CHAPTER ONE
1.0 METAL CLEANING AND SURFACE FINISHING

1.1 Metal Cleaning

Metal cleaning operations are the practical applications of chemical and physical forces to impart the desired properties to a metal surface. The selection of cleaning process is influenced by the type of soil and other contaminants to be removed (see fig.1.1), the required degree of cleanliness, and the cost. Various types of soils often encountered and the cleaning methods for them are listed below:

- Pigmented drawing compounds: emulsion cleaning (EC), alkaline cleaning (AlC), electrolytic alkaline cleaning (EAC), acid cleaning (AC), vapour degreasing (VD) and solvent cleaning (SC).
- Un-pigmented oil and grease: (EC, VD, SC, AC, AlC, EAC).
- Chips and cutting fluids on steel parts: (EC, AlC, EAC, VD, SC, AC)
- Polishing and buffing compounds: (SC, EC, AlC, EAC, AC)
- Residue from magnetic particle inspection: (EC)
- Rust and scales

  The removal of rust and scales is the problem one often encounters with mill products, forgings, castings and fabricated metal parts.

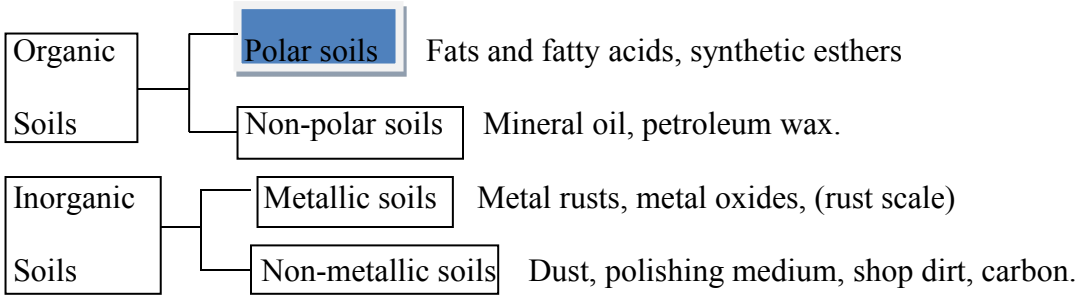

Fig. 1.1: Classification of Soils

The practical application sites of industrial cleaning include:

i. Pre-plate cleaning
ii Pre-paint cleaning
ii. Heat treatment lines
iii. Cold rolling strips cleaning
iv. Parts washing in machining lines
v. Pre-treatment for phosphate conversion treatment

Metal working oils which normally constitute contaminant of work pieces and have to be removed before further processing include:

i. Cutting oil
ii. Machining oil
iii. Spinning lubricant
iv. Lubricant
v. Drawing oil
vi. Rust preventives
vii. Stamping oils

viii Rolling oil
ix. Quenching oil
x. Others (grease, wax)
xi. Heavy sulphurized drawing oils, phosphated and soap draw.

1.2 Removal of Rust and Scales from Metal Parts

The cleaning methods for removal of rust and scales from metal parts are discussed in details below:

i. **Abrasive Blasting**: with a wide choice of abrasives, it is suited for all sizes and shapes, and all metals without affecting their heat treatment. However, it may abrade corners, alter dimensions, and cause surface etching / roughness in extreme cases.
ii. **Tumbling:** it is the least expensive process. Parts configuration and size are the primary limitations of the process. Tumbling in dry abrasives (debarring compounds) is effective for removing scale and rust from small pars of sample shape. Complex shaped parts with recesses and irregularities require more time.
iii. **Brushing:** it is used for removing light rust or loosely adhering scales. It is least expensive method, suited for work pieces made from tubing.
iv. **Pickling:** it is used for complete removal of scale from mill products of fabricated parts in hot, strong solution of sulphuric or hydrochloric acid. By adjusting formulations, it can be used for removing scale of ferrous and nonferrous parts. It is adaptable to products of virtually any size or shape. In case of high carbon alloys, it can be potential source of hydrogen embrittlement. Some metal (up to 3%) may be lost in pickling. Necessary care of dispose of fumes and spent acid is required. Sometimes excessive pitting may occur on cast steels and irons. This process is usually used as supplementary treatment following abrasive blasting or salt bath descaling.
v. **Electrolytic Pickling:** it can remove scale twice as fast as pickling process, but it is costly. It utilizes 30% HCl at 55^{o}C and 3 to 6 volts for 2 to 3 minutes.
vi. **Salt Bath Descaling:** it is an effective means of removing or conditioning scales. The reduction or oxidation of scale is almost instantaneous when work piece attains the bath temperature (385^{o}C to 520^{o}C). There is no loss of metal or danger of hydrogen embrittlement. High bath temperature relieves stress but may result in cracking or warping of complex work pieces.
vii. **Alkaline Descaling:** it is more costly and slower in action than acid pickling, but there is no loss of metal by this method. Bath contains about 60% sodium hydroxide and is maintained at room temperature and in some cases up to 95^{o}C. Immersion time is dependent on thickness of scale to be removed. The use of current increases the rate of oxide removal.

Figure 1.2 shows the surface conditions of rolling strips before cleaning.

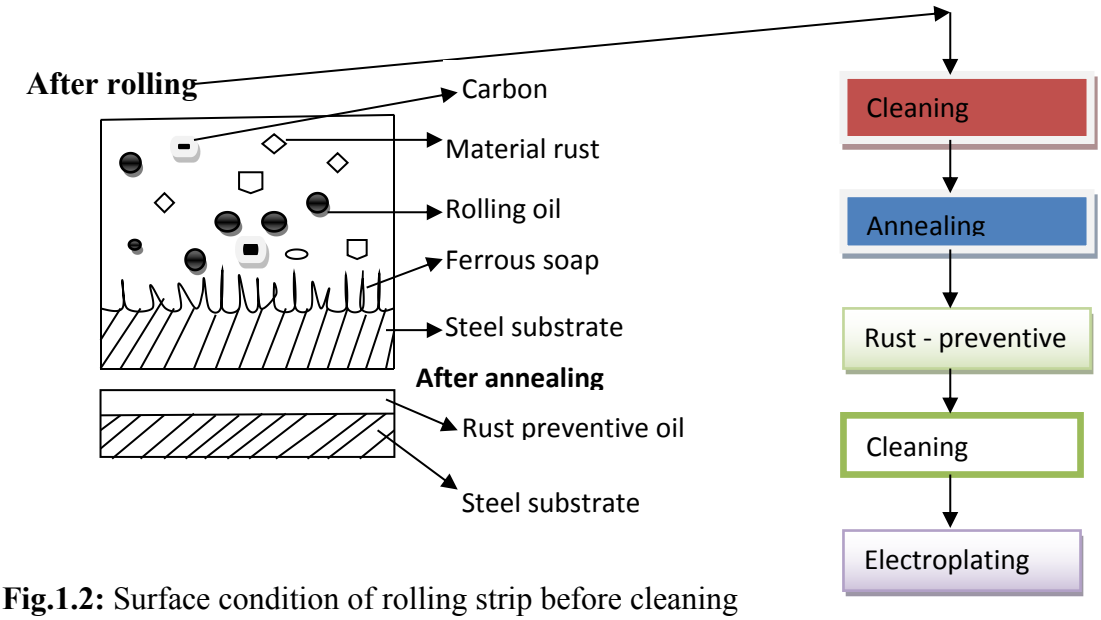

Fig.1.2: Surface condition of rolling strip before cleaning

1.3 Methods of Cleaning Metals

The several methods of cleaning metals are discussed below in brief:

I. **Alkaline Cleaning:** this method is used for removal of oily, semi-solids from metals before they are electroplated. The solutions used depend on their detersive properties for cleaning action and effectiveness. Agitation of the solution and movement of work pieces also helps. The principal methods employed for alkaline cleaning are soak, pray, electrolytic, barrel, steam-gun, spray rotary etc. The cleaning effectiveness of alkaline compounds is attributed mainly to the action of builders (compounds to provide alkalinity and other desirable properties at low cost) which are the principal bulk components of the formulation.

II. **Emulsion Cleaning:** it is a process for removing oil, grease loose metal chips, and other contaminant from the surface of metal by the use of common organic solvents dispersed in an aqueous medium with the aid of an emulsifying agent. The cleaning is done at room temperature to 80^{o}C depending on the solvent used. Emulsion system is generally a hydrocarbon and water. Emulsion cleaning is used when rapid superficial cleaning is required and when some protection by a light residual film of oil is desirable.

III. **Solvent Cleaning:** it is used to remove oil, grease, loose metal chips, and other contaminants from the surface of metal parts by common organic solvents. Cleaning is usually performed at, or slightly above, room temperature. Parts are cleaned by being immersed and loaded in the solvent, with or without agitation large parts are sprayed with the solvent. Higher operating temperature will invariably increase the cleaning efficiency of a solvent. Good agitation usually eliminates the need for prolonged soaking.

IV. **Vapour Degreasing**: it is a cleaning process that employs the hot vapours of a chlorinated solvent to remove oil, waxes and grease. Degreasing is possible by (a) vapour only (b) vapour-spray-vapour system (c) warm liquid-vapour system (d) boiling liquid-warm liquid-vapour system.

V. **Acid Cleaning:** it is a process in which a solution of mineral acid, organic acid or acid salt, in combination with a wetting agent and detergent, is employed to remove oxide, slop soil, oil, grease and other contaminants from iron and steel surfaces. The difference

between acid cleaning and acid pickling is a matter of degree. Various methods of application are wipe-on wipe-off, spray cleaning, immersion barrel acid cleaning and electrolytic cleaning.

VI. **Pickling:** it is the process of chemical removal of surface oxides (salt) from metal by immersion in an acid solution. Wide variations are possible in the type, strength and temperature of the acid solutions used. It can be adapted to continuous operations. Sulphuric acid is commonly used for pickling, because in comparison to HCl, it has lower cost, produces less fumes and has less volume to be handled. However, H_2SO_4 produces darker surfaces and smelt on light-carbon steel, and requires to be heated to high temperature. Inhibitors are added to acid pickling solutions primarily to protect the steel being cleaned, by retorting or stopping the chemical action of the acid on the basic metal.

VII. **Electrolytic Pickling:** it overcomes some of the difficulties encountered in still pickling. While rust Fe_2O_3 gets removed by still pickling, black magnetic oxide Fe_3O_4 is removed by electrolytic pickling. This process is much rapid because of greater evolution of hydrogen.

VIII. **Salt Bath Descaling:** These processes could be either reducing, or oxidizing or electrolytic. Salt bath for the oxidizing process are most stable and least costly. The educing and the electrolytic processes are more effective in attacking heavy, tightly adhering scale, electrolytic process usually provides more thorough scale removal than the reducing process. Since it operates at a lower temperature, it is advantageous for descaling metals that undergo a change in properties at higher temperatures.

IX. **Abrasive Blasting Cleaning:** this process entails the forceful direction of abrasive particles either dry or suspended in a liquid-against the surfaces of metals or products, to remove contaminants or to condition the surfaces for subsequent finishing. This process is used for removal of scale, rust etc., or roughening of surface in preparation for bonding, painting or other coating, or removal of burrs. The abrasives used are grit (angular metallic particles), short (spherical particles), sand etc. Metal cleaning methods may be classified as stated in fig 1.3.

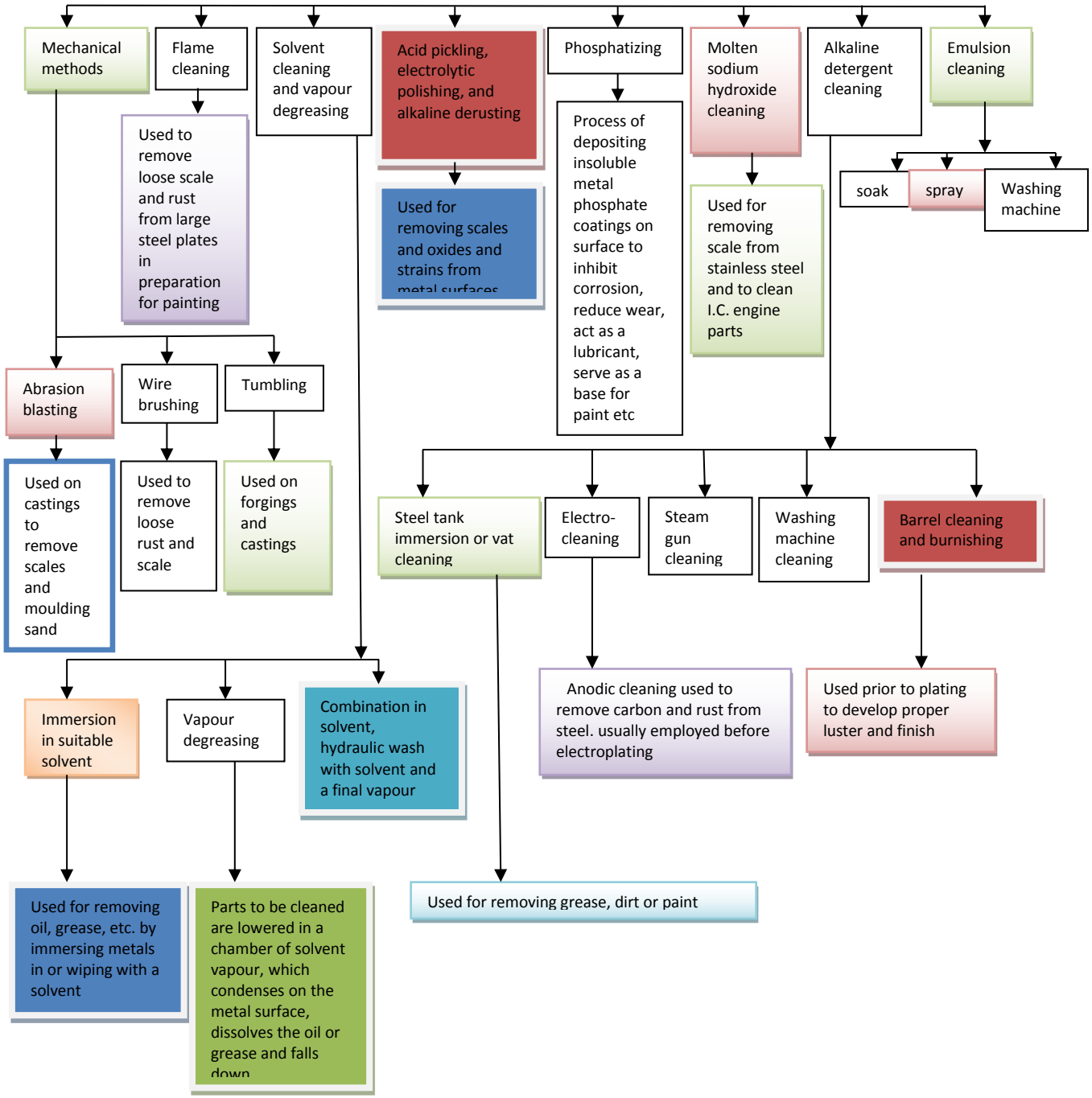

Fig. 1.3 Different Types of Industrial Cleaning Methods

1.4 Mechanical Finishing

Very often parts have to be finished by mechanical means. The mechanical finishing processes include – polishing and buffing, barrel finishing, shot-peening and power brush cleaning and finishing.

Polishing: is an abrading operation employed for the removal or smoothing out of grinding lines, scratches, pit, mould, monks, parting lines, tool marks, stretcher strains, etc. Polishing is

performed with either a belt or a wheel to which an abrasive is bonded. The process removes metal, and causes some plastic working of the surface. Emery and corundum are the natural abrasives commonly used on polishing wheels. Polishing wheels are usually made of muslin.

Buffing: is a process for producing smooth, reflective, scratch-free surfaces on work piece by bringing them into contact with revolving cloth or buffs charged with suitable compounds. The action of the wheels, together with that of the compound, either cuts or flaws the metal, thus removing minor defects and imparting a smooth, lustrous finish. Most buffing compounds consist of an abrasive that is immersed in a binder-carrier. The abrasive serves as the principal cutting medium, the binder provides lubricant, prevents over heating of the work, and firmly cements the abrasive to the wheel face. Binders must not chemically etch, corrode or mar the metal surface.

Barrel Finishing: involves the tumbling or rolling of parts in rotating barrels or the agitation of parts in shaker containers, vibratory tubes for cleaning, deburring, shine rolling and burnishing. It can be performed either dry or wet and can be applied to parts ranging from rough casting to delicate parts. Water is usually used as the liquid in wet barrel finishing. A finishing medium, usually metallic materials in bulk or chunks, is used in the barrel. Cleaning, descaling, deburring, burnishing and shine rolling can be performed in a barrel depending on the compound used in the barrel.

Shot-Peening: is a process in which a stream of shots is impinged at the metal surface at high velocity and under controlled condition to induce compressive stresses in the exposed surface layers of metallic objects. It not only cleans the surface being peened, but also increases fatigue strength. It also relieves tensile stresses that contribute to stress-corrosion cracking and tests the adhesion of silver plating on steel. The peening action (rounded depression in the surface) improves the distribution of stresses in surfaces that have been disturbed by grinding, machining or heat treating. Shot peening is especially effective in reducing stress concentration effects of notches, fillets, forging pits, surface defects, and decarburization. A higher residual stress , approaching yield strength, can be obtained by strain peening, which consists of peening the surface while it is being strained in tension as in the case of springs.

Power-drive wire or non-metallic-fibre-filled rotary brushes: are widely used for cleaning, deburring, edge blending and surface finishing of metals. The brush may be constructed using straight wire, twisted wire, crimped wire, or natural or synthetic fibre. Trim (length or fill material extending from the retaining member to the brush face) may be short, medium, or long. Density of fill may be heavy, medium or light. The selection of a power brush for a specific cleaning or finishing operation depends primarily on selection of the proper combination of variables in brush construction and operating procedure.

Burnishing Machines: External burnishing machines are used for finishing the external diameters of soft, cylindrical components. The process of burnishing being a process of cold-rolling does not produce the peaks or valleys but actually removes these by turning over the peaks into the valleys. This increases the bearing area of the component, and its tolerances remain stable. This process has the advantages that it remains stable. The process is extremely fast; requires no consumables; having practically no scrap; produces a surface of very high

surface finish, and provides greater life to the component. It substitutes finish-grinding. This process is most economical and is stable and used for pressed-bar of sawing machine; etc. The burnished surface accepts electro plating as a finishing process.

High Pressure and Steam Jet Cleaning Machine: these machines are robust, mobile and ideally suited for the removal of grease, sticky vehicle components, plant and machinery, shop floors, containers and pipes, hot water or steam is ejected through the equipment under pressure which can be adjustable and chemical detergent stored in built tanks can be added in controlled quantities to further accelerate the cleaning process.
The equipment consists of a reciprocating type slow speed piston pump and an oil fired burner with a heat exchanger. Safety devices to safeguard the operator and machine are provided. The most obstinate deposits in inaccessible areas can be removed with the utmost of ease. These cleaners are extremely useful in automobile, defence and railway workshops and industries like chemical, cement, earth moving equipment, breweries, dairies, mining, food processing and fertiliser plants.

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1.5 General Cleaning Methods

Yuken Industry Co. Ltd classified cleaning as follows:

a. **Aqueous Cleaning**: is accomplished through interfacial action of surfactants as a principal ingredient and saponification as chemical reaction.
b. **Mechanical Cleaning (aqueous and solvent)**: these include: ultrasonic, spraying, barrel, electro-cleaning, scrubbing, wiping, grinding, blasting (hydro -, vapour -,) and vacuum cleaning.
c. **Solvent Cleaning:** these include petroleum-based solvents, chlorinated solvents and terpenes.
d. **Burn-off Cleaning:** this is done particularly in heat-treatment lines.

Characteristics of the water-based Cleaners

The characteristics of the water-based cleaners are as follows:

i) **No ozone depleting**: they are free of chlorinated solvent.
ii) **Environmentally friendly:** they are biodegradable and free of volatile organic compounds (non VOC)
iii) **Safe to use:** they are nonflammable and nontoxic
iv) **Less cost:** their cost is less and reasonable
v) **High performance:** they have high performance in terms of result.

The fig. 8.4 shows the system structure for aqueous cleaning.

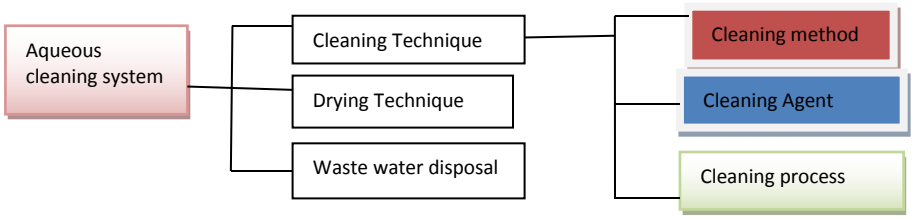


Fig.1.4 *System structure for aqueous cleaning.*

1.5.1 Design of cleaning Technique

*T*he design of the cleaning technique will look at cleaning method, cleaning agents, and cleaning process.

Cleaning method: cleaning method considers the following:

i. Peculiar shapes of workpieces (blindhole, etc)
ii. Permissibility to scar and transformation
iii. Racking condition

Cleaning agents: consideration for cleaning agents, include the following:

i. compatibility with materials
ii. Soils to be removed (quantity, and type etc)
iii. Presence or absence of rinsing step

Cleaning process: considerations for the cleaning process include:

i. Cleanliness required from subsequent process
ii. Floor space for cleaning facility
iii. Presence or absence of rinsing step

The Principle of Aqueous Cleaning

Chemical and physical Actions

Aqueous cleaning is the combination of both chemical and physical action. Interfacial action include; penetration, emulsification, dispersion, spray, ultrasonic, electrolysis, fluid-agitation, work-agitation, scrub and barrel.

Ingredients of water-based cleaners

The ingredients of water based cleaners are shown in figure 8.5.

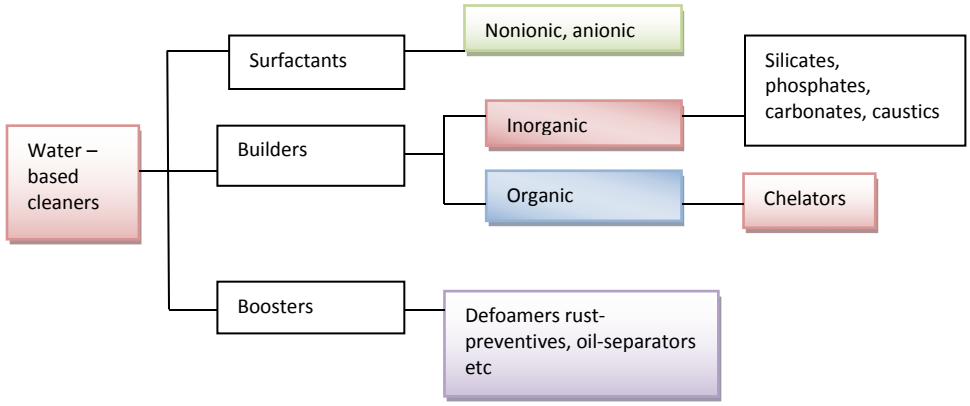
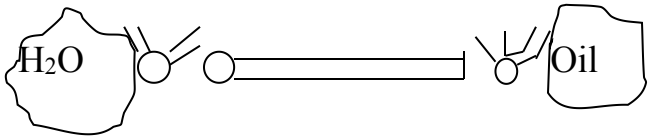


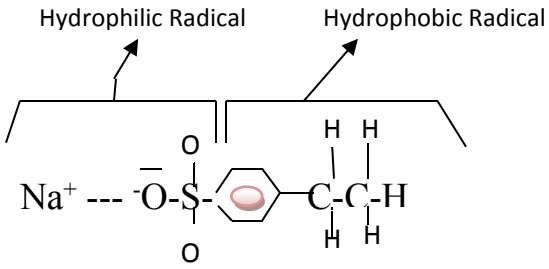
Fig.1.5: Ingredients of water-based cleaners

Surfactants

Type of structures

The typical structure of a surfactant is shown below:





The hydrophilic end gets attracted to water while the hydrophobic end gets attracted to the oil removing it.

The behavior of Surfactant against Oil Droplet.

The behavior of surfactants against oil droplet is illustrated; likewise the behavior at air/ liquid interface

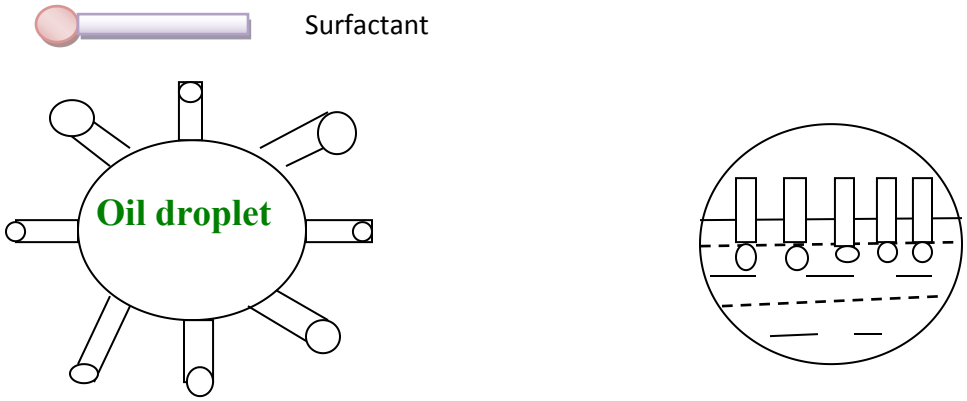


Fig. 1.6: a) Behavior of surfactant against oil droplet. b) Behavior of surfactant at air/ liquid interface.

The Behavior of Surfactants in Aqueous Solution.

The behavior is illustrated in fig. 1.7

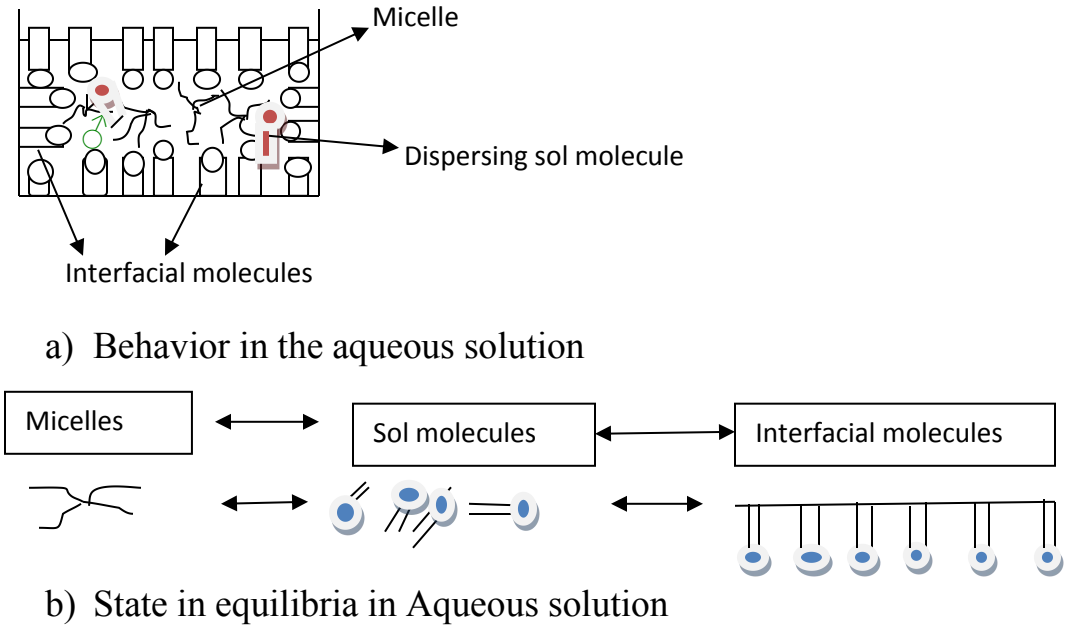


Fig. 1.7: The behavior in Aqueous solution

The functions of surfactants in cleaning

The functions of surfactants in cleaning include:

i. Wetting and penetration effect
ii. Emulsification effect
iii. Dispersion effect
iv. Recontamination preventing effect

Water –based cleaning Mechanism

Wetting-penetration: through the use of surfactants, the cleaner penetrates and loosen the substrate-soil bond by lowering surface and interfacial tension

Rolling-up-Displacement: soil is rolled-up and removed as smaller particles dispersed in the solution. In this step, the mechanical actions are very effective for soil removal, such as work-piece agitation, fluid agitation, etc.

Saponification: the reaction between organic oil containing reactive fatty acids and free alkali forms soaps. Insoluble fatty acid + Alkali = water soluble soap

Solubilization and/ or Emulsfication: the soils are dispersed and/ or emulsified to prevent it from agglomerating.

Anti-recontamination: surface is then coated with a thin film of surfactants to prevent it from recontamination.

Electro-cleaning

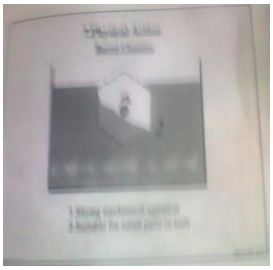
At the anode electro-dissolution of the substrate takes place as a result of oxidation atmosphere from oxygen which causes the organic soils to be removed easily and the pH of the cleaning medium to drop to neutral.

At the cathode hydrogen gas removes the oil physically. The reducing atmosphere at the cathode causes the pH to rise almost to 14 which makes the fats and fatty acids to saponify much more. The reducing atmosphere causes activation and derusting at the cathode. Electro-deposition of metal ions must be avoided.

The cleaning mechanism is illustrated in fig. 1.8.

(a)

Physical Action (Barrel cleaning)
1. strong mechanical agitation
2. suitable for small parts in bulk

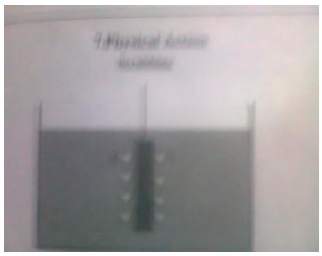


(a)

(b)

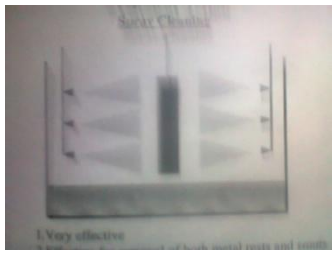
Physical Action (Ultra Sonic Cleaning)
1. Cavitation effect (20 – 50 KHZ)
2. Effective for hermetically sealed portion

(b)



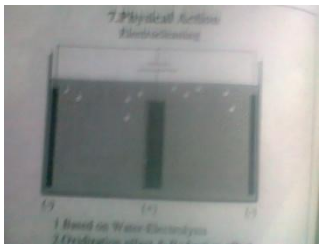
(d)

Physical Action (Scrubbing)
1. Very strong mechanical agitation
2. For flat shape parts only



(e)

Physical Action (Spray Cleaning)
1. Very effective
2. Effective for removal of both metal rusts and smuts



(f)

Physical Action (Electrocleaning)
1. Based on Water-Electrolysis
2. Oxidation effect & Reduction effect
3. Suitable for precision cleaning

Fig. 1.8: Cleaning Mechanism

1.5.2 Cleaning Process in Electro-Zinc-Plating Line

A typical example of cleaning process is the cleaning process in a zinc plating line which is shown in fig. 8.9 below:

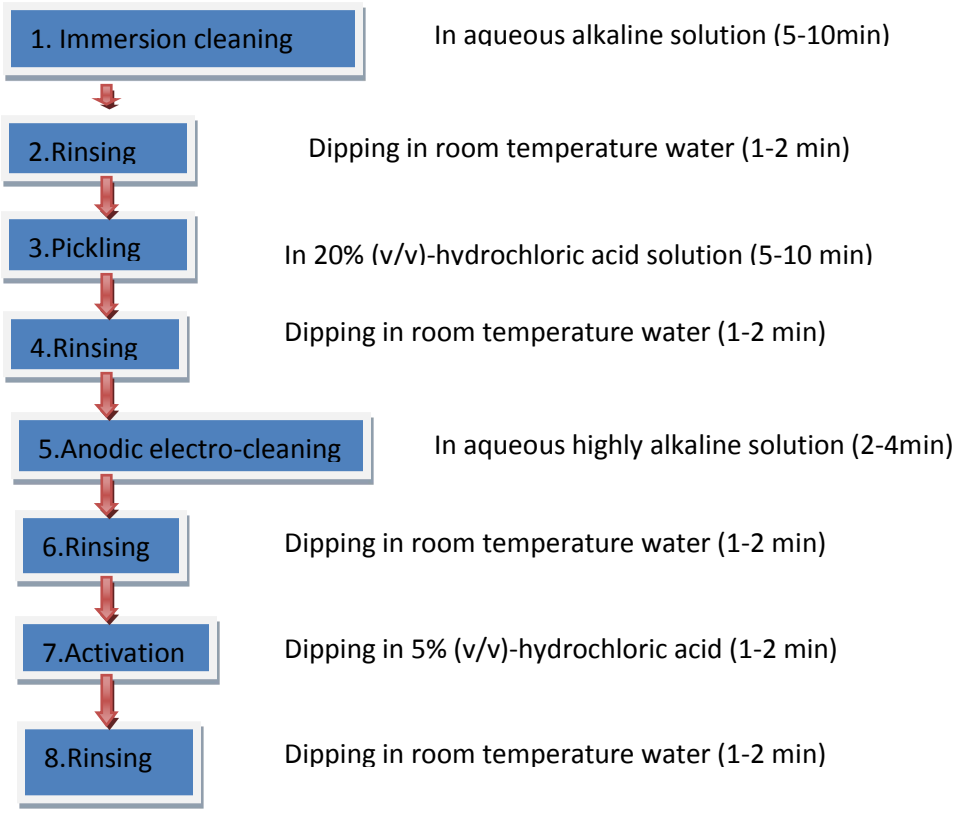


Fig 8.9: Cleaning Process in Electro-Zinc Plating Line

Practical Exercise on Degreasing

i. Soak Degreasing-Test
Cleaner: pakuna 100HK-N: 3%
Temp: 60°C
Cleaning time: 2, 5, 10 mins
Then rinse and dip in 0.3% H_2SO_4

The rusted area of the specimen will determine the degree of degreasing and the effectiveness of the cleaner chemical.

ii Spray Degreasing Test

Oil to be degreased: Quenching oil
Spraying pressure: 0.1MPa
Cleaner: pukuna FDN-26: 3%
Temp: 60°C
Cleaning time: 2, 60, 90 secs

At the end of the spraying time the specimen is removed and evaluated using visual evaluation of the cleaned surface and the result expressed in percentage. Existence of stains shows that the cleaning is not complete.

Note: the reader should take note that it may not be possible for me to disclose the chemical composition of some of the chemicals I may have mentioned, and in such situations only the product name will be mentioned as indicated above. Compositions are normally top company secrets even when obtaining patents they don't normally give full details. Chemicals are available for pretreatment and plating operations and companies specialize in the manufacture of these chemicals. For instance Uyemura & Co. Ltd 3-2-6 Doshomachi, Chuo-ku, Osaka 541-0045, Japan, phone; 81-6-6202-8944, produces pretreatment chemicals and plating chemicals for all types of plating operations. Pakuna is a degreasing agent used in pretreatment operations for all sorts of metal surface treatment activities.

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2.0 CHAPTER TWO

A Focus on New Ceramics for Surface Modification in Industry

2.1 Introduction

In recent times various kinds of oxides, nitrides, carbides, and borides are playing an important role as new ceramics for surface modification in industry because of their excellent characteristics and performance [1]. Ceramics occupy the number one position on the list of industries with the greatest potential for commercial development, according to data that has been compiled by Japan's Ministry of International Trade and Industry [2]. The highly desirable characteristics offered by these new ceramics will impact a broad segment of the industrial sector such as the automotive, electronics, aerospace, medical and telecommunications segments. New ceramics will no doubt play a vital role in the development of smart and intelligent materials in the 21st century. Coatings and bearings for orthopedic or dental implants are also available. Some of these materials function as resorbable materials to provide temporary support until the human body can gradually replace it, while others are surface active materials which form a bond with the surrounding tissue in order to stimulate growth. The use of ceramic coatings in automobile engines by Japanese companies has lead to the development of engines which are 30 to 40% more fuel efficient than the current generation of engines, and furthermore, these engines run at higher temperatures without lubrication or cooling [2].

These ceramics such as nitrides, carbides, oxides, and borides are coated in order to give their effective properties and performance to materials surfaces [3]. The ceramic coating is a process which produces composite material consisting of ceramics as film and other materials e.g metals as substrate. Therefore ceramic coating will be given a great deal of attention not only as a coating technology but also as a manufacturing process for composite materials or preliminary process for joining [3]. As representative process of ceramic coating, chemical vapor deposition (CVD), physical vapor deposition (PVD), chemical densified coating (CDC), molten salt method, spray coating, ion implantation etc, are mentioned in this paper. And in addition diamond coating and sol-gel processes are recently developed and being advanced very actively. They too are mentioned in this paper. Table1 shows the classification of surface treatment for surface modification of materials.

The objective of this chapter is to review various ceramic coating processes which mainly produce the film of nitrides, carbides, oxides, and borides. This will be dealt with from the viewpoint of their properties, performance, and coating methods, and the principle that develops the effective technology for surface modification.

Table 2.1: Classification of Surface Treatment

Basis	Process	Examples
Electro-chemistry	Cathodic process	Electroplating-single metal, Cu, Ni, Cr, Zn, Cd, Au, Ag, etc. Alloy: Cu-Zn, Sn-Pb, Ni-Sn, etc Electroforming –Cu, Ni, Fe, etc
	Anodic process	
		Electropickling, electrocleaning (or degreasing) PR electroforming (or cleaning)
		Electropolishing-stainless steel, Al, electroetching etc Anodizing –Al, Mg, Zn, Pb, etc
chemistry	Chemical process	Acid dipping, acid pickling, -descaling, activating, degreasing, cleaning Chemical polishing Chemical plating (cementation, contact, reduction) calorizing, (bronzing etc) Chemical conversion process (phosphating, chromate, etching, photoetching, chemical milling)
Coating	Hot dipping Metal spraying Powder spraying Cladding Painting Resin spraying Ceramic spraying Enamelling	Zn, Sn, Sn-Pb, Al, Pb Metalicon, Pb-homogen, plasma metal spraying Low melting metal, mechanical plating (Zn) Clad plate, printed circuit, explosion plating Spaying, electrostatic painting, E.D., Powder painting Lining Al_2O_3, Cr_2O_3, TiO_2, ZrO_2 (Plasma, flame etc) Glass enamelling, cloisonné, antiacid enamelling
Diffusion penetration	Metalizing Hardening	Al, Zn, Cr, Si Carburising, nitriding, boriding, siliconizing, etc
Vacuum penetration	Physical Chemical	Carburization, sputtering, ion-plating, etc (PVD) CVD, plasma CVD
High densified energy	Laser, laser plating, laser CVD, electron beam, ion-beam, etc	
Others	Quenching, shot-blasting, liquid-honing, etc.	

2.2 Ceramics, Ceramic Films and their Significance

2.2.1 Ceramics

Ceramics occupy the number one position on the list of industries with the greatest potential for commercial development, according to data that has been compiled by Japan's Ministry of International Trade and Industry [2]. The markets for structural ceramics are projected to total between $1billion and $5 billion in the year 2000 and the principal ingredients of these markets are presented in figures 1 and 2. This new generation of fine ceramics bears little resemblance to the sand and clay combinations of terrestrial materials utilized by homo habilis in the Mesolithic and Neolithic periods for the fabrication of earthenware utensils. These new materials feature

minerals such as aluminum oxide, silicon nitride and silicon carbide which are manufactured as extremely pure, fine powders prior to consolidation at high temperatures to yield a durable dense structure. The control of these new ceramics provides the design engineer with a class of ceramics which are stronger, lighter, and harder than most metallic competitors. Furthermore, the ceramics can operate at much higher temperatures and they do not degrade significantly due to oxidation as do commercial metals such as the irons and steels [2,4].

These materials do, however, have an Achilles heel: brittleness. This brittleness is associated with a number of extremely small flaws such as cracks, voids, and impurities present in the material, and also the amount of energy required in fracturing the material in the presence of these flaws. Thus the manufacturing processes must be extremely and carefully controlled, since flaw as small as 10 to 50 micrometers can reduce the strength of a ceramic part to only a few percent of its ideal strength thereby rendering the part useless. While material toughness is a major limitation of the current generation of advanced structural ceramics, the many significant advantages of these have not deterred further research on these compounds while other research efforts are focused on this limiting material characteristic. These latter efforts are typically focused on synthesizing tougher materials through the prosecution of research on microstructural design, transformation toughening, and ceramic composites where the incorporation of ceramic particulates, whiskers, or continuous fibres in a ceramic matrix can yield a composite material that absorbs more energy during fracture, than a geometrically identical part fabricated in the matrix material alone [2, 4].

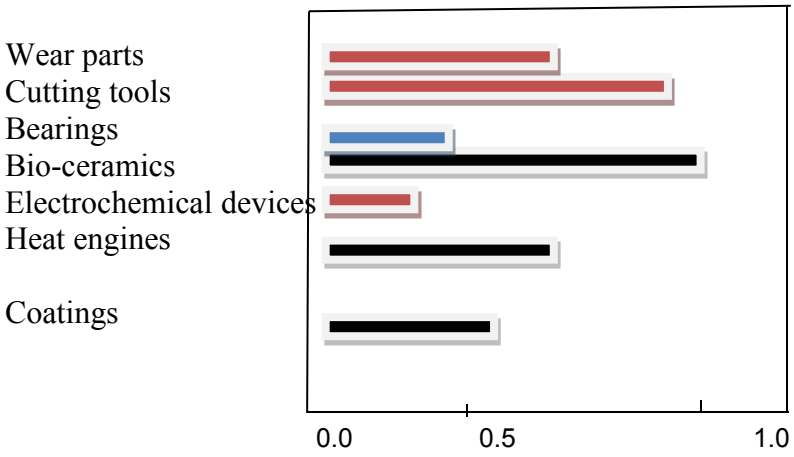

Figure 2.1: Projected US Markets for Structural Ceramics in the Year 2000. Source: Gandhi and Thompson (1992)

Applications	Performance advantages	Examples
Wear parts - **Seals** - **Bearings** - **Valves** - **Nozzles**	High hardness, low friction	Silicon carbide, alumina.
Cutting Tools - **Lathe tools** - **Milling cutter**	Hot hardness, high strength	Silicon nitride
Heat Engines - **Diesel components** - **Gas turbines**	Thermal insulation, high temperature strength, fuel economy.	Silicon carbide, silicon nitride, zirconia.
Medical Implants - **Teeth** - **Joints**	Surface bonds to tissue, corrosion resistance, biocompatibility	Bioglass, alumina, zirconia, hydroxylapatite.
Construction - **High ways** - **Bridges** - **Buildings**	Improved durability, lower overall cost	Advanced cements and concrete.

Figure 2.2: Future Applications of Structural Ceramics.

2.2.2 Ceramic Films and their Significance

Ceramics are classified into carbides, nitrides, borides, oxides, silicides etc. in the carbide group we have, TiC, VC, TaC, WC, NbC, ZrC, MoC, Cr_7C_3, Cr_3C_2, B_4C, SiC, etc. TiN, VN, TaN, NbN, ZrN, HfN, CrN, Si_3N_4, BN, AlN etc are listed in the nitride group. TiB_2, VB_2, TaB_2, WB_2, ZrB_2, MoB_2, NbB_2, CrB_2, AlB, SiB_2 etc, are in the boride group. TiO_2, ZrO_2, Nb_2O_5, TaO_5, Al_2O_3, MgO, SiO_2, Cr_2O_3, Fe_3O_4, In_2O_3, SnO_2 etc are in the oxide group. And in addition various silicides such as TiSi, MoSi, ZrSi, and CrSi are in the silicide group. Various sulphides, BP, C, B, i-carbon, diamond, etc are also listed as ceramics. It must be noted that some of these ceramics are not yet in general usage but still undergoing research and development.

Generally speaking ceramics mentioned above have high melting point, surface hardness (1000-2000 HV) good oxidation resistance, acid and alkaline resistance but they are brittle. Their coefficients of thermal expansion are about 5-10 x 10^{-5} /^{o}C. Therefore one can select a certain ceramic and utilize it as coating according to the purpose. On the other hand ceramic coating films are classified into two large groups from the viewpoint of applications, i.e those use as construction materials, and electronic (functional) materials. The former needs corrosion resistance, surface hardness, heat resistance, wears resistance, acid resistance and so on. And the later requires the properties of semiconductor (insulation, passivation), magnetism, dielectric properties (thin film condenser, surface wave device, pressure sensitive element), photoelectric properties (thin film laser, transparent electrode, optical coating). Khurmi and Sedha in 2011, commenting on the wonders of the ceramic materials said ‘it is quite possible for a common person to think that copper is a good conductor of electricity. But it will be interesting to know that ceramic can be a better conductor of electricity than copper. Scientists have discovered

recently high temperature superconducting ceramic materials. At ≤ 100k, these materials offer no resistance to the conduction of electrons. Besides this, such materials reject magnetic flux lines so that a magnet can be suspended in the space above the semiconductor. In Japan, a high-speed levitated train is being developed based on this principle called 'meissner effect'. Coating a conducting material with the above mentioned ceramic may greatly increase its conductivity this may form a basis of research, hopefully very soon. But the discovery of new properties will lead us to more useful applications in future [1, 2, 6].

2.3 Nitrides and Carbides

Properties of various nitrides and carbides are shown in Tables 1-2. Most nitrides have high melting point (<2000^{o}C). Their resistivity ranges from 10 - 20 μΩ.cm; these include ZrN and TiN. Si_3N_4 has a resistivity of greater than 10μΩ.cm. Their hardness is more than 1200kg/mm^2 e.g Si_3N_4 (2600-3200kg/mm^2) and TiN (1800-2100kg/mm^2), but generally their elasticity is low and they are brittle.

On the other hand, density of carbides ranges widely from 2.5-15g/cm^3 the same goes for nitrides. The specific resistivity for TaC ranges from 20 - 175μΩ.cm and SiC from 10^9 -10^{11} μΩ.cm. in carbides there are no insulators such as Si_3N_4 and melting points of carbides are generally higher than that of nitrides. They have melting point which is more than 2500^{o}C. Thermal conductivity of carbides is generally larger than that of nitrides, and they can be applied to various uses. Microhardness of carbides is much higher than that of nitrides, for example 1800kg/mm^2 for TaC and 3000 - 3500kg/mm^2 for SiC. Elasticity of carbides is slightly higher than that of nitrides but they have also low elasticity and are brittle in general. Although these ceramics as thin film they deviate slight from their intrinsic properties, however the tendency of their property remains constant [1,6]. According to Khurmi and Sedha [15] graphites are known to be refractory, light-weight and corrosion resistant materials. Such properties are essential for many applications, e.g. dies for continuous casting, rocket nozzles and heat exchangers for the chemical industry. However, the relatively poor resistance of graphites to wear and oxidation limits their use. The addition of titanium carbide (TiC) coatings greatly extends the use of graphites. The TiC coatings possess excellent resistance to wear, oxidation and corrosion as well as having other desirable properties. Other TiC coated parts include quartz parts.

2.4 Oxides and Borides

Various properties of oxides and borides are shown in Table 3 and 4. Density of oxides ranges from 4 - 10g/cm^3. Melting point of oxides is lower than that of both nitrides and carbides. Specific resistance of oxides is much higher than that of nitrides and carbides (10^7 - 10^{22} μΩ.cm), and many oxides can be use as insulators. Thermal conductivity ranges from .001 to .01 (CGS), which can be deduced from the value of specific resistance, and is very low in general (however, thermal conductivity and specific resistance of BeO is exceptionally high). Both microhardness and elasticity of oxides are lower than those of carbides and nitrides. Al_2O_3 and Cr_2O_3 however have high hardness which can be utilize in various applications [1, 6]. On the other hand the densities of borides range from 4.5-12g/cm^3 which are similar to those of the other three compounds.

Melting point of borides is much higher than that of the other compounds (and is similar to that of several carbides whose melting point is very high). This property will be utilized for high heat resistance in the future. Specific resistivity of borides ranges from 6 to 30μΩ.cm, and is lower than that of carbides. This property will be utilized for special

purpose like conductors at high temperature. Thermal conductivity of borides ranges from 0.04 to 0.15 (CGS). Hardness of boride is the highest in the four compounds, generally greater than 2000kg/mm^2, and it is very important that this hardness property be applied to practical uses. But elasticity is also very low and brittle as well as the other compounds. These ceramics have low thermal expansion

Table 2.2: Properties of Various Nitrides

Nitrides / **Properties**	**TiN**	**ZrN**	**HfN**	**VN**	**TaN**	**NbN**	**BN**	**Si_3N_4**	**AlN**	**CrN**	**Cr_2N**
Crystal system	cubic	cubic	cubic	Cubic	Cubic	cubic	Hexagonal cubic	Hexagonal (α, β)	Hexagonal	cubic	Hexagonal
Density (g/cm^3)	*5.44*	*7.35*	*13.94*	*6.08*	*14.1*	*8.26-8.4*	*2.15-2.27 3.48-3.49*	*3.18 3.19*	*3.25-3.30*	*6.1*	*6.51*
Melting point (°C)	2900-3220	2930-2980	3300-3307	2050-2360	2980-3360	2050	Decomposition 2720-3000	Decomposition 1900	Decomposition 2200-2300	1500	-
Specific resistance (μΩ.cm)	22-130	11.5-14.0	32	86	135	200	1.7x1019	>1019	2x1017	600-680	79-89
Thermal Conductivity (CGS)(RT)	0.07	0.04	0.052	.027	.021	.009	Orientation	.035-.041	.004	.0261-.0307	.0514-.0523
Microhardness (kg/mm^2)	1800-2100	1400-1600	1500-1700	1500	1060	1400	-	2670-3260	1225-1230 (KH)	1000-1188	1522-1629
Elastic modulus (kg/mm^2)	25500	-	-	-	58700 (ε-TaN)	49300	1160-8370 (α-BN)	5620-21800	28100-35200	-	-
Coefficient of thermal expansion	9.31-9.39 (25-	7.24 (20-	6.9 (20-	9.2 (20-	3.6 (20-	10.1 (20-	0.5-1.7 (α-BN)	2.75 (20-1000)	4.8 (20-300)	2.3 (20-800)	9.41

(10^6deg-1)(^{O}c)	1100)	1100)	1100)	1100)	700)	1000)					(21-1100)

SOURCE: Oki, T (2008)1

Table 2.2: Properties of Various Carbides

Carbides / Properties	**TiC**	**ZrC**	**HfC**	**VC**	**TaC**	**NbC**	**WC**	**B_4C**	**SiC**	**Cr_3C_2**	**Cr_7C_3**
Crystal system	Cubic	cubic	Cubic	Cubic	cubic	cubic	hexagonal	rhombohedral	Cubic hexagonal	orthorhombic	trigonal
Density (g/cm^3)	4.85-4.93	6.44-6.9	12.2-12.7	5.36-5.77	14.48-14.65	7.82	15.6-15.7	2.5-2.54	3.21-3.22	6.68	6.92
Melting point °c	3180-3250	3175-3540	3885-3890	2810-2865	3740-3880	3500-3800	2627-2900	2350-2470	Decomposition 2200-2700	1895	1782
Specific resistance (μΩ.cm)	70-170	50-64	60	150-160	20-175	74-254	53	$.3x10^4$-$.8x10^4$	10^9-10^{11}	70-80	105-113
Thermal conductivity (CGS)(RT)	.041-.06	.049	.053	.010	.053	.034-.041	0.070	1.065-1.069	.098-.100	.045-.047	.035-.038
Microhardness (kg/mm^2)	2900-3200	2600	2533-3202	2800	1800	2400	2400	2400-3700	3000-3500	1800	1882
Elastic Modulus (kg/mm^2)	31600-44800	32300-48900	43300	26000-27400	37100-38900	34400	53600-72100	29500-45800	34450-42200	38000	-
Coefficient of thermal expansion ($10^6.deg^{-1}$)(°c)	7.95 (25-1000)	7.01 (25-1000)	6.80 (25-1000)	7.25 (25-1000)	7.09 (25-1000)	7.21 (25-1000)	3.84 -	4.5 25	4.7 (20-2127)	11.7 (20-1100)	9.4 (20-1100)

Table 2.3: Properties of Various Oxides

Oxides / Properties	**TiO_2**	**ZrO_2**	**HfO_2**	**V_2O_5**	**Ta_2O_5**	**Nb_2O_5**	**WO_3**	**Al_20_3**	**Cr_2O_3**
Crystal system	**Tetragonal**	**tetragonal**	**Cubic**	**Orthorhombic**	**Orthorhombic**	**hexagonal**	**Tetragonal**	**Hexagonal**	**orthorhombic**
Density (g/cm^3)	4.24	6.27	9.68	3.36	8.73	4.95	6.47	3.97	5.21
Melting point (^oc)	1855-1885	2900	2780-2790	670-685	1755-1815	1470-1510	1473-2130	2050	2309-2359
Specific resistance ($\mu\Omega.cm$)	$3x10^{10}$	-	-	$3x10^7$	$1x10^{11}$	-	$2x10^{11}$	$1x10^{22}$	-
Thermal conductivity (CGS)(RT)	.008-.015	.0047	.0011	.0010	-	-	-	.095	-
Microhardness (kg/mm^2)	1000	1300-1500	940-1100	-	890-1290	726	-	2300-2700	2915
Elastic modulus (kg/mm^2)	24000-29000	25000	-	-	-	-	-	37000	-
Coefficient of thermal expansion ($10^6.deg^{-1}$)(^oc)	8.85 (25-1000)	10.8 (25-1200)	6.45 (20-1700)	-	-	-	-	8.1 (20-1000)	9.6 (20-1400)

Table 2.4: Properties of Various Borides

Borides / Properties	TiB_2	ZrB_2	HfB_2	VB_2	TaB_2	NbB_2	W_2B_5	CrB_2	FeB	Fe_2B
Crystal system	hexagonal	hexagonal	Hexagonal	Hexagonal	Hexagonal	hexagonal	hexagonal	Hexagonal	Orthorhombic	tetragonal
Density (g/cm^3)	4.38	6.17	10.5	5.06-5.28	12.38	6.97	11.0	5.22	7.15	7.34
Melting point (^oc)	2790	3200	3250	2400	3037	3000	2370	2200	1650	1410
Specific resistance ($\mu\Omega.cm$)	6.4-9.1	9.7	10.6	22.7	32.5	25.7	22.0	30	80	38
Thermal conductivity (CGS)(RT)	.154	.138	.122	.101	.038	.057	.125	.076	.029	.072
Microhardness (Kg/mm^2)	3310-3430	2230-2274	2400-3400	2797-2813	2460-2540	2600	2650-2675	2020-2180	1600-1700	1290-1390
Elastic modulus (kg/mm^2)	54000	35000	-	27300	26200	65000	79000	21500	35000	29000
Coefficient of thermal expansion ($10^6.deg^{-1}$)(^oc)	4.6 (27-1027)	5.9 (27-1027)	6.3 (27-1027)	7.6 (27-1027)	8.2 (27-1027)	8.0 (27-1027)	7.8 (27-1027)	10.5 (27-1027)	~12 (400-1000)	11.5-12.1 (20-800)

Source: Oki, T. (2008)

coefficient, good heat resistance, corrosion resistance, electric properties, although their thermal – shock resistance and mechanical strengths are not good yet. The low elasticity of these ceramics is detrimental rather than beneficial. The new ceramics coating is one treatment which can resolve such a disadvantage by combining these brittle new ceramic films with ductile substrates. Therefore it might be regarded as a composite manufacturing process. Recently the differences in properties between ceramic films and ceramics themselves have become clear, which is very interesting in the view point of surface functions of these ceramics [1, 6].

2.5 Significance of Fine or New Ceramic Coating

Ceramic coatings can give some new functions, particularly the properties which are composite to the material substrate surface. Main applications of the ceramic coatings are described as follows: components for wear resistance, hot resistance and packing parts, and mechanical seals; these are coated with Al_2O_3, TiN, TiC, SiC etc. Electrical materials (functional materials) such as transparent conductive films are In_2O_3, SnO_2, etc, for infrared cut filters and strong dielectric substances $BiTi_3O_{12}$ is used, and for piezoelectric films ZnO is used. In addition Al_2O_3 is applied in the coating of lens by utilizing its transparency. AlN is used as insulative film Si_3N_4 and SiC as semiconductor devices, TiN, TiC, TaN, and TaC as emitter materials, and transparent SiO_2 thin film as infrared ray cut filter, resistant devices, dielectric substances and lens coating [1, 2, 6]. It is normally required nowadays that mechanical components should undergo higher loading, and that electronic materials have more diversified functions. Materials usages are inclined to increase more and more in this twenty first century, if the properties of ceramics are studied and revealed further (e.g. the electric, magnetic, thermal and mechanical properties of non-stoichiometrical compounds by reactive ion plating, etc), the uses of new ceramic coating will definitely increase more and more. Recent trends in the application of new [1, 3, 6] ceramic coatings with new properties is very significant.

Ceramic coating processes can be classified as follows:

i). **Chemical Vapour Deposition (CVD)**

CVD utilizes chemical reactions in gas phases in order to coat the new ceramic on a substrate. Low pressure CVD for controlling the surface state and plasma CVD which promotes reactions at relatively low temperatures are recently being developed.

ii) **Physical Vapour Deposition (PVD)**

All PVD processes are considered as vacuum vapor deposition as well its application process. For new ceramic coatings there are many processes utilizing chemical reactions, e.g vacuum vapor deposition, sputtering, ion plating and so on with and without reactive gases. Low temperature plasma is utilized effectively to improve reactivity and characteristics of produced films. Ion implantation being new in the lime light is one of PVD processes and very interesting (1, 7).

iii) **Chemical Densified Coating Process (CDC)**

This process utilizes the decomposition reaction of compounds crated on the substrate. The coating of chromium oxide is utilized in practical uses to improve the wear resistance of components and materials [1, 8] some rocket parts and jet engine components are coated using this process.

vi) **Other Processes**

Besides the above mentioned processes, carbide coating, and boride coating using molten salts, ion nitriding, ion carburizing, spray coating, composite plating, diamond coating and i-carbon coating are being developed. These processes have the characteristic that film

formation takes place through catalytic contact reactions of the interface between substrate and gas phases or liquid phases, [1,8]. This various properties will be explained.

2.6 CHEMICAL VAPOR DEPOSITION (CVD)

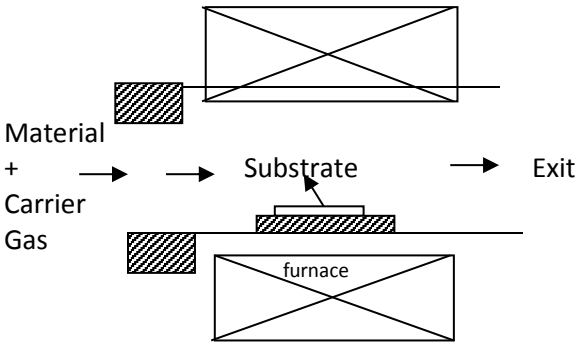

Figure 2.3, Schematic Illustration of CVD Process

Basic apparatus is shown schematically in figure 2.3. CVD is the process in which metal nitrides, carbides, borides and other compounds are deposited on material substrate surfaces through catalytic contact reactions at the interface between substrate and vapor phases. For example the following reactions take place on the surface of steels to produce titanium carbide and tantalum nitride.

$3TiCl_3 + C_3H_8 + 2H_2 \xrightarrow{1000^0C} 3TiC + 12HCl$

$2TaCl_5 + N_2 + 5H_2 \xrightarrow{700^0C} 2TaN + 10HCl$

In many CVD processes, excessive heat affects film formation, elevated temperatures in the range of 700^0C to 1000^0C normally create adhesion problem. In order to avoid this disadvantage intermediate undercoating is sometimes required. Recently plasma CVD in which low temperature plasma makes the film formation at relatively low temperature possible is being investigated to overcome such disadvantage. Representative CVD processes are listed below:

Substrate reaction method: $Ti + 2BCl_3 + 3H_2 \xrightarrow{1000^0C} TiB_2 + 6HCl$

Thermal decomposition method: $CH_3SiCl_3 \xrightarrow{1400^0C} SiC + 3HCl$

Hydrogen reduction method: $WF_5 + 3H_2 \xrightarrow{700^0C} W + 6HF$

Reaction Vapor deposition method: $TiCl_4 + C_3H_8 + H_2 \xrightarrow{1000^0C} 3TiC + 12HCl.$

Gas phase transport method: $Ti + TiCl_4 \xrightarrow{1000^0C} 2TiCl_2 \xrightarrow{600^0C} Ti + TiCl_4$

On the other hand diamond and i-carbon coating by plasma CVD are of recent research interest and many studies are going on in this area [7].

$CH_4 + nH_2 \longrightarrow C$ (diamond, i-carbon, graphite) + $(n+2)\ H_2$.

The diamond has high hardness and good thermal conductivity, in spite of its high insulation. Therefore diamond coatings are very interesting and it is expected that the technology will develop more in the future [7].

Kazuki kawata in his paper tittled Development of mass-production-type plasma chemical Vapour Deposition equipment and its application to various dies'' explained the development of a PCVD equipment and its applications to dies where it is used in producing different types of ceramic coatings on the dies. According to him there are generally two processes namely chemical vapour deposition (CVD) and Physical Vapour Deposition (PVD), for surface treatment of dies, however, these processes have advantages and disadvantages. In the CVD process, the adhesion and throwing power of the film are excellent, but the process tends to cause deformation and a change in dimensions due to high temperatures in the 1273k range required during the treatment stage. On the contrary, the PVD can suppress deformation and a change in dimensions during low temperature treatment, but the adhesion and throwing power are inferior to those of the CVD process. Consequently there have been a large number of laboratory investigations on the plasma chemical Vapour deposition (PCVD) process which is believed to offset the defects of both the CVD and the PVD processes.

2.6.1 Comparison of various surface treatment processes

Table 2.5 compares the characteristics of the various surface treatment processes in use. From Table 2.5 it can be seen that the PCVD process which involves low temperature treatment is applicable to dies requiring high degree of dimensional accuracy. Under the PCVD process, processing pressures are between those of the CVD and PVD processes and the feedstock gas can be feed from all directions. For these reasons, the PCVD process gives much greater film throwing power than the PVD process does. The film adhesion under the PCVD process has also improved substantially over that obtained in traditional processes for reasons of higher plasma density, diffusion hardening treatment etc.

Since all feedstock is fed in gaseous form, dense films free from pinholes and droplets can be formed. It is easy to apply partial coatings; no lapping is needed after surface treatment under the PCVD process. This process is also suited to surface treatment of large, heavy and long objects.

Table 2.5: comparison of various surface treatment Processes

Parameter (units)	PCVD	CVD	PVD
Temperature (k)	573-873	1273	573- 873
Pressure (Pa)	1.3-1.3x 10^3	6x 10^3-1x10^5	1.3x10^{-2} - 1.3
Adhesion	good	good	inferior to CVD
Throwing power	superior to PVD	Good	bad
Density	good	bad	inferior to PCVD
Partial coating	possible	difficult	possible
Dimensional accuracy	good	bad	good
Post-lapping	unnecessary	necessary	unnecessary
Pre-washing	easy	easy	care required

2.6.2 Outline of Equipment

A drawing of the mass-production–type PCVD equipment is given in fig.2.4 and the specifications of workpieces treated by this equipment are 460mm in diameter and 800mm in height. Dies of mass 100kg or more each can be treated. The equipment is of external-heating construction, and thyristor control of a four-zone heater provides a uniform temperature distribution. An example of a gas composition in TiN film coating is as follows: N_2: Ar: H_2: $TiCl_4$ = 18.8:4:75:2.2. By selecting an optimum rotation speed, the out-furnace motor with inverter causes the work-pieces either to rotate and revolve or only to revolve, thereby improving the film thickness distribution and temperature distribution. Once the work-piece in process is set on the work-table, computer-controlled fully automatic operations including temperature increase, surface treatment and cooling are performed, making manpower almost unnecessary.

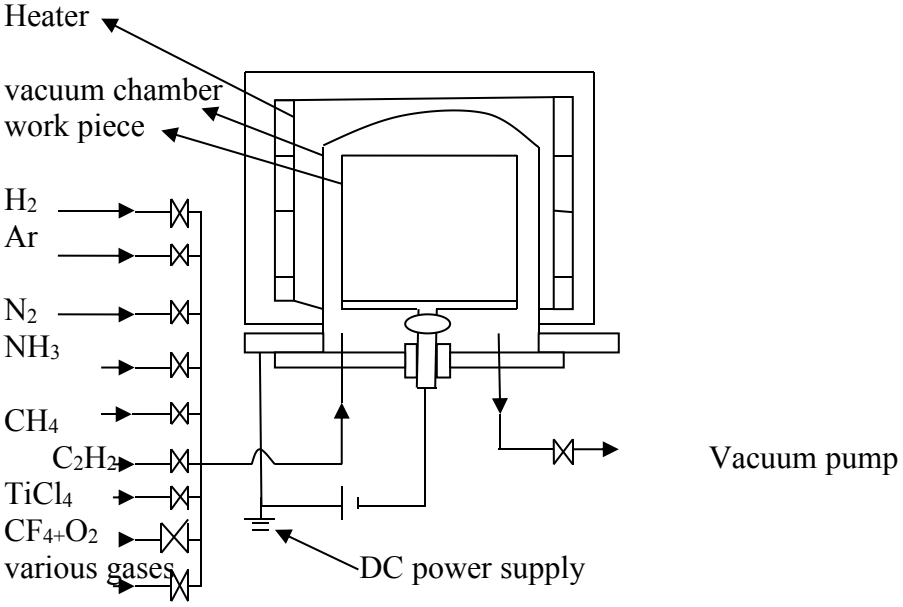

Fig.2.4 Schematic Diagram of the Mass-Production Type PCVD

Characteristics of film

TiN films produced by the PCVD process have a strong preferred orientation of (200) and approximately the stoichiometric composition. These films had a Vickers hardness equal to

that of films produced by the CVD and PVD processes, i.e, approximately 2000HV for TiN, approximately 3000HV for TiC and a value between those of TiC and TiN for Ti(C,N). The TiN films are found to have a more dense texture than that of the fracture surface in fig.2.5 as viewed by a scanning electron microscope.

Fig.2.5: Scanning Electron Micrograph of a PCVD TiN Film Coated on M2 Steel

Examples of actual application to dies
Cold –working dies
Generally, high temperature processes, such as the CVD process and the molten salt immersion process (TD process), are applied to cold working dies. However, the PVD process which gives a shorter life than high temperature processes has sometimes been employed for surface treatment of cold-working dies, requiring a higher degree of dimensional accuracy. The PCVD process has been applied to a wide range of cold-working dies with better results than those obtainable with the high temperature processes. Some of the better results are indicated in Table 2.6.

Table 2.6: Examples of Effectiveness of Plasma Chemical Vapour Deposition Application to Cold-working Dies

Applications	**Materials of dies**	**Durability Effects**
Cold-blanking punches (material worked, low carbon Steels, plate thickness, 3.1 mm)	M2 Steels (high speed tool steels)	non-coating, 20,000 shots PCVD, 330000 shots
Cold-heading dies (material worked, low alloy steels, Plate thickness, 5mm)	M2 steels (high speed tool steels)	CVD (TiC) 15,000 shots PCVD, 48,500 shots
Cold-forming dies (material worked, austenitic Stainless steels, plate Thickness, 1.6 mm)	D2 steels (cold-worked die steels)	TD process (VC) 25000 shots PCVD, 120,000 shots

Trimming dies	PM high speed tool Steels	CVD (TiC), 30000 shots PCVD, 61900 shots
Cold forging punches	M35 steels (high speed tool Steels)	non coating, 45,000 shots PVD (TiN), 45000 shots CVD (TiC +TiCN +TiN), 75000 shots PCVD, 150000 shots
Cold-working mandrels (material worked, austenitic Stainless steels)	PM high speed tool steels	TD process (VC), 530 pieces CVD, 780 pieces PCVD, 1200 pieces

Plastic moulds

Generally, the PVD process is applied to plastic moulds in terms of the dimensional accuracy required and surface roughness. However, the PVD process has disadvantages, such as the tendency to form pinholes or droplets and inadequate throwing power. The PCVD process gives such a highly dense film and long mould life that it is applied to peculiar moulds for optical discs demanding the highest degree of dimensional accuracy of all plastic moulds. This process is also applied to various types of plastic mould.

Hot working dies

The PCVD has the following advantages when applied to aluminium die casting dies.

1. Low temperature treatment does not cause deformation or a change in dimensions with pins and die cavities.
2. Good film throwing power enables uniform coating to be carried out in die cavities of complex shapes.
3. Combination with diffusion –hardening treatment gives aluminium die casting dies a high resistance to soldering, erosion, thermal checking and thermal cracking
4. Unlike the case of nitriding and sulphiding-nitriding, repairs involving welding are made easier because gases are not produced.
5. PCVD process applied to aluminium extrusion dies give it a much longer life than the nitriding process does since it permits coating of narrow and deep slits.

2.7 Physical Vapor Deposition (PVD)

Generally speaking, PVD is the process in which vaporized materials deposit as compounds on the substrate through reactions with reactive gases, ceramic coating can be achieved by evaporation or sputtering ceramics e.g several oxide films are produced only by evaporation. PVD processes are mainly classified into the vacuum vapor deposition, the reactive sputtering and the reactive ion plating. See figure 2.6 for the schematic illustration of the processes.

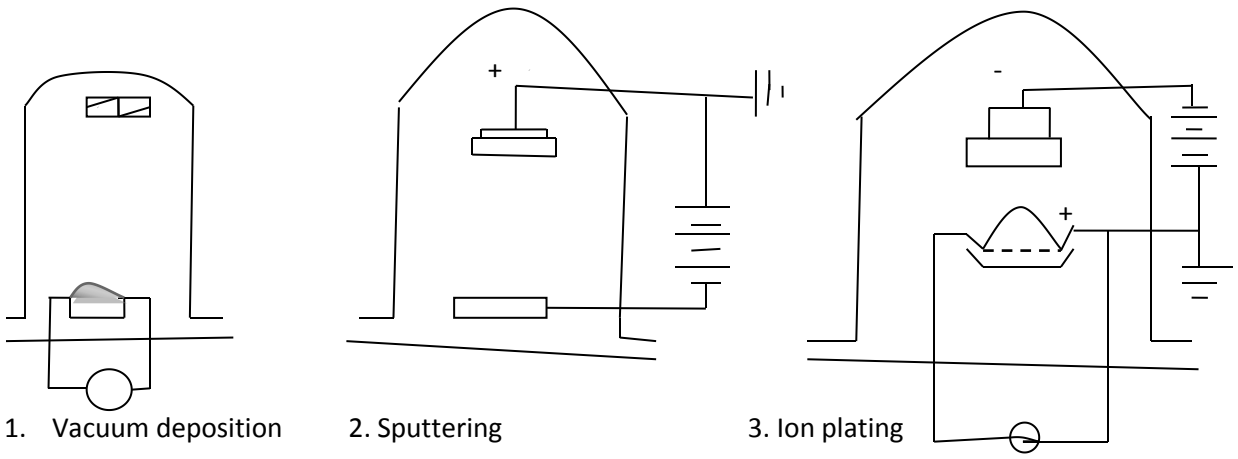

Figure 2.6: Schematic Illustration of PVD Process.

In the vacuum vapor deposition process, the system is evacuated at 10^{-4} - 10^{-7} mmHg to have various compound films deposited on the substrate.
In the sputtering processes, Ar gas is induced into the vacuum chamber at 10^{-3}-10^{-2} mmHg. Voltage of 1 - 5kv is applied to the intended ceramics as negative electrode. And glow discharge takes place in the vacuum chamber, where positive argon ion collides with the negative ceramic target and sputters part of it to deposit on the substrate. Prominent features of this process are to produce films of high melting point materials at relatively low temperatures, to keep the composition constant from target to film and to be able to form various kinds of ceramic film by reacting with induced gases. It`s very interesting to consider sputtering as one method of vaporizing at low temperatures.
Reactive ion plating is the process in which vaporized metal is ionized or activated to produce compound film on material surfaces through reaction with environmental gases. In this process plasma promotes the chemical reactions and adhesion of produced films at relatively low temperatures. Ion plating is classified into various types from the view point of the way of ionization or activation, see figure 2.7

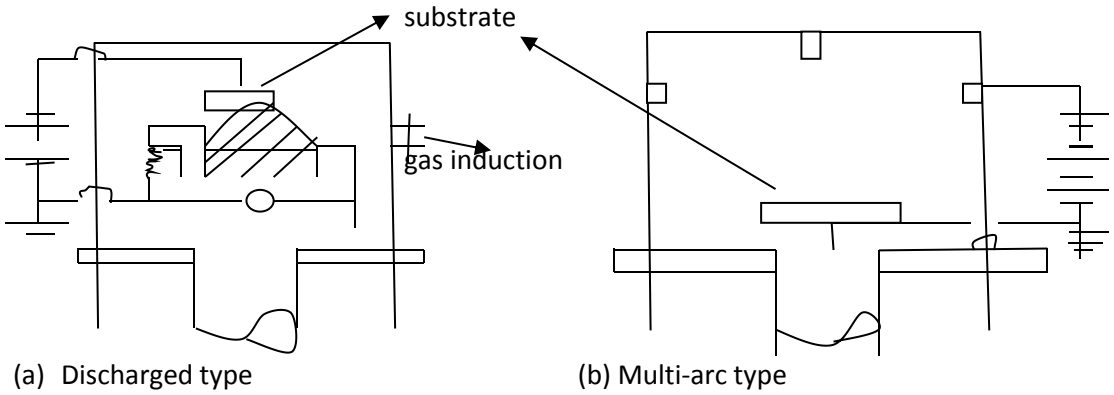

Figure 2.7: Schematic Diagram of some ion Plating Devices

For example total reactions for the formation of titanium carbide and titanium nitride is described as follows:

$Ti + 1/2C_2H_2 \longrightarrow TiC + H_2$

$Ti + 1/2N_2 \longrightarrow TiN$

Reactive ion plating makes it possible to produce Al_2O_3, TaC, ZrC, ZrB_2, SiC, films, etc as the reaction in this process proceeds in the non-equilibrium state, various phases of titanium nitrides and carbides are produced on the surface of the substrate. The principle leads to the development of the coating process of new ceramics which is term the artificial new ceramics.

The mechanism can be generally described as follows:

$M \longrightarrow M_{gas} \xrightarrow{\text{ionized, activated}} M^+ + M^* \longrightarrow$ Reactive compound films on substrate.

Reactive gas $\xrightarrow{\text{ionized, activated}}$ reactive gas^+ + reactive gas* → reactive compound films on substrate.

For the formation of nitride films, N_2 and NH_3 gas are used as reactive gas, CH_4, C_2H_2, C_2H_4, C_3H_3, etc for carbide films, O_2 gas for oxide films and BH_3 and BCl_3 for borides [7,9,10]

2.8 Chemical Densified Coating and Other Process

2.8.1 Chemical Densified Coating (CDC)

This process utilizes the chemical- thermal decomposition to coat porous structural ceramic films and to densify them. The example of the coating is chromium oxide as explained below:

A hydrous chromic oxide is dissociated by heat. The reaction can be described as follows:

$2CrO_3 \longrightarrow Cr_2O_3 + 3/2O_2$

Cr_2O_3 is deposited by this reaction. In practical uses, the substrate is coated by SiO_2-Al_2O_3 compound called 'base coat' at the thickness of about 30 -100μm, chromium acid solution as binder is added into the film and heated. As a result, the ceramic film of more than 1200-1300 HV can be coated on the substrate. Even if the base coat is not used, a thin Cr_2O_3 film can be coated. This is one of the best and prospective surface modifications in the aspect of making use of the good properties of Cr_2O_3 [1, 6]. Ceramic coating by chemical thermal decomposition will advance surface modification technology further as research to perfect the process continues [8].

2.8.2 Carbides Coating and Borides Coating. Process by Molten Salt

When materials containing carbon are immersed into molten neutral or borax salts into which carbide forming elements are added as powder, carbide films form on material substrate surfaces. And the treatment in boron containing molten salts leads to the formation of FeB or Fe_2B; the hardness range is 1800 - 2100kg/mm^2. This process enables low grade steels to have high wear resistance, heat resistance and corrosion resistance. Composite films such as V-Nb-C and Ti-V-C can be produced by this process. The disproportionate reaction is considered as the main mechanism [1, 6].

2.8.2.1 Boriding Process

In the boriding process using molten salts, a material is treated by placing it in a salt bath containing boron- in which borax is generally the main constituent-and adding boride metals that contain boron (B) or halogenated boride salts. The material undergoes treatment when it is subject to replacement reaction or reduction reaction at 900-1000^{0}C. This can be done either by a simple immersion method or by electrolytic method.

Borides are extremely hard and have excellent abrasion resistance, corrosion resistance, and heat resistance. When iron and steel is treated in a borax-containing molten salt bath at 950^{0}C, a layer of FeB (with a hardness of Hv 1,500) is formed on the surface and a layer of Fe_2B (with a hardness of Hv 1,200) is formed beneath the FeB layer. The formation of the boride layers is quicker with the electrolytic boriding process comparison to other methods.

2.8.3 Spray Coating

These processes; such as high temperature plasma spray coating, explosion spray coating and so on requires high temperature or energy. They are not suitable for ceramics decomposing at elevated temperatures. Ceramic films are inclined to be porous, as the melting points are generally high. If this tendency is taken into consideration, the process has no problem with ceramic coatings. Low pressure spray coating inhibits the change of components by oxidation. A bit of binder is applied to improve the adhesion, when the mixture does not hinder the properties of the ceramics. Even with this treatment the problem of pores, do remain unsolved sometimes [8].

2.8.4 Composite Plating

Ceramics such as SiC, WC, TiC, Cr_7C_3, Al_2O_3 are dispersed in plating metal e.g. Nickel, which results in the improvement of wear resistance. Nickel plating dispersed SiC has been put to practical use [11].

2.8.5 Sol-Gel Process

Metal alkoxides sol such as $Al(OC_2H_5)_4$, $Al(OC_4H_9)_3$, $Ti(OC_3H_{11})_4$ and so on, painted on materials becomes thin films through thermal decomposition and hydrolysis. The calcination temperatures depend on the properties of the produced films and is about 100-1100^{O}C [1].

2.9 Points and Characteristics for Application

These processes mentioned above are generally applicable to various material substrates. But one has to pay attention to softening temperatures of substrate, their elasticity and the difference in thermal expansion between substrate and coated ceramics, this is important for ceramic coatings at elevated temperatures. For this purpose undercoating is often required (particularly for the coating on metal surfaces). As the thickness of the film grows, the larger the effect of thermal expansion becomes. Thermal expansions of various ceramics are summarized in Table 5. For steels multilayer coatings are sometimes needed. For aluminum; one must pay attention to the oxide surface film and softening, but anode oxide films are often applicable. For copper alloys, low temperature treatments are required to get a good adhesion. If all these points are addressed, ceramic coating can be widely used. It is expected that the processes will be developed by the study on the properties of produced films [1].

Table 2.7: Coefficient of Thermal Expansion α [10^{-5}/ ^{O}C]

Element	**Nitride**	**Carbide**	**Oxide**
Ti(0-100°C) 8.9	TiN(180-27^{O}C) 3.02-4.78	TiC (25-1000^{O}C) 7.95-8.58	TiO_2 (20^{O}C) Ti_2O_3 (20^{O}C) 7.5 9.0
Zr (0-100°C) 4.4	ZrN (-180-27^{O}C) 4.09-4.62	ZrC (25-1000^{O}C) 7.01-7.42	ZrO_2 (20^{O}C) 3.8
Hf (0-100°C) 6.0	HfN (20-1000^{O}C) 6.9	HfC (20-1000^{O}C) 6.8-7.13	HfO_2 (20^{O}C) 3.8
V (0-100^{O}C) 8.3	VN (-180-27^{O}C) 9.2	VC (25-1000^{O}C) 7.25-7.45	-
Ta(0-100°C) 6.5	TaN(20-700^{O}C) 3.6	TaC (25-1000^{O}C) 6.5-7.12	-
Nb (0-100°C) 7.2	NbN (20-1000^{O}C) 10.1	NbC (25-1000^{O}C) 6.88-7.25	-
W(0-100^{O}C) 4.5	-	WC(25-1000^{O}C)	WC_2 (20^{O}C) WO_3(20^{O}C) 2.6 16.4
Al(0-100°C) 23.5	AlN(20-300^{O}C) 4.8	-	Al_2O_3 (20°c) 5.4
Cr(0-100°C) 6.5	CrN(20-800°c) 2.3	Cr_7C_3(20-1000^{O}C) 9.4	Cr_2O_3 (20^{O}C) 8.8
B (20^{O}C) 4.7	α-BN(20^{O}C) 1.8	B_4C (20^{O}C) 4.5	-
Si(0-100°c) 9.6	Si_3N_4(20-1000^{O}C) 2.75	β-SiC(25-1000^{O}C) 4.7	SiO_2 (20°c) 10.3

Source: Oki,T. (2008)[1]

2.10. Prospects for the Future

Various properties and new performance of new ceramics or artificial ceramics has been found, which made this technology more applicable as high performance surface, modified surface, composite surface, and functional surface. For example the practical applications of nitride and carbide films are shown in Table 6 and 7. Some coating processes such as ion

plating can produce non-equilibrium phases on the surface, application field will expand more and more, particularly in this 21st century of advanced technology [13].

It is expected in future that new functional materials by ceramic coating such as semi-conductor, metallic materials, ceramics and plastics will be investigated and developed, and that new thin films such as ultra fine particle films, amorphous films, super conducting films and diamond films will be developed, and that structural materials on which corrosion resistance, heat resistance, wear resistance films, are formed will be developed. These areas are currently receiving serious studies and investigations, and great deal of progress is been made [1, 2, 12, 14].

Table 2.8: Properties and Application of Various Nitrides

Nitrides	Properties					Application
	Density(g/cm^3)	**Melting point (^oc)**	**Specific resistance (μΩ.cm)**	**Microhardness (kg/mm^2)**	**Coefficient of thermal expansion [$10^{-6}\ ^oC$]**	
TiN	5.44	2900-3200	22-130	1800-2100	9.35	Wear resistance, cutting tool, die, ornaments, cases for watches.
TaN	14.1	2980-3360	135	1060	3.6	Wear resistance, cutting tools, and ornaments.
AlN	3.25-3.30	Decomposition 2200-2300	$2x10^{17}$	1225-1230 (KH)	5.0	Heat resistant insulator, ultra-hard heat resistant structural materials
BN	2.15-2.27 3.48-3.49	Decomposition 2200-3000	$1.7x10^{13}$	4700	4.8	Heat resistance,corrosion resistance, die cast, insulation, electronic materials, and thermal conductivity
Si_3N_4	3.18-3.19	Decomposition 1900	$>10^{13}$	2570-3260	2.75	Heat resistance

HfN	13.94	3300-3307	32	1500-1700	6.9	Corrosion resistance
NbN	8.26-8.4	2050	200	1400	10.1	Electric conductance, electric tube for sending images.

Table 2.9: Properties and Application of Various Carbides

Carbides	**Properties**					**Application**
	Density (g/cm^3)	Melting point (^oC)	Specific resistance ($\mu\Omega cm$)	Microhardness (kg/mm^2)	Coefficient of thermal expansion [10^{-4} /^oC]	
TiC	4.85-4.93	3180-3250	70-173	2900-3200	6.4	Wear resistance, heat resistance, cutting tool, ceramic tools.
WC	15.6-15.7	2627-2900	53	2400	3.7	Wear resistance, heat resistance, hard metal tools (WC-Co)
TaC	14.48-14.65	3740-3880	20-175	1800	5.6	Wear resistance, ceramic tools, heat resistance
B_4C	2.50-2.54	2350-2470	0.3-0.8	2400-3700	4.5	Wear resistance, electron

						absorber.
SiC	3.21-3.22	Decomposition 2200-2700	10^9-10^{11}	3000-3500	3.3	Wear resistance, heat resistance, corrosion resistance, high grade materials for furnaces
HfC	12.20-12.70	3885-3890	60	2533-3202	4.9	Heat resistance
ZrC	6.44-6.9	3175-3540	50-64	2600	4.0	Heat resistance, heat resistant alloys.
VC	5.36-5.77	2810-2865	150-160	2800	6.2	Wear resistance.

Source: Oki, T.[1]

2.11. Conclusion

New ceramic coating processes will be developed as outstanding technical innovations and this will be dreams and hopes come true for the engineers and material scientists. This breakthrough will introduce diversified and complex technology to our industrial world. The current ceramic coatings have no doubt contributed in raising performance, functionality, durability and efficiency in most machineries and systems it is believed that new ceramics will play a major role in the development of advanced materials and smart materials which are expected to characterize the 21st century.

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3.0 CHAPTER THREE
UTILIZATION CHARACTERISTICS OF MOLTEN SALTS IN SURFACE FINISHING

3.1 Introduction

Surface finishing (property modification) is the process of imparting various desired functions to the surface and surface films of materials such as metallic materials, including ceramics.

It can be said that molten salts are solvents with many properties that make it possible to employ them in industrial use. Depending on the purpose, molten salts are often superior to water solvents. In general, if proper selection is made, molten salts can dissolve many substances, including metals, non-metals, oxides, and various salts. In various combinations such as these, it is possible to impart various chemical or physical properties to molten salts. Water solvents can be used from normal room temperature to about $100^{O}C$. Meanwhile, molten salts range from NaCl-KCl-$AlCl_3$- based molten salts with a fusion point of $89^{0}C$ to those used in molten salt electrolysis of aluminium with a fusion point of approximately $1000^{0}C$. Moreover, by choosing salts such as fluoride –based salts, it is possible to use molten salts over wide temperature ranges up to more than $1300^{0}C$ as a liquid medium, heat medium, and chemical medium. It can be said that molten salts are excellent media that can adjust reactivity, heating effects, etc. in addition the film effects of these molten salts reduce the effect of the atmosphere and gaseous substances. It can be said that molten salts have the characteristics that enable high-temperature chemical reactions and high-temperature physical processing with simple devices.

Meanwhile, with regard to electrochemical properties, the decomposition voltage of water solvents is about 1.0 volt. In comparison, molten salts have high decomposition voltages- 2.6 volts at $700^{0}C$ for eutectic composition of CaCl-$MgCl_3$ and 3.5 volts at $700^{o}C$ for the eutectic composition of LiCl-KCl. Through the electrolysis of various salt constituents that use this as media, it is possible to obtain metals with an electrochemical potential more negative than hydrogen, that is not possible with water solvents, and these metals can also be made to contribute to surface finishing reactions. Molten salts are used in neutral heating and surface heat treatment by taking advantage of their characteristics such as heat capacity, heat conductivity, and reactivity. For low temperature heat treatment baths ($150\text{-}550^{o}C$), nitrous acids soda (fusion point: $280^{O}C$), potassium nitrate (fusion point: $336^{O}C$), potassium nitrite (fusion point: $297^{o}C$), nitric acid soda (fusion point: $310^{o}C$), and other nitric salts, as well as mixed salts composed of potassium hydroxide, caustic soda, and metal salts, are used. These low temperature molten salts are also used for cooling during quenching, but this group of molten salts develops high oxidizing properties when the temperature exceeds $450^{o}C$. They are also used for oxidizing the surface of steel after nitriding treatment. Medium temperature molten salts ($570\text{-}900^{O}C$) are also used for heating, but they are important as neutral molten salt baths used primarily for preventing the oxidation or decarburization of base material steel. They are primarily mixed salts consisting of NaCl, KCl, $CaCl_2$, and $BaCl_2$, and $BaCl_2$-KCl, $BaCl_2$-NaCl, $BaCl_2$-$CaCl_2$-NaCl, KCl-LiCl, NaCl-KCl, $BaCl_2$-Na_2CO_3, etc. are used. For high temperature molten salts ($1000\text{-}1300^{o}C$), a wide variety of added salts comprised primarily of $BaCl_2$ are used. There are also mixed salts

containing borax ($Na_2B_4O_7$). This group of molten salts has problem with viscosity, hydrosolubility, etc. therefore, a wide variety of treatment is possible with the group of $BaCl_2$ salts.

3.2 Surface Reaction in Molten Salts Solvents

In order to achieve the desired surface treatment of materials by using chemical reactions or electrochemical reactions of molten salts, it is necessary to have the desired metals or non-metals constituents reach the material surface in a clean state. The process of surface reaction that takes place for this is thought to be as follows:

1. **Formation of desired constituents by electrolysis**: within molten salts, the metallic constituents of molten metal salts are generally produced metal ions (M^{2+}) through electrolytic dissociation, and non-metallic constituents similarly produce non-metal ions (N^{2-}) through electrolytic dissociation. At the cathodes and anodes, the desired constituents are produced by electrolysis through the following reaction:

   $M^{3+} + 3e \longrightarrow M \qquad N^{n-} \longrightarrow N + ne$

   At the time they are generated, the active M and the active N react with the basal plate and form an alloy film, a compound layer, etc. on the surface and thus used for surface finishing.

(2) **Chemical Replacement Reaction:** Through a chemical replacement reaction between the desired constituents in the molten salts and the base material (basal plate), the desired metal is made to precipitate on the surface of the basal plate, and the surface property is modified through the formation of alloys or compound in the process of the dispersion of the desired precipitated metal into the interior of the base material.

MCln + source material $\longrightarrow$ M (on negative base plate) + (source material constituents) Cln

(3) **Collision Reaction**: The desired constituent elements are made to be present in the molten salts beforehand (melted or dispersed). Surface property is modified through reaction and formation of alloys by taking advantage of the fusion point of the desired constituent elements and the source material.

M (dispersed or melted) + source material $\longrightarrow$ M – source material (surface)

(4) **Molten Salt Disproportionation Reaction:** Disproportionation reaction causes MCln, a constituent in the molten salt, to form the desired constituent element M on the surface of the basal plate material, and this M forms an alloy or compound on the surface of the material surface, resulting in surface modification.

MCln $\longrightarrow$ $M+MC_{n-1,}$ M + source material $\longrightarrow$ M - surface material (surface)

Material property modifications for the required purpose are achieved by primarily using these reactions and imparting physical and chemical properties to the material surface, I would like to discuss these surface property modifications by separating them into surface heat treatment and surface alloy / compound formation process.

3.3 Surface Heat Treatment using Molten Salts

In the case of employing the molten salts process, low temperature molten salts (150-550^{O}C) are used in heat treatment of light metals, tempering of steel products, and in austempering treatment, or in the cooling stage such as martempering and marquenching in the process of quenching steel products. As mentioned earlier, these low temperature molten salt baths are recommended to be used below 450-500^{O}C in order to avoid

changes or deterioration in properties and oxidizing effect that generally occur with nitrate salt-based molten salt baths at higher temperatures. Medium temperature molten salts (570-900^{o}C) are generally used in the quenching of steel products, mold steel, and tool steel, as well as in preheating, tempering, or austempering of high speed steel. High temperature molten salts (1000-1300^{o}C) are used in such processes as the quenching and solution treatment of stainless steels, austenitic stainless steel, and high speed steel.

With regard to molten salts used in surface hardening treatment, there are such processes as the carbon- nitriding process and the soft nitriding process, in which cyanide salts are primarily used; a process that primarily consists of the sulfurizing process, in which sulphide salts are added to cyanide salts; and the boride process, in which borate salts are primarily used.

3.4 Liquid Caburizing (carbon-Nitriding) process

This process is a method to carburize the surface of iron and steel by using molten salt reaction for the purpose of hardening iron and steel in order to improve their abrasion resistance and sliding properties. Although its objective is carburizing treatment, this process generally uses cyanide salts as the main constituent for the desired carbon additive molten salts. It is called carbon nitriding because in addition to the penetration of carbon, a nitriding effect takes place at the same time. As indicated in the formula below, cyanide salt break down into various types of salt as a result of the change in properties of the molten salts constituents due to oxidation at the processing temperature, as well as a result of the carbon nitriding effect. This makes it necessary to keep the constituents under control in order to maintain the carbon nitriding power. One of the base salts is comprised of such constituents as 10-23% NaCN, 0-25% KCl, 20-40% NaCl, up to 30% Na_2CO_3, and 0-10% alkaline metal salts (specific gravity: 1.76 (900^{o}C)). The reaction that occur within the molten salts are listed here:

$$2NaCN \longrightarrow Na_2CN_2 + C \quad (1)$$
$$2NaCN + O_2 \longrightarrow 2NaCNO \quad (2)$$
$$NaCN + CO_2 \longrightarrow NaCNO + CO \quad (3)$$
$$NaCNO + C \longrightarrow NaCN + CO \quad (4)$$
$$4NaCNO + 2O_2 \longrightarrow 2Na_2CO_3 + 2CO + 4N \quad (5)$$
$$4NaCNO + 4CO_2 \longrightarrow 2Na_2CO_3 + 6CO + 4N \quad (6)$$

These reactions occur, resulting in the formation of NaCNO, CO, N, Na_2CO_3, and C. The generated CO and C contributing to the carburization, and N become involved, depending on the conditions.

$$Fe + 2CO \longrightarrow Fe\,[-C] + CO_2 \quad (7)$$
$$\left\{\begin{array}{l} 2CO \longrightarrow C + CO_2 \\ Fe + C \longrightarrow Fe\,[-C] \end{array}\right\} \quad (8)$$

In the case of thin film quenching steel, high cyanide salt concentrations are used for the low temperature side in the range of 845-900^{O}C. when seeking eutectoid carbon content concentration of 0.8% for use as iron and steel material, the base salt mentioned above is used. In case the hypoeutectoid carbon content concentration is less than 0.8%C, the

temperature and the cyanide salt concentration level should be lowered. In contrast, when hypereutectoid carbon content concentration that is greater than 0.8%C is sought, the cyanide salt concentration level must be raised. In case of thick film quenching steel, the base to be used at 900- 955^{O}C should be 6-16% NaCN, 30-55% $BaCl_2$, 0-20%KCl, 0-20% NaCl, up to 30% Na_2CO_3, and 0-10% alkaline metal salts (specific gravity: 2 (925^{O}C)). When the NaCN concentration exceeds 30%, carbon scum is generated due to the breakdown of NaCN. Therefore, it becomes necessary to lower the concentration of NaCN in case of a high – temperature bath. For example, the standard would be 14-23% at 815^{O}C and 6-12% at 955^{O}C. When the temperature is relatively low, nitriding becomes dominant.

$$5NaCNO \longrightarrow 3NaCN + Na_2CO_3 + CO_2 + 2N \qquad (9)$$

3.5 Soft Nitriding Process

Alkaline salts that primarily have the cyanogen radical or the cyanic acid radical are used as molten salts for the soft nitriding process. This process mainly involves nitriding, which occurs as a result of active N, which is formed when NaCN, KCl, NaCNO, KCNO, etc break down. Reactions such as in formulas, 2), 3), 4), etc. are important. In addition, as a result of the formation of N and C due to reactions such as

$$3NaCNO \longrightarrow NaCN + Na_2CO_3 + C + 2N \qquad (10)$$

As well as

$$4NaCNO + O_2 \longrightarrow 2Na_2CO_3 + CO_2 + 4N + C \qquad (11)$$

Nitriding and slight carburization occur at temperatures of 570-580^{O}C in the ratio of roughly C: N: 1:4. This ratio grows smaller with the rise in the temperature. This is because it is at this temperature that N, which has a high dispersion speed within iron, penetrates deep. The basic bath consists of 0-3% cyanogens salt and 34-36% CNO salt, and takes place in device bath materials of Ti or inconel materials. There are reports of nitriding Ti cathode material by adding KNO_3, KNO_2, Li_3N, etc. to LiCl-KCl at 450^{O}C by employing electrolytic reactions.

3.6 Sulphurizing Process

When treating iron or steel with molten salts by mixing sulphide salt into molten salts consisting of neutral salts or reducing salts in order to reduce the friction coefficient of the surfaces of iron or steel or improve their abrasion resistance, the sulphide salts break down at the processing temperatures to form loose ions, etc. as a result of this, sulphurizing takes place. It is also possible to employ a method in which NaCN, etc, are used and surphur compounds are mixed with them. With this method, however, it is necessary to take the stability of the baths into consideration. The basic composition of molten salts for sulphurizing is as follows: 70% NaCNO-Na_2CO_3 system (eutectic temperature: 450^{O}C) and 74% NaCN-Na_2CO_3 system (eutectic temperature: 550^{o}C), and NaCNO-NaCN-Na_2CO_3 system (eutectic temperature: 400^{O}C), and as added sulphur compounds for sulphurizing effects, Na_2S, Na_2SO_4, $Na_2S_2O_3$, Na_2SO_3, etc, are used. $Na_2S_2O_3$ is stable up to about 100^{O}c, but starts to break up gradually around 120^{o}C. near 120^{o}C,

$$Na_2S_2O_3 + 3O_2 \longrightarrow SO_2Na_2SO_4 \qquad (12)$$

At 310-385^{O}C, reactions such as below take place.

$$Na_2S_2O_3 \longrightarrow Na_2SO_3 + S \quad (13)$$

Furthermore, at 400- 500^{O}C, active sulphur formed due to such reactions as

$$4NaS_2O_3 \longrightarrow 3Na_2SO_4 + Na_2S_2 \quad (14)$$
$$Na_2S_2 \longrightarrow Na_2S + S \quad (15)$$

Begin to take effect as chemical species for the sulphurizing process. At 550^{o}C, the sulphurizing layer is thin-less than 0.1mm. when the temperature rises to 570^{o}C, however, the layer becomes defaced and eroded. In this instance, the sulphurizing effect that normally takes place does not proceed by itself alone. Since nitriding and carburizing brought about by the cyanogens salt that is the main constituent of the salt bath also takes place, a nitriding layer is present inside the sulphurizing layer, and FeS is formed on the surface. On the other hand, there is an electrolytic sulphurization method (Caubet process: at 180-200^{O}C) in which the material to be processed is immersed in a molten salt bath containing low-temperature rhodan salt. If the material is connected to an anode and electrolyzed, S is produced and sulphurization takes place, with FeS forming on the surface.

$$MSCN \longrightarrow M + SCN^-, \quad Na_2S \longrightarrow Na^+ + S^{2-} \quad (16)$$
$$SCN^- + 2e \longrightarrow S^{2-} + CN^-, \quad S^{2-} \longrightarrow S + 2e \quad (17)$$
$$Fe + S \longrightarrow FeS \quad (18)$$

With this kind of sulphurisation process the friction coefficient can be as lowered to 0.04

3.7 Carbide Film Process

If carbide –forming elements such as V, Cr, and Nb are added to a borax bath that is heated to 800-1200^{O}C and basal plate consisting of iron or steel that contains carbon is immersed in the bath a carbide film is formed on the surface of the basal plate. In addition it is possible to form various transition metal carbide films on the basal plate surface by using 29%NaCl-29%KCl-14%NaF-14%metal fluoride-14%metal system. Surface films consisting of such substances as VC, NbC, and CrC have excellent abrasion resistance, heat resistance, seize resistance, oxidation resistance.

3.8 Boriding Process

In the boriding process using molten salts, a material is treated by placing it in a salt bath containing boron-in which borax is generally the main constituent-and adding boride metals that contain boron (B) or halogenated boride salts. The material undergoes treatment when it is subjected to replacement reaction or reduction reaction at 900-1000^{O}C. This can be done either by a simple immersion method or by electrolytic method. Borides are extremely hard and have excellent abrasion resistance, corrosion resistance, and heat resistance. When iron and steel is treated in a borax-containing molten salt bath at 950^{o}C, a layer of FeB (with a hardness of Hv 1,500) is formed on the surface and a layer of Fe_2B (with a hardness of

1200Hv) is formed beneath the FeB Layer. The formation of the boride layers is quicker with the electrolytic boriding process comparison to other methods. A TiB_2 film is a material with high hardness and high corrosion resistance. It can also be obtained through electrolysis in a molten salt bath containing boric acid at (900^OC) or in a molten salt bath containing fluorides (at 700^OC). In addition, it is possible to obtain boride layers by adding Al, Ti, Mg, Ca, B_4C, SiC, etc. to this molten salt bath and producing active B.

3.9 Oxidized Film Process and Other Method

The process in which a fine film of magnetite (Fe_3O_4) is formed on the surface of a material to be treated in nitric acid salts used in molten salt baths for medium-temperature surface heat treatment can be applied to iron and steel materials to improve their corrosion resistance and seize resistance. There are also cases in which the process is used in applying color to Ti plates, etc. at 500^oC for a period of 120-900 seconds, such colors as gold, purple and blue can be imparted to Ti materials. With a 10% Na_2CO_3 - 4% Ferroniobium-10% Al_2O_3-20%NaCl-20% KCl system, NbC is formed on the surface of iron and steel, and if Ferroboron is added to this, a carbon boride layer is formed. If carbonate is used, a layer of carbide can be formed even if there is no carbon present in the base material. On the other hand, it is possible to obtain a film of TiC if such substances as K_2TiF_6 are added to a KCl-$BaCl_2$, NaCl-$BaCl_2$, or KCl-NaCl system and carbon –containing material is immersed in it. Next I would like to touch on the process that uses KCl-$BaCl_2$-NaF and KCl-NaCl-NaF system as base salts.

3.10 Mechanism for Disproportionation Reaction within Molten Salts and Surface Film Formation

Disproportionate reaction takes place in molten salts as a type of chemical transport method. In general disproportionate reaction results in a state of low valence at high temperatures, and at low temperatures, the reaction disproportionate into a high valence state and metals. In a general formula, it can be shown as follows:

$$nM + (z-n)\,M^* + TYT_{2Z}M^{(z-n)+} \quad (z-n>0,\ T_1>T_2) \qquad (16)$$

If, at this time, the M formulation reaction causes the activity of the material component M to form alloys of compounds, it will be possible to make a low valence disproportionation reaction and metal formulation disproportionation reaction to occur at the same time.

$nM(a_1) + (z-n)M \rightarrow zM(3-n)+2M^{(2-n)+}$ + basal plate$\rightarrow$nM (a_2, within alloy, within compound) + $(z-n)M^{2+}$ (activity a1> activity a2)

These two reactions can be shown together as follows:

M (a1) + basal plate$\rightarrow$ M (a_2, within alloy, within compound formed with the basal plate) in this way, it is possible to have the two reactions occur at the same time taking advantage of the change in activity of the disproportionation reaction and thus generate the surface film. The following shows an example of a reaction for the formulation of a silicide film on a Ni basal plate:

$$2Si + 2Si^{4+} \rightarrow 4Si^{2+} \qquad (17)$$

$$\underline{4Si^{2+} + 5Ni \rightarrow Ni_6Si_2 + 2Si^{4+}} \qquad (18)$$
$$2Si + 5Ni \rightarrow Ni_5Si_2$$
$$(a_1) \qquad (a_2)$$

3.11 Method by Alloying or Compounding with the Base Material Constituents

(i) **Alloying Film Formulation Process**

As an overall reaction within a KCl (-NaCl)- $BaCl_2$-NaF-MFn- M system molten salt, it can be considered a chemical transport dispersion reaction method that turns out as M (a_2 in source) → M (a_2 in alloy) ($a_2 > a_2$). Formulation of Fe-Si and Fe-Cr films is possible.

The Fe-Cr system can be shown in the following formulae:

$Cr + F^- + CrF^{7-} \rightarrow 2CrF^{4-}$

CrF^{4-} + Fe (basal plate)→Cr-Fe + F^- + CrF^{7-}

2) **Carbide Film Formulation Process**

$Ti + 6F^- + TiF_6^{2-} \rightarrow TiF_6^{4-}$

$2TiF_6^{4-}$ + C (within basal plate)→TiC + $6F^-$ + TiF_6^{2-}

$V + 2VCl_6^{9-} \rightarrow 3VCl_4^{2-}$

$3VCl_4^{2-}$ + C (within basal plate)→VC + $2VCl^{3-}_6$

The above reaction result in the formulation of films of TiC (1,750 Hv), VC (3,400 Hv), ZrC (1,490 Hv), and Cr-C (1,200-2,000 Hv)

3) **Borides**

Formulation of boride films is possible with the KCl (-NaCl)-$BaCl_2$-NaF-B_2O_3-

Ferroboron system. For example, with the following reactions:

$B + 2BF^{4-} \rightarrow 3B^{2+} + 8F^-$

$3B^{2+} + 8F^-$ + 2Fe (basal plate)→Fe_2B + $2BF^{4-}$

It is possible to obtain surface hardening films such as Fe-B film (1600 Hv), Ni-B film (1000 Hv), and Cr-B film (2,900Hv)

Formulation of Films of Compounds of Constituents not Found in Source Materials

The desired film of a compound for the surface of a material to be treated is formulated through a process involving disproportionation reaction of the molten salts, in combination with the reaction taken to the next level and so on.

(1) Alloy Film Formulation

Considering the formulation of a chrome silicide film on carbon steel, for example, the chromizing process takes place in the first phase and siliciding takes place in the second phase.

Phase 1: $Cr + Cr^{4+} \rightarrow 2Cr^{3+}$, $14Cr^{3+} + 3C$ (within basal plate)$\rightarrow Cr_7C_3 + 7Cr^{6+}$ (or Cr-Fe)

Phase 2: Cr_7C_3 (or Cr-Fe) + $Si \rightarrow CrSi^{2+}$ + C (or Fe)

Formulation of the film progresses depending on the reactions.

(2) Boride Film Formulation

Boride films with hardness of 3,000-4000 Hv, such as TiB_2, VB_2, and CrB_2, are formed by preparing carbide and alloy film layer in advance and subjecting these desired constituents to boriding process.

Phase 1: $Ti + Ti^{4+} \rightarrow 2Ti^{2+}$, $2Ti^{2+}$ + C (or Fe)$\rightarrow$TiC (or Ti-Fe) + Ti^{4+}

Phase2 : TiC (or Ti-Fe) + $6B^{2+} \rightarrow TiB_2$ + C (or Fe) + $4B^{3-}$

(3) Formulation of Nitrides and Carbide Films

Nitride films are formed by nitriding steel materials in the first phase, and the subsequent desired metallization causes nitride films to form on the surface. For example, by using 55% (NaCN + KCN)-25%(NaCNO + KCNO)-10%(Na_2CO_3 + K_2CO_3) + 10%(KCl + NaCl), etc, and treating the steel material at $570^{O}C$, Fe_3N, etc, are formed on the surface. This is then subject to chromitization process to form a CrN film. In carbide film formulation, the steel material is subject to a carburizing process in the first phase, and then subject to the desired metallization process, after which a metallic carbide film is formed.

M (metallization process) + C (carburizing process) $\rightarrow$MC (Film)

3.12 Application of Molten Salt Disproportionation Reaction to Surface Hardening

Introduction

Disproportionation reaction refers to reactions in which a single valence state (ionic valency) of a transition element, which shows more than two valence states as seen often in transition metal elements, changes to a zero valence state and another valence state (ionic valency), or to two different valence states. These reactions are expressed in the following formulas:

$M^{a+} \rightleftharpoons M + M^{c+}$ 1

$\mathbf{M}^{b+} \rightleftharpoons M^{a+} + M^{c+}$ 2

(provided that M: metal or element with more than two valence states: a,b,c, positive integers, a<b<c)
In the case of the well-known element titanium (Ti), the following reaction is often used:
$2TiCl_3 = Ti + TiCl_4$
(←:>1273K, →:<873K)
In the case of aluminium (Al), the following reaction is often used:
$3AlCl = 2AlCl_3$
(←:>1273K, →: <973K)
These reactions fall under the reactions in (1) shown above. Other than these, there are reactions that fall under (2) above, and one of these is as follows:

$2TiCl_3=TiCl_2 + TiCl_4$

The reaction involving titanium as in the example for the formula shown in (1) above is used as a chemical transport process, which is one form of the chemical vapor deposition (CVD) process, or as a gas phase transport process. This is carried out as follows: first as a result of the following reaction:

$Ti(s) + TiCl_4 (g)= 2TiCl_3 (g)$ (>1,273)

Titanium chloride gas (TiCl (g)) is produced, produced, and this gas is produced , and this gas is brought to a basal plate under approximately 873K to bring about the following reaction at the basal plate:

$2TiCl_2 (g) = Ti (S) + TiCl_4 (g)$ (873K)

To finally form a metallic titanium film on the basal plate. To give a detailed overview of the wide application of disproportionation reaction by providing a number of examples of disproportionation reaction in which molten salts are used. Generally, with molten salts, the various valence states in the molten state, unlike the case of gases, can be shown as the ionic states. Therefore, disproporttionation reactions in molten salts can occur as shown in the following formulas:

$3Al^{+} = 2Al + Al^{3+}$

$2Ti^{2+} = Ti + Ti^{4+}$

$3B^{2+} = B + 2B^{3+}$

$(3B^{+} = 2B + B^{3+})$

$2Si^{2+} = Si + Si^{4+}$

It is therefore possible to use these reactions effectively for surface hardening in various ways.

When metals or elements that dissociate and separate as a result of disproportionation reaction at a certain temperature are in a state in which they are able to disperse within the target basal plate material at that temperature, these metals or elements form a diffused layer, alloy layer, and compound layer by diffusing through the surface of the basal plate material, and impart special functions to the surface, such as, for example, surface hardness, corrosion resistance, abrasion resistance, and other properties. The reaction transition of the desired constituent M that has undergone disproportionation reaction occurs at the same temperature, and the overall reaction-upon taking the amount of activity into consideration- can be shown as follows:

M (within the material) →M (within the alloy or compound formed on the surface)

(activity a_1) (activity a_2)

Provided that $a_1>a_2$

Here, I would like to take up the topic of the direction and application of methods to harden the surface of metal materials, such as iron and steel, as well as other materials, by using this kind of disproportionation reaction. (These hardening processes can be considered chemical transport hardening process).

Surface Hardening Capable Target Constituents and their Effects.

various constituents and their various compounds that make surface hardening possible through disproportionation reaction will be shown here by citing examples with the objective of surface hardening through the high hardness carbides, nitrides, borides, and silicides.

Hardness of Substances of the Carbide Family

Various carbides that can be used for surface hardening are listed in the table below, along with their hardness (Hv) and melting point (^{O}C):

Table 3.1: **Hardness of Substances of the Carbide Family**

Carbide	Hardness (Hv)	Melting Point (^oC)
TiC	2900-3200	3180-3250
ZrC	2600	3,175-3540
VC	2800	2,810-2865
TaC	1800	3740-3880
HfC	2,533-3202	3,885-3890
NbC	2400	3,500-3,800
WC	2400	2627-2900
B4C	2400-3700	2350-2470
SiC	2,200-2700	3,000-3500
Cr-C	1663-1800	1518-1895
Mo-C	1499-1500	2680-2700

In this way, if surface hardening can be carried out by having a single substance or compounds that exhibits high hardness form on the material surface, improved abrasion resistance can be expected. In addition, hardness and abrasion resistance at high surface temperatures can be expected to be achieved if the melting temperature is high.

Hardness of Substances of the Nitride Family

Various nitrides that can be used for surface hardening are listed in the table below, along with their hardness (Hv) and melting point (^oC):

Table 3.2: **Hardness of Substances of the Nitride Family**

Nitrides	Hardness (Hv)	Melting Point (^OC)
TiN	1800-2100	2900-3220
ZrN	1400-1600	2930-2980
HfN	1500-1700	3300
VN	1500	2050-2360
TaN	1060	2980-3360
NbN	1400	2050
Si_2N_4	2670-3260	1900 (decomp)
AlN	1225-1230	2200-2300(decomp)
CrN	1000-1188	1500
BN(c)	4695-8600	1980(decomp)

If surface hardening can be carried out by having a single substance or compounds that exhibit high hardness form on the material surface, improved abrasion resistance can be expected. In addition, hardness and abrasion resistance at high surface temperatures can be expected to be achieved if the melting temperature is high. However, since oxidation can occur in the presence of oxygen, the absence of oxygen is preferred. Nevertheless, such substances as Si_2N_4 and AlN can be used in the presence of air at high surface temperatures. In addition, sialon, which composed of Si_2N_4, AlN, and Al_2O_3, has high strength and oxidation resistance.

Hardness of Substances of the Boride Family

Various borides that can be used for surface hardening are listed in the table below, along with their hardness (Hv) and melting point (^oC):

Table 3.3: Hardness of Substances of the Boride Family

Borides	Hardness (Hv)	Melting point (^oC)
TiB_2	3310-3430	2790
ZrB_2	2230-2270	3200
HfB_2	2400-3400	3250
VB_2	2797-2813	2400
TaB_2	2460-2540	3037
NbB_2	2600	3000
W_2B_3	2650-2675	2370
CrB_3	2020-2180	2200
FeB	1600-1700	1650
Fe_2B	1290-1390	1410
MoB	2350-2500	2180
WB	3700	2870-2970
ZrB	3500-3600	2942-3042

In this way, substances of the metal boride family exhibit high hardness in comparison to those of the nitride and carbide families. If surface hardening can be carried out by having a single substance or compound form on the material surface, improved strength and abrasion resistance can be expected. In addition, hardness and abrasion resistance at high surface temperatures can be expected to be achieved if the melting temperature is high.

Hard Substances of the Silicide Family.

Various silicides that can be used for surface hardening are listed in the table below, along with their hardness (Hv) and melting point (^oC)

Table 3.4: Hardness values of Silicides

Silicides	Hardness (Hv)	Melting point (^oC)
$MoSi_2$	1295	1980-2080
$TaSi_2$	1000-1200	2200
WSi_2	1090	2180
Ti_5Si_3	986	2120
ZrSi	1000	2095 (decomp)
$NbSi_2$	---	2000
$CrSi_2$	1150	1575

These substances of the metal silicide family have lower hardness in comparison to those that have been listed so far, but they have high melting points and can also be used in the presence of oxygen. Since they can be used as materials with oxidation resistance, corrosion resistance, and thermal resistance, they are added to metal carbides and hard substances of the metal boride family to improve their oxidation resistance. If surface hardening can be carried out by having a single substance or compound that exhibit high hardness and thermal resistance form on the material surface, high

hardness and abrasion resistance at high surface temperatures can be expected because of improved abrasion resistance due to surface hardening and because of excellent oxidation resistance.

Hard Substances of the Oxide Family

Various oxide that can be used for surface hardening are listed in the table below, along with their hardness (Hv) and melting point (^oC):

Table 3.5: Hardness Values of Oxides

	Hardness (Hv)	Melting point (^oC)
TiO_2	1000	1855-1885
ZrO_2	1300-1500	2900
Al_2O_3	2300-2700	2050
Cr_2O_3	2915	2309-2359
Ta_2O_5	890-1290	1755-1815
Fe_3O_4	1300-1400	---
HfO_2	940-1100	2780-2790

If surface hardening can be carried out by having a single substance or compound that exhibit high hardness form on the material surface, improved surface hardening and abrasion resistance can be expected, and as a result of the high oxidation resistance of the materials themselves, high hardness and abrasion resistance at high surface temperatures can be expected. There is interest in such substances as lanthanum chromate ($LaCrO_3$) that exhibits conductivity at high hardness. In addition, stabilized zirconia with a 5%-10% mixture of oxides, such as magnesia (MgO), Calcia (CaO), and yttria (Y_2O_3), and partially stabilized zirconia with the oxides slightly added can be used as materials with high hardness, strength, and toughness.

Disproportionation Reaction in Molten Salt Systems

Disproportionation reactions occur in various states of existence such as in gas systems, water solvent systems, and molten salt systems, and while they can be used under these conditions, the desired systems for these reactions are selected according to the various relationships of the reaction and formulation conditions.

Surface hardening reactions bring about diffusion, alloy formation, compound formation, etc, surface hardening properties can be made more effective in comparison to simple, physical formation of these films if gradient material properties are imparted as a result of adhesion, diffusion, alloy formation, etc. therefore, it is preferred that these reactions occur under conditions under which diffusion or alloy formation can occur- for example, temperatures at which these reactions occur.

Taking these points into consideration, processing reactions at temperatures of 500^oC- 1300^OC can easily be set up and implemented by selecting the molten salt structure accordingly. In addition, since the molten salts make it easy to isolate the processing from the external atmosphere, they also very favorable as a thermal reaction medium in comparison to gas and water solvent systems. Of course, disproportionation reaction occurs in gas systems, as in such cases as the formation of titanium coatings, for example. There is a surface hardening process in which titanium coatings, titanium diffusion layers, and titanium compounds are formed by adjusting the processing temperature through the following reaction:

$2TiCl_2 \rightarrow Ti + TiCl_4$

However, proper adjustment of the reaction conditions is complicated. In contrast, since disproportionation reaction in molten salt systems is a liquid system, the use of this reaction can be readily handled. Due to these reasons, I will move on with discussion on surface hardening reaction processing through disproportionation reaction using molten salt systems, but since processing can be carried out using other systems based basically on the same line of thinking, it can be said that the application is broad. In addition, there is a wider selection of reaction options and optimization of reactions is easier to achieve in comparison to reactions in the molecular state in gas systems because ionic-type disproportionation reactions can be used in the case of molten salt systems in systems in which chemical species are present. Here, I would like to present the methods for surface hardening processing through disproportionation reaction within molten salt systems by citing examples with regard to the possibilities and directions of these methods.

Molten salts are the source of supply for reactive materials necessary for reactions. They serve as the thermal source for disproportionation reaction and diffusion reaction of the desired constituents on the surface layer of basal plates. In addition, molten salts have an isolation effect that prevents ambient air from coming in contact with and affecting the basal plates and the hardened layers that have been formed.

Gay and others were the first to attempt using disproportionation reaction in moltensalts. They diffused nickel base plate material into compound molten salts consisting of KCl-NaCl-NaF-Na_2SiF^{6-}-Si and brought about silicide processing of nickel according to the following formula:

$4Si^{3+} + 5Ni \rightarrow Ni_6Si_2 + 2Si^{4+}$

Here, it is possible to bring about such reactions as diffusion of the formulated metallic silicide into the basal plate material; alloy formation; and compound formation resulting from the Si^{2+} formation reaction and disproportionation reaction occurring at the same reaction temperature.

I will now explain a number of representative transition elements that are the desired constituents for carrying out surface hardening by using disproportionation reaction within molten salts to bring about surface modification of the basal plate material and their disproportionation reaction within molten salts. If I give an explanation here by citing a case using fluoride ions, which are more stable as complex negative ions, easy to handle for processing, and difficult to hydrolyze, the following reaction:

$Cr + F^- + CrF^{7-} \rightarrow 2CrF^{4-}$

And, subsequently, the following reaction at the same temperature:

$2CrF^{4-} + M \rightarrow Cr\text{-}M + F^- + CrF^{7-}$

Result in forming a surface-hardening constituent (Cr-M) layer by reacting with basal plate and the constituent (M) within the basal plate. However, if a is designated here as the amount of activity of chromium, it must be provided that aCr> aCr-M

Similarly, here are the explanation on such elements as vanadium (V), titanium (Ti), zirconium (Zr), and tantalum (Ta):

V: $V + VF_6^{3+} \rightarrow 3VF_4^{2-}$

$2VF_4^{2-} + M \rightarrow V\text{-}M + 2VF_6^{3-}$

Ti: $Ti + 6F^- + TiF_6^{2-} \rightarrow 2TiF_6^{4-}$

$2TiF_6^{4-} + M \rightarrow Ti\text{-}M + 6F^- + TiF_6^{2-}$

Zr: $Zr + 6F^- + ZrF_6^{2-} \rightarrow 2ZrF_6^{4-}$

$2ZrF_6^{4-} + M \rightarrow Zr\text{-}M + 6F^- + ZrF_6^{2-}$

Ta: $2Ta + 4F^- + 3TaF_7^{2-} \rightarrow 5TaF_6^{2-}$

$5TaF_6^{2-} + 2M \rightarrow 2Ta\text{-}M + 4F^- + 3TaF_7^{2-}$

In basal plates consisting of these elements and transition elements in which diffusion, alloy formation, and compound formation occur at the same temperature, it is possible to bring about surface hardening through surface modifications using these disproportionation reactions.

Surface Hardening through Formation of Metallic

Surface hardening through disproportionation reaction within molten salt systems is possible by forming metallic carbide layers with a hardness of 1000-3000Hv, such as, for example, TiC, VC, ZrC, TaC, and Cr-C, on the surface of a carbide-containing basal plate material. As supporting electrolytic molten salts, representative supporting electrolytic molten salts of the KCl-NaCl-NaF (in the ratio 2:1:1 in terms of weight) group are used. Compounds with 10%-15% content of the desired constituents (those that are soluble in the supporting electrolytic molten salts) and 10%-15% content of the desired metals and their alloys (for the desired metal quantity) are added to the supporting electrolytic molten salts. The target surface hardening material is immersed in this at the designated temperature of 600^{o}C-1000^{O}C for a designated length of time to have a hardened layer form on the surface of the basal plate.

In this case, if the basic reactions sought are to be shown exclusively in terms of the direct and primary disproportionation reactions, the reactions are as follows:

TiC: $2TiF_6^{4-} + C \rightarrow TiC + 6F^- + TiF_6^{2-}$

Cr-C: $2CrF^{4-} + C \rightarrow Cr\text{-}C + F^- + CrF_7^-$

ZrC: $2ZrF_6^{4-} + C \rightarrow ZrC + 6F^- + ZrF$

VC: $3VF_4^{2-} + C \rightarrow VC + 2VF_6^{2-}$

TaC: $5TaF_5^{2-} + C \rightarrow TaC + 4F + 5TaF_7^{3-}$

(Here, C is carbon contained in the carbon-containing basal plate material)

When carbon steel with a carbon content of 0.6-1.2% was used as the basal plate material, a hardness of 1255-2188Hv was achieved with a Cr-C layer, 1,490 Hv with a ZrC-layer, 1,750 Hv with a TiC layer, 3,400Hv with a VC layer, and 2,800-3,000 HV with a TaC layer. In this way, it is possible to obtain metallic carbide films with surface hardened layers registering 1,200-3,400 HV through disproportion reactions within molten salt systems.

Surface hardening through formation of metallic boride layers

Metallic boride film formation reactions result in forming metallic boride layers when activated boron ions are formed as a result of disproportional reaction of boron ions in molten salt systems – as indicated in the following formula – react with the desired boride-forming constituent (M) contained in the basal plate.

$3B^{2+} \rightarrow B + 2B^{3+}$

or

$3B^{+} \rightarrow 2B + B^{3+}$

and

$B + M \rightarrow MB$

The composition of the molten salt system used here has the KCl-BaCl-NaF group of molten salts as the supporting electrolytic molten salt (KCl : $BaCl_2$: NaF = 2 : 2 : 1 ratio by weight), with 5% content of boric oxide and 10% content of boron, or boron alloys or borides of the equivalent weight added to this. In this case, the activity level of the boron contained in the boron additives must be greater than the activity level of the boron in the metallic boride films that are formed. In addition, it is possible to use sodium chloride and their mixtures in place of calcium chloride. The reaction temperature is selected from a range of 600^{o}C – 900^{o}C.

The initial reaction involved in the formation of disproportionation reaction species of boron ions is as follows:

B: $B + 2B^{3+} \rightarrow 3B^{3+}$

B: $2B + B^{3+} \rightarrow 3B^{+}$

Boronation takes place as a result of disproportionation reaction of the low-valence boron ions produced here. Next, if the basic reactions for producing metallic borides and various types of metallic boride layers are to be shown in terms of the direct and primary disproportionation reactions, there are such reactions as follows:

MB: $3B^{2+} + M \rightarrow MB + 2B^{3+}$

$3B+ + 2M \rightarrow 2MB + B^{2+}$

TiB_2: $Ti + 6B^{2+} \rightarrow TiB_2 + 4B^{3+}$

$2Ti + 6B^{+} \rightarrow 2TiB_2 + 2B^{3+}$

ZrB_2: $Zr + 6B^{2+} \rightarrow ZrB_2 + 4B^{3+}$

$2Zr + 6B^{+} \rightarrow 2VB_2 + 2B^{3+}$

Cr-B: $Cr + 3B^{2+} \rightarrow Cr\text{-}B + 2B^{3+}$

$2Cr + 3B^{+} \rightarrow 2Cr\text{-}B + B^{3+}$

FeB: $Fe + 3B^{+} \rightarrow 2Fe\text{-}B + B^{3+}$

Taking Fe-B as an example, the structure of the layer that is formed changes depending on the activity level of the raw material boron. If the raw material boron with an activity level greater than that of the compound FeB is used, the structure of the layer appears from the surface as FeB-Fe_2B-Fe(B)-Fe. When 18 Cr-8Ni stainless steel (SUS304) was used as the basal plate material, a surface hardened layer consisting of CrB compounds was formed that registered a high hardness of 3200Hv, with a titanium alloy basal plate, a TiB_2 surface hardened layer with a hardness of 4200 Hv was formed; with a vanadium-containing basal plate, a VB_2 surface hardened layer with a hardness of 3700 Hv was formed; with a carbon steel basal plate, a FeB-Fe_2B surface hardened layer registering a hardness of 1600-2500Hv was formed, and with a zirconium compound basal plate, a ZrB_2 surface hardened layer with a hardness of 3000Hv was formed (the hardness indicated here refers to surface hardness)

In performing surface hardening that involves the formation of a metallic boride-type hard substance on the surface of a material and it is to have a fresh metallic boride film form on the surface of a basal material that does not contain any of the constituents of the desired metallic boride, the following methods are conceivable:

(1) First, have the boron constituents form an alloy within the surface layer of the basal material through disproportionation reaction. Next, provide a metal for boride formation through disproportionation reaction, and have the desired metallic boride-type film form on the basal plate surface.

(2) First, have the metallic constituents of the desired metallic boride form an alloy within the surface layer of the basal plate material through disproportionation reaction. Then, provide the boron constituents through the next round of disproportionation reaction process to complete the formation of the desired metallic boride-type film.

In these two methods, the essential requirement is that the affinity between the basal plate material and the constituents provided as a result of the disproportionation reaction in the initial stage must be smaller than the affinity between the boron and the metal within the desired metallic boride layer sought to be obtained through disproportion reaction in the second stage. Decision on which of the two methods mentioned above should be selected must be made upon thoroughly taking this requirement into consideration, and this will determine the success of failure of the surface hardening method. As an example, the formation of a titanium boride (TiB_2) surface hardened layer on a carbon steel surface will be taken up. If this is to be done according to method (1) above, Fe-B-type compounds and alloys are formed on the carbon steel surface layer by first having boron form an alloy within the carbon steel through disproportionation reaction. Next, if titanium (Ti) is provided to this surface layer through disproportionation reaction in the second stage in order to obtain a titanium boride (TiB_2) surface hardened layer, the desired titanium boride surface hardened layer cannot be obtained.

This is because the following reaction does not occur at all or does not occur easily, and the task, therefore, cannot be accomplished:

$2FeB + Ti \rightarrow TiB_2 + 2Fe$

On the other hand, if method (2) is to be followed, Fe-Ti-C-type compounds and alloys are formed within the carbon steel surface layer by having titanium form an alloy within the carbon steel through disproportionation reaction. Primarily, TiC, Fe-Ti, etc are obtained here. Next, if boron (B) is provided to this surface through disproportionation reaction in the second stage, the desired titanium boride type surface hardened layer can be obtained through the following reaction:

$Ti\text{-}Fe\text{-}C + 2B \rightarrow TiB_2 + C + Fe$

The overall reaction that takes place here will be listed here sequentially, but for the sake of simplicity, ionic system will be used to show the formulas

$Ti + Ti^{4+} \rightarrow 2Ti^{2+}$

$2Ti^{2+} + C \rightarrow TiC + Ti^{4+}$

$2Ti^{2+} + Fe \rightarrow Ti\text{-}Fe + Ti^{4+}$

$TiC + 6B^{2+} \rightarrow TiB_2 + C + 4B^{3+}$

$TiC + 3B^{+} \rightarrow TiB_2 + C + B^{2+}$

$TiFe + 3B^{+} \rightarrow TiB_2 + Fe + B^{2+}$

By employing the similar two-stage disproportionation reaction process within molten salt systems, it is possible to carry out surface hardening processes to form films other than the Ti-B-type metallic boride films, such as the V-B, Cr-B, Zr-B, and Ta-B type metallic boride-type hard films, regardless of the composition of the basal plate material.

Surface Hardening through Formation Of Metallic Nitride Layers

Among the metallic nitride family, CrN, TiN, ZrN, VN, etc. have a high hardness, registering values of 1000-3000Hv. It is thought that they can be used effectively as surface hardened films.

When attempting to form a metallic nitride-type surface film, disproportionation reactions using nitrogen ions is unlikely. Therefore, it is assumed that basal plate materials with sufficient nitrogen content for reactions or those with surfaces that have been nitride in advance will be used. In this case, it would suffice if the constituents in the basal plate material and the desired metal nitrides are formed as a result of the nitriding process, but that will not be taken up here. It is possible to use the nitrogen that is present in the surface layer as a result of nitriding and bring about the formation of the desired metal nitride-type surface film by introducing the metal constituents in the desired metal nitrides into the surface layer through disproportionation reaction within a molten salt system.

The following is an example of the formation of a chromium nitride surface layer: first, carbon steel is subject to a nitriding process in a molten salt bath containing 55% cyanide (NaCN + KON) -25% cyanide(NaCNO + KCNO)- 10% carbonate ($Na_2CO_3 + K_2CO_3$)-10% Chloride (NaCl + KCl) at a temperature of 570^{o}C. In this case, a nitride layer equivalent to FeN is obtained. Next, for the disproportionation reaction process for the formation of chromium nitride, 29% NaCl-29%KCl-14%NaF-14%CrF_3-14%Cr is used for the molten salt system and when the process is carried out at 900^{o}C, a chromium nitride-type surface layer can be obtained through the following disproportionation reaction:

$2CrF^{4-} + N\ (in\ Fe) \rightarrow CrN + CrF_7^{-} + F^{-}$

$4CrF^{4-} + N\ (in\ Fe) \rightarrow Cr_2N + CrF^{7-} + F^{-}$

And

$2CrF^{4-} + Fe\text{-} \rightarrow Cr\text{-}Fe + CrF^{7-} + F^{-}$

The various types of metal nitride film formation reactions induced by disproportionation reactions can be shown in formulas using only positive ions as follows:

CrN: $Fe\text{-}N + 2Cr^{3+} \rightarrow CrN + Cr^{6+} + Fe$

$Fe\text{-}N + 3Cr^{3+} \rightarrow Cr_2N + Cr^{6+} + Fe$

$2Cr^{3+} + Fe \rightarrow Cr\text{-}Fe + Cr^{6+}$

TiN: $Fe\text{-}N + 2Ti^{2+} \rightarrow TiN + Ti^{4+} + Fe$

$2Ti^{2+} + Fe \rightarrow Ti\text{-}Fe + Ti^{4+}$

ZrN: $Fe\text{-}N + 2Zr^{2+} \rightarrow ZrN + Zr^{4+} + Fe$

$2Zr^{2+} + Fe \rightarrow Zr\text{-}Fe + Zr^{4+}$

VN: $Fe\text{-}N + 3V2+ \rightarrow VN + 2V3+ + Fe$

$3V^{2+} + Fe \rightarrow V\text{-}Fe + 2V^{3+}$

Besides these, surface hardening is also possible with transition metals that have the potential to form hard metallic nitrides if special metallic nitride-type surface layers are formed by using similar disproportionation reaction within molten salt systems.

Surface Hardening through Formation of Metallic Sillicide Layers

When trying to form a metallic silicide surface layer through disproportionation reaction within a molten salt system, the disproportionation reactions for silicon primarily employed are based on the following reaction:

$2SiF_6^{4-} \rightarrow Si + SiF_6^{2-} + F^-$

Carbon steel will be taken up as an example to explain the formation of silicate films consisting of metal constituents of a basal plate material on the surface of that basal plate material. By using 33.8%NaCl-33.8%KCl-13.1%NaF-13.1%Na_2SiF_6-6.2%Si as the basic molten salt system, a Fe-Si layer was obtained by causing a reaction at 900^{O}C. This layer registered a hardness of approximately 700Hv. The results of an x-ray analysis showed that silicide layers were formed inward from the surface in the order of $FeSiO_2$, FeSi, Fe_3Si, etc. this occur as a result of the following reaction:

$2SiF_6^{4-} + Fe = Fe\text{-}Si + SiF_6^{2-} + F^-$

On the other hand, as an example of a case in which a surface coating of chromium silicide films consisting of constituents not present in the basal plate material is sought, the formation of chromium silicide films will be explained here. In case case, the first stage involves carrying out chromium processing and the second stage involves carrying out silicon processing through disproportionation reaction within a molten salt system. After this, the desired chromium silicide films were formed. Steel was used as the basal plate material for processing in this case. Using carbon steel (carbon content: 0.8-0.9%) as the basal plate material for processing, chromium processing in the first stage was conducted at 900^{o}C, using 29.5%KCl-29.5%$BaCl_2$-14.7%NaF-4.41%NaF-4.41%CrF_3-22%Cr for the molten salt system.

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4.0 CHAPTER FOUR
TOYOTA DIFFUSION (TD) PROCESS

4.1 Introduction

This process is a method of forming a carbide layer on the surface of materials such as steel, cemented carbide, etc. by immersing them in a fused salt bath being kept at high temperature. The carbide layer produced by this method consists of carbide itself, including very few substrate constituents other than carbon; thus, as shown in plate 1, it has fine composition without porosity.

When the constituent of the VC layer is investigated with the EPMA as shown in Fig. 4.1, V and C exist throughout the layer, and there is almost no iron or boron which might be penetrated by the salt bath. TD process is a process of soaking the substrate in a hot salt bath containing vanadium, niobium, or chromium. Then these metals diffuse into the substrate and react with carbon in it to form carbide coating which covers the substrate with thickness of several microns. This super hard coating is superior in wear resistance, seizing resistance, and resistance to high temperature oxidation. Generally, simultaneously with the coating formation the heat treatment is carried out to secure the strength of the substrate. With a similar process, the boride coating can be formed by diffusing boron on the substrate. Some areas of application include, drawing mandrels, nipple for plastic extruder, die for pressing, die for automobile, etc. fig.4.3 shows a TD Process equipment with some processed components

Fig. 4.1 Micrograph of Carbide Layer Formed using TD Process Investigated with the EPMA

4.2 Principle of the TD Process

Atoms or ions of carbide constituents dispersed in the salt bath combined with C atoms contained in the substrate; then the carbide layer is formed on the surface of the substrate. Thereafter, the layer is expanded by reaction between C and the carbide constituent on the formed carbide layer and the continuous supply of C atoms from the substrate. See fig. 2.

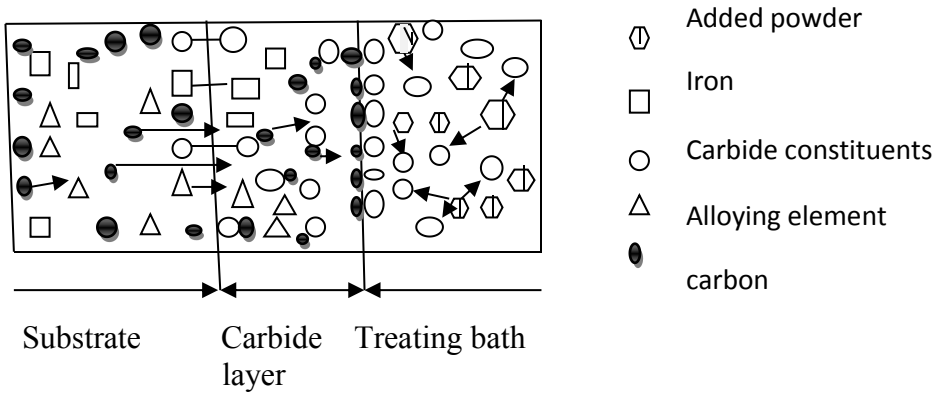


Fig.4.2 Profile of Expansion of Carbide layer Formed on Steel Surface in the Borax Bath.

Fig.4.3 TD Process Bath and Some Processed component

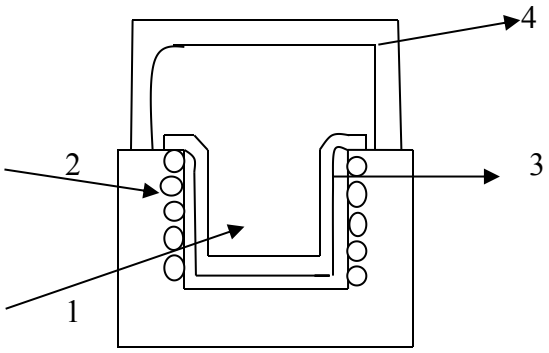
4.3 Features of the TD Process

a. Foaming of the coated layer and hardening of substrate can be simultaneously accomplished
b. Partial coating can be applied
c. Retreatment can be conducted. (the retreating up to 8 times in practice)
d. Uniform coating is attainable in the complex shape of work pieces. (possible onto even internal surface of small holes)
e. No post-treatment is required because surface finish will suffer no change. (if more than 1μ of R_{max} is not allowed, diamond lapping is required)
f. Easy to adjust thickness of carbide layer
g. Uniform layer quality is easily obtainable. Composition, structures and property of layers have no relation with treating conditions and kinds of steel.

4.4 Method of the TD Process

The carbide is formed by immersing a work piece into a fused salt bath set in an electric furnace as shown in fig.4.4 within the range from 800 to 1050^{O}C (up to 1,250^{O}C is

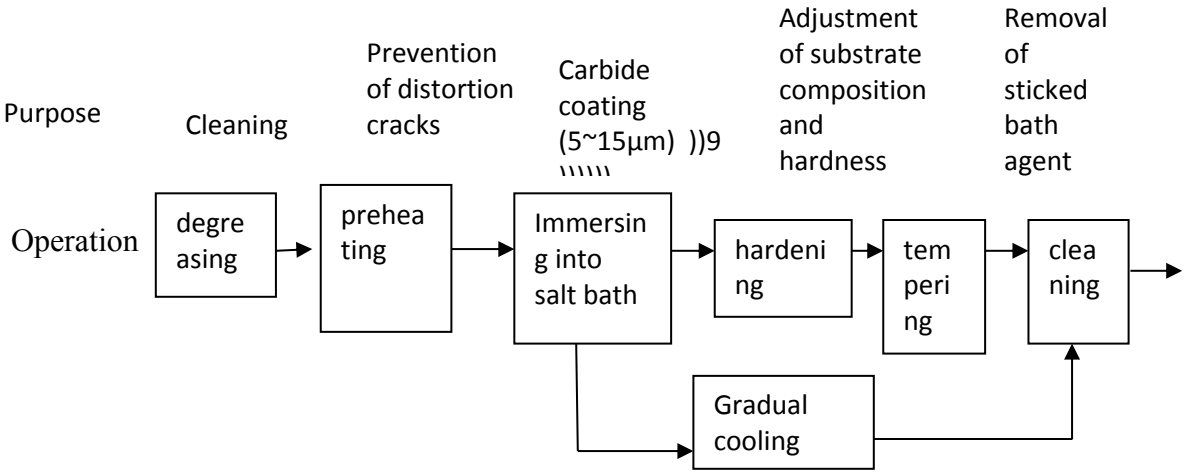
available if the furnace construction is moved from the salt bath for further hardening and tempering. The process is treated according to the steps shown in fig. 4.5.

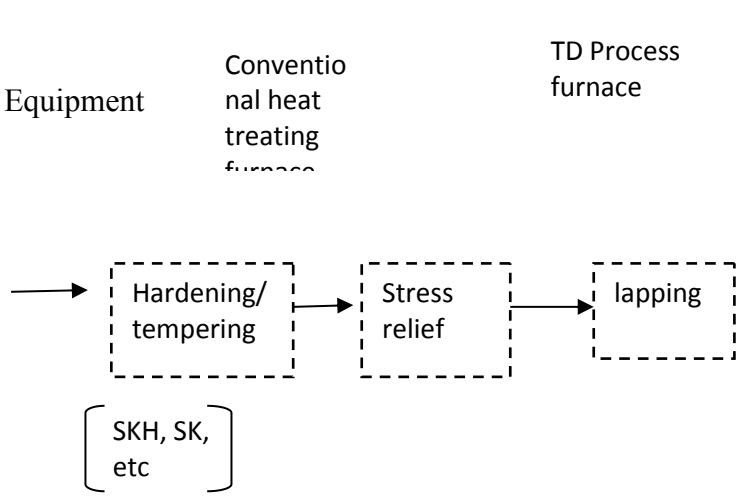


1. salt bath agent
2. heating element
3. Heat resisting steel pot
4. top cover of furnace

Fig.4.4 Furnace for TD Process

Steps of TD Process





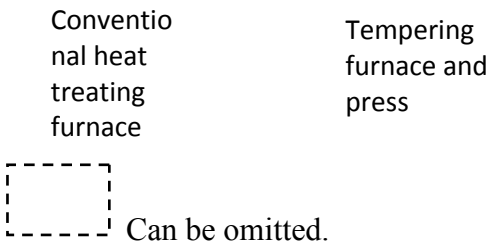


Fig.4.5 Steps of the TD Process

Fig.4.5 shows the steps involved in the processing of work pieces using TD process. This process was developed by Toyota Company. It entails the cleaning of the work piece for degreasing, then preheating to prevent distortion and cracking of the work piece before immersing into the salt bath for carbide coating of 5-15 microns. Thereafter hardening and tempering is carried out on the work pieces to adjust substrate composition and hardness. Other steps like hardening/tempering, stress relieving and lapping obtainable in conventional heat treatment can be omitted for ordinary steels. However, for SKH, SK, and other alloy steels (tool steels) the dotted steps above may be necessary.

4.4 Characteristics of Materials Treated by the TD Process

The materials treated by TD process have surpassing properties in wear-resistance, seizure-resistance, corrosion-resistance and oxidation-resistance as well as peeling-resistance and toughness. The materials treated by TD Process feature:

(a) Far higher hardness than cemented carbide (over 3000 Hv).
(b) Wear-resistance equivalent to or higher than cemented carbide.
(c) Seizure-resistance surpassing cemented carbide.
(d) Corrosion-resistance and oxidation-resistance better than stainless steel
(e) Peeling-resistance far better than chromium plating, PVD and the like.

Fig.4.6 shows the comparison of hardness of surface layers of various processes with TD process. The figure shows that TD process has higher hardness value.

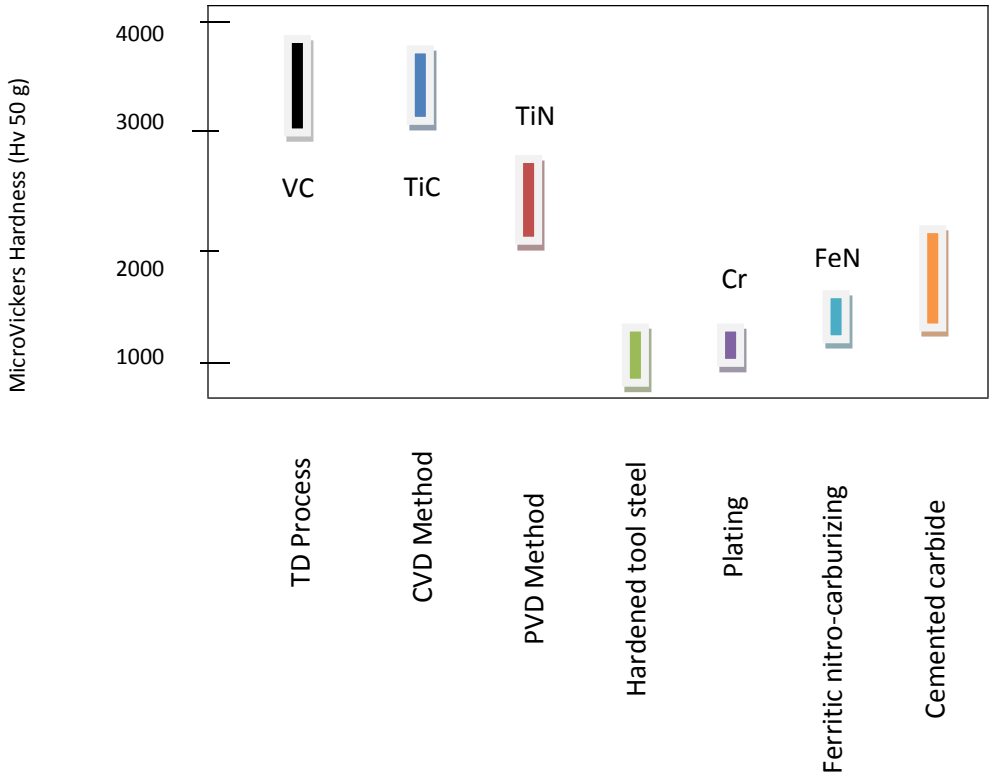


Fig. 4.6 Comparison of hardness of surface layers

4.5 Wear Resistance

Carbide layers produced by TD Process show remarkable wear resistance against any materials such as steel, nonferrous metal, plastic, rubber and so forth.

4.6 Seizure resistance

The materials treated by the TD Process show excellent seizure and score resistance against steel, nonferrous metals and so forth. See Tables 4.1 and 4.2

Table 4.1: Comparison of Seizure Resistance by Ring Compression Test

Ring Test / Compressed plate	Room temperature			1200°C
	S45C	SUS304	A1050	S45C
Hardened and tempered steel (SKD11)	X	X	X	X
Cemented carbide (16%Co-WC)	◎	X	—	—
VC coated steel (SKD11)	◎	○	△	◎

◎No seizure ○ little seizure △A little seizure X Remarkable seizure ____No testing
Size of ring: 20Ø x 10Ø x 5mm
Surface roughness of compressed plate:
R_{max} = 0.08µm (hardened and tempered steel cemented carbide)
R_{max} = 0.06µm (VC coated steel)
Compressibility: room temperature 20≈45%
1200°C, 20 minutes, 30%.
Lubricant: none

Table 4.2: Comparison of Score Resistance by Ring Compression Test

Test Piece \ Mating ring	SUS 304	FC 20	Al-Si
Hardened and tempered steel	2.7	4.1	2.5
Cemented carbide	7.7	4.0	2.1
VC coated steel	7.8	11.8	3.0
Cr-C coated steel	4.2	-	3.1
Nb coated steel	7.7	11.2	2.4
TiC coated steel	7.5	-	-
Chromium plated steel	3.6	-	-
L_o	4.2	-	-
Sulphurised steel	2.4	-	-
Ferro-TiC steel	4.1	-	-

(Pressing the dice test piece to the mating ring. No lubricant. 2.6 m/sec) score initiating load (kg)

4.7 Oxidation-resistance

The Cr-C coated steel shows very excellent oxidation-resistance with very small weight increment even under 900°C. In the case of VC and NbC, oxidation is found at high temperatures of over 500°C, but they can be used for application where it is exposed to high temperatures for only a short time.

Izod impact test, shows that the impact values of VC and NbC coated steels are equivalent to that of hardened and tempered steel, regardless of the material of the substrate. Therefore, if a material having high impact resistance is selected for the substrate, it will be effective against breakage, chipping-off and the like.

4.8 Corrosion Resistance

The materials treated by the TD Process have superior corrosion resistance as compared with stainless steel. The corrosion resistance was obtained by immersing test pieces into nitric acid solution and

hydrochloric acid solution. The corrosion resistance of VC, NbC, and Cr-C coated steels immersed in the solution of HCl and HNO_3 is very excellent, no corrosion is evidenced in the test piece soaked in a 36% HCl solution while stainless steel is corroded.

4.9 Peeling Resistance

Unlike plating, the coated layer produced by the TD Process will not easily peel off. Test results obtained by observing the peeling off of the layer and the cracks on the surface after repeated-strikes on to a same spot with an acuminated hammer showed that TD process coated samples do not peel easily as compared with plated samples.

4.10 Cutting and Shearing Performances

The materials treated by the TD Process have excellent performance when they are used as cutting and shearing tools for various metals and nonferrous materials such as rubber, plastics, etc. The result of measurement of the width abraded at the nose of cutting tools after turning resin materials with glass fiber content showed minimal width abrasion. This proved that the wearing out of tools is remarkably improved by applying the TD Process.

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5.0 CHAPTER FIVE
ACTIVE SCREEN PLASMA NITRIDING TECHNOLOGY

5.1 Introduction

Active Screen Plasma Nitriding Furnace is still under development in Japan. Those in current use in the country were bought from Australia. Researchers in Japan are working on developing it locally and to change the colour of the products processed using this furnace [1]. This same kind of approach can be adopted here in Nigeria. Active Screen Plasma Nitriding (ASPN) is a novel alternative for plasma nitriding, and J.N. Georges was the inventor of the active screen technology at plasma metal SA Luxembourg. This novel active screen technology was first presented for the first time at the International Federation of Heat treatment and Surface Engineering Congress in Melbourne November, 2000. Since then several authors like Prof. Tom Bell, Prof H. Spies and Prof. H. Biermann, and Prof. D. Doyle had both published several papers [1] regarding this novel and innovating technology. Furthermore the European Community decided to allocate the CRAFT project G5ST-CT-2002-50324 to investigate on ASPN surface engineering of austenitic stainless steel components [1].

The active screen, on which plasma is applied, radiates heat to the workload. The latter is brought to the desired temperature under vacuum. The active screen generates highly energized species, which are directed on the workload by gas flow and bias. The use of plasma technology in furnaces today is on the increase and one of the reasons is because less heat is generated; causing the components to retain their shape after the nitriding process. Active screen plasma nitriding is a further improvement of the plasma nitriding process. Apart from the conventional nitriding other nitriding processes include; gas carbonitriding, plasma carbonitriding , direct current plasma nitriding (DCPN), ASP nitrocarburizing, plasma nitriding, and salt bath nitriding [2]

The issue of the environment has become very important, in the words of Kyazze [3] ‘’we at UNESCO are convinced that the depletion of, or disrespect for the environment is one of the most crucial problems facing human kind today. We are also convinced that the global change is largely a result of man’s abuse of the environment. We know that environmental issues can only be dealt with effectively if tackled globally, and internationally. The air, the seas, oceans, and rivers are never, limited to national boundaries”. These words no doubt stress the need for processes like the ASPN which is environmentally friendly.

The objectives of this chapter are to explain the principle of operation of the ASPN process and to stress the importance of using environmentally friendly processes in order to save the environment from the current state of abuse by man.

5.2 NITRIDING PROCESS

Nitriding process is a heat treatment to diffuse nitrogen into steel. By nitriding steel, steel surface hardens to form nitrides (Al_xN, Cr_xN, V_xN,…) This imparts improved abrasion resistance to the surface of the steel and also corrosion resistance and fatigue strength. The nitriding temperature is less than 873K (600^oC). This process does not need surface hardening by quenching as carburizing [4]. Table5.1, shows the comparison of nitriding processes, from the table it can be seen that the plasma techniques have good characteristics. The diagram of the structure of nitrided steel is shown in figure1. The diagram illustrates the structure of a nitrided steel showing the compound layer, diffusion layer and the substrate.

Table 5.1: Comparison of Nitriding Processes [4]

		Plasma nitriding	Salt bath nitriding	Gas carbonitriding	Gas nitriding
Atmosphere		Gas(in low pressure)	Liquid	Gas (in atmospheric pressure)	Gas (in atmospheric pressure)
Adaptation for steels		All steels	All steels	All steels	SACM,SCM
Nitriding temperature		623k	823k- 873k	823k-853k	773k-803k
Heating method		Grow discharge	Heater outside chamber	Heater outside chamber	Heater outside chamber
Nitriding time		15min- 100hr	15min-3hr	15min-3hr	<100hr
Source		N_2 +H_2 mixture gas	XCN-XCNO(X= K, Na)	NH_3 gas, R_X gas	NH_3 gas
Partial nitriding		Easy	Difficult	Difficult	Difficult
Control of nitriding		Discharge current and voltage. Easy	Ratio of salt and research salt difficult	Degree of separation of ammonia. Commonness	Degree of separation of ammonia. commonness
Distortion of steel after nitriding		Small	Larger	Larger	Larger
Cleaning after nitriding		Unnecessary	Necessary	Necessary	Unnecessary
Assessment of	Waste liquid	Unnecessary	Necessary	Necessary	Unnecessary

the environment	treatment				
	Cleaning of toxic wastes	Unnecessary	Necessary (salt)	Necessary	Unnecessary (exhaust gases)
Working conditions		Very good	not good	not good	Not good
Porous layer of surface		Not formed	Easy formation	Easy formation	Formation
Control of ε and ŕ layer		Possible	impossible	Impossible	Impossible
consumption	Gases	Very small	-	Large	Large
	Electricity consumption	Smaller	Large	Large	Large

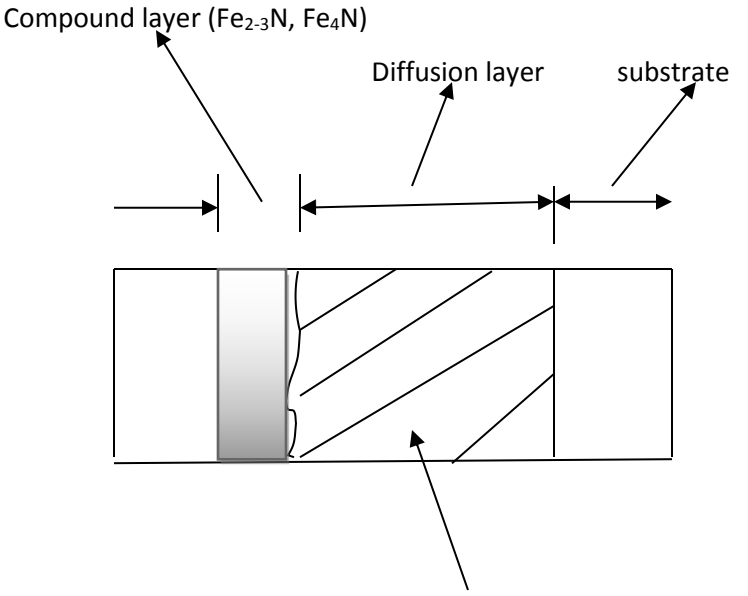


Figure 5.1 Diagram of Nitrided Steel in Cross-section.

5.3 Plasma Nitriding

During nitriding nitrogen diffuse into the surface of steel or iron to form iron nitrides and a diffusion layer. It is possible to achieve nitride level and thickness of nitriding layer by controlling nitrogen ratio in mixture of gases the nitriding temperature is from 653K- 873K. Plasma nitriding can select the nitriding part of works easily, it can also easily nitride stainless steel and titanium. This plasma technology applies plasma of non-equilibrium state to heat treatment. The plasma of non-equilibrium state is created by abnormal glow discharge [5].

5.4 Ion Nitriding

Ion nitriding also has a long history; in 1920 Franz Skaupy of Germany invented a heating furnace which utilized the heat of ion discharge in inert gas. Also for nitriding, Egan of America proposed an ion nitriding method which use arc discharge or corona discharge in NH_3 gas or N_2 gas at the atmospheric pressure, but did not succeed with the method. In 1932, Bernhard Berghaus of Germany invented the ion nitriding method utilizing glow discharge. This method which causes glow discharge by putting N_2 gas or NH_3 gas in a vessel kept at low pressure was initiated by the recognition of the advantage of nitriding treatment in ionized gas [6]. Table 5.2 shows surface treatments using DC glow discharge which is the fallout of the breakthrough by Bernhard Berghaus [6].

Table 5.2: Surface Treatments using Direct Current Glow Discharge

Treatment	Source gases	Process temperature	Characteristic (merit)	Adaptation of steel grade
Plasma nitriding (ion nitriding)	N_2, H_2, Ar	673k-823k	*low temperature *no oxidizing treatment *easy masking *Nitriding of stainless steel *nitriding of Al, Ti, etc *pollution-free and good condition for workers. (small H_2S consumption) *Easy operation *Easy variable treating condition	SPCC, SKD11, SKD61, Ti, SCM, SKH51, SACM
Plasma carbonitriding	N_2, H_2, Ar, CH_4	773K- 853K		SPCC, SS, SC
Plasma sulf-nitriding	N_2, H_2, Ar, H_2S	773K-853K		SKD61, SCM, SACM, SUS, SK, SC, SS SUS, Ti
Plasma carburizing (using HCD)	N_2, H_2, Ar, CH_4	1073K-1273K		Ti, SUS, Cr
Radical nitriding (using external heating)	N_2, NH_3, Ar	673k-773k		SKH51, SKD11, SKD61

5.5 Radical Nitriding Process

Radical nitriding was co-developed by NDK and Sumitomo metal mining co. ltd. This is plasma nitriding method based on a new idea. The process produces flat and smooth surface condition. No compound layer. It is applied to the duplex surface treatment with PVD. The

specimen is nitrided with NH radical using electrical discharged energy which is small in size compared to plasma nitriding [7].

4.4 Environmental Concerns

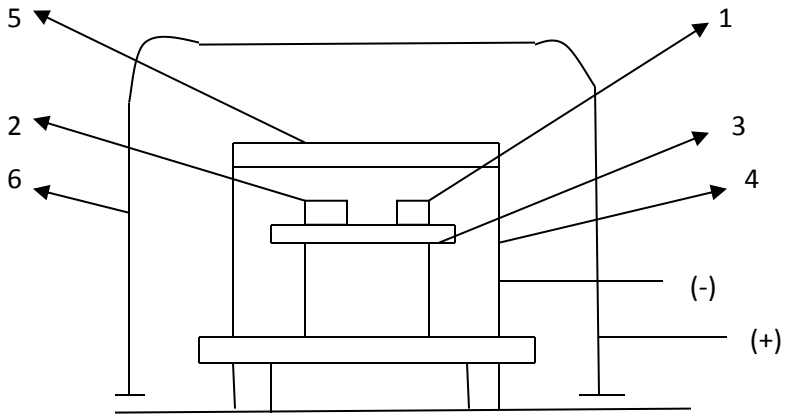
Man's activities and industrialization has continued to exert harmful impact on the environment and is now threatening the very existence of living things on the planet earth. A CNN documentary on the impact of man's activities on earth has it that aquatic life on the rivers, seas, and oceans is drastically reducing [8]. There is global warming, and polar ice is melting very fast. Recent findings about the ozone layer depletion, polar ice melting, and depletion of the polar bears are alarming. This has informed the attention being given to the environment by countries like USA and China who hitherto have been adamant and indifferent to the call by environmentalist that the earth is in peril.

Every attention is now given to actions and production activities that are eco-friendly. It is now the stand of many countries including Nigeria to eliminate processes, actions and activities that would further aggravate the damage that has already been done to the planet earth. According to Kyazze [2] ''we at UNESCO are convinced that the depletion of, or disrespect for the environment is one of the most crucial problems facing humankind today. We are also convinced that the global change is largely a result of man's abuse of the environment we know that environmental issues can only be dealt with effectively if tackled globally, and internationally. The air, the seas, oceans, and rivers are never, limited to national boundaries." In the words of A.B. Boveri the balance between mankind's needs and the conservation of the natural resources of our planet depends on clean and efficient technology [2]. These words therefore stress the need for uses of eco-friendly processes and technology across the globe.

5.7 Active Screen Plasma Nitriding (Aspn): An Environmentally Friendly Process.

The novel active screen technology was presented for the first time at the IFHTSE congress in Melbourne November, 2000. Since then authors like Prof. Tom Bell of the university of Birmingham (UK), Prof. H. Spies and Prof. H. Biermann of the Bergakademie Freiberg Demark, and Prof. D. Doyle of Swinburne university of technology , Melbourne Australia have each published several papers [1] regarding this novel and innovating technology. Furthermore the European community decided to allocate the CRAFT project G5ST-CT -2002-50324 to investigate on ASPN surface engineering of austenitic stainless

steel components [1]. Figure 2 shows a schematic diagram of active screen plasma nitriding equipment. The plasma is applied to the screen and no longer to the parts; in industrial equipment a bias is applied to the parts in order to direct the active species to the work-load [1]. Figure 3 shows the industrial version of ASPN, while Plate 1 shows the ASPN on the workshop floor.



1. *Sample 2. Dummy shape for temperature control 3. Isolated sample table 4. Mesh cylinder cathode 5. Top lid cathode 6. Furnace wall anode*

Figure 5.2: Schematic Diagram of Active Screen Plasma Nitriding Equipment.

The Role of the Active Screen

Active screen plays the following important two roles:

1. The active screen, on which plasma is applied, radiates heat to the work load. The latter is brought to the desired temperature under vacuum.
2. The active screen generates highly energized species, which are directed to the workload by gas flow and bias.

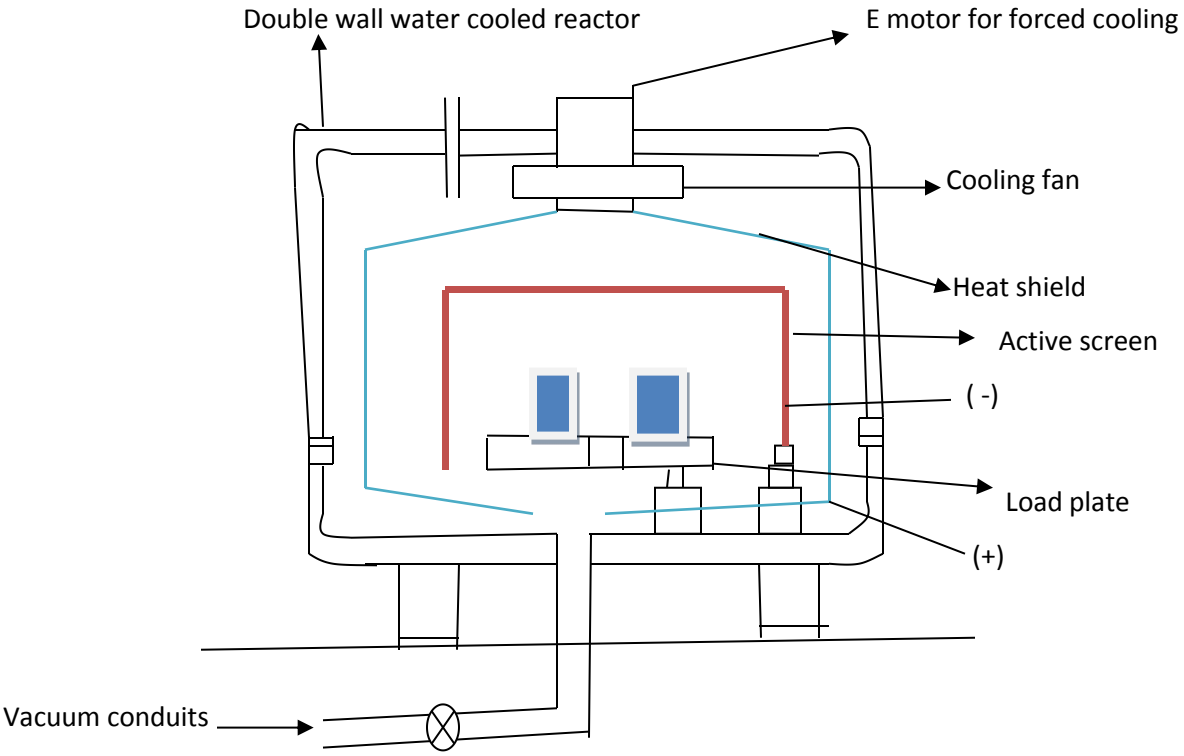


Figure 5.3: Shows the Industrial Version of ASPN

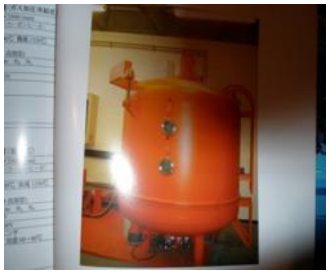


Plate 1: Shows the ASPN on the Workshop Floor

5.8 Comparing DC Plasma Nitriding and ASPN

In a study conducted by C.X. Li, Tom Bell, and H. Dong they both discovered that ASPN has a slightly bigger compound layer than DC Plasma nitriding. This is shown in figure 4. The studies also showed that nitrogen in-take is higher in ASPN, which confirms the correctness of figure 4. This is illustrated in figure 5, which is the plot of nitrogen (wt.%) versus depth (ɥm). ASPN curve is higher than that of DCPN [1]

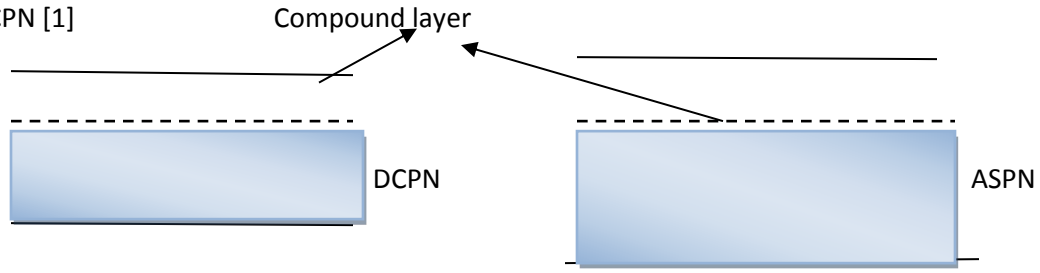


Figure 5.4: Comparing the Compound Layer of DCPN with that of ASPN

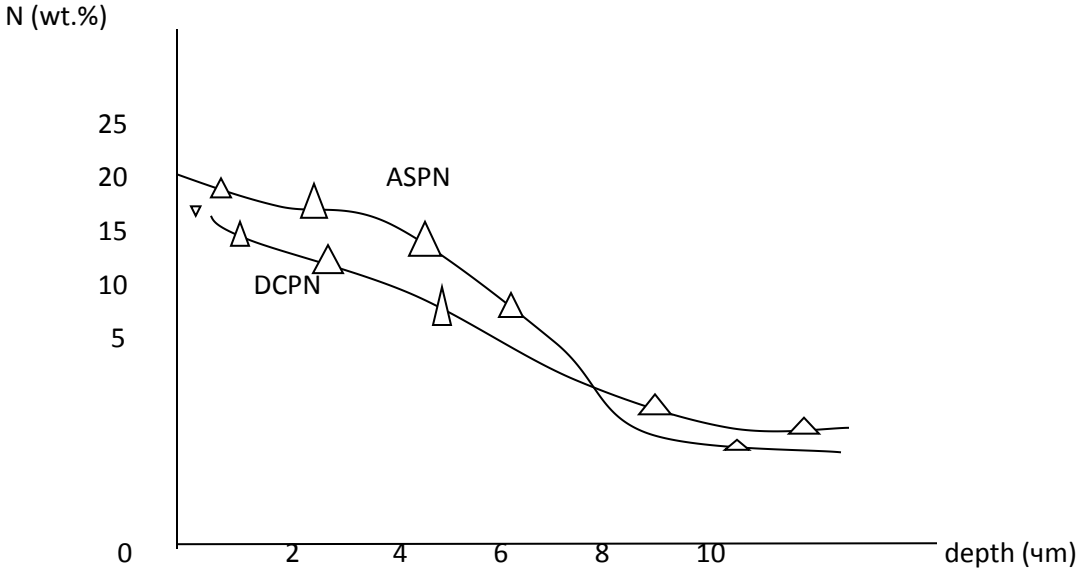


Figure 5.5: Nitrogen Distribution in New Surface of AS and DC Plasma Nitrided 722M24 Steel

X- ray diffraction patterns of a DC and AS Plasma nitrided 722M24 sample surface showed that both consist of a mixed structure of gamma prime and epsilon, however it seem that ASPN facilitates the formation of epsilon layer. Hardness profiles of both DCPN and ASPN are identical in test conducted [1]. ASPN may replace any other plasma assisted nitriding or nitrocarburizing equipment.

5.9 ASPN Mix Load Examples

Different items can be nitrided using ASPN this include: small size gears the system can take about 23,000 piston rings at the same time, hydraulic parts, and other parts are nitrided with no edge

effects and no decolouration of the parts. It is possible to also mask parts in areas where nitriding is not required

5.10 ASPN Nitriding of Stainless Steels

ASPN nitriding of stainless steels can result in the formation of an S-phase, this is a solid solution of nitrogen. It is essential not to form CrN as in this case the steel will no longer remain stainless. S-phase layers have a thickness of up to 10 microns and a hardness of up to 1000HV0.1. S-Phase is a good solution for problems, where corrosion resistant steels also need to be wear resistant. The fields of application are numerous, e.g. medical, food, chemistry, aviation, space, etc. Tests have proven that the S-Phase treated austenitic steels have a better corrosion resistance than untreated steels. The work done under the CRAFT project G5ST-CT-2002-50324 [1] has clearly proven that the ASPN technology is actually the sole technology which gave the best results compared to all today known nitriding technologies.

S- Phase can be realized not only with nitrogen, but it is also possible to do s-phase with carbon and nitrogen. Furthermore it is possible to do carbon S-Phase. The nitro-carbon s-phase is a duplex layer having excellent wear and corrosion properties this process is patented by NITRUVID, France. This very process ASPN carburizing can be used for carburizing of medical implants [1].

4.11 ASPN Bulk Nitriding of Small Articles

As there is nearly no plasma applied to the parts, logically no severe (damage) arcing, hollow cathode, etc can occur. It is therefore obvious to imagine a tumbling system, able to slowly move small articles, in the highly energized species atmosphere of an ASPN. Indeed the bulk nitriding system is suitable for parts of all kinds of steels. The nitriding can be achieved with or without compound layer. Stainless steel parts, nitralloy, 4140 steel parts etc can all be bulk nitrided using ASPN [1].

5.12 ASPN and Economy

The process is economical for the following reasons:

- ASPN needs only 60 to 200L/ h gas mix
- ASPN needs no ammonia
- ASPN allows mixed loads
- ASPN allows very dense charges
- ASPN allows mechanical masking

- ASPN needs no skilled operator
- ASPN works fully automatically
- ASPN is equipped with forced cooling
- ASPN accepts steam cleaned parts.

5.13 ASPN as an Environmentally Friendly Process (Eco-friendly)

One can claim that ASPN does no harm to the environment. Indeed ASPN only uses pure gases like nitrogen, Hydrogen, methane, oxygen, argon. The unused gases are released to the atmosphere through the vacuum pumping system. ASPN further needs no effluent burning systems. ASPN nitriding uses only 10% gas as compared to gas nitro-carburizing equipment.

Table 5.3 Comparing Effluent Emissions of Gaseous Nitrocarburizing and ASPN Nitrocarburizing.

	Plasma	Gaseous	Reduction (%)
Amount of gas used, m^3/ h	0.6	6.0	90.00
Total carbon emission via CO/CO_2, mg/m^3	504	137253	99.63
Total amount of NOx gas, mg/m^3	1.2	664	99.82
Output of residual C-bearing gas, mg/h	302	823518	99.96
Output of residual NOx gas mg/h	0.72	3984	99.98

Table 5.3 above clearly shows that effluent emissions from ASPN nitrocarburizing are far less low than emissions from gaseous nitrocarburizing equipment. The process is therefore environmentally friendly and it is recommended for a world like ours which is already experiencing the effects of global warming [9]

5.14 ASPN is Safe

The plasma reactor is not considered as a pressurized chamber. The top of the chamber only rests on the bottom part and is kept closed by vacuum. No ammonia reservoirs are needed. The system

is computer controlled and a possible failure of a component is immediately detected and a safe shut-down takes place.

5.15 Conclusion

The issue of environmental degradation, pollution, and global warming has become a very serious problem to the entire world. This calls for the use of technology that is environmentally friendly to cut-down on the harm already done to the earth. ASPN is one of such technology, after analyzing it we have safely drawn the following conclusions:

- ASPN may replace any other plasma assisted nitriding or nitrocarburizing equipment.
- ASPN is economically and ecologically friendly and safe.
- ASPN makes nitriding of stainless steels easy and more efficient
- ASPN is suitable for nitriding small articles in bulk

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6.0 CHAPTER SIX

SURFACE COATING (HOT DIP GALVANIZING, THERMAL SPRAYING, SHIPPO CLOISONNE, POWDER COATING)

6.1 Introduction

Technology is constantly improving likewise surface finishing technology. There are different types of surface coating and surface finishing processes. The choice of any type depends on factors like cost, quality, functionality and durability. Other considerations can go down to corrosion resistance, wear resistance, esthetics and heat resistance. The intention of this chapter is to specifically examine the following surface finishing technologies: hot-dip galvanizing, thermal spraying technology, shippo cloisonné, and powder coating technology. Products treated with these surface finishing technologies are widely used at home, oil sector, construction, automotive, space and aeronautic sectors. Another good reason why these processes are used is to protect and preserve scarce resources. These processes help in preventing the waste of limited resources. TOCALO also agrees with the above and I quote his views `today, surface modifying technology is an integral part and widely employed in the fields requiring energy-saving, efficiency, product-reliability and other advantages, such as power generation, steelmaking, car manufacturing, electronics, space development, medical field. The fig.6.1 below shows the areas of application of surface modification.

Fig.6.1 surface modification is applied to aeronautic, space technology and computer technology.

6.2 Hot Dip Galvanizing/ Hot Dip Aluminizing in Practice

6.2.1 Zinc Metal

Evidently zinc was known in ancient times, because it was used in the brasses and bronzes produced by primitive man. Metallic zinc, known then as spelter, was produced and used in Europe as early as the sixteenth century. Zinc has considerable resistance to atmospheric corrosion because, as is the case of aluminium, the oxidation formed initially on its surface protects it from further attack. For this

reason it is used as a protective coating for iron sheets, zinc is rolled into sheets to be used for making electric dry battery cells and for some construction purposes increasingly large amounts of zinc are being used for making diecastings. The most common source of zinc is the zinc sulphide ore known as sphalerite or zinc blende. Zinc ore is crushed, concentrated by gravity concentration methods or by flotation, and roasted, all by much the same procedures as those used for copper ores. After roasting, metallic zinc is extracted from the calcine by electrolysis or by distillation either in retorts or by an electrothermal process. Zinc extracted by electrolysis is of the highest purity of any commercial grade, and is used for die casting. It has a purity of about 99.9%. Iron and steel may be protected from corrosion by application of a surface coating of zinc; the coating forms a thin layer of iron-zinc alloy, covered by a thicker layer of pure zinc. Even when a break occurs in the continuity of the coating, the presence of zinc provides electrolytic protection against corrosion of the iron. Such a coating may be applied by one of the processes known as galvanizing. In the hot dip process, the ferrous metal is cleaned by pickling in dilute acid, and then is immersed in molten zinc. This process produces on wrought iron a coating that is from 25 to 40 percent thicker than that obtainable on other varieties of iron and steel. For objects too large to be dipped, molten zinc is sprayed on by a gun; this is known as metalizing. Other methods of applying a coating of zinc are electrodeposition, also called electrogalvanizing, and sherardizing, accomplished by heating small articles packed with powdered zinc at a temperature of about $650^{O}F$ ($343.3^{O}C$) . **Hot Dipping:** hot dipping coatings can be used for coating high melting point metals such as iron and steel, zinc, tin, lead and alloy of lead and tin called terne. The coating metal should be of such a composition that it forms an alloy at the interface between the base metal and the coating. If the coating does not form an alloy, precoating with a metal which alloys both with a base and principal coating can be used. Zinc forms a more protective coating on iron than tin and terne, but it is unsuitable for the preparation and storage of food, where tin coatings are quite satisfactory. This is due to the frequent acid nature of foods which are strong enough to dissolve

the zinc but do not attack tin. Terne coating is never used for food preservation due to danger of lead poisoning.

6.2.2 Hot Dip Galvanizing

It is the name given to the coating of zinc by hot dipping. The quality of the coating is directly related to its thickness which is measured in gms/m^2 of surface for all products except sheet where it is measured in gms/m^2 of sheet (2 sides). Heavy coatings of zinc are most easily applied by hot dipping than electrolytically. The purity of zinc affects its bonding property and the appearance of the coating, and besides that it has no effect. So where bonding does not matter, low grades of zinc can be used. It is mainly used in roofing, wire fencing for gardens, etc., buckets and water cans, steel pipes and for structure purposes exposed to atmosphere.

Hot dip galvanizing is commonly used in Nigeria for the coating of steel coils and corrugated steel sheet. Nigerian industrial standard NIS 180: 2003 has specification for galvanized corrugated steel sheet. The Nigerian industrial standard was prepared by the technical committee of standards organization of Nigeria on iron and steel, to assist manufacturers and purchasers to keep abreast of technological development in the galvanized corrugated steel. It specifies types of sheets classified according to the mass of zinc coating, brand symbol; re-test criteria, and chemical composition in percentage which are essential requirements to enable manufacturers produce quality products. The standard specifies the materials profiles, and dimensions of hot dipped galvanized corrugated steel for general purposes and defined some key terminologies in galvanizing as below:

Hot-dipping: is the insertion of a substrate in a hot solution

Galvanizing: is the process of coating steel with zinc

Coating: is a process of putting an outer layer of a substance on a substrate.

Dross: is a product of oxidation and contamination of the zinc bath

Fluxing: is the process by which the base metal is protected against oxidation

Pickling: the process of removing oxide scale on steel before fluxing

Standard dimensions: are the reference length, width and thickness

Pitch: is the shortest distance between two corrugation peaks

Depth of corrugation: is the perpendicular distance between the trough and the peak

The standard specifies zinc with a minimum purity of 98.5% for use in the bath. The aim of galvanizing is to protect steel from rusting see figure 6.1

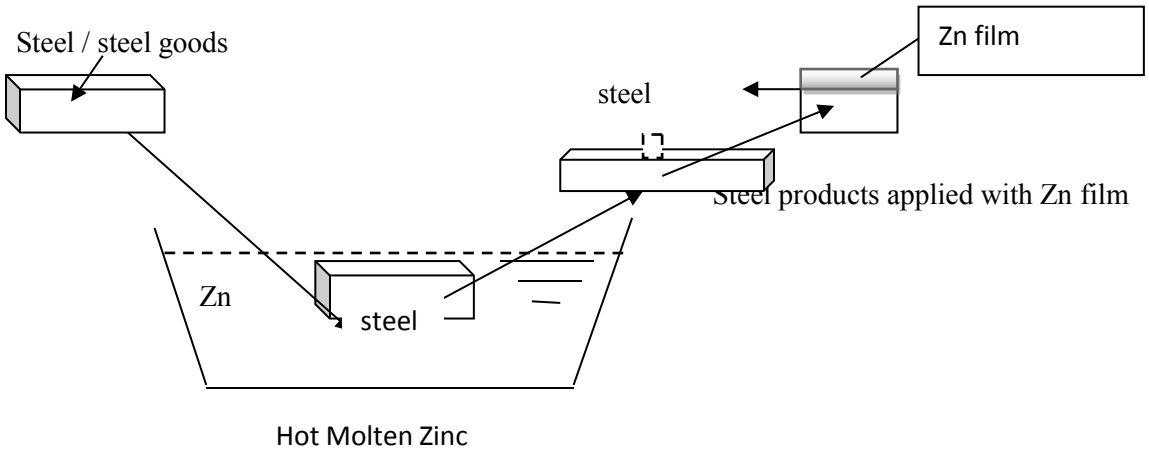


Figure 6.2: Outline of Hot Dip Galvanizing

Hot dip galvanizing products have excellent features such as:

1. Superior corrosion resistance
2. Cost effectiveness
3. Uniform coating
4. High adhesion

Superior corrosion resistance

Zinc offers a protective covering for the steel metal substrate. It also has a sacrificial tendency to protect the substrate from corrosion. See illustrations below:

	Zinc	Steel	Paint coating
Substrate	Zn	steel	coating steel
Rust formed	Rust($znO+Zn(OH)_2$) Zn Fine thin rust layer formed	Rust (Fe_2O_3) Steel Coarse rust formed	coating Steel Coating film deteriorates
After forming rust	Rust($znO+Zn(OH)_2$) Zn Fine thin rust layer formed acts as protective film	Rust (Fe_2O_3) Steel steel rust formed as it is poorly protective	rust coating steel substrate corroded

Figure 6.3 protective action of zinc.

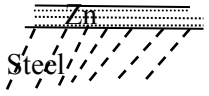
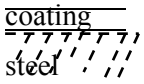
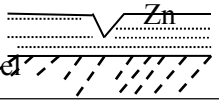
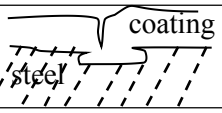
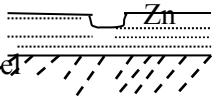
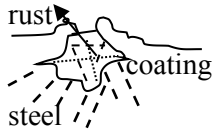
	Zn plating	Paint coating
Initial stage		
Scar generated		
Permeation of water	 sacrificial corrosion protection action of zn prevents corrosion of steel substrate	 coarse rust widely damages coating film and corrosion develops.

Figure 6.4 Sacrificial corrosion protection of zinc

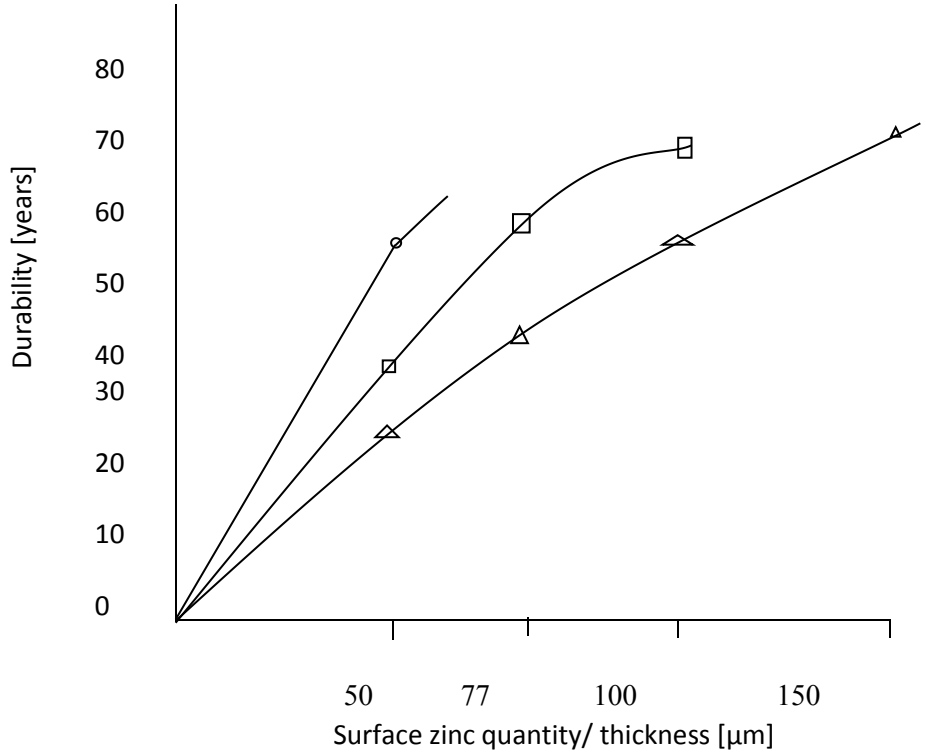


Figure 6.5: Durability of Hot Dip Galvanizing

Cost Effectiveness

Hot dip galvanization is cost effective in a study conducted by Arita Industries co. ltd Japan. The company showed that galvanizing is more cost effective than two –lay Three-layered coating red coating in terms of ₦1200/Ton of materials coated over the years. The cost of hot dip galvanizing remains constant as the years go by see figure 6.6, cost effectiveness.

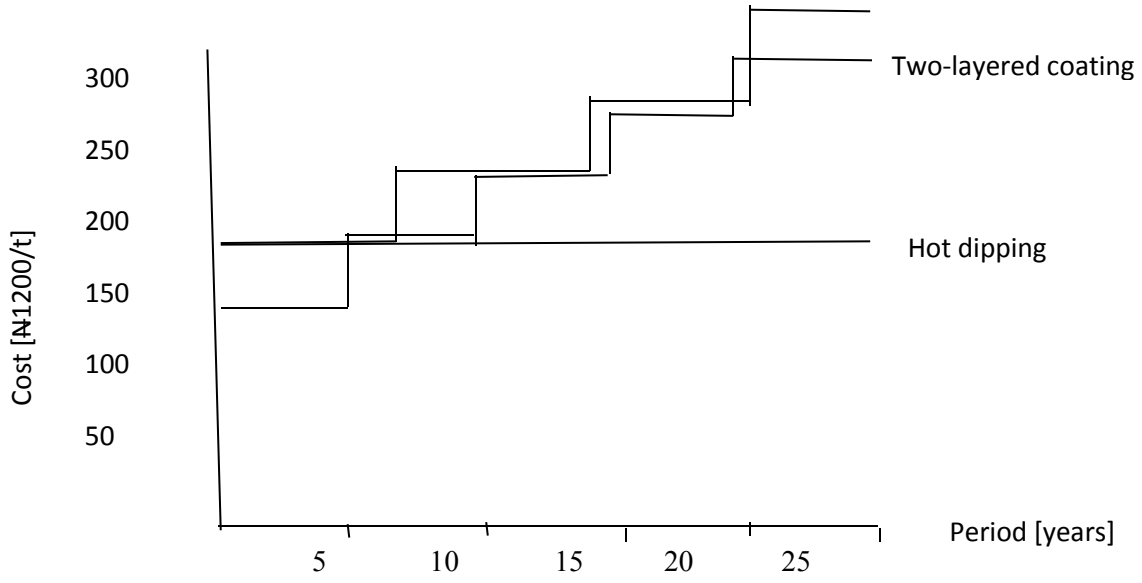


Fig.6.6 Cost Effectiveness of Hot Dip Galvanizing

Uniform coating: hot dip galvanizing provides uniform coating for even intricate shapes. Sharp corners and edges on dipping all get coated as shown in fig.6.7.

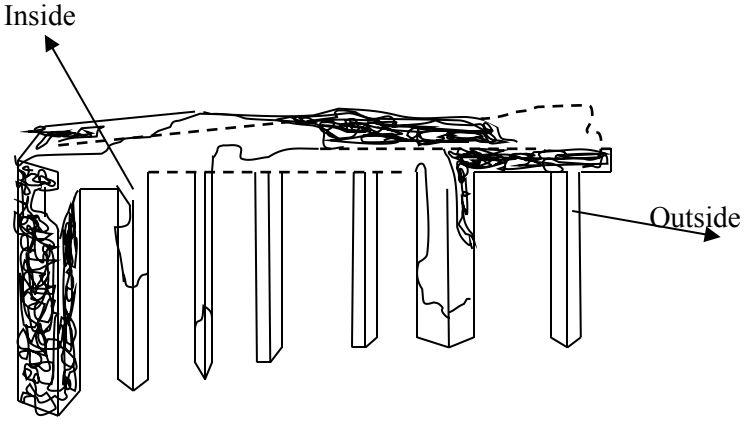


Fig. 6.7 Hot Hip Galvanizing Provides Uniform Coating

High Adhesion

Hot dip galvanizing has high adhesion to the steel substrate. A section through a galvanized steel plate will show an oxide layer, pure zinc layer, alloy layer and the steel substrate see fig.6.8 below:

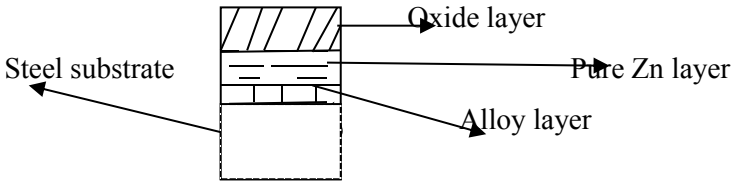


Fig.6.8 A section through a galvanized steel plate

6.2.3 Galvanizing process

The galvanizing process in a galvanizing plant normally starts with materials received. The materials are inspected and documented properly before they are assigned for processing. The materials are first sent to the degreasing tank to remove greases and oils. The tank is kept at $75^{O}C$- $90^{o}C$, sodium hydroxide is used for the degreasing and the process takes place for 5 minutes to 1hr depending on the size of the material and degree of contamination. The material is then transferred to the next tank which is for acid cleaning, the solution contains hydrochloric acid (HCl) the process of cleaning is known as pickling and it is done for 2 hrs. The next stage is the fluxing tank the fluxing tank contains a solution of $ZnCl_2$ and NH_4Cl, the solution contains 30% of the two chemicals. The temperature of the bath is normally at $60^{O}C$ and the use of the flux is to ensure that zinc adheres to the substrate. Hollow products without vents are very dangerous. They could cause explosion during galvanizing. To avoid explosion the products should be dried or vented after fluxing. The coating thickness on the product is determined by the resident time. Companies have data that guide them on the resident time. Resident time of 1- 4 minutes is commonly used when products are immersed in the galvanizing tank. Molten zinc has a specific gravity of 6.5 and purity of 99%, the others are trace elements like lead, aluminum and others. Galvanizing tank is normally heated from underneath using gas burners to a temperature of $430^{O}C$- $450^{O}C$. Ammonium chloride is added to enhance fluxing; immersed products are removed from the galvanizing tank and quenched in water bath for few minutes to stop the alloy reaction and have a stable coating on the surface the temperature of the water is normally 40-$50^{O}C$. Even if the thickness of galvanized sheet is like the sheet of a paper it can last for 50 years or more. The pretreatment baths are checked every 2 days to ensure that they are still effective. The product can also be cooled in air. Finishing and inspection involves using grinders and files to remove rough surfaces. The inspection involves checking the appearance of the

product and also checking the thickness of the coating. Products that are certified to meet the standard are then shipped for delivery.

Hot Dip Aluminizing in Practice

10000T/ year of hot dip aluminizing is carried out, in Japan about 100 companies are involved in the business with a production capacity of 1.0MT/ Yr. it is carried out on various products for heat and corrosion resistance. The substrate used for hot dip aluminizing can be steel and stainless steel. the substrate is first cleaned by dipping in HCl bath and rinsing in water bath before moving it to hot aluminium bath which normally contain 95%Al and 5%Zn and fluxes the composition of which is given below. The bath is normally at 706^{o}C and a depth of 1m of molten aluminium, the work piece is normally dipped for 4 minutes and removed. It is then water cooled before air-cooling. The bath has a chiney attached for fumes extraction. The bath is stirred before dipping the work piece for two times and thermit reaction takes place after the 4 minutes. HNO3 acid bath is used to remove coated aluminium. When the flux in the bath becomes much it is removed and it takes 30-40 minutes to remove the flux. Materials for aluminizing include, jigs for heat treatment facilities, cast iron and stainless steel steam boilers.

Secondary Diffusion Process

Aluminizing can be carried out on bolts and nuts, here the aluminized parts are heated in the furnace to the austenizing temperature and held for sufficient length of time for the formation of diffusion layer. The treatment increases the heat resistance of the material. For the bolts and nuts the wear resistance is also increased. Welded stainless steel is normal heat treated before aluminizing and mechanical cleaning is carried out to remove excess aluminium from bolts after aluminizing. The thickness of aluminizing is normally between 20µm- 100µm. the melting point of the flux used is 680OC and the composition is given below

The mixing of the flux

- NaCl 50g
- KCl 50g
- Na_2AlF_6 50g
- AlF_3 25g

6.2.4 Quality Control

6.2.4.1 Evaluation Method

Corrosion protection period is in proportion to coating thickness. The performance is evaluated according to Zn plating thickness.

6.2.4.2 Coating Weight Test

JIS HDZ- 55 (550g/ m^2 = 77µm) the value must agree for a good coating. The value is arrived at by subtracting the initial weight by the final weight after galvanizing and dividing by the surface area, this gives the coating weight. This method is referred to as the direct method. The coating mass is obtained by weighing the test piece before and after coating and calculating the increase in weight.

Operation and calculation of coating mass: after pickling, washing and drying the test piece as done before the substrate represented thereby, weighing it and carrying out coating. Weighing it again and obtaining the coating mass by dividing the increased amount by the surface area of the test piece.

6.2.4.3 Indirect Method

Principle: the hot dip galvanized coating is dissolved in hydrochloric acid and the resultant loss in mass is determined by weighing the test piece before and after the coating is dissolved.

Operation: the test piece shall be weighed before zinc dissolves. The accuracy shall be 1% or under of the presumed coating mass (the prospective coating mass). The quantity of the test solution shall be determined so as to be minimum 10ml per 100mm^2 of the surface area of the test piece. The test piece shall be dipped completely in the test solution at room temperature, and left until the coating film is completely dissolved. The progressive generation of hydrogen in the solution stops, this shows that the dissolution is completed. Then, rinse the test piece in running water, wipe it well with cotton cloth, dry it sufficiently, or immerse the test piece in alcohol and dry it immediately, and weigh the mass again with the accuracy. After weighing, obtain the area S (mm^2) with the accuracy of measurement of 1% or under of the actual surface area.

Calculation of coating mass: the coating mass shall be calculated from the following formula:

$A = \frac{W1 - W2}{S} \times 10^6$ Where, A: Coating mass (g/m^2), W_1 : mass of test piece before removing coating layer (g), W_2: mass of test piece after removing coating layer (g), S: Surface area of test piece (mm^2)

6.2.4.4 Electromagnetic Thickness Test

Principle: the coating thickness of product is measured by means of an electromagnetic measuring apparatus. From this measured coating thickness, the coating mass is obtained through conversion. The method for obtaining the converted coating mass from the measured value of thickness shall generally be in accordance with the following formula by taking the density of galvanized coating as 7.2g/cm^3.

A = 7.2 x t

Where, A: Zinc coating mass (g/m^2), t: coating thickness (µm)

6.2.4.5 Methods for Adhesion Test

Method by visual inspection: the presence of cracks or exfoliation of the coating layer due to the ordinary handling shall be examined. The visual inspection method is applied to products which are not subject to the hammer test or bending test.

Bending test: when bent by a specified angle with an inner side radius of specified times the diameter or thickness of the test piece, the surface condition of the coating layer such as the bent part or welded part shall be examined.

Hammer test: the surface condition of the coating layer which has been subjected to hammer blows is normally examined. The apparatus is shown in fig.6.9.

Operation : the test surface shall be horizontal and the hammer shall be allowed to fall freely from the position where its arm is vertical centering the support table. Blows shall be applied to 5 parallel positions at 4mm intervals and the exfoliation and embossment between their traces shall be examined. The area within 10mm from the corner or end shall not be tested. Each position shall be stuck only once. This test is carried out at an ordinary temperature.

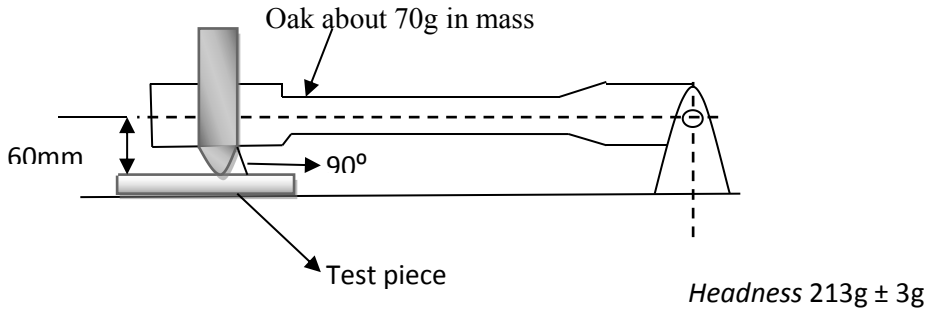


Figure 6.9 Apparatus for Hammer Test

6.2.4.6 Acceptability Judgment

The acceptability judgment for the adhesion test is as follows:

a) As a result of the adhesion test by visual inspection, coating layers on which is cracking or exfoliation is observed is deemed acceptable.
b) As a result of the bending test, coating layers on which no embossment or exfoliation is observed is deemed acceptable
c) As a result of the hammer test, coating layers on which no exfoliation or embossment is observed between the data is deemed acceptable.

Phenomena Appearing on Coating Surface

a) **Uncoated area:** areas on the substrate which are not coated with film, with the surface being locally exposed, when uncoated area is small, it has only a minor influence on corrosion

resistance thanks to the self sacrificing protective function of surrounding zinc. The size of uncoated area covered by this function is experimentally Ø 5.5mm or 5mm in width

b) **Burn:** parts of coating which lack gloss of metallic zinc and whose surface shows delustering or grey, in extreme cases, it becomes dark grey. This phenomenon is the exposure of alloy layer on the surface of coating and it does not influence the corrosion resistance in the air. If adhesion is sufficient, a burn is not practically a defect. This should be when setting the criteria on appearance. Moreover, the gloss of metallic zinc is lost as oxidation progresses, and it turns into the tone resembling the surface of burn. The silicon content is different depending on the steel manufacturing process (deoxidation process) and frequency of occurrence of burn is different by its influence.

c) **Lumpiness and run:** adhesion of excessive amount of zinc on parts or and parts of substrate. Generally speaking, substrate easily generating burns, since they are galvanized at a low temperature, are likely to cause lumps and runs as well since the lowered galvanizing temperature reduces the fluidity of zinc. When lumps and runs are smoothed out with means such as files care should be taken not to expose the substrate surface, unless they can be detrimental to practical use, lumps and runs should be left untouched.

d) **Seam:** linear and characteristic unevenness of the coating on the surface of substrate which has flaws. Removal of seams is not essential because the coating film is formed. Attempts to smooth out the surface may cause exposure of the substrate surface.

e) **Skimming:** significant amount of zinc oxide or flux residue sticking to the surface. Such residue generally has adverse effect on corrosion resistance. They should be removed with files or other means when found on the coating

f) **Rough deposit:** fine particle shaped projections on which suspended matter (dross) adheres. It does not affect the corrosion resistance of the coating.

g) **Flaw:** mark generated by the contact of a coating implement with the crating surface. The adversity of the flaw on the coating surface should be judged by their position of generation, size and depth.

h) **Discoloration:** discoloration of crating surface caused by the adhering of chemicals during storage or at the time of raising from coating bath.

i) Discolorations caused by raising from the coating bath is caused by interferences and reflection of light and do not have any effect on corrosion resistance.

j) **White corrosion:** the corrosion product of basic zinc carbonate and the like produced by the adhering of rain water, dew formation and the like during storing. The exhaustion of coating film due to white corrosion is small in extent and has little effect on corrosion resistance of the coating.

6.2.4.7 Classification and Symbols

Classification and symbols of coatings is as given in Table 6.1.

Table 6.1 Classification and Symbols

Class	Symbol	Example of Application
Class1A	HDZ A	Rolled steels and steel products up to and include 5 mm in thickness steel tubular products, bolts and nuts 12 mm and over in diameter and washers over 2.3 mm in thickness
Class1B	HDZ B	Rolled steels and steel products over 5mm in thickness, steel tubular products, castings and forgings
Class2 35	HDZ 35	Rolled steel and steel products with a thickness I mm or over up to and include 2 mm in thickness, bolts and nuts 12 mm or over in diameter and washers over 2.3 mm in thickness
Class2 40	HDZ 40	Rolled steels and steel products over 2 mm up to and include 3 mm in thickness, and castings and forgings
Class2 45	HDZ 45	Rolled steels and steel products over 3mm up to and include 5 mm in thickness, and castings and forgings
Class2 50	HDZ 50	Rolled steels and steel products over 5 mm in thickness and castings and forgings
Class2 55	HDZ 55	Rolled steels and steel products, castings and forgings to be used under severe corrosion environmental conditions

Notes

1. *The coatings of HDZ 55 should be required for articles whose substrate are at least 6 mm thick, when applying it for those of substrate with thickness under 6mm.*
2. *The thickness and diameter given in example of application'' column in the above table are nominal dimensions*
3. *Severe corrosion environmental conditions mean areas such as sea side where the concentration of sea salt particles is high, or areas where snow melting agents are sprayed.*

6.2.4.8 Weak Points about Hot Dip Galvanizing

The weak points of hot dip galvanizing include the following:

a. limitation to substrate size
b. work piece must not have hollow or sealed section

c. long term corrosion protection in coastal area could not be expected
d. severely attacked by acid and alkali
e. initial brightness does not last

Areas of application of hot dip galvanizing are as follows:

a. used for roofing sheets
b. plant steel frames
c. steel tower for power transmission
d. pipes for water supply
e. micro wave steel tower
f. telecommunication tower
g. cable bridge
h. transformer station
i. some parts of ship
j. steel tubes for structural purpose
k. Rolled steel: steel plates, sections, steel flats, steel bars etc.

6.3 THERMAL SPRAYING

Thermal spraying is a very versatile technology. There are different types of thermal spraying with different sources of energy. This technology has attended sophistication and is gradually replacing electroplating in some areas. Thermal spray process include, plasma transfer arc, atmosphere plasma spray, vacuum plasma spray, gas thermal spray, the various processes can be used to apply ceramic coating, carbide coatings, metal coatings, alloy coatings and composite coatings. Atmosphere plasma spraying has a short flame while vacuum plasma spraying is free of oxidation and it also has a longer flame than atmosphere thermal spraying. Chemical densified coating has a higher density and higher corrosion resistance than the thermal spray process. Thickness of thermal spray wire can be 2-3 mm but the coating will be porous. Using the other thermal process (VPS, PTA) thickness will be 30μm-800μm. thermal spraying normally start with the turning and the grinding of the work piece which is then followed by blasting using abrasive material. There are different types of abrasive materials and alumina is one of them. Hand blasting device is used to blast small work pieces. Specially made blasting chambers are used for larger materials. Thermal spraying using spraying gun is very portable because work pieces can be sprayed on site. The equipment is made up of oxygen cylinder, propane cylinder, air cylinder, wire (aluminum, brass, zinc, aluminum-zinc alloy etc) spraying gun. The work piece is blasted before spraying. The feeding speed has to be controlled for quality deposition. The oxygen, propane and the air has to be controlled. Compressed air is used for atomizing or spraying. The oxygen and propane is used for combination. The spraying can be localized and different materials can be used as spraying metals as well as ceramics

Developing economical and long-lasting, antirust/ anticorrosion technologies for several steel structures, including large bridges, is an especially important challenge in the 21st century when environmental conservation and energy saving are important. JACC thermal spraying committee started its operation in 1983 in order to evaluate antirust/ anticorrosion thermal spraying and to improve thermal spraying technologies. In fiscal year 2001, thermal spray committee carried out the investigation research under contract of the National Institute for Materials Science and produced Antirust/anticorrosion thermal spraying, which uses zinc and aluminium etc. requires an objective evaluation based on long term tests, but such long term tests performed in actual field are not reported so often. In addition, some marine exposure tests performed in Japan reported that thermal-sprayed steel pipe piles have a poor anticorrosion property while other tests reported that they are excellent in a long term anticorrosion property.

Since the antirust/anticorrosion mechanism of thermal spray coatings is significantly dependent on the system of a series of thermal-spray processes including a substrate preparation, the sample materials with a clear and detailed processing history had to be used. 12 thermal sprayed steel pipe piles were prepared using JIS-authorized plat and installed them in the natural tidal zone at Chikura beach in Chiba prefecture in May 1986 to begin the marine exposure test, the committee reported the 10th year observation results in "Bouseikanri (rust prevention and control, a monthly magazine). The committee was carrying out an objective evaluation every year. This report covers part of the endurance data (mainly, for the appearance observation reports) collected in the initial 15 years, since a great amount of detailed data exist, the committee is working on a separate report with these data.

Applications of Metal-spraying.

(1) Corrosion Protection: the most extensive use of metal spraying is the application of aluminum and zinc into iron and steel. Calorizing is frequently accomplished by spraying 0.1 mm aluminum on steel and then heating the parts to form iron aluminum compound on the surface.

(2) Hard and noble surface. One big application of metallizing is the application of special metal surface on large masses of less costly metal e.g. big shaft required to be corrosion resistant need not be made completely of stainless steel. It might be made first of any metal

and hen metallized with the noble metal. Similarly the metallizing my be applied for abrasion or wear resistance, corrosion protection and electrical or magnetic properties etc. most of the regular hard surfacing materials are available in powdered form and can be sprayed when thin coatings are prepared.

(3) Soldering surfaces. Sprayed copper is usually used on non-metallic parts when it is desired to attach parts by soldering. The procedure may be also adopted on hard solder metals such as magnesium, when galvanic corrosion is not a consideration.

(4) Electrical conductivity. Conductive coating of copper and silver can be obtained on poor conductor e.g. by spraying copper on most of carbon brushes for motors and generators for better electrical connection.

(5) Thermal conductivity. Sometimes it is desirable to have surface to carry away heat from hot spots on poor conductors. In this case copper can be sprayed and it has further advantage of perfectly fitting into non-conducting part and gives best efficiency.

(6) Its other applications are in having decorative films, reflecting surface and special metal forms.

6.3.1Thermal-Sprayed Piles for Exposure

Materials, Shape, and Size

The test steel pipes are carbon steel pipe normally used for plumbing (JIS G3452, SGP-B100A, 114.3 mm Ø x 2,000 mm L x 4.5 mm t). Both ends were closed by arc-welding, the rolled steel plates for general structure (JISG3101S3400) was used to make a test pile.

6.3.2 Spraying Specification

For pre-processing, they performed the air-pressure and dry-type blasting that is defined in JIS H9300 (1977) “Recommended Practice for Zinc Thermal Spraying on Iron and Steel” and JIS JIS H9301 (1977) “Recommended Practice for Aluminium Thermal Spraying on Iron and Steel”. # 20-40 fused alumina (WA) was used as an abrasive, and steel grit (G70 and G100 were mixed 2:1) was used during the pre-processing of thermal spraying of some aluminium. The blast was finished to a Sa 2½ of ISO8501 – 1 or higher standard. Grain size of the abrasive was designated to control the surface roughness. Thermal spraying was carried out within an hour after the blasting operation.

As a thermal spraying method, wire flame spraying (oxygen and acetylene flame) and electric arc spraying were selected so that their anticorrosion characteristics could be compared. A wire of 2.0 mm Ø was used for the electric arc spraying of aluminium while wire of 3.1 mm Ø for the other spraying operations. A thermal-spray-coating thickness of 175 ± 25μm was adopted in accordance with the standards, such as BS2569, AWSC 2.2, JIS H8300 and JIS H8301 (1971). A thickness of 40 μm was additionally adopted for the aluminium thermal spraying because 0.4-0.5 mm spraying is described in JISH8301, AS 7 and thick coating with electric arc spraying method is often used for special cases. The committee used thermal spraying equipment by Metallisation Limited for the electric arc spraying and another piece of equipment called IIE by Sulzer Metco for the flame spraying. The equipment was respectively operated at the optimal condition for the spraying operation. Table 6.2 shows the spraying, sealing and painting specifications of the test piles used for the exposure test.

Thermal spraying only was performed for Nos. 1-5. Sealing with epoxy was treated for Nos. 6-9 after the thermal spraying operation, and heavy-duty painting was performed for Nos. 10-12. The sealing treatment was performed by brushing the cold-setting epoxy resin (Epicote 828) diluted

with thinner (at the mixture ratio of 100:50) twice within 24 hours after the thermal spraying operation. The selected heavy-duty painting was the same as those used by the Honshu-Shikoku Bridge Authority and panting was performed by Steel Bridge Painting Corporation.

Test materials for storage were also prepared at the same time for a comparison with the test piles at the completion of the exposure test. The comparative evaluation test are appearance, coating thickness, cross-section micrograph, and flattening, as well as destruction tests such as EPMA and XPS, using these test results, the committee planned to examine any changes in coating performance.

Table 6.2 Spraying Sealing and Painting Specifications for Test

No	Spray Metal	Spray Method	Coating Thickness (μm)	Sealing Treatment	Painting Specification	Quantity
1	Zn	Flame	175 ± 25	None	-	1
2	Zn87-Al13	Flame	175 ± 25	None	-	1
3	Al	Flame	175 ± 25	None	-	1
4	Al	Arc	175 ± 25	None	-	1
5	Al	Arc	400 ± 25	None	-	1
6	Al	Arc	175 ± 25	Epoxy	-	1
7	Zn87-Al13	Flame	175 ± 25	Epoxy	-	1
8	Al	Flame	175 ± 25	Epoxy	-	1
9	Zn	Flame	175 ± 25	Epoxy	-	1
10	Zn	Flame	175 ± 25	-	WP + PE (100 μm x 3) + PU (100 μm x 1)	1
11	Al	Flame	175 ± 25	-	Primer + Special PU (MITSERON386) (3	1

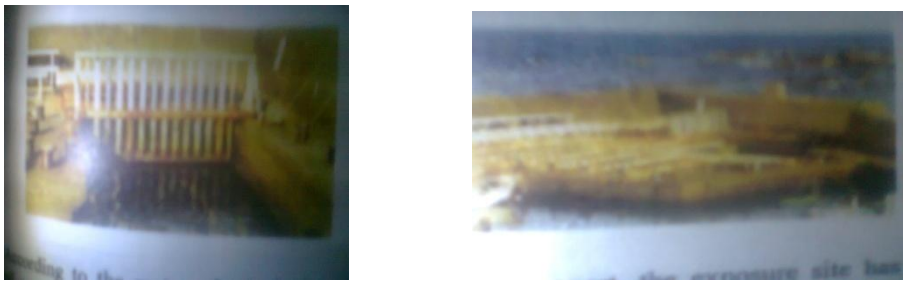
					mm x 1)	
12	Al	Arc	400 ± 25	-	CP + PE (100 μm x 3) + PU (100 μm x 1)	1

Al: JIS H2102 (Al 99.7% or more)
Zn: JIS H2107 Zn (Zn 99.9% 0r more)
WP: wash primer
CP: calcium plumbatel epoxy-type primer
PE: epoxy resin painting
PU: polyurethane resin painting

6.3.3 Exposure Test

Site and Environment for the Exposure Test

The test was carried out using a part of the Chikura beach exposure site of Kausai Paint Co. Ltd at Chikura-cho, Awa-gun in Chika prefecture (at 34 degrees 56 minutes north latitude and 139 degrees 58 minutes east longitude). Regarding the exposing environment, the sprayed piles were aligned and vertically installed in a trestle as fig.6.10 shows. The following three environments were set up onto one test pile: the sea-air, splash, and tidal zones divided by the under-the-sea portion and the sea surface. The trestle was located inside the fishing port sea wall but was totally exposed to waves during a typhoon.



a b

Fig.6.10 a) Installing condition, b) Installing environment

According to the meteorological observatory report, the exposure site has an average annual maximum temperature of 30°C, a minimum temperature of 1.9°C, average total solar radiation energy of 11-12 Mj / m^2 / day, an annual rainfall of 1,800-2000 mm, and an average monthly relative humidity of 65-90%.

The sea salt particle amount and composition are: NaCl (1.6-2.9 g /dm^2 / day on average), SO_4 – (0.03-0.04 g /dm^2 / day on average), and NO_3- (0.03-0.05 g /dm^2 / day on average).

Table 6.3 Analysis Method of Seawater Quality

No	**Analysing Item**	**Test Method**	**June 1, 1989**	**June 20, 1994**
1	Ph	K0101 Glass electrode method	8.6	8.7
2	Na ion	K0101 Flame hardness method	15,300	11,400
3	Mg ion	K0101 ICP emission spectroscopy method	1300	1,400
4	Ca ion	K0101 ICP emission spectroscopy method	412	450
5	K ion	K0101 Flame hardness method	19	21
6	NH_4 ion	K0101 Absorptiometry method	1.6	0.04
7	NO_3 ion	K0101 Absorptiometry method	1.7	0.09
8	Cl ion	M0202	23,100	21,200
9	SO_4 ion	M0202	2,320	2,690
10	COD	K0101	1.4	1.3

Investigated Item and Method

The committee carried out an appearance observation and took photos as well as measured the coating thickness every year since 1987, the year after the exposure commencement. At the time

of observation of the appearance, Mosses and other objects adhering to the surface were removed with seawater using a soft brush before the items described in Table 6.4 were investigated.

Table 6.4 Changes and Defects Observed and Noted

1. Blisters 2. Peeling 3. Cracks 4. Rust (white rust) 5. Exfoliation 6. Deterioration	7. Red rust 8. Change in colour 9. Adherence of living things 10. Indentation (scratch) 11. Transferred rust (rust transferred from other objects) 12. Others

Investigation was performed regarding the sea-air, splash and tidal zones. Visual observation was conducted on the surfaces on both the sea and land, sides were sketched. Photos were taken from three angles every 120 degrees with the sea side at their centre. The thermal spray coating thickness was measured at 24 locations using an electromagnetic thickness gauge. Table 6.5 shows an evaluation standard of the appearance.

Table 6.5 Evaluation Standard of the Appearance

Evaluation	State of Appearance of Thermal Spray Coating
A	No change in the thermal spray coating. It is in good condition
B	The coating is partially spotted with white rust on the surface. Shells, algae and oil residue are adhered.
C	The coating is heavenly spotted with white rust. The painted film changes in colour tone and micro-blisters occur.
D	The surface of the coating is partially deteriorated and slightly blisters and peels off. Spotted red rust occurs on substrate.
E	The deteriorated and damaged coated film causes red rust all over the surface of substrate.

6.3.4 Result and Examination of the Exposure Test

1. Observation Result

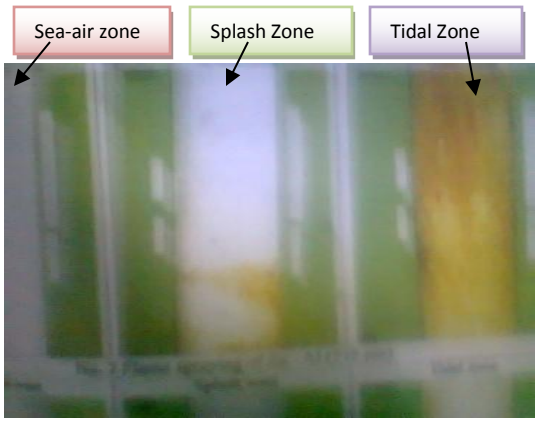
Fig.6.11 shows the photos taken after 15 years of exposure. The observation was performed at three locations, i.e. the sea-air, splash and tidal zones, from three directions. Since there is hardly any difference by direction, these photos include only the 5 major test piles that were taken from a single direction.

Since rust generated on the thermal spray coating sometimes disappears in the following year, the thermal spray coating must be evaluated comprehensively by recording deterioration with age. This report explains the progress made in 15 years using the five-scale evaluation system (A-E) as Table 6.5 shows. Actually, it is which item should be included as part of the evaluation standard as well as what level of significance (or harmfulness) must be set for each item. For instance, one of the most radical viewpoints asserts that it is acceptable if no iron rust can be found on the base material; the objective of thermal spray coating is to protect steel piles, and

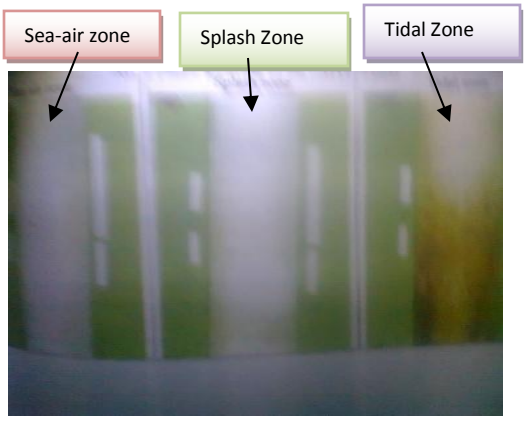
therefore it is natural for the coating to be deteriorated from the view-point of its being a sacrificial anode.

On the other hand, another view point may show that deteriorated sealer or rust on the thermal spray coating will directly ruin the anticorrosion mechanism; our objective should be long-term antirust / anticorrosion. However, we still do not know exactly how harmful the deteriorated sealer or rust on the coating can be for the anticorrosion mechanism of the base material. In this way, an evaluation of the anticorrosion mechanism using the appearance observation is extremely difficult, and the evaluation standard in Table 6.5 is controversial. Therefore, this evaluation result maybe slightly distorted but the progress up to the 15^{th} year was judged in accordance with Table 6.5.

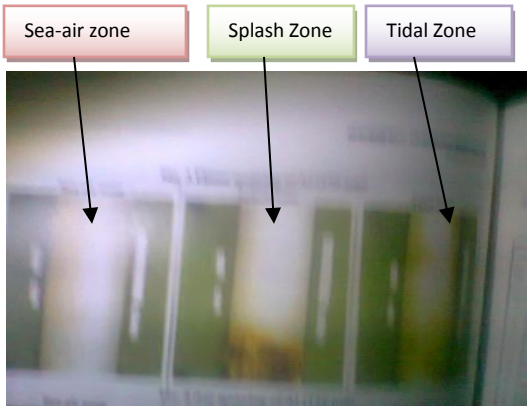
Deteriorated sealer and transferred rust are secluded from the evaluation condition, because, in accordance with the anticorrosion performance of the thermal spray coating. However, since the objective of the painted sample piles (nos. 10-12) is to examine the anticorrosion performance of the painted films, the painted films of these sample piles were examined in terms of their change in colour, deterioration, swelling and cracking, etc.



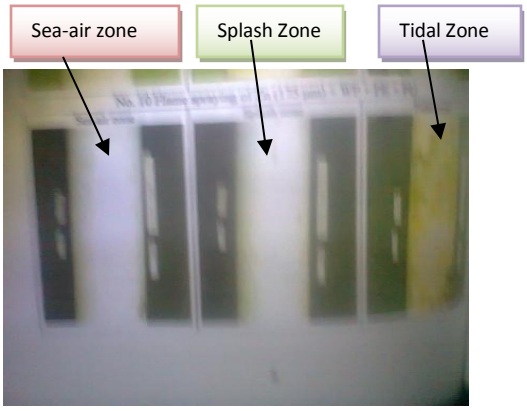
No. 1 Flame Spraying of Zn (175µm)



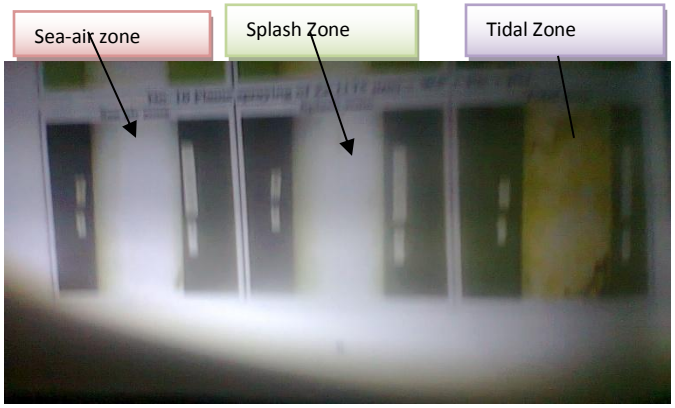
No.2 Flame Spraying of Zn-Al (175µm)



No.3 Flame Spraying of Al (175 µm)



No.4 Arc Spraying of Al (175µm)



No.10 Flame Spraying of Zn (175µm) + WP + PE + PU

Fig. 6.12 Pictures of the Test Specimens after 15 Years of Exposure

Table 6.6 shows the exposure results after 7, 10 and 15 years in accordance with the appearance evaluation standard.

Table 6.6 Results of Appearance Examination for Each Zone after the Exposures of 7, 10, and 15 years

Marine exposure period		**7-Year exposure**				**10-Year exposure**				**15-Year exposure**			
No	Spraying specification	Sea-air	Splash	Tidal	Overall	Sea-air	Splash	Tidal	Overall	Sea-air	Splash	Tidal	Overall
1	Flame Spraying of Zn (175µm)	AB	AB	AB	AB	AB	AB	E	E	AB	E	E	E
2	Flame spraying of 87Zn-13Al (175µm)	AB	AB	AB	AB	AB	AB	AB	AB	AB	AB	AB	AB
3	Flame Spraying of Al (175 µm)	AB	D*	B	B	AB	E*	B	E	AB	E*	B	E
4	Arc Spraying of Al (175 µm)	AB	B	A	AB	AB	B	A	AB	AB	B	A	AB
5	Arc Spraying of Al (400 µm)	AB	B	A	AB	AB	B	A	AB	AB	B	A	AB
6	Arc Spraying of Al (175 µm) + Epoxy sealing	A	A	AB	A	A	A	AB	A	A	A	AB	A
7	Flame spraying of 87Zn-13Al	A	A	A	A	A	A	A	A	A	A	AB	A

	(175µm) + Epoxy sealing												
8	Flame Spraying of Al (175 µm) + Epoxy sealing	A	A	AB	A	A	A	B	B	A	A	B	B
9	Flame Spraying of Zn (175µm) + Epoxy sealing	A	AB	C	C	A	AB	E	E	A	E	E	E
10	Flame Spraying of Zn (175µm) +WP + PE(300µm)+ PU(100µm)	AB	A	AB	AB	C	C	C	C	C	C	C	C
11	Flame Spraying of Al (175 µm) + primer + special PU(3000µm)	A	A	A	A	A	A	A	A	A	A	A	A
12	Arc Spraying of Al (400 µm) + CP+PE(300µm) + PU(100µm)	AB	AB	AB	AB	C	C	C	C	C	C	C	C

Note: The mark * indicates that an initial flaw on the coating is assumed to have generated the rust.

These results lead to the following conclusions as of the 15th year:

1. **No. 1 (flame spray of Zinc (175µm)**

   A significant antirust effect was maintained at the sea-air zone. At the tidal zone, however the coating thickness started to change at approximately the 6th year, causing the base material to corrode and generate red rust from the 7th year. The rust further developed after that.

2. **No. 2 (flame spray of 87 Zn – 13 Al (175µm)**

   It is generally in good condition, what looks like red in the photo of the tidal zone is not rust but a kind of seaweed. The coating is intact.

3. **No. 3 (flame spray of Al (175µm)**

   Although the overall evaluation is E, it is assumed that a flaw, which initially existed on the coating outside the observed area in the splash zone at the time of installation, was developed and sprayed into the observed area. The other part of the coating is intact.

4. **No. 4 (Arc spraying of Al (175µm)**

   It is generally in good condition

5. **No. 5 (Arc spraying of Al (400µm)**

   It is generally in good condition

6. **No. 6 (Arc spraying of Al (175µm) + Epoxy sealing)**

   It is generally in good condition. What look like a spotty pattern in the photo of the tidal zone is residual sealer material.

7. **No. 7 (flame spray of 87 Zn – 13 Al (175µm) + Epoxy sealing)**

   It is generally in good condition.

8. **No. 8 (flame spraying of Al (175µm) + Epoxy sealing)**

It is generally in good condition.

9. **No. 9 (flame spraying of Zinc (175µm) + Epoxy sealing)**

   This pile trace almost the same progress as the one without sealing treatment did (No. 1).

10. **No. 10 (flame spraying of Zinc (175µm) + WP + PE (300 µm) PU (100 µm)**

    The painted film swells and peels off here and there. The thermal spray coating is only lightly damaged with no signs of rust developing from the mother material.

11. **No. 8 (flame spraying of Al (175µm) + Primer + Special PU (300 µm)**

    In good condition, with almost no changes since the time of installation.

12. **No. 12 (Arc spraying of Al (400µm) + CP + PE (300 µm) + PU (300 µm)**

    The painted film swells and peels off here and there. The thermal spray coating is only lightly damaged with signs of rust developing from the mother material.

6.3.5 Measurement Result of the Changes in Coating Thickness

Any change in thickness was measured at fixed point of the sea-air, splash and tidal zones of both the sea and land sides. The following shows only its overview:

a. The test piles having special significant changes in coating thickness are No 1. and No. 9. The coating thickness of No 1.was on both the sea and land sides of the splash zone as well as of No. 9 in the splash and tidal zones have become more than twice as thick (500 µm or more) than the initial value after the 6^{th} year, consequently, exceeding the measured thickness in some parts.

b. Comparing the thermal sprayed layers of an alloy of Zn – Al with and without sealing treatment (namely between No. 2 and No. 7), the coating thickness tended to increase in the sea-air and splash zones when sealing was not treated. On the other hand, there was

no significant difference between No. 1 and No. 9, No.3 and No. 8 and No.4 and No. 6, regardless of whether sealing treatment was done.

c. Comparing the thermal spraying method of aluminium between No. 3 (flame type, without sealing) and No. 4 (Arc type, without sealing) did not show any significant difference.

d. Conclusion

Some of the thermal sprayed layers of aluminium and of an alloy of Zinc and aluminium still maintain an excellent anticorrosion mechanism even after 15 years have passed. This project initially started as a 5-year exposure test, but since most of the coatings were intact, it was extended to 10 years. Then the differences due to thermal spray material started to emerge, thereby making us recognise the importance of a long-term exposure test. We have just completed the site inspection of the 16th year, in keeping with our goal of 20 year. When 20 years have passed for the exposure test, it is expected that several phenomena can be elucidated through various analyses, such as a destructive test observation that includes cross-section cutting, and chemical analysis inside the thermal spray coating [7].

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6.4.1 Wire Flame Spraying

Wire flame spraying is one of the major gas spraying methods, liner-shaped spray materials are continuously fed into a burning flame of oxygen-acetylene or oxygen-propane in other to melt them, and the melted particles that are atomized with compressed air are protected in order to form a coating. As a thermal spray material, metal materials that can be processed in a liner state can be sprayed: low melting temperature materials such as zinc and aluminium as well as carbon steel, stainless steel, and molybdenum. Materials that cannot be easily processed in a liner state, such as ceramics or cermet are filled into a flexible tube and then sprayed. The method features portable spraying equipment that can be operated on site without heating base materials, and a broad range of thermal spray coating thicknesses (0.1 – 10 mm). The equipment is shown in fig.6.13 below

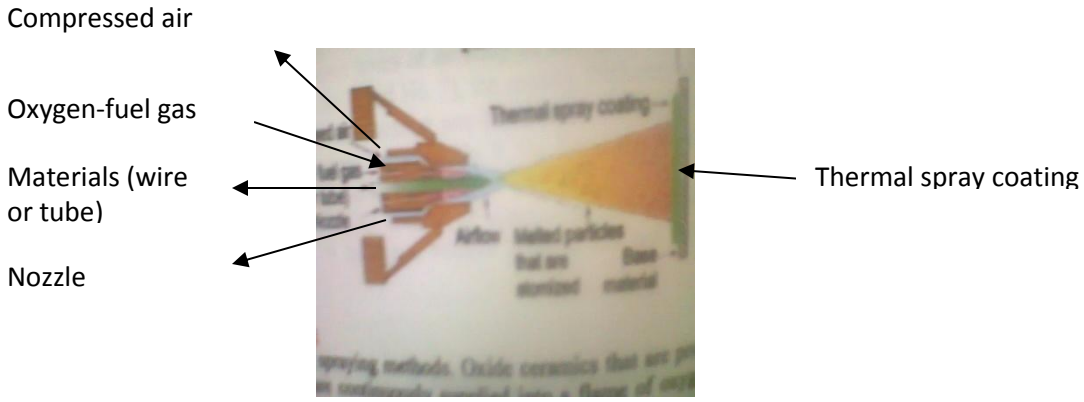


Fig. 6.13 Wire flame spraying device

6.4.2 Ceramic Rod Flame Spraying

This is one of the flame spraying methods, oxide ceramics that are processed in a 4.7 – 6.0 mm diameter rod state are continuously supplied into a flame of oxygen-acetylene in order to melt them, and particles that are atomized with compressed air are projected in order to form a coating. Oxide ceramics, such as aluminium oxide, zirconium oxide, and chrome oxide, are sprayed. Since completely melted materials only are sprayed, the sprayed coating does not include unmelted particles, thereby strengthening the bonding forces among the particles. This method therefore features the production of relatively tough coating. (see fig. 6.14)

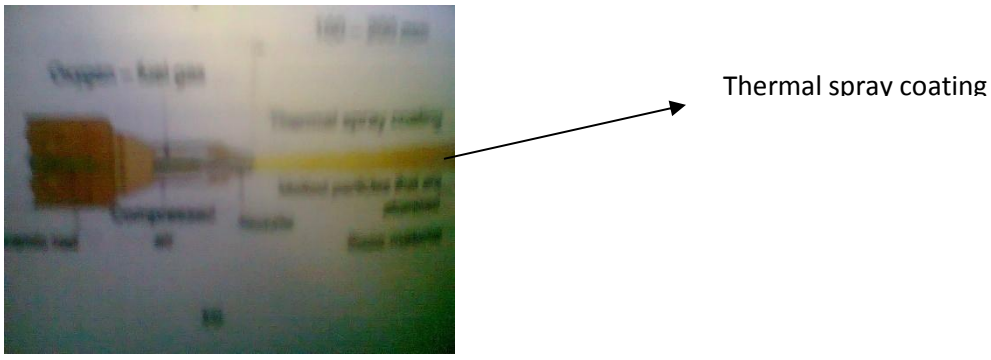


Fig.6.14 Ceramic rod flame spraying machine

6.4.3 Powder Flame Spraying

Powdered spray materials are projected into a flame of oxygen-acetylene (or hydrogen, propane) in order to melt them in the flame, and are simultaneously accelerated using a combustion gas stream in order to collide the melted powders with the base material. Although almost all of the metals, alloys and cermets can be sprayed, this method is

generally and widely used for self-fluxing alloy spraying that involves a remelting process after the spraying operation, for abradable spraying such as nickel graphite, and for plastic spraying. This method features a light and easy-handled thermal-spray gun, relatively high thermal spray efficiency, and low noise. (see fig.6.15)

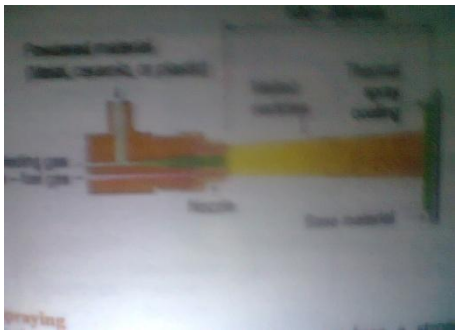


Fig. 6.15 powder flame spraying device

6.4.4 High Velocity Flame Spraying

This is the thermal spraying method developed to produce a strong colliding force through sprayed particles flying at high velocity that result in a thermal spray-coating that is fine-grained and highly-adhesive. In this method, high temperature combustion gas, which is produced with oxygen-propylene, oxygen-hydrogen, oxygen-kerosene, and air-kerosene, etc. is throttled in the nozzle to increase the velocity of the gas stream. Then, powdered spray materials are melted in the nozzle and simultaneously accelerated by the high-velocity gas stream so that they collide with the base material at a much higher velocity than the speed of sound to form a coating. The coating with this high velocity spraying method is higher-density, more-highly-adhesive, and harder than those applied using the other thermal spraying methods even using the same spray materials. This method is widely used for wear-resistant spraying that uses WC cermet materials.

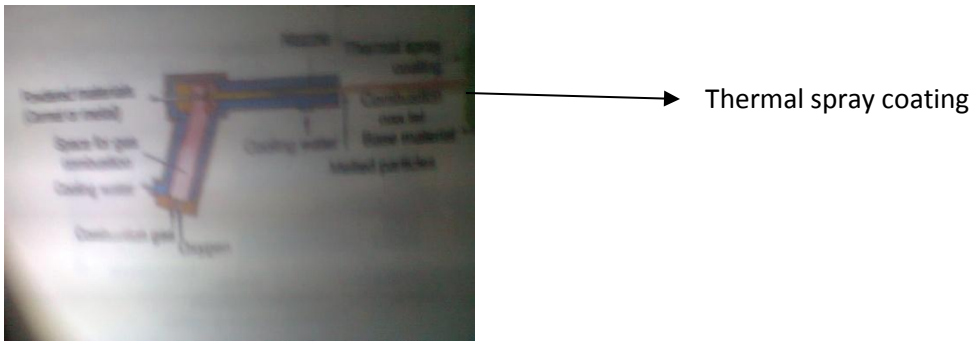


Fig.6.16 High velocity flame spraying

High Velocity Oxy-Fuel (HVOF) Spraying Process

HVOF spraying process is a process increasing the pressure in the combustion chamber of the spraying gun to produce high-speed flame comparable to detonative combustion flame, feeding the powdered spray materials into the middle of the flame jet stream to make them melt or half –melt, and continuously spraying the materials at high speed. As the molten fine spray materials collide with the substrate at very high speed, extremely high density coatings with high bonding strength can be produced. This spraying process proves its merits especially in forming wear resistant coatings with carbide cermets. Unlike this spraying method, in case of the method using detonative combustion flame in which the thermal spraying is carried out intermittently, the discontinuous spray pattern (pop marks) shown on the individual coating sometimes becomes an issue. Areas of application include plastic film making machine, extruding screws, sink roll in continuous galvanizing line and paper mill roll.

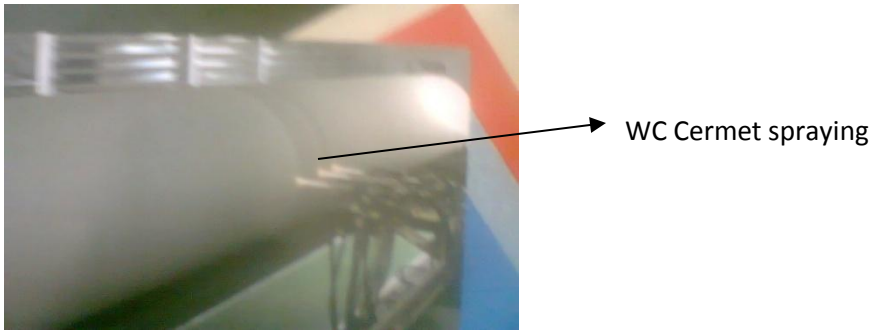


Fig. 6.17 WC Cermet spraying on paper mill roll using HVOF

6.4.5 Plasma Spraying

This is the spraying method in which a DC arc of a strong current is discharged in a gas, such as Argon, in order to form a high-temperature and high-velocity plasma jet inside the thermal spray gun, and then produced spray materials are projected into this plasma jet so that the materials can be melted and accelerated in order to form a coating. Since the plasma having an extremely high energy density can generate high temperatures exceeding 10,000oC, most of the materials can be sprayed, including metals with high-melting point, cermet and ceramics. Since the temperature of the plasma jet can be selected depending on the generating condition. This method features a relatively free choice of materials and a highly adhesive property between the base material and the thermal sprayed coating.

Plasma Oxy-Nitriding: the process involves nitriding and the oxidation to get Fe_3O_4 on the surface of the substrate.

Fig. 6.18 Plasma Spraying Device

Vacuum Plasma Spraying

The figure below shows a vacuum plasma spraying equipment called VPS thermal spraying equipment. Areas of application include turbine blade, gas turbine rotor of power generator, and energy industry. (See fig.6.20) Plasma spraying carried out in the chamber under an inert atmosphere at controlled low pressure is called VPS process. This process has the following characteristics.

- Since original properties of material are maintained, coating can be produced with characteristics as designed.
- Activated metals such as Ti can be thermal-sprayed.
- As the fly speed of molten particles is faster than that in the air coatings with higher bonding strength and higher density can be produced. VPS process is indispensable for forming highly functional coatings closely related to the investigation of various advanced technologies.

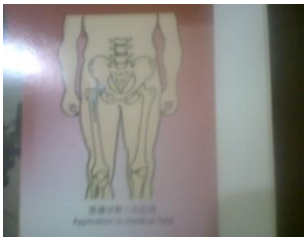
Fig.6.19.a). VPS Thermal Spraying Equipment

b). Inner structure of VPS thermal spraying equipment

Application to energy industry

Application to gas turbine rotor of power generator

Application to turbine blades



Application to Medical Field

Fig.6.20 Areas of Application of VPS Thermal Spraying Equipment.

Atmospheric Plasma Spraying (APS) Process

The process in which plasma spraying is carried out in the common air is called APS process to distinguish from VPS process. Incidentally, the simple expression `plasma spraying process' means APS process. Atmospheric plasma-sprayed coatings produced under severe process controlling and with properly selected spray materials and coating design in due consideration of every characteristic of manifold ceramic materials and their working conditions, are now playing active part in a variety of areas. APS is applied to tuyeres of blast furnace in the steel making industry, hearth rolls in continuous annealing line, insulated bearing for traction motor, roofing tile machine and mouthpiece. (see fig. 6.21 below)

Application bearing for traction motor

Application to steel making industry

Fig. 6.21 Areas of Application of Atmospheric Plasma Spraying

Plasma Transferred Arc (PTA) Process

In this process build up welding is carried out using powdered metals, alloys, and cermets as weld materials, and employing plasma transferred arc as the heat source. As powdered materials are used, it is possible to make weld depositing of various materials including cermets containing carbides, a kind of ceramics. Applicability of this process is now expanding unlimited. We have facilities which can deal with various weld depositing such as TIG, MIG, and submerged arc welding process, as well as PTA process. Areas of application ball valves, side guide rolls in hot strip mill, cartridge for atomic power industry. (see fig.6.22)

Fig. 6.22 Plasma Transferred Arc used on Cartridge for atomic power industry

6.4.6 Electric Arc Spraying

This is one of the electric spraying methods in which an electric arc (electric spark) is generated between two metal wires to use the discharged energy for melting the wires. The wires are fed according to the melting speed while the melted metal is atomized with compressed air so that this can be sprayed onto the base material to form a coating

continuously. Compared to the flame spraying method, this method features a higher spraying capacity (a larger spray coating amount that can be formed per hour) and more highly adhesive coating against the base material because the spray materials are sufficiently melted at a high temperature. Although the electric arc praying equipment can be operated using alternating current (AC), direct current (DC) is generally used for stabilising the arc. Since the wires are used as an electrode, the spray materials must have electric conductivity. (see fig.6.23)

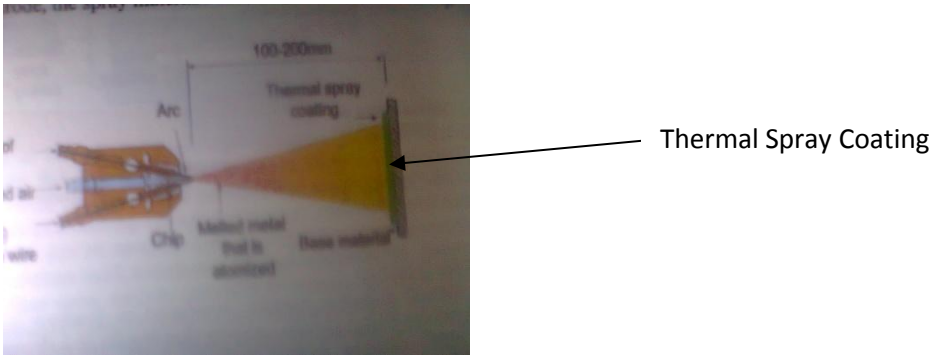


Fig.6.23 Electric Arc Spraying Equipment

6.4.7 Wire Explosion Spraying

This is one of the electric spraying methods in which a material with electric conductivity is processed into a liner state so that a strong impulse current is conducted on the material in order to discharge and explode the material in the air or inactive gas. The thermal spray material that is instantly melted with the strong current is atomized and scattered, and then collide with the base material to form a thermal spray coating. Since the collision speed is fast and the melted particles temperature is high, the coating is well adhered to the base material.(See fig.6.24)

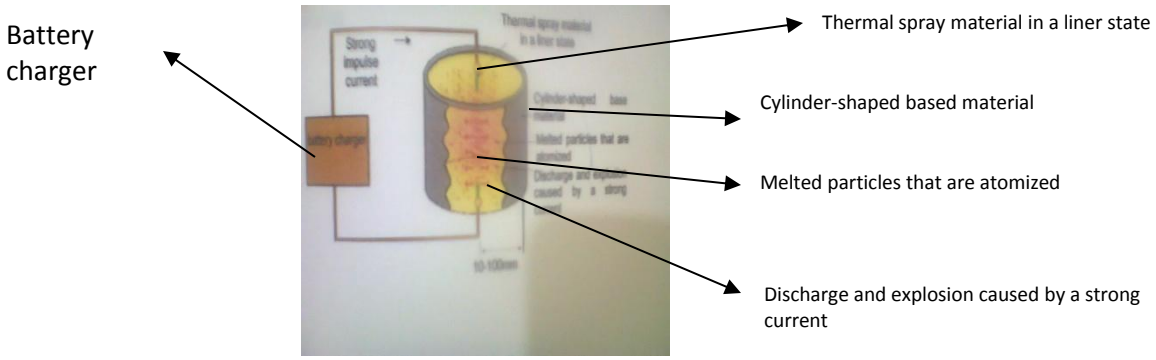


Fig.6.24 Wire Explosion Spraying

Wire Spraying Process

Wire spraying is a general term for thermal spraying using metal and alloy wire as the spray materials, and combustion flame, electric arc or plasma as the melting heat source. The wiry material is continuously melted and the produced drop-shaped melt are atomized immediately and sprayed on the substrate by using compressed air. All metals and alloys that can be made into wire, from low melting point metals such as aluminium, copper, and bronze, to stainless steel, high carbon steel, and molybdenum, are applicable as the spray material for the wire spraying. The word `metallicon' which is occasionally used for the thermal spraying with the main object of rust-proofing is a coined word derived from metalizing. Areas of application include boilers, hydraulic ram, bridges etc (see fig.6.25)

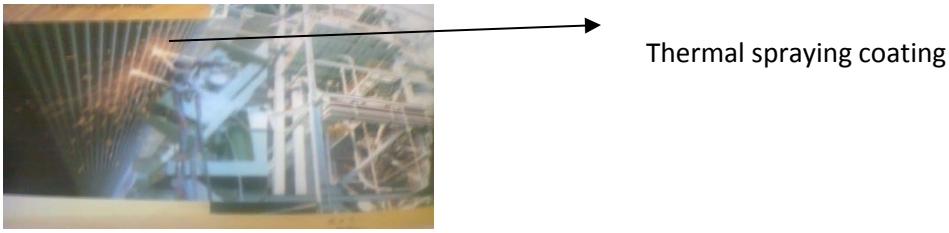


Fig.6.25 Spraying of Boiler using wire spraying process

6.4.8 Symbol Expressing Thermal Spraying Method

The symbol expressing thermal spraying method is as given in the table below:

Table 6.7 Thermal Spraying Method and its Symbol

Thermal Spraying Method	**Symbol**
1. Wire flame spraying	WF
2. Rod flame spraying	RF
3. Powder flame spraying	PF
4. High velocity flame spraying	HVF
5. Detonation flame spraying	DF
6. Electric arc flame spraying	ES
7. Plasma spraying	APS
8. Low pressure plasma spraying	LPS
9. Water stabilized plasma spraying	WPS
10. Wire explosion spraying	WES

6.4.9 Post Treatment and Post Processing Symbols

The symbol expressing post treatment expresses the treatment to be applied to the sprayed coating as post processing of the thermal spraying (see Table 6.8 below). The symbol expressing the post processing method applied is also shown in Table 6.9.

Table 6.8 Symbol Expressing Post Treatment

Grade of Post Treatment	**Symbol**
1. Sealing	SE
2. Heat resistant sealing	HRS
3. Diffusion treatment	DT
4. Painting	PA

Table 6.9 Symbol Expressing Post Processing Method

Processing Method	**Symbol**
1. Machine grinding	G
2. Machine cutting	C
3. Hand finishing	F

6.4.10 Thermal Spraying Method as Outlined by JIS H8300

Thermal spraying shall be as follows:

a. Thermal spraying shall be carried out after the parent metal surface has been prepared by abrasive blasting, within a period that ensures that the prepared surface is still clean, dry and not visibly oxidized when spraying commences.

b. This time delay shall be as short as possible. The process should be carried out typically within at least four hours of the blast completion depending upon the environmental conditions.

c. Thermal spraying process shall not be carried out under conditions leading to condensation of humidity on the surface to be sprayed, and the surface shall be maintained at a temperature of at least 3^{o}C above the dew-point to avoid blistering. If deterioration of the surface to be coated is observed, any affected areas shall be prepared again to bring them to the required quality.

6.4.11 Sealing

Sealing according to JIS H8300 shall be as follows:

a. The purpose of sealing is to fill up the inherent porosity of thermal spray coating. Natural sealing shall be such that the porosity of thermal spray coating is filled up with oxides or hydroxides, which are secondary and naturally generated by oxidation under normal environmental exposure conditions.

b. Artificial sealing shall be achieved either by chemical conservation of the coating surface (by phosphating etc.) or by applying an appropriate sealant to fill up any porosity. The sealant shall be applied before the coating can take up any moisture.

6.4.12 Measurement Method

Measurement method for thermal spray thickness includes; the use of magnetic thickness tester, coating appearance (visual inspection), micrographic cross-section examination, and adhesion test. Coating hardness test, heat resistance test, chemical corrosion resistance test method, tensile test and the degree of cohesion between particles are other tests associated with thermal coatings.

6.4.13 Methods of thickness measurement for sprayed coating

The kinds of test methods are as follows:

a. Test method by micrometer
    1. Direct method
    2. Masking method
b. Test method by microscopical examination of cross section
c. Test method by magnetic force
d. Test method by eddy current
e. Test method by scanning by profilometer

6.4.14 Measuring Method by Micrometer

Direct Method

Employing a micrometer, measure the thickness of substrate before spraying, again measure the thickness of the spot of the sample after spraying, and obtain the thickness of sprayed coating from the difference between both measurements.

Masking Method

Carry out the shielding treatment (also referred to as masking) from spraying on the part of substrate adjacent to the spot to be measured. After spraying, measure the difference in level between the coated surface and substrate surface to obtain the thickness of sprayed coating.

The number of measuring spots shall be at least 3 spots for the typical significant surface, and their average value shall be considered the thickness of sprayed coating of the product.

6.4.15 Test Method by Microscopic Examination of Cross Section

Observe the vertical cross section of the sprayed coating with a microscope to measure the thickness of sprayed coating.

Apparatus and Instrument

For this test, the following apparatus and instrument shall be used:

a. Micrometer microscope or metallographic microscope
b. Photographic apparatus for micrograph (unnecessary when micrometer microscope is used)
c. Slicing machine
d. Material for embedding
e. Polisher for test piece

Procedures

Preparation of Test Piece for Microscopic Observation

The preparation of test piece for microscopic observation shall be as follows:

a. Cut the test piece for microscopic observation, measuring about 20 mm in length and about 10 mm in width, from a suitable place of the sample so that the cut section is perpendicular to the sprayed surface. In this case, be careful not to destroy the sprayed coating.
b. If the size of the product is smaller than the size shown in (a), the product shall be used as a test piece for microscopic observation.
c. With care not to destroy the sprayed surface, polish and finish glossily the surface to make the surface to be observed at right angle to the sprayed coating. In this case,

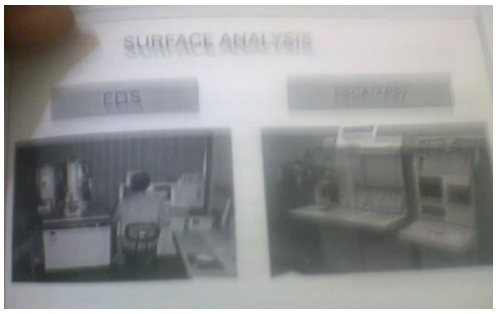
sufficient observation shall be paid not to give ‘slandering’ when polishing, and to prevent abrasive from being embedded in sprayed coating.

d. If the sprayed coating is soft or very thin, polish it after the test piece is embedded in resin or the like.
e. After polishing, if the boundary between the sprayed coating and the substrate is obscure, etch it with suitable etchant.

6.4.16 Observation of Cross Section of Sprayed Coating and Measurement of its Thickness

The observation of the cross section of sprayed coating and the measurement of its thickness shall be as follows:

a. Magnify the cross section of sprayed adequately using a micrometer microscope, measure the distance from the boundary of substrate to the surface of coating to obtain the thickness of coating.
b. When using a metallographic microscope, take photographs on which the cross section of sprayed coating is adequately enlarged to measure the thickness of the coating.
c. The magnifying power of microscope shall be chosen so that the measuring accuracy is not more than 5% of the thickness of sprayed coating.
d. Carry out the measurement at 5 spots by equal spaces in one visual field of microscope for one place, and their average value shall be considered the thickness of sprayed coating at the place.
e. Take at least 3 places for measurements, and the average value of the thicknesses of the sprayed coating shall be considered that of products.



6.4.17 Test Method by Magnetic Force

The thickness of paramagnetic coating deposited on the metal substrate which is ferromagnetic is obtained by measuring the magnetic resistance at a magnetic circuit passing through magnetic pole, sprayed coating, and substrate metal, or alternatively by measuring the magnetic attraction working between the permanent magnet and the substrate metal through the sprayed coating.

If the substrate metal is already magnetized, this method shall not be applicable.

Apparatus

a) Electromagnetic Measuring Apparatus

These apparatus are classified into 2 types according to the substrate of detector. An example of the apparatus is shown in fig.6.26.

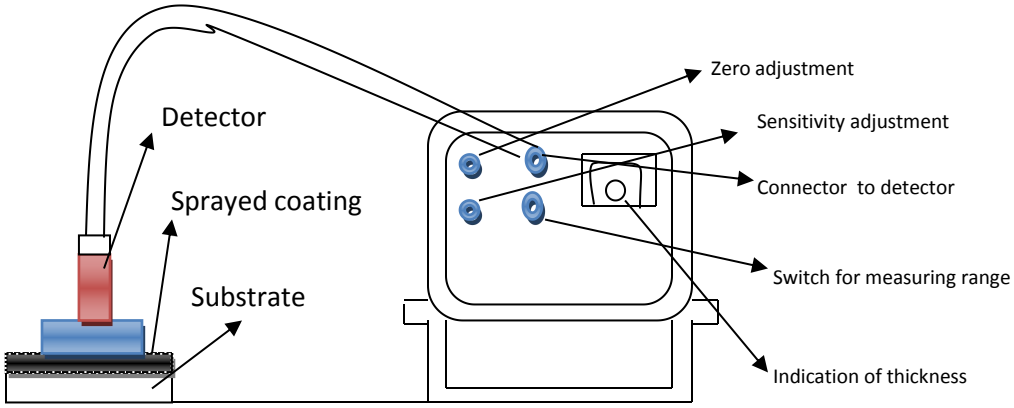
1. Unipolar type (with single measuring head)
2. Bipolar type (with double measuring heads)

b) Permanent Magnet-type Measuring Apparatus

c) An example of this apparatus is shown in fig. 6.27.

d) The minimum scale of these apparatuses shall be limited to 5 μm for the measuring

e) range from 0 to 100 μm, and 10 μm for the range from 100 to 500 μm.



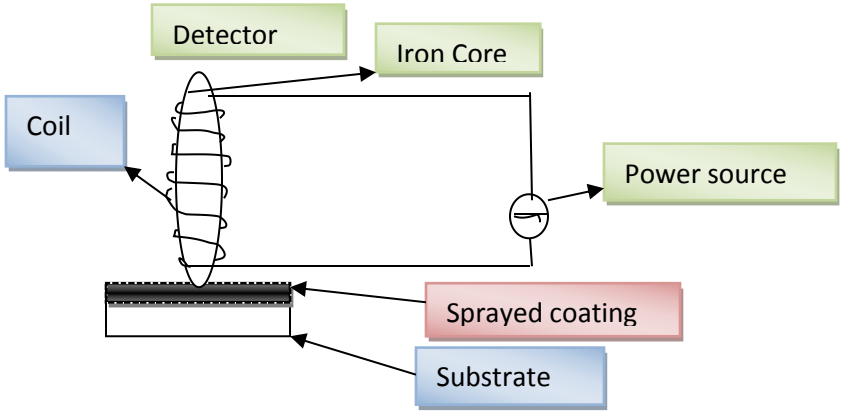


Fig. 6.26 Example of Electromagnetic Measuring Apparatus

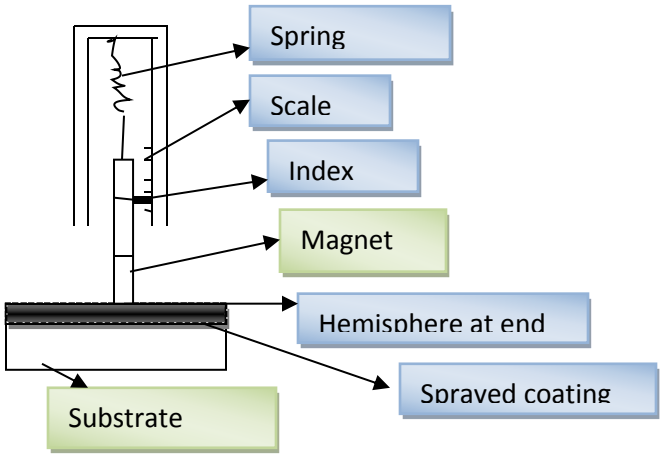


Fig. 6.27 Example of Permanent Magnet-type Measuring Apparatus

Adjustment of Apparatus

a. Prior to thickness test for sprayed coating, adjust the apparatus completely depending on its respective characteristic. Additionally, while test, the adjustment is necessary at suitable intervals.

b. Carry out the adjustment with paying attention to the following matters:

    1. The substrate to become a significant surface of product in future or the substrate whose material, shape, and thickness are similar to those of products. Indicated surface roughness may case errors, therefore care shall be taken.
    2. Carry out the adjustment on nearly the same place as that for measurement.
    3. The reference plate for adjustment shall be a thin plate with uniform thickness and without flaws, unevenness and warpage, and it shall have thickness nearly the same as that of sprayed coating.

       The reference plate shall be used to ensure that it is closely in contact with the substrate.

       Note, use the reference plate whose thickness error to that of indicated thickness is within 2%. Beryllium copper plate specified in JIS H3130 is suitable for the plate because its material is considerably free from flows, unevenness, or warpage.
    4. Carry out the adjustment to control the thickness measurement within 5% of the thickness of reference plate.

6.4.18 Procedure

a. Carry out the procedures in conformity with the instruction manual of each measuring **Apparatus.**

b. Apply the detector perpendicularly to the sprayed coating. If it is too strong, a dent takes place on the sprayed coating, and if too soft, it is not closely in contact with the sprayed coating, accordingly in both cases the right value of thickness cannot be obtained.
c. When the real thickness of sprayed coating to be measured is in vicinity of the upper limit of measuring range of apparatus, a large error may occur, therefore adequate range of measurement shall be selected.
d. Some apparatus may be influenced owing to gravity or the magnetic field caused by surrounding electrical appliances, so much influence shall be carefully observed.
e. Carry out at least 3 measurements at one place, and average the values to determine the thickness of the sprayed coating at the place.
f. Choose at least 3 places per nearly equal area. When the area of significant surface is over $1m^2$, carry out one measurement or more per 1/3m2, then average the thickness values measured at each place to obtain the thickness of sprayed coating on the product.

6.4.19 Test Method by Eddy Current

Measure the thickness of sprayed coated deposited on paramagnetic metal using the charge of amplitude and phase of eddy current which is generated on the surface of substrate metal or in the sprayed coating when high frequency current is flowed through the coil of a detector.

An example of a measuring apparatus by Eddy current is as shown in fig.6.26.

6.4.20 Test Method by Scanning with Profilometer

Carry out thermal spraying after shielding a part of the substrate adjacent to the measuring point on the sprayed coating surface from spraying, measure level difference between the substrate and

sprayed coating surface using a stylus scanning-type surface roughness meter, make a sectional profile to obtain the thickness of sprayed coating. See fig.6.27.

Surface roughness tester

Fig.6.27 Surface Roughness Tester

Thickness of sprayed coating by scanning method by stylus: when the thickness of sprayed coating is obtained on the profile curve, there are two methods:

a. Coating thickness between centre lines: Distance between the centre line of profile curve drawn on the sprayed coating surface.
b. Coating thickness between apexes: Distance between the apex of profile curve drawn on the substrate surface and the apex drawn on the sprayed coating surface.

Standard length: when making measurement of coating thickness between centre line or coating thickness between apexes, standard length shall be, unless otherwise specified, If there are slackening, swellings, or chippings on the part with level difference, set up the standard length after the length L resulted by such flaws was eliminated.

Fig. 6.28 Coating Thickness Testing Devices

6.4.21 Test Methods of Tensile Adhesive Strength for Thermal Sprayed Coatings

Test Method

The spray deposit is peeled from the parent metal by pulling in the vertical direction with respect to the parent metal surface, and adhesiveness is examined.

The apparatus used are (a) the tensile testing machine specified in JIS B 7721 (b) tensile Jig.

The tensile adhesive strength of the coating is calculated using the following formula, and the mean value of the tensile adhesive strengths obtained from three test pieces is rounded to integers.

$T = P / A$

Where, T: tensile adhesive strength (N/mm^3)

P: breaking strength (N)

A: sectional area of test piece (mm^2)

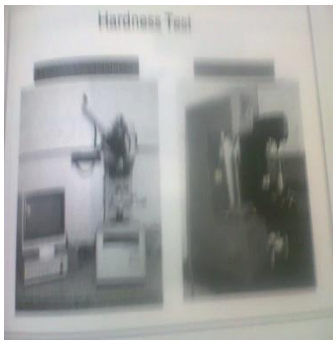
6.4.22 Test Methods

Appearance Test

In the appearance test, observe spray deposit with the naked eye at a place of the brightness of about 200 ix from the distance of about 60 cm from a test surface.

Surface Hardness Test

A standard practice of the surface hardness test is a method using a Brinell hardness tester and a test piece sample. However, when the hardness of spray deposit is directly measured, a method using a portable shore hardness tester may be used.



Micro-Vickers and Rockwell hardness tester

Micro-Vickers hardness tester

Fig.6.29 Micro-Vickers and Rockwell Hardness Tester

6.4.23 Conclusion

Details on other testing methods on thermal spray coating can be read from JIS handbook on metal surface treatment (2007).

6.5 POWDER COATING

Paint coating film is formed on the substrate surface by spraying or immersing into powder resin (powder paint) followed by baking. Companies have different methods of spraying powder coatings for instance Arita Industries Co. Ltd of Japan specialises on the electrostatic powder coating. Using Epoxy / Polyester this company produces coatings on iron and steel, zinc, aluminium, copper, tin, titanium, cadmium and other materials which have high coating hardness, excellent resistance to corrosion and several areas of application. For instance, road / civil works,

here bridge railings, lighting columns, sign posts, fences, car stop etc. are coated. Architecture: is another area of application, here building materials, handrails, gates, staircase etc. are coated. Other areas of application include monuments interior items, electric appliances, cosmetic parts etc.

Powder Spraying Process

'Powder flame spraying' using self flux alloys as the spray materials is called `powder spraying' by usage. Self flux alloys mean alloys with low melting point of around 1000^{o}C containing nickels and / or Cobalt as the base metal, and boron and silicon as the fluxing materials. After the sprayed coating attains the desired thickness, the coating is given the fusing treatment to get rid of open pores and to form alloy layer with the substrate. As the result the sprayed coating gains bonding strength comparable to the welded coating. In the fusing and solidifying process, the coating deposits the solid layer of borides and carbides which add excellent wear resistance to the coating. In addition to these features, the coating has sufficient corrosion-resistance to most chemical solutions and excellent erosion and cavitation erosion resistance and hot hardness characteristics. Application areas are die casting plungers, glass moulding plungers, etc

a) Powder spraying in the chamber

b)

c)

Fig.6.30 a) Powder Spraying in the Chamber, b) Special Patterns using Powder Spraying c) Application Area on a Bridge

6.6 Shippo Cloisonne

In Japanese, shippo literally means ``seven gems'', identical as gold, silver, emerald, shako, agate, pearl and maie in the Buddhist scriptures. The cloisonné works in Japan were named ``shippo'' because their beauty resembles those seven precious stones. Manufacturing shippo cloisonné is a traditional industry which has been handed down from generation to generation in shippo. Each piece is hand made using an elaborate, delicate process. Shippo was name after these cloisonné works that the people love so much. The same kind of shippo cloisonné existed in ancient Egypt and many pieces are believed to have found their way into Japan through the trade routes of India, China, and Korea. One early example of cloisonné believed to have been made in Japan is a mirror presently exhibited in the Shosoin Treasure House in Kyoto. Unfortunately, the line of Shippo cloisonné craftsmen died out sometime in the 18^{th} or 19^{th} century. Around 1830, Tsunekichi kaji, a metal worker, discovered shippo cloisonné from an old book, and he tried to make it in vain. He obtained a cloisonné dish and broke it into pieces, finally discovering that the glazing had been done using copper wire to separate the colors. Later a shippo peddler named shogoro Hayashi heard of Kaji's success in improving the cloisonné technique, and was very interested in acquiring it. He managed to obtain the technique from Kaji's grandson in 1856. After the Kaji line of craftsmen died out, Hayashi taught this technique to many people. Their successors have carried on the local industry in the Toshima area of Shippo, and Shippo cloisonné has flourished ever since. The fig.6.31 Shows some items made by shippo cloisonné method.


Fig. 6.31 Shippo Cloisonne Manufacturing Process

Shippo cloisonné is a handcraft that uses simple tools and equipment. The craft produces ornaments and decorative items. Colourful necklaces, emblems' jugs and so on can be produced using copper plate and glazes of various colours. The procedure is as follows:

i. A copper sheet is used as the base for the vase. The vase is pounded into shape by both hammer and machine.

ii. The design is painted on the surface of the vase.

iii. Silver strips are attached to the copper vase, following the outline of the design.

iv. Many different colours of glaze are painted into the design between the silver strips.

v. The vase is fired in an electric kiln for 5-15 minutes. This process of glazing and firing is repeated 3 to 7 times.

vi. The surface is polished to a high sheen

vii. Finally, ornamental metal rings are attached at the top and bottom of the vase

Quality Testing Equipment in a Surface Finishing Engineering Outfit

Testing equipment are required both for the creation of new coatings as well as for quality assurance of produced products. Some of the equipment commonly found in the R and D laboratories of some companies include, hardness tester, coating thickness tester, x ray diffraction analyser, scanning electron microscope, energy dispersible spectronmeter, powder particle size analyser, multifunctional tensile bond tester, surface roughness measuring

instrument, evacuate heat treatment chamber, abrasion tester, corrosion tester, microhardness tester, optical microscope and many others. Fig.6.32 shows equipment used in quality testing

Thickness Tester

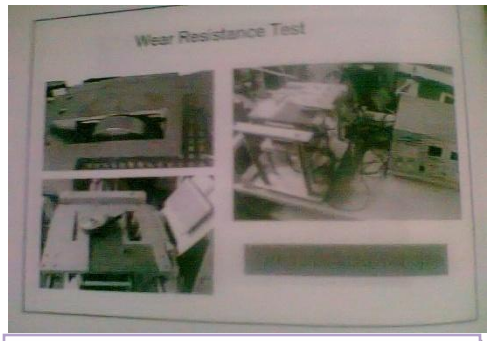
Coating Thickness Tester

Micro-Vickers hardness

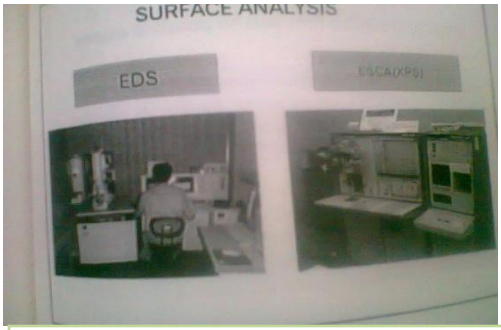
Surface Roughness tester

Corrosion Test (salt spray test: CASS Test) NaCl 5%, pH7, 35^{o}c

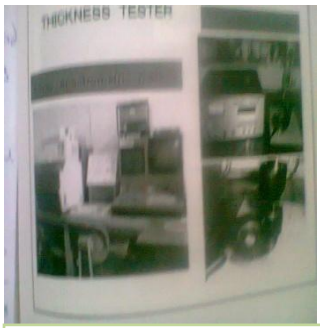
Surface Analysis: AES (Auger Electron Spectroscopy



Wear Resistance Test (reciprocating motion)



Surface Analysis (EDS and ESCA (XPS))



Thickness Tester
X-ray spectrometric method and
Coulometric method

Disk revolution wear resistance test and jet wear resistance test equipment

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7.0 CHAPTER SEVEN

DRY PROCESSES FOR SURFACE MODIFICATION BY SURFACE ALLOYING

7.1 Introduction

Dry processes for surface modification by surface alloying have gained wide acceptance in the technological arena. Today the sophistication of the technologies used for surface alloying of materials is becoming amazing. The areas of application of these technologies is also widening with super properties and surface finishing of high class being imparted unto materials. Dry processes for surface modification include physical vapour deposition, chemical vapour deposition, hot dipping, lead coating, metal cladding, diffusion, sherardizing, calorizing, chrome-diffusion, siliconising, parkerizing, etc. these have found application in aviation sector, space technology, medicine, automobile sector, manufacturing, building and construction sectors, etc, the advanced technology era is greatly assisted by these processes.

7.2 Surface modification methods.

Tin plating by hot dipping: tin plating has a pleasing appearance, good corrosion resistance and it solders well. Copper wire is very often tin-plated to increase its suitability for soldering. This coating is usually applied by hot-dipping before the wire has been drawn down to final diameter and the subsequent operations drawn down the copper and tin together. The various application of tin plating includes tin can for food, biscuit-tins, kitchen utensils, copper wire, copper tube used in refrigerator etc.

Lead coating: the lead coating for hot dipping process contain 2 ½ % tin and 2% of antimony, the presence of which strengthens the coatings considerably. The coatings used generally are thicker than terne but thinner than zinc. To compensate for the drawback of poor adhesion of coatings lead has decided advantage because it does not alloy with steel. The steel is

not embrittled and can be used for deep drawing etc. It takes paints and solders well. To obtain the best possible adhesion, the steel must be perfectly cleaned before coating. Lead coating is a cheaper substitute for terne and it can be used for spinning and deep drawing operation.

Metal-cladding: cladding is usually performed by attaching plates of relatively thick metals together such as by welding and then rolling them down together. The centre core and plated metal retain their proportion as the cross-section is reduced. It is much used in air-craft construction. In a like manner steel may be clad with copper, cupro-nickel, and rolled gold is made by rolling a gold alloy into a brass or cupro nickel-base. This method in general allows the protection of a material which combines the strength of core with the corrosion-resistance of the plated material. Unlike electroplating there is danger of porosity.

Diffusion: It resembles the process of cementation for making steel and case hardening. The article being treated is heated in contact with the metal being diffused which penetrates into the surface thereby producing an alloy. The concentration of diffused metal in the article is highest at the surfaces and falls off rapidly within less than 1.25mm. Steel is treated chiefly with four metals which forms useful diffusion alloys at the surface, namely zinc, aluminum, chromium and silicon. Hardly any dimensional change occurs in the treated articles.

Sherardizing: so called after the name of its originator is the name given the zinc diffusion process which has been used extensively. The parts to be treated are trembled in a barrel to 350^{o}C with powdered zinc or a powder of zinc and zinc oxide known as blue powder. The period of heating depends upon coating required, varying from 3 to 12 hours for a coating of (0.025 to 0.075mm) thickness. However, there is a drawback of brittleness in this process and so its use is restricted to treatment of small nuts and bolts exposed to atmosphere, and small castings etc.

Calorizing: it is a diffusion process of aluminum powder mixed with roughly equal proportion of aluminum chloride. This is carried out at a much higher temperature (about 900^{o}C), i.e. well above the melting point of aluminum. The time of process is 4 to 6 hours, but this may be followed by retaining for such a longer period at 950^{o}C out of contact with aluminum in order to homogenize the layer and to increase its depth. Calorized parts are resistant to both corrosion and at elevated temperature are protected by the impervious alumina films which occur in furnace and exhaust pipes.

Chrome-diffusion: it produces a surface layer similar to stainless steel. It is carried out by heating the steel articles in a mixture of 55% of chromium powder or powdered ferro-chrome and 45% of alumina in the presence of hydrogen atmosphere. The temperature used is above 1000^{o}C at which one hour is sufficient to produce coating of about 0.1 mm thickness and containing 10 – 20% of chromium. These coatings are used where the corrosion or wear is severe, but this application does not merit considerably because of its higher cost. Also it is not a good substitute as compared to stainless-steel because coating produced by diffusion tends to brittle.

Siliconizing: it is carried out for two hours at above 1000^{o}C in a mixture of silicon-carbide and ferro-silicon in an atmosphere of chlorine. The parts siliconized are very hard and process is carried out for wear resistance, corrosion resistance, or heat resistance. A typical application is in valves, valve seats, and guides of internal combustion engines.

Parkerizing: it is a process used for making thin phosphate coatings on steel to act as a base or primer for enamels and paints. In this process steel articles are dipped in a heated solution of magnesium dihydrogen phosphate at temperature of 88^{o}C for about 45 minutes. During the dipping period, the phosphate from magnesium dihydrogen phosphate decomposes and phosphate separates out and forms a thin coating on the steel articles.

Electroforming: the electroformed part is transferred to the aluminium cast part of the casting die. The process of producing dies for car parts, airplanes, micro-parts for electronics and even bath tabs involves many steps which start with the design using CAD and CAM. The first step is to produce the mould for the master mould/ model which is then used for electroforming. The electroformed part can be used directly or machined or transferred to be coupled with other parts to make the final die mould.

7.2.1 CDC-ZAC Coating Process

This process is quite unique method to form ceramic coatings by using chemical reactions. CDC means Chemical Densified Coating which is complex ceramic coating containing chromium oxide as the main component. On the surface of the substrate, the structure in which metallic components of the substrate is mixed with ceramic components of the coating is made and the coating obtains high bonding strength. Even small parts and narrow sections of machines which are hard to be sprayed can be produced with this coating process. Areas of application include step-cones for drawing machine, pump impeller, various plungers, textile machine parts etc. see fig.7.1 below

Fig. 7.1 Step-cones, pump impeller, plungers and textile machine parts.

7.3 Chemical Vapour Deposition

Protective coatings on various types of substrates are applied to change certain characteristics of the surface to enhance its appearance or useful life. In engineering applications, various surface characteristics required are corrosion resistance, wear resistance, and oxidation resistance. A coating may be defined as a layer of any substance used as a cover, protection, decoration, or finish. Three basic types of coatings are overlay, conversion, and combination of these two. Overlay coatings are deposited by applying a new material onto surface of component. Conversion coatings are applied by modifying composition of a surface by an in-situ process. In combination coating, an interface is formed having properties different than those of the substrate and the coating.

The techniques of vapour deposition fall in two categories, viz. chemical vapour deposition and physical vapour deposition. In chemical vapour deposition (CVD) technique, a mixture of gases interacts with surface of a substrate at a relatively high temperature, resulting in the decomposition of some of the constituents of the gas mixture and the formation of a solid film or coating of a metal or a compound on the substrate.

CVD process thus requires a source of precursor gases (inert gases and a variety of reactive gases), a heated reaction chamber, and a system for the treatment and disposal of exhaust gases. In conventional CVD process, reaction temperature is of 900 – 2000^{o}C. Temperature can be lowered to 500 – 850^{o}C by using metal organic precursors which decompose at lower temperatures. Reaction temperature can be lowered by facilitating more energetic activation of the vapour phase reactions (plasma assisted, plasma enhanced, or laser). In these processes, the chemical reactions in the vapour phase are activated by the creation of plasma in the gas phase or by shining a laser beam into the gas mixture. The decomposition of a coating by CVD occurs by one or more of a variety of chemical reactions like thermal decomposition, reduction, oxidation,

hydrolysis, and co-reduction. The deposits are formed by a reaction between the various precursor gases in the vapour phase (resulting in overlay coatings). The example of conversion coatings is the formation of nickel aluminide coating on the surface of nickel by a reaction between $AlCl_3$ and hydrogen in the vapour phase and the nickel substrate.

The CVD technique is readily applicable for the deposition of refractory metals. The precursors for the deposition of metals, and most compounds, are the respective metal halides. It is necessary to decompose these halides at relatively moderate temperatures (around 2000^{o}C). For metal whose halides are stable in this temperature range, their organometallic compounds as well as metal carbonyls are used.

A very important application of CVD is in making powders and whiskers of refractory materials. Whiskers have tremendous potentials in the development of composites. The addition of whiskers of extremely fine dimensions (in the range of microns) to ceramics has shown significant improvements in the toughness of such composites.

The coatings deposited by CVD are used in various applications requiring wear resistance, oxidation resistance, corrosion resistance, and electrical, optical, or tribological properties. Depending upon the applications, the characteristics of coatings may be varied by controlling process parameters and equipment. Purity of coating is critical in some applications.

7.3.1 Plasma Chemical Vapour Deposition Equipment and its Application to Various Dies

Generally there are two processes, namely chemical vapour deposition (CVD) and physical vapour deposition (PVD), for surface treatment of dies; however, these processes have advantages and disadvantages. In the CVD process, the adhesion and throwing power of the film are excellent, but the process tends to cause deformation and a change in dimensions due to high temperatures in the 1273 K range required during the treatment stage. On the contrary, the PVD

process can suppress deformation and a change in dimensions during low temperature treatment, but the adhesion and throwing power are inferior to those of the CVD process. Consequently there have been a large number of laboratory investigations on the plasma chemical vapour deposition (PCVD) process which is believed to offset the defects of both the CVD and the PVD processes.

This outlines the mass-production-type PCVD equipment produced Oriental Engineering Co. Ltd of Japan which is actually in operation and describes in some details how it performs surface treatment functions. Fig.7.2 shows PCVD equipment and some components and dies treated with PCVD process.

(a) (b) (C)

Fig. 7.2 a) PCVD equipment, b) and c) various components including dies treated using PCVD.

7.3.2 Comparison of Various Surface Treatment Processes

Table7.1 compares the characteristics of the various surface treatment processes in use. From Table7.1 it can be seen that the (PCVD process which involves low temperature treatment is applicable to dies requiring a high degree of dimensional accuracy.

Under the PCVD process, processing pressure are between those of the CVD and PVD processes and the feedstock gas can be fed from all directions. For these reasons, the PCVD process gives much greater film throwing power than the PVD process does. The film adhesion under the PCVD process has also improved substantially over that obtained in traditional processes, for reasons of higher plasma density, diffusion hardening treatment etc.

Since all feedstock is fed in gaseous form, dense films free from pinholes and droplets can be formed. It is easy to apply partial coatings; no lapping is needed after surface treatment under the PCVD process. This process is also suited to surface treatment of large, heavy and long objects.

Table 7.1 Comparison of Various Surface Treatment Processes

Parameter (units)	**PCVD**	**CVD**	**PVD**
Temperature (K)	573 -873	1273	573 -873
Pressure (Pa)	1.3 – 1.3 x 10^3	6 x 10^3 – 1 x 10^5	1.3 x 10^{-2} - 1.3
Adhesion	Good	Good	Inferior to CVD
Throwing power	Superior to PVD	Good	Bad
Density	Good	Bad	Inferior to PCVD
Partial coating	Possible	Difficult	Possible
Dimensional accuracy	Good	Bad	Good
Post-lapping	Unnecessary	Necessary	Unnecessary
Pre-washing	Easy	Easy	Care required

7.3.3 Outline of Equipment

A drawing of a mass-production-type PCVD equipment is given in fig 7.3 and its specifications are listed in Table 7.2. The effective dimensions of work pieces treated by this equipment are 460mm in diameter and 800mm in height. Dies of mass 100 kg or more each can be treated. The equipment is of external-heating construction, and thyristor control of a four-zone heater provides a uniform temperature distribution. An example of gas composition in TiN film coating

is as follows: N_2: Ar: H_2: $TiCl_4$ = 18.8: 4: 75: 2.2. By selecting an optimum rotation speed, the out-furnace motor with inverter causes the work pieces either to rotate and revolve or only to revolve, thereby improving the film thickness distribution and temperature distribution. Once the work piece in process is set on the work-table, computer-controlled fully automatic operations including temperature increase, surface treatment and cooling are performed, making manpower almost unnecessary. See fig.7.3 for schematic diagram of the mass production type PCVD.

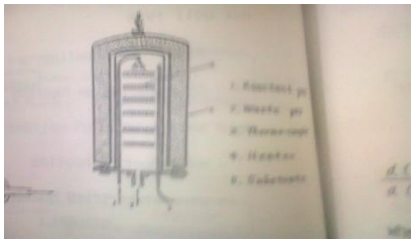

Fig.7.3 Schematic diagram of the Mass-Production-Type PCVD.

7.3.4 Characteristics of Films

TiN films produced by the PCVD process have a strong preferred orientation of (200) and approximately the stoichiometric composition. These films had Vickers hardness equal to that of films produced by the CVD and PVD processes, i.e. approximately 2000 HV for TiN, approximately 3000 HV for TiC and a value between those of TiC and TiN for Ti (C, N). The TiN films are found to have a more dense texture than that of the fracture surface in fig.7.4, as viewed by a scanning electron microscope. The results of scratch test on various types of film illustrated in fig.7.5 shows that the films produced by the PCVD process have a higher critical load value than those produced by the CVD and PVD processes. During scratch testing, the sliding speed was 10 mm min^{-1} and the loading rate was 100Nmin^{-1}.

Fig.7.4 Scanning Electron Micrograph of a PCVD TiN film coated on M2 Steel.

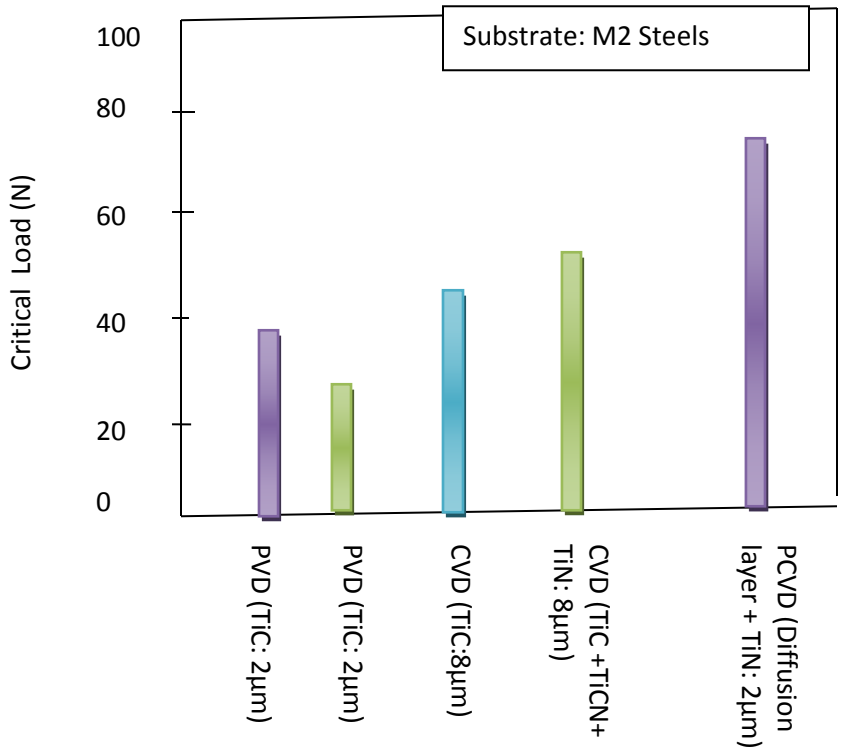

Fig.7.5 Results of Scratch Tests on Various Types of Film

7.3.5 Example of Actual Application to Dies

Cold-working Dies

Generally, high temperature processes, such as the CVD process and the molten salt immersion process (TD process), are applied to cold-working dies. However, the PVD process which gives

a shorter life than high temperature processes has sometimes been employed for surface treatment of cold-working dies, requiring a higher degree of dimensional accuracy.

Table7. 2 Specification of Equipment

	Specification
Application	Coating and diffusion-hardening treatment of dies, tools, Wear-resistant machine parts, electronic components, etc.
Films that can be produced	TiC, TiN, Ti(C,N) (in addition, it is possible to combine With the diffusion-hardening treatment)
Effective dimensions of Work piece	460 mm in diameter and 800 mm in height (objects of mass greater than 100 kg each can be treated)
Temperature used	Normal, 573 – 873 K Maximum, 1073 K (low temperature treatment up to 873 K and intermediate Temperature treatment up to 1073 K are also possible)
Temperature distribution	Within ± 278 K (at 773 K)
Film thickness distribution	Within ± 10% (at effective dimensions)
Treating pressure	1.3 – 1.3 x 10^3 Pa
Heating methods	External heater + d.c. plasma

The PCVD process has been applied to a wide range of cold-working dies with better results than those obtainable with the high temperature processes. Some of the better results are indicated in Table7. 3. Figure 4 illustrates the various types of cold-working die to which the PCVD process has been applied.

Fig.7.6 Cold-working dies

Table7.3 Examples of Effectiveness of Plasma Chemical Vapour Deposition Application to Cold-working Dies

Applications	**Material of dies**	**Durability Effects**
Cold-blanking punches (material worked, low carbon Steels; plate thickness, 3.1 mm)	M2 steels (high speed tool steels)	Non-coating 20000 shots PCVD, 330000 shots
Cold-hardening dies (material worked, low alloy Steels; plate thickness, 5 mm)	M2 steels (high speed tool steels)	CVD (TiC), 15000 shots PCVD, 45000 shots
Cold-forming dies (material worked, austenitic stainless steels; plate thickness, 1.6 mm)	D2 steels (cold-worked die steels)	TD process (VC), 25000 shots PCVD, 120000 shots
Trimming dies	PM high speed tool steels	CVD (TiC) 30000 shots
Cold-forging punches	M35 Steels (High speed tool steels)	Non coating,45000 shots PVD (TiN), 45000 shots CVD (TiC +TiCN+TiN), 75000 shots PCVD, 150000 shots
Cold-working mandrels (material worked, austenitic stainless Steels)	PM high speed tool steels	TD process (VC), 530 pieces CVD, 780 pieces PCVD, 1200 pieces

7.3.6 Plastic Moulds

Generally, the PVD process is applied to plastic moulds in terms of the accuracy required and surface roughness. However, the PVD process has disadvantages, such as the tendency to form pinholes or droplets and inadequate throwing power. Equally CVD has dimensional problems, CVD is carried out at a very high temperature this results in dimensional change.

The PCVD process gives such a highly dense film and long mould life that it is applied to specular moulds for optical dies demanding the highest degree of dimensional accuracy of all plastic moulds. This process is also applied to various types of plastic moulds. Figure 5 illustrates the optical disc moulds to which the PCVD process is applied.

Fig.7.7 Optical Disc Moulds

7.3.7 Hot-working Dies

The PCVD process has the following advantages when applied to aluminium die-casting dies.

1. Low temperature treatment does not cause deformation or a change in dimensions with pins and die cavities.
2. Good film throwing power enables uniform coating to be carried out in die cavities of complex shapes.

3. Combination with diffusion-hardening treatment gives aluminium die-casting dies a high resistance to soldering erosion, thermal checking and thermal cracking.

Fig.7.8 shows the comparison of the effects of the various surface treatment processes with respect to aluminium die casting pins. See fig.7.9 for aluminium diecasting dies

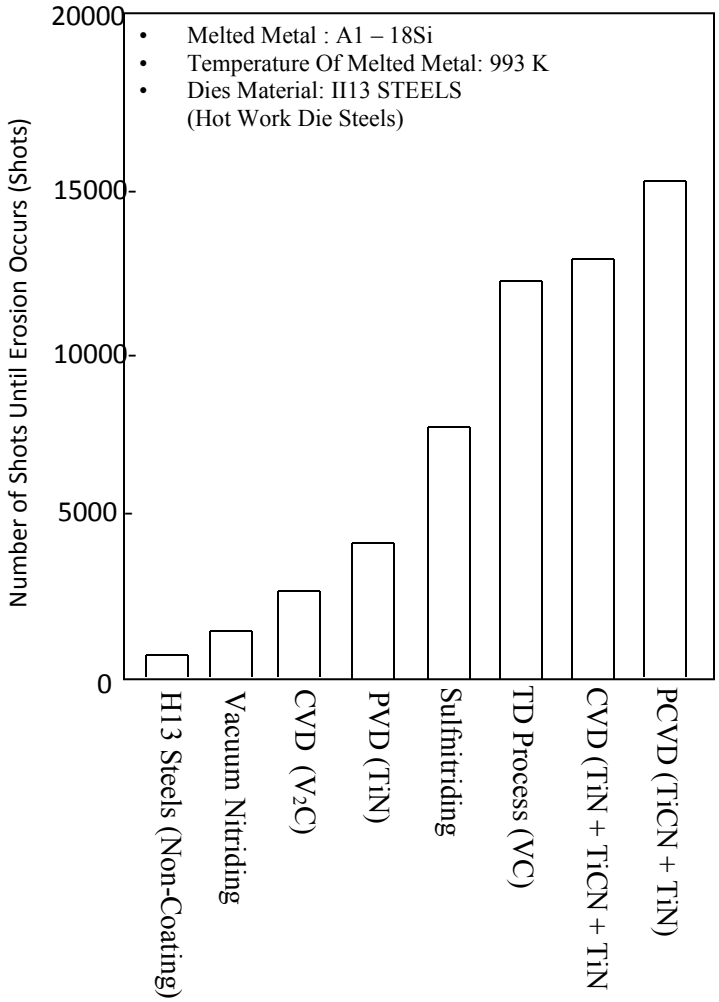

Fig.7.8 Comparison of the Effects of the Various Surface Treatment Processes with respect to Aluminium Die Casting Pins.

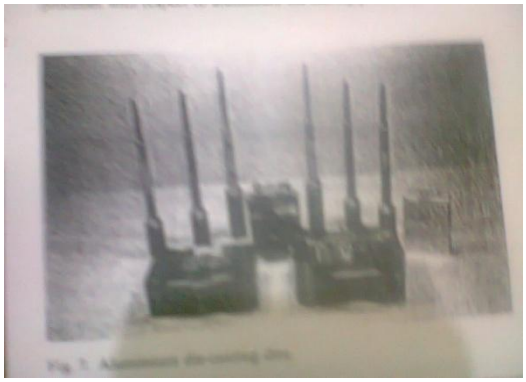

Fig.7.9 Aluminium Die casting Dies

7.4 Formation of Amorphous Carbon Thin Films by Plasma Source Ion Implantation

Ion implantation is a quite effective method to improve not only the electronic properties of materials but also their surface physical and mechanical properties, such as wear, corrosion, fatigue and friction. There have been an extensive number of publications on the ion implantation technique. However, its application for industrial purposes is limited due to its relatively high capital cost and its inability to implant three-dimensional substrates- ``line of sight'' process. Recently, Plasma Source Ion Implantation (PSII) and Plasma Immersion Ion Implantation (PIII) invented by Conrad and coworkers and Tendys et al respectively, have been used as alternative ion implantation methods. In both PSII and PIII processes, pulsed high negative bias voltage is applied to the target immersed into plasma. Ions are accelerated in a direction perpendicular to the target surface, across the plasma sheath. As a result, the total surface of the target is implanted, unlike the conventional ion implantation technique without any sample manipulation and sputtering of the substrate. Implantation of many targets simultaneously is also possible by both techniques. As a result, the PSII technique is more cost effective for industrial non-planar target applications. Carbon ion implantation into steel and amorphous carbon films coating on steels have been used to improve surface properties such as wear, friction and corrosion. The structure of the implanted layer and films is important in

understanding the mechanism for improvement of properties and optimization of process parameters. In this section I report on the results of CH_4 plasma source ion implantation of carbon ions into silicon wafer and martensitic stainless steel as was carried out by Baba and Hatada in 1998. According to the researchers in PSII, samples are placed in a CH_4 plasma and pulse high negative bias voltage (- 20 kV) is applied to samples. All samples are subsequently characterized by Scanning Auger Microscopy and Raman spectroscopy. The surface properties were estimated by reciprocating sliding tester and scratch tester. The plasma source ion implantation apparatus used for the work is shown in fig.7.10. The vacuum chamber, 50 cm in diameter and 65 cm in length, is made from 304 stainless steel. The negative high voltage pulse is generated by solid state switches and capacitors, and applied to a substrate folder by an insulated copper cable. The implantation voltage and current are monitor using a voltage divider and a current transformer, connected to a digital oscilloscope.

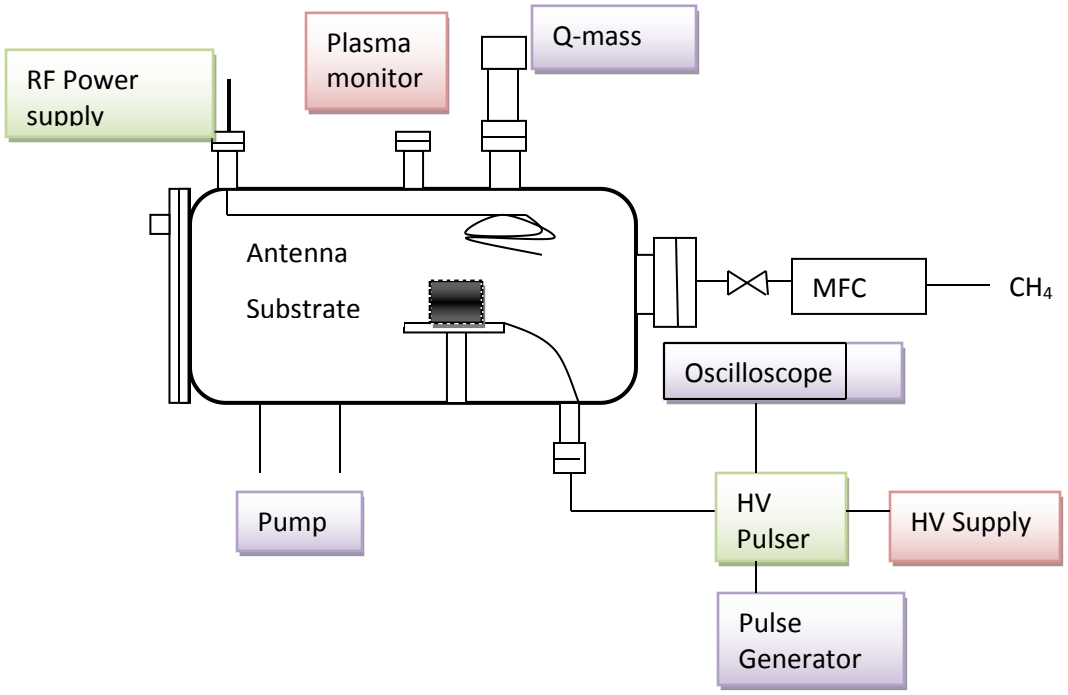

Fig.7.10 Schematic diagram of the PSII system

7.4.1 Ion Implantation and Coating

The base pressure of the vacuum chamber is $7x10^{-5}$Pa. the plasma is generated by the application of a 13.56MHz radio frequency power on the antenna located inside the chamber through a matching network. The maximium voltage and current of the generator were – 50kV and 30A, respectively. The repetition range is 10Hz-5 kHz, and the maximum pulse duration is 1% of the repetition period. Commercial grade martensitic stainless steel type 440C and (100) silicon wafer are used as substrates. The steel substrates used are ground and polished to obtain a mirror-like surface. The substrates are mounted on a holder and placed in the PSII chamber. Methane gas is introduced into the chamber at a constant flow rate of 20.0sccm. the vacuum pressure during the process is around $2.5x10^{-1}$ Pa. 30 radio frequency power is applied to the antenna to generate the plasma. The implantation is carried out at a constant pulse repetition rate of 100Hz and a constant pulse width of 50μs. the target bias was -20, -10, and -5kV. The process time is 2hrs for all samples.

Surface Characterisation

The surface morphology is observed by a field emission scanning electron microscope (SEM). The chemical structure of the surface layer of the substrate is evaluated by a micro-Raman spectrometer (Renishaw system 2000). The surface stoichiometry is determined with the aid of a scanning Auger electron spectroscope (AES). The friction coefficients of the surface layers are measured by a reciprocating sliding tester. The tribology behavior is measured by reciprocal sliding of a 10mm diameter 304 stainless steel ball at a speed of 1 mm/s. the normal load is fixed at 0.245N. After 1000 cycles of sliding the surface structure of the specimens is observed by SEM. The adhesive strength of the films is estimated by scratch tester (CSEM microscratch tester MST). The testing parameter is 30N/min loading rate, 10mm/min scratching speed and

diamond indenter ground to a 120^{o} cone with a spherical apex of 200μm radius. Baba and Hatada said amorphous carbon films were deposited by methane plasma source ion implantation on silicon wafer and 440C stainless steel substrates.

7.4.2 Deposition of Diamond-like Carbon Films by Plasma Source Ion Implantation with Superposed Pulse

Diamond-like carbon (DLC) films have been the subject of considerable attention because of their unique mechanical properties such as high hardness and low friction coefficient. Many methods have been applied to prepare DLC films. Plasma source ion implantation (PSII) and related methods have possibility to give high adhesion and good surface coverage for DLC films. In a PSII method plasma is generated by an additional plasma source excited by a radio frequency or a microwave. Baba and Hatada reported a new idea to prepare DLC films without additional plasma sources. Negative DC voltage superposed on high negative pulse voltage is applied to the substrate to generate plasma. Continuous plasma could be generated by the application of negative DC voltage to the substrate. This method has some advantages such as, simple construction, easy to scale-up and good coverage. DLC films were prepared by using this method from CH_4 and C_2H_2 plasma. All samples are subsequently characterized by scanning electron microscopy (SEM) and Raman spectroscopy. Hardness and wear properties are estimated by an indentation method and ball-on-disc tests. Baba and Hatada explained that diamond-like carbon (DLC) films were prepared on silicon wafer substrate by plasma source ion implantation with superposed negative pulse. Methane and acetylene gases were used as working gases for plasma. A negative DC voltage and a negative pulse voltage were superposed and applied to the substrate holder. The DC voltage was changed in the range from 0 to -4kV and the pulse voltage was changed from 0 to -18kV. The surface of DLC films was very smooth. The

deposition rate of DLC films increased with increasing in superposed DC bias voltage. Carbon ion implantation was confirmed for the DLC film deposited from methane plasma with high pulse voltage. I_D/I_G ratios of Raman spectroscopy were around 1.5 independent on pulse voltage. The maximum hardness of 20.3GPa was observed for the film prepared with high DC and high pulse voltage.

7.5 Ultra-Microcrystal Diamond Coated End Mill Development

Diamond coating of a tool nose having a complicated shape has become possible by means of CVD (Chemical Vapour Deposition) with this technology, end mills with complicated shapes can be coated so that they can be used as cutting tools.

7.5.1 Improvement of surface finish Roughness

Since diamond coating is made of almost 100% pure diamond it has high deposition resistance against aluminium and other nonferrous metals. Because of this diamond has been considered for use in drills and end mills. However, diamond coating is an aggregate of diamond crystal grown from small diamond cores generated on the base metal surface. An aggregate of approximately 5-10μm crystal is found on the coating surface. When this is coated over the tool surface and use for cutting aluminium material, the irregularity of diamond coating surface will be reflected on the cutting finish surface of aluminium material.

By micro-crystallizing the coating, coating toughness can improve. Since diamond crystal grown in the shape of a column from a diamond core generated on the base of metal surface, coating tends to destroy easily as cracks progress along the boundary between crystals. On the contrary, micro-crystallization of the coating will prevent cracks and improve toughness of the coating.

OGS's new patent for ultra fine diamond coating is made from ultra fine diamond crystals in an innovative new process. This coating can be easily distinguished from other diamond coatings by its shiny finish. According to OGS this new diamond coating will give better finish and better performance and is only available from OGS. The surface structure of the ultra fine diamond coating and other diamond coating is shown in fig.7.11.

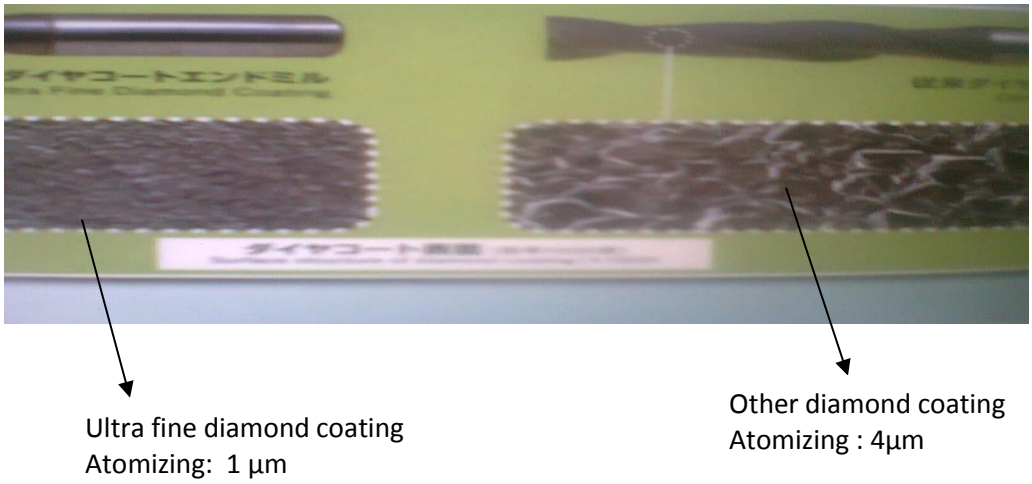

Fig.7.11 The surface structure of the ultra fine diamond coating and other diamond coating.

7.5.2 Characteristics of ultra Fine Diamond Coating

1. High Efficiency Milling: the fine and smooth coating ensures high-precision milling while maintaining the same level of wear resistance as the conventional diamond coating.
2. Superior galling resistance: this coating makes it possible to perform finish milling, dry milling, or semidry milling of aluminium alloys.
3. Beautiful finished surface with minimal surface roughness: ultra fine diamond crystals produce the same milling surface roughness as non-coated carbide tools.
4. High durability: the ultra fine diamond crystals improve the toughness of the coating and make it is highly durable when working in materials that are difficult to cut. OSG's DLC coating provides a shining surface. This shining and smooth surface optimizes end mill performance particularly in flattened aluminum alloys that required galling resistance and

lubricity. It can also be applied to HSS products. Table 7.4 shows the features of ultra fine diamond compared with other coatings

Table 7.4 Features of Ultra Fine Diamond Compared with other Coatings

Material name	**Hardness (Hv)**	**Thermal conductivity (cal/cm.sec.^{o}C)**	**Thermal Expansivity (x 10^{-6}/^{o}C)**
Tungsten Carbide (WC)	2,200	0.3	5.1
Titanium carbide (TiC)	3,200	0.04	7.6
Titanium Nitride (TiN)	2,000	0.07	9.2
Cubic crystal boron(c-BN)	4,500	3.1	4.7
Diamond (C)	>9,000	5	3.1
Tungsten carbide	1,800	0.19	5
HSS	800	0.04	11

7.6 Ion-beam Based Techniques for Surface Modification

The useful life of many materials is determined as to how their surfaces react with environment. Thus surface finish and treatment deserve serious attention. Surface characteristics can be modified by ion beam-based techniques at low temperature without altering tolerances. In ion-beam based techniques, high energy ions provide energy (not heat) for reactions to occur and thus form new compounds or alloys. Ion implantation (shallow penetration of ions to modify

surface) and ion-assisted coatings are used on non-electronic materials to improve surface properties.

Ion implantation process is carried out in a vacuum (10^{-6} torr) in an ion implanter which contains an ion source (ions created from a plasma) and a chamber in which items to be treated are housed. The ions are fired as a beam from source to the object to be treated. Ions being in the form of a beam, the process is line-of-sight. When an ion enters the surface, it collides with the atoms of the solid and keeps moving in, blazing a trail ahead, behind, and to the side of its path as it knocks atoms away. The displaced atom collides with several others for about 10^{-11} sec. This is known as a collision cascade and often visualized as very localized spike of thermal energy which causes very fast heat and quench of surface in a region of 0.1 micron long and 0.02 micron diameter. The effects of this rapid heat-quench cycle together with the new atoms lodged in the original material gives the ion implantation process some of its unique properties. Since ions become integral part of the material, the implanted layer can't flake or peel off. Thus implanted ions can combine with atoms of the solid or with each other, to form conventional alloys or compounds. Implanted material is buried beneath surface and can't come off. There is no measurable change in surface dimensions after implantation. Controllable addition of desired ions for desired surface characteristics is possible. Use of multi-energy implants can offer tailored depth profile.

Three types of ion implanters in use are: mass analysis, nitrogen implanters, and plasma source ion implanters. In ion-assisted coating process, ion beam is used for chemical vapour deposition. Ion beam can also be used to mix the coating into the substrate to improve coating adhesion. Ion beam being easier to define, control, and use, it is more readily acceptable to different substrate materials and geometries than plasma. Ion-assisted coatings are generally used for high-precision

surface treatments. Because of their adaptability, reproducibility, and low temperatures, they offer a relatively rapid and controllable method of developing new coating or treating new types of materials. Fig.7.12 shows arc ion plating equipment and some cutting tools coated using the arc ion plating method. The method is used for creating TiN, TiCN, and TiAlN coatings with excellent wear resistance. The method was used at OSG Coating Services Co. Ltd Japan.

Fig.7.12 a) Arc ion plating equipment, b) and c) coated cutting tools.

7.7 Thin-film Vapour Phase Deposition Techniques

Surface properties of substrates may be modified by a wide variety of thin film vapour phase deposition techniques. Figure7.13 shows in schematic form the process of vapour phase deposition system. This system basically consists of effective generator of vapour flux, effective capture of vapour flux, effective establishment of surface conditions to control film growth from the vapour flux. PVD solid material at low temperature (500^{o}C) is physically evaporated to form physical deposition on the material. Ion plating equipment include; electron beam apparatus and arc discharge apparatus. These two differ as explained below.

Electron beam apparatus.

The apparatus is rotated as the plating is going on. Chamber and jigs can be rotated. Coating is done on small parts.

Operation.

1. Vacuum state creation; this is necessary because the film is very thin any foreign matter on the surface may become a defect this has to be avoided.
2. The chamber is then heated to 450-500oc, the workpiece is heated to increase adhesion.
3. Negative voltage is charged on the work piece
4. Electron beam temperature is about 2000oc
5. The target metal temperature is around 1100oc
6. Electron beam is focused on the target for melting
7. Methane and nitrogen are supplied as reaction gas
8. Direct current at +200V is supplied to give a positive charge to the vapour so that it can be attracted to the work piece

Arc Discharge System

Work pieces are in a vertical position. They are rotated inside the chamber.

The principle of operation

1. The target material is on the side of the chamber the work piece is in the middle of the chamber.
2. Vacuum state is created
3. Work piece is heated to 450-500oc
4. Work piece is negatively charged
5. Arc discharge is used to melt the target metal. Arc discharge is around 4000oc at this temperature the metal immediately vaporizes, and ionization of the vapour is positive. The discharge has two purposes first to vaporize and secondly to ionize the vapour
6. Reaction gas will then be injected to effect the coating.

7. The arc discharge generates the plasma. 1-3 hours give a thickness of 10μm. the total coating time is normally 4-12 hours depending on the work piece too. The equipment cost around N150,000,000.

Looking at the two processes; electron beam process gives smooth coating while arc discharge process is like shaving out the metal, the part that is shaved out will be large so that the coating film formed on the surface will be porous. However the holes are about 1μm. different films like TiN, TiCN, CrN and others can be formed.

Nitriding and coating

Conventionally the two process cannot be done at the same time, but Yuken company Ltd have developed the process of removing the compound layer. Nitriding is carried out then the compound layer is removed and coating is the carried out. In the case of PVD no heat treatment after coating but polishing can be done, while for CVD tempering is normally administered after coating. Ion plating has a weakness in that it is difficult to coat inner diameter. Application of PVD increases life cycle from 200 shots to 10000 shots.

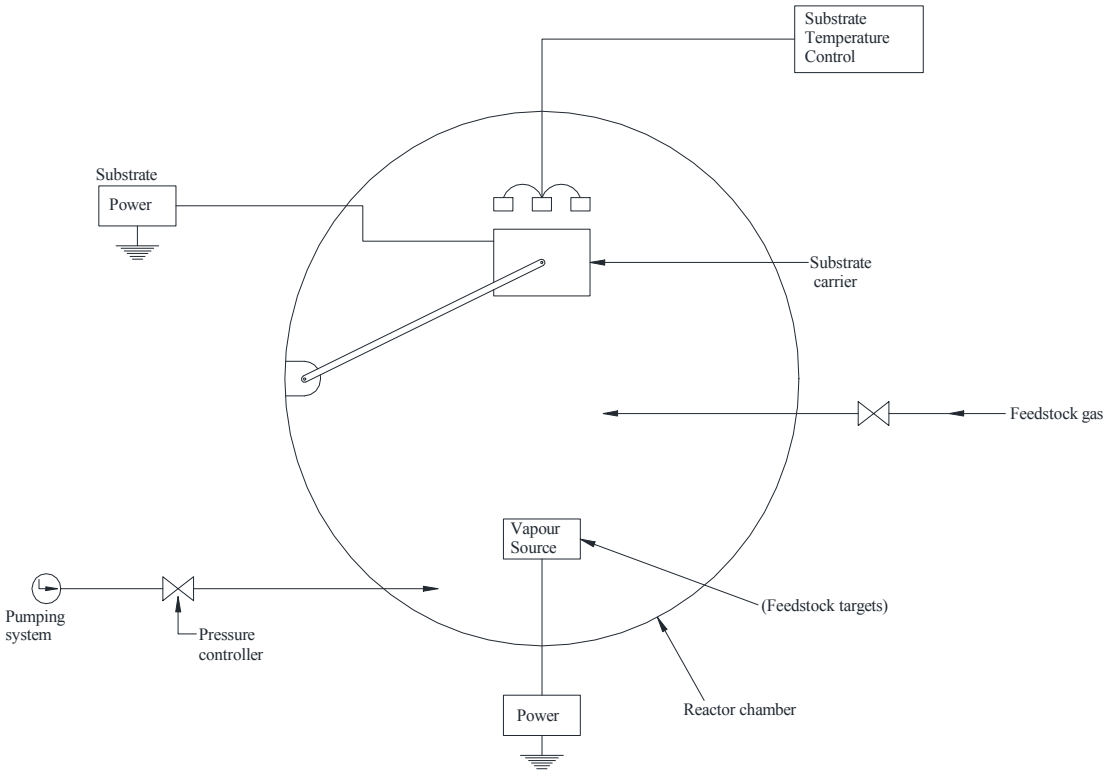

Fig. 7.13 Schematic form of the process of vapour phase deposition system

Vapour source is a solid feed stock which is connected to a power source. The feedstock supply rate and the power level are used in conjunction with the chamber pressure control system to vary the composition, flux, and level of excitation of the vapour during the process. The substrate carrier is electrically excited and temperature controlled so that the desired film growth conditions are established. Overall deposition system pressure is controlled by the chamber pressure control system. The three surface modification techniques under this category are: glow discharge deposition, planar magnetron sputtering, and ion beam sputtering. All these processes

have the following common aspects which have important influence on the quality of surface modification.

(i) Control of the composition, flux, and degree of excitation of the vapour,

(ii) Positioning of the substrate to intercept the correct vapour flux composition to achieve the desired condensation rate on the surface,

(iii) Control of the substrate surface conditions which influence the growth of the coating.

In glow discharge deposition techniques, the vapour fluxes are created by dissociation and excitation of feedstock gases by glow discharges. The planar magnetron sputtering and ion beam sputtering deposition techniques use glow discharges as a source of high energy, noble gas (like argon) ions, which in turn excite the vapour fluxes by sputtering atoms from feed stock targets. Sputtering excites materials into the gas phase by momentum transfer. In the sputtering technique, high-energy ions or neutral atoms supplied by the glow discharge collide with the surface of the feed stock target and transfer their momentum to the target material; and some of the feedstock material is ejected from the surface of the target as a result of the momentum transfer.

The composition of the excited vapour is controlled by the composition of the feedstock target.

The flux is varied by controlling the vaporization rate of the feedstock and the area of the feedstock target .The shape and area of the feedstock target influence the shape and total flux density in the space between the source and the substrate.

The degree of excitation of vapour is controlled by the sputtering ion's incident energy and the energy lost by collisions with the background gas as the sputtered atom moves to the

substrate. Glow discharge deposition is like chemical vapour deposition with free radicals formed in the discharge. This process takes place at lower operating temperature of 400 ^{o}C because of the highly excited state of the feedstock gases in the glow.

In planer magnetron sputtering technique, the glow discharge is an ion source and a means of dissociation and excitation of reactive gases. The glow is ignited by applying an r.f or d.c potential between the cathode and anode surrounding it. The electron confinement is achieved with magnets.

In ion beam deposition system, the substrate is completely separated from the glow discharge and thus the environment of the substrate can be independently controlled. The glow discharge comprises of ions for the sputtering process. The d.c glow is ignited between the hot

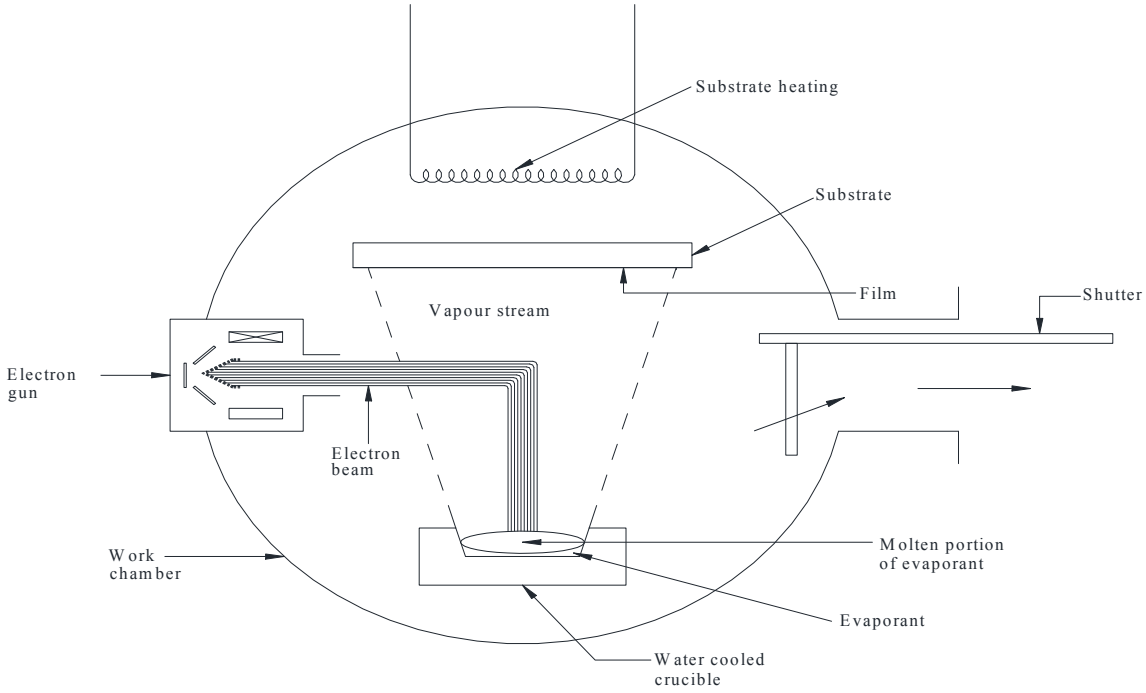

Fig.7.14 Thin- film Vapour Phase Deposition using Electron beam.

filament cathode and the anode in about one milli torr of argon. Ions are extracted from the glow through the holes in the screen grid and accelerator grid. The deposition rate on the substrate is controlled by the cathode erosion rate and the substrate collection efficiency. The target erosion rate is controlled by the ion current voltage and the orientations of the target and ion beam. The condensation rate is controlled by the orientation location of the substrate with respect to the vapour flux from the feed stock target.

Quality Control of Coatings of PVD

1. XRF Coating Thickness Gauge Machine

   The X-ray fluorescence machine is used to test the thickness of coatings made from PVD X-ray is released by the machine onto the specimen the rays are reflected back the intensity of the reflected rays is matched against already stored data back in the machine to determine the thickness of the test specimen.

2. Scratch Testing Machine

   The specimen is mounted on the load is applied and the indenter slides on the surface until a scratch is made. The plot of the scratching is displayed on the screen of the computer attached to the machine, likewise the acoustic intensity. The specimen is viewed under a microscope to determine whether peeling occurs, if it does it is rejected.

3. Surface Roughness Testing Machine

   The test specimen is placed under the stylus, the stylus moves on the surface of the specimen as the profile is plotted by computer attached to the machine. The computer gives both the plotted profile and the numerical values of the surface roughness of the specimen. The sample as received is tested and then the polished sample is again tested.

Specifications are normally given by customers and the tested sample must conform to specification or else it is returned for polishing.

7.8 Laser Treatment for Surface Modification by Surface Alloying

Engineering failures at surfaces occur due to fatigue, corrosion, friction and wear because stresses are highest at surfaces and they are exposed to the environment. Best solution is therefore to provide material with surface properties which are different from those of the bulk. Laser can be used to surface hardened steels and cast iron to enhance fatigue, wear, and corrosion properties. Laser surface modification processes are designed to alter the compositions and microstructures of surface layers. Laser parameters can be controlled to obtain the desired surface alloy compositions with unusual microstructures. Laser surface modification processes could be either laser surface alloying type or laser cladding type.

The benefits of laser treatment are conservation of strategic and expensive alloying elements, formation on non-equilibrium crystalline and amorphous phase, refinement of grains, homogenization of microstructures, increased solid solubilities of alloying elements, and modification of segregation patterns. With laser technique, it is possible to control power density precisely, ensuring heating to a controlled depth and thereby reducing distortion. Laser technique can also be used to alloy inaccessible and localized areas. Considerable changes in chemical and microstructural features occur due to rapid heating and subsequent quenching rates. Large temperature gradients (of the order of 106-108^{o}C/s) exist across the surface layer and the underlying substrate. Substrate by itself acts as heat sink and thus no additional quenching medium is required.

Laser cladding can be accomplished either by prior placing of the coating in the form of loose powder or by pneumatically injecting the powder into the melt pool during laser processing.

The powder is carried by the stream of argon. Powder flow rate is one of the key factors affecting the shape of cladding, porosity, dilution, and adherence of the coating. Laser cladding enables applying of cladding alloys of high melting point on low-melting point work pieces, controlled dilution localized application of coating, good fusion bond, fine microstructures, minimal heat affected zone, and homogeneous and flawless coatings.

7.9 Electron Beam Coating

This process is based on evaporation in a vacuum to produce thin films. The electron beam as an energy carrier serves to heat the evaporant in the crucible directly. Electron beam is generated in the electron gun, and by suitable focusing and deflection, is passed through the work chamber to the evaporant. Both the work chamber and the beam generating system are evacuated to enable generation and unimpeded propagation of electron beams. When the beam hits the evaporant, the kinetic energy is converted into heat (useful energy and evaporation) and losses encountered are back scattered electrons, secondary electrons, thermionic electrons and x-radiation.

Fig.7.15 shows the principle of electron beam evaporation. Plant consists of a work chamber with a vacuum pumping system, a crucible for an evaporant, an electron gun, a shutter, and a substrate with its fixtures and heating appliance.

The evaporant is heated by the beam that impinges directly into its surface. The surface is therefore brought to such a high temperature that it becomes the source of a vapour stream. The substrate to be coated is arranged in this vapour stream, and part of the vapour condenses on it in the form of a thin film. Evaporation from cooled crucible allows the production of high purity films because reactions with the crucible walls are avoided almost completely.

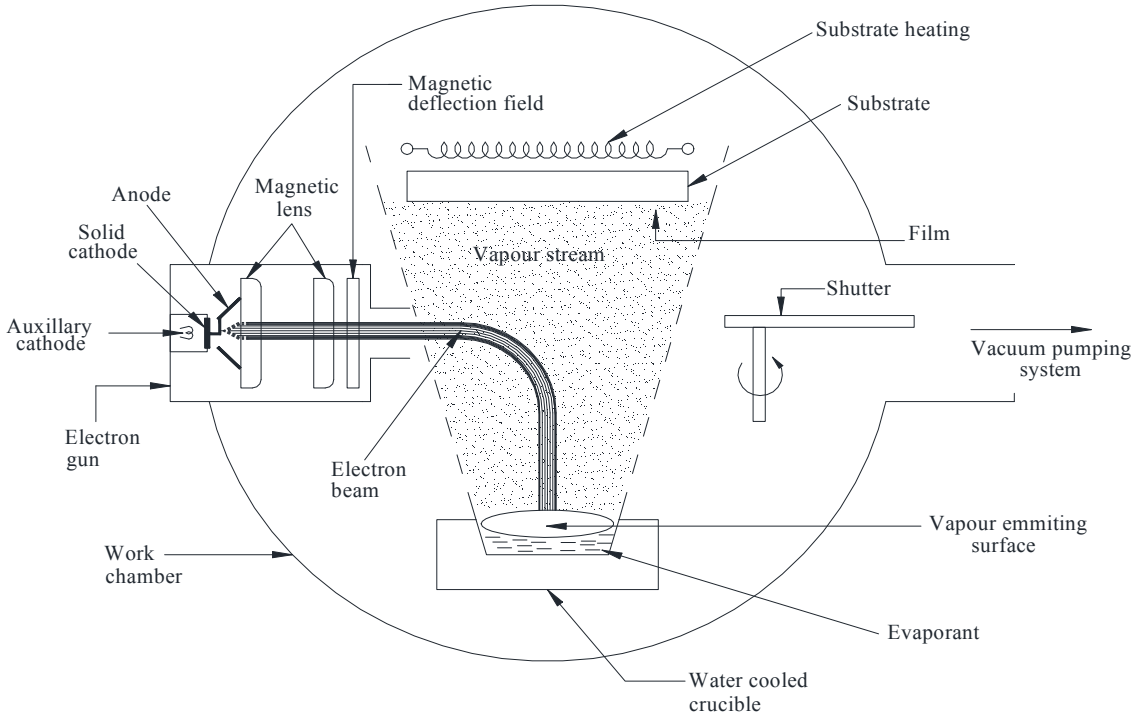

Fig. 8.4

Fig.7.15 The Principle of Electron Beam Evaporation.

Fig.7.16 Electron Beam (EB) Method Equipment

OSG Coating Services Co. Ltd uses EB method to create smooth TiN, TiCN, and CrN coatings with superior welding resistance. The EB equipment is shown in fig.7.16 above.

7.9.1 Plasma Treatment

Plasma surface treating produces diffusion coatings (of nitrogen, carbon, boron etc.) which are quite distinct from over lay coatings. It uses the phenomena of electrical glow discharge to activate the gas species. It permits better control over final work surface composition, structure and properties. Electrical glow discharge gives faster deposition rate at lower surface temperatures. It can produce the required active species in a low pressure gas mixture. Proper plasma surface treatment includes both vacuum degassing and sputter cleaning steps before the addition of desired species.

Nitriding, carburizing and boriding with positive ions derived from the plasma of an electrical glow discharge is an effective surface treatment for cast iron and alloyed steel. The glow discharge used for plasma treating occurs by application of voltage between two electrodes positioned within a gas mixture at some suitable partial pressure. Work surface forms cathode and a vacuum retort forms the anode for an electrical glow discharge. A regulated voltage pulse is applied between cathode and anode to produce a positive ion glow of some selected chemical species to the surface of the work piece. The pulse power supply permits regulation of ion concentration gradient at work surface.

7.9.2 Plasma Nitriding

Nitriding process is a heat treatment to diffuse nitrogen to steel, particularly nitriding steel, steel surface hardens to form nitride (AlxN, CrxN, VxN...) by nitriding steel; steel surface is improved in terms of abrasion resistance, corrosion resistance and fatigue strength. Nitriding is normally done at a temperature below 873K ($500^{O}C$ to $550^{O}C$). Nitriding process does not need surface hardening by quenching as carburizing after nitriding. The aim of this book is not to so much due on conventional methods. Therefore we move onto plasma nitriding technology.

7.9.3 Plasma Nitriding Technology

Plasma technology is the technology to apply plasma of non-equilibrium state to heat treatment. This plasma technology has new characteristics in comparison with conventional heat treatment. Plasma of non-equilibrium state is created by abnormal glow discharge. The characteristics include:

- Iron or steel surface form iron nitrides, and nitrogen diffuse into the steel to make diffusion layer
- You can select nitride and thickness of nitriding layer by control nitrogen ratio in mixture gases
- Nitriding temperature is from 653K to 873 K
- Plasma nitriding can select the nitriding part of works easily.
- Plasma nitriding process can easily nitride stainless steel and titanium. Plasma nitriding equipment is show in the fig.7.17. Below

Fig.7.17 Plasma Nitriding Equipment

The nitriding process requires cleaning the work pieces. Then setting them in work table from where they are transferred into the chamber by inserting them in an orderly manner. Nitriding is started after closing the chamber by starting the glow discharge followed by cooling, taking out, visual inspection of work pieces, then rust proof treatment, packaging and delivery inspection. Area of application include, plastic forging die, worm forging die, hot forging die, aluminium die casting sleeve, cam , gear, shaft, dram, light electrical appliance parts, boats and ship parts.

7.9.4 Merits and Demerits of Plasma Nitriding

Plasma nitriding process can nitride all steels

- Plasma nitriding temperature is from 623K to 863K
- Plasma nitriding process is eco-friendly process
- Plasma niriding process can easily nitride a part of work
- Plasma nitriding process can select the structure of nitriding layer by how to use works
- Plasma nitriding process can nitride stainless steel
- Plasma nitriding can be carried out with small distortion
- Plasma nitriding surface of work is beautiful
- Plasma nitriding compound layer is not porous

Demerits

Plasma nitriding process is difficult to form compound layer over 10μm.

- In plasma nitriding process, dirts of work surface can become a problem.
- Plasma nitriding process cannot nitride small hole and gap of work.

7.9.5 Radical Nitriding Process

Radical nitriding was co-developed by NDK and Sumitomo Metal Mining Co. Ltd all of Japan. This is plasma nitriding method based on a new idea. The characteristics of the process are:

- Flat and smooth surface condition
- No compound layer
- Application to the duplex surface treatment with PVD.

The difference between radical nitriding and plasma nitriding is that in radical nitriding the heating method is a heater located outside of the chamber and NH radical produces the nitriding on the work. The gas in the chamber is NH_3 and NH radical. Nitriding of the work in plasma

nitriding is however by ion bombardment and N ion causes the nitriding. Areas of application include punching tools, cold press die, injection moulding machine parts. I have intentionally with held the details of these technologies because they will not make meaning to the targeted readers at this point in time. Fig.7.18 shows radical nitriding equipment.

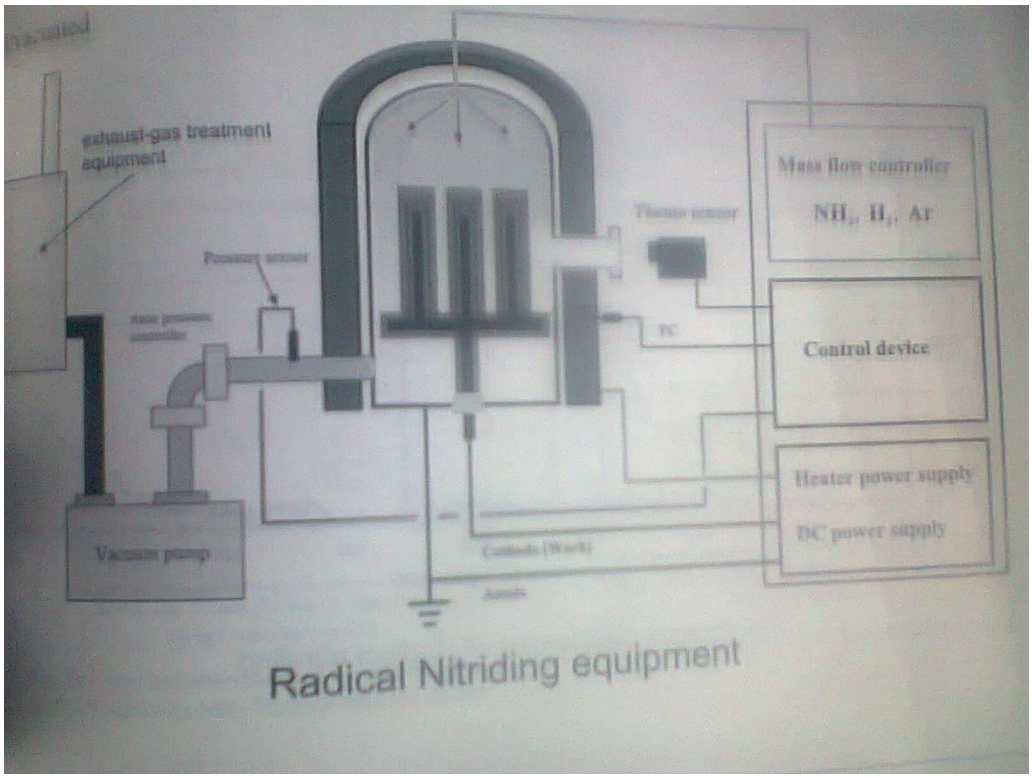

Fig.7.18 Radical Nitriding Equipment.

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8.0 CHAPTER EIGHT

ELECTROPLATING AND ELECTROLESS PLATING (WET PROCESS)

8.1 Introduction

This chapter looks at some electroplating processes, otherwise referred to as the wet process of electroplating. This wet process can be either electroplating or electro-less plating. Processes like the CVD, PCVD, PVD etc are referred to as dry processes. In electroplating the material for surface coating is normally referred to as the substrate and the bath which contains the material which supplies the substances is referred to as the electrolyte. The electrolyte is normally in the bath into which the substrate must be immersed. The bath also contains a cathode and anode which are linked to power supply. In the case of the electro-less process this is also provided but to a limited level and that is why it is called electro-less plating. The purpose of surface modification is multidimensional and includes the reinforcement of surface, passivation or decoration of surface, development of composite materials and application of functional devices. Coating materials can be metals, ceramics and semiconductors and even plastics. Substrate materials can be metals, ceramics or graphite, glass and polymer (Oki, 2008)

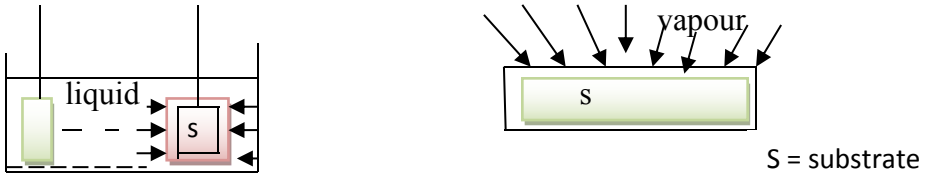
8.1.1 Classification of Coating Techniques

- Electrodeposition
- anodic oxidation
- electroless plating
- sol-gel method
- painting and baking
- molten salt dipping
- thermal spraying
- chemical vapour deposition (CVD)
- Physical vapour deposition (PVD)

Wet process

Dry process

The dry process and wet process is illustrated below



(a) Wet process (b) dry process

Fig. 8.1 Illustration of the Wet and Dry Process of Coating.

8.2 Electroplating

8.2.1 Zinc Plating and Conversion Coatings

Zinc plating and conversion coatings are normally carried out for corrosion protection; prevention of waste is metal resources. The committee on cost of corrosion in Japan estimated that the cost of corrosion in Japan was 1.8% of GNP (5,800 Billion Naira) in 1976 and 0.77% GNP (7,800 Billion Naira) in 2000 (Nogochi, 2008). The prevention measures were 58% for painting coating, 28% for surface finishing. Other measures were anti-corroding metal material,

inhibitor, cathodic protection etc. 120 million ton of steel products was protected in Japan in 1973, 30% of which was steel coil strip.

Corrosion Prevention of Iron and Steel

The following measures are employed to prevent corrosion of iron and steel; painting and surface finishing.

Surface finishing: several surface finishing methods are in use for corrosion prevention of iron and steel. Conversion coating include processes like phosphating and chromating.

Zinc plating can be done using several techniques such as electroplating, galvanizing (hot dipping), zinc lamella systems (ex. Dacromet), metal spraying and vacuum plating. Other materials like Ni, Cu, Sn, Cr, Ni-Cr, Al can also be plated on iron and steel to prevent corrosion. Corrosion of iron and steel can equally be achieved using other methods.

8.2.2 **Zinc Plating**

Zinc is not a noble metal and acts on steel by sacrificial corrosion protection. It forms a stable zinc oxide carbonate film, which attains passivation by chromating. Zinc has excellent cost performance. Electro zinc plating can be carried out in a jobbing shop as well as large scale as in a steel company where it is used for steel strip by continuous, high speed processes. In jobbing shop the bath could be alkaline or weak acidic.

Alkaline: cyanide solution (low, middle, or high concentration) and zincate solution.

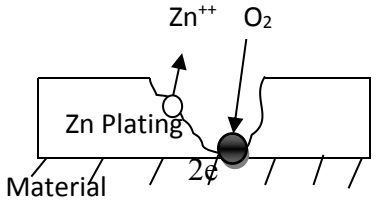
Weak acidic: ammonium chloride solution, potassium chloride solution and zincate solution. For steel company steel strip the bath could be made up of mainly sulphate zinc solution and rarely chloride zinc solution.

Zinc plating using zinc cyanide plating was started in 1910, and by 1960 regulation of air, water pollution and development of non-cyanide processes of zincate bath and chloride bath was

started. In the 1980s the development of zinc alloy plating with high anticorrosion properties was started using Zn-Ni, Zn-Fe, Zn-Sn, Zn-Co alloys. Chromate passivation was developed in the USA in the 1940s, to increase the corrosion resistance of Zn plating. Green chromating was started in the 1960s to eliminate the harmful effect of hexavalent chromium. The year 2000 was set in Europe as the date to end the use of hexavalent chromium from passivation film.

Anti corrosive Property of Zinc Plating.

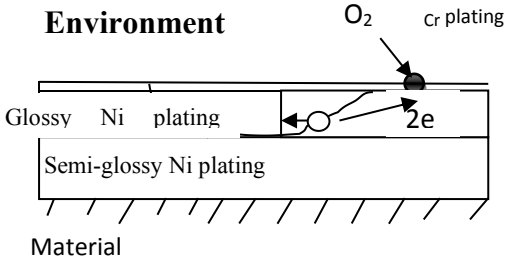
As in the model shown in fig. 8.1, plating films can be classified into the following categories according to their electrochemical anti-corrosive effects (1) sacrificial dissolution type plating; and (2) barrier type plating. Representative of the first type is zinc plating on iron and steel.



O anodic reaction: $Zn \longrightarrow Zn^{2+} + 2e$

Cathodic: $H_2O + 1/2O_2 + 2e \longrightarrow 2OH^-$

1) Sacrificial dissolution type plating film



O anodic reaction: $Ni \longrightarrow Ni^{2+} + 2e$

Cathodic reaction: $H_2O + 1/2O_2 + 2e \longrightarrow 2OH$

2)Barrier type plating film

Fig. 8.2 Plating Film Corrosion Model

Table 8.1 shows major oxidation–reduction reactions related to plating and their electrode potentials. The normal electrode potential of zinc is -0.76v. Compared to iron, whose electrode potential is -0.47v, zinc is electrochemically inferior. Therefore, when iron and Zinc are electrically linked, zinc is oxidized first, resulting in preventing iron from being corroded. This is referred to as sacrificial corrosion prevention or sacrificial dissolution. Moreover, under normal atmospheric conditions, basic zinc carbonate, which is relatively stable and has a low corrosion rate that is 1/20 of the corrosion rates of iron and steel, is formed on the surface of zinc. This is very effective as an anti-corrosive film. However, attention should be paid to the fact that when the temperature exceeds 60oc, the electrode potentials of zinc and iron become reversed, resulting in the loss of sacrificial dissolution property.

In the other type of plating (2), films that are highly resistant to corrosion such as those formed in the tin plating and nickel-chromium plating on iron and steel, acts as a barrier to block the substrate from a corrosive environment. In order to enhance anti-corrosive strength it is important to reduce pinholes in the films, for this reason it has become popular practice not only to simply increase the thickness of the films, but also to adopt a multilayer structure, such as the double or triple layer structure in semi-glossy and glossy nickel plating. The sacrificial corrosion effect works in these processes by taking advantage of the slight differences in electric potential between the various layers.

Table 8.1 Standard Electrode Potential

Elemental species	**Reaction formula**	**Electrode potential**
Oxygen	O2+4H+ +2e = H2O	+ 1.229
Silver	Ag+ + e = Ag	+0.80
Copper	Cu2+ + 2e = Cu	+0.34
Hydrogen	$H^+ + e = 1/2H_2$	0
Nickel	Ni2+ + 2e = Ni	-0.27
Iron	Fe2+ + 2e = Fe	-0.47
Zinc	Zn2+ + 2e = Zn	-0.76
Water	$H_2O + e = 1/2H_2 + OH^-$	-0.83
Manganese	$Mn^{2+} + 2e = Mn$	-1.19
Zincate	$Zn(OH)_4^{2-} + 2e = Zn + 2OH^-$	-1.245
Zinc cyanide	$Zn(CN)_4^{2-} + 2e = Zn + 4CN^-$	-1.26
Aluminium	Al3+ + 3e = Al	-1.66
Lithium	Li+ + e = Li	-3.05

Table 8.2 Hydrogen (10^{-2} A/ dm^2)

Metal	**Over-potential (V)**
Pt	0.024
Platinum black	0.015
Fe	0.4
Cu	0.48
Ni	0.56
Zn	0.72
Hg	0.9

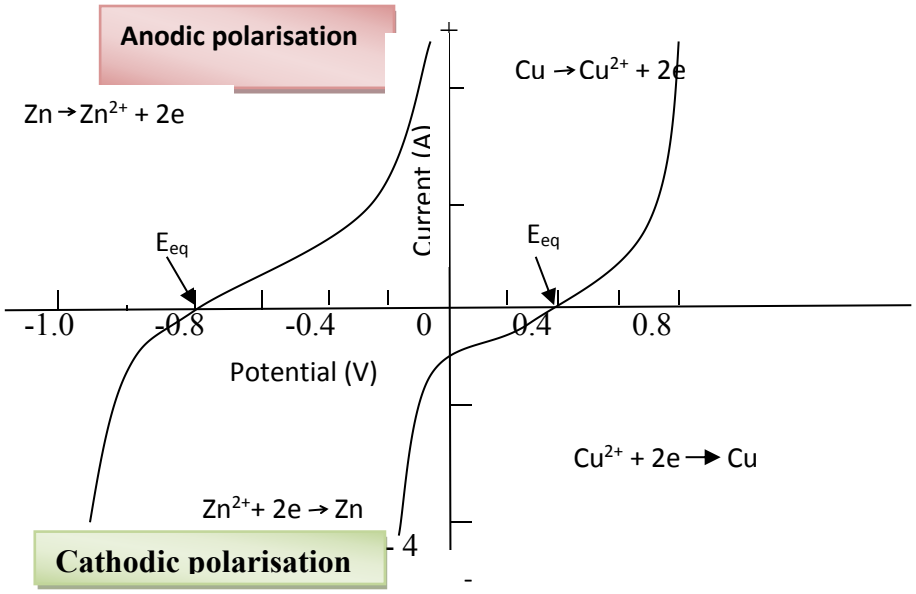


Fig.8.3 Current- Potential Plot (polarization curve)

Fig.8.3 shows the relationship between the current and potential of the electricity flowing through an electrode. This relationship is shown as a graph, called a current-potential plot, or polarization curve. Copper ions (cu^{2+}) undergo cthodic polarization; cathodic current flows when the potential is less than +0.34V; and plating takes place. Similarly zinc ions (Zn^{2+}) are plated

when the potential is below -0.76V. However, if the plating solution is acidic and many hydrogen ions are present, the hydrogen ions undergo discharge at 0V or less, and hydrogen gas is generated. In this case, once zinc is deposited, only a small amount of hydrogen is generated and zinc plating becomes dominant because the hydrogen over-potential on zinc is very high. Cathodic polarization curves are normally shown by reversing the top/ bottom and the right/left orientation of the graph in fig.8.2. Shown in Table 8.2 are the hydrogen over-potentials of major metals on zinc at 1mA/dm^2. The values of the over-potentials of the metals over platinum are very small, but large over zinc and mercury. Zinc separates from zinc chloride plating baths when the potential is below -0.76V. In contrast, zinc separates from zinc cyanide and zincate baths, which are alkaline, when the potential is below -1.26V, as shown in table 1. Highly alkaline and with only slight amounts of hydrogen ions present, reduction of water occurs when the potential is below -0.83V, making it easy for hydrogen gas to be generated. Satisfactory plating cannot be achieved for cast iron or high-carbon steel in cyanide or zincate baths because more hydrogen is generated than zinc. For aluminum, zinc is separated in a zinc chloride bath when the potential is -1.66V, and this the reason that electroplating in an aqueous solution is impossible. Therefore, electroplating of aluminum is done using non-aqueous solutions or molten salts.

8.2.3 Plating Elementary Reaction and Effects of Brightening Agents

Metal ions in plating solutions are surrounded by such ligands as water:

1) Metal ions, while surrounded by ligands, move closer to the plating surface (electrode) by migrating and dispersing from the solution bulk (dispersion stage)
2) They release the ligands and turn into bare metal ions (chemical reaction stage)

3) Bare metal ions receive electrons from the electrode and turn into neutral adsorption elements (adatoms) (charge transfer stage)
4) Adatoms move across the surface of the electrode, become incorporated into crystal lattices, and turn into a metal (crystallization stage)
5) These processing stages are linked in series and the observed reaction speed (plating speed) undergoes rate controlling during the slowest stages. The neutral metal adatoms now generate at the electrode as a result of reduction during the crystallization stage move across the electrode surface. They are incorporated into kinks where the surface energy is high, and since growth occurs at only certain faces of the crystal, the crystal becomes very large. In the case of zinc, which is a hexagonal system, the crystal has a hexagonal face (0002). This is indicated very well in fig. 8.4, which shows the results of observing with a scanning electron microscope the surface of plating achieved in a zinc chloride-potassium chloride bath.

   If suitable substances with adsorption properties are now present in the plating solution, they are adsorbed specifically at kinks and other active points, inhibiting the incorporation of metal atoms into certain regions. Consequently, the metal element adheres to other regions, resulting in the formation of fine crystals. The irregularities on the plating surface become refined as much as the wavelength of light or less, producing a glossy surface when diffuse reflection of light disappears. This explains the qualitative effect mechanism of brightening agents. Most brightening agents are organic. They are selected for practical use according to the type of metal or the constituents in the plating bath. The composition of brightening agents, such as saccharin and butynediol used in nickel plating, are rarely known. Many of them are corporate secrets, and their details are

practically unknown. Brightening agents generally consists of a base component that has a level effect and a brightening component that has a brightening effect. By dispersing and being adsorbed to the convex areas, the leveling component suppresses deposition at the uneven surfaces that are greater than the surface irregularities that are considered when discussing luster. Meanwhile, the concave areas are plated and become level. Therefore, along with the brightening component, the leveling component also has a brightening effect. The polyamine series are used as a brightening agent in zinc cyanide baths. In zincate baths, various polyamines are used as the base component, while aromatic aldehyde is used as the brightening agent. In zinc chloride baths, nonionic surfactants are used as the base component, while aromatic aldehyde is also used as the brightening agent. The addition of brightening components results in increasing cathode polarization in the current-potential curve shown in fig.8.4

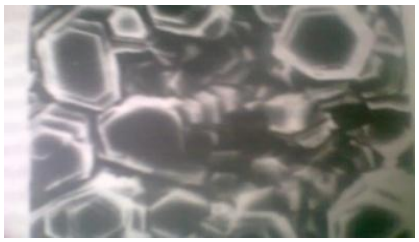


Fig.8.4 Microstructure of zinc coating plated in zinc chloride-potassium chloride bath using SEM.

8.2.4 Types of Zinc Plating and their Characteristics.

In zinc plating with sacrificial dissolution as its anti coorosion principle, the anti corrosion strength is generally stipulated by film thickness (amount of deposition). The structural materials for power transmission line towers and bridges require long-term corrosion resistance for 50- or 100 years period. Hot-dip galvanizing, in which thick coatings are easily produced, is adopted for these materials. Here we will take up zinc

electroplating that aims at corrosion resistance for periods of several years or between 10-19 years. Zinc plating baths that plating specialists use are roughly classified into alkaline baths and acid baths as shown in Table 8.3. The former is further broken down into zinc chloride baths and zincate baths. Among acid baths, chloride baths are the type used by plating specialists. Sulphate baths, which are used by steelmakers in continuous plating of steel strips and wire rods, are mentioned here. Zinc baths are used for plating auto parts. Zinc cyanide baths are sometimes specified for plating household electrical appliances. The zinc chloride baths are used for plating bolts and other fastener components.

Plating solution composition and plating properties according to bath type-with zinc alloy plating processes will be discussed below.

Zinc Cyanide Bath

Due to aversion towards the highly toxic property of cyanides, the volume of zinc cyanide plating baths have been on a downward trend. However, compared with zincate baths and zinc chloride baths, zinc cyanide baths have superior characteristics: they are highly resilient to preprocessing flaws; the films are flexible and have excellent secondary processing property; and there is little occurrence of whiskers. As a result a certain amount of demand still exists. Zinc cyanide baths are primarily used for static zinc plating.

Depending on the concentration of sodium cyanide, zinc cyanide baths are divided into high concentration, medium concentration, and low concentration cyanide baths. While the majority of these are medium concentration cyanide baths, low concentration cyanide baths are being converted to zincate baths. Table 8.3 shows the composition of

Zinc Cyanide Baths and Zincate Baths.

In zinc cyanide baths, zinc is present in the form of $Zn(CN)_4^{2-}$ and $Zn(OH)_4^{2-}$ complexes as in the following formula: $Na_2Zn(CN)_4 + 4NaOH = Na_2Zn(OH)_4 + 4NaCN$.

The deposition potential of Zinc from the two complexes are quite close: -1.26V and -1.22V, respectively. The balance in the presence of these two complexes is known to

Have substantial effects on the current efficiency, leveling property, and uniform electrodeposition property. The value of all sodium cyanide concentration removed with zinc concentration is called the M ratio. This is commonly used in the management of baths. By setting the M ratio at the proper value, a starch syrup-coloured film with a semi-glossy to glossy external appearance can be obtained from a solution with the basic composition without adding brightening agents. In addition, the external appearance is enhanced by immersion in diluted nitric acid.

Table 8.3 Composition of Alkaline Plating Baths

Types of Bath	**Zinc cyanide bath (g/L)**			**Zincate bath (g/L)**	
Type of chemical	High Concentration	Medium concentration	Low concentration	Conventional bath	Uniform electrodeposition property
Zinc oxide	42	25	10	12	15
Sodium hydroxide	90	70	70	120	140
Sodium cyanide	90	40	10	-	-
Brightening agent	Moderate amount			Moderate amount	
Bath temperature (^{O}C)	20-30			20-30	20-40
Current density	0.5-8	0.5-8	0.5-8	0.5-5	0.5-8
Current efficiency %	50-90	50-90	50-90	60-90	50-85
M ratio	2.7	2	1.25	-	-

8.2.5 Zinc Baths

Zincate baths are of a highly alkaline liquid composition in which cyanides have been removed from low concentration cyanide baths. They consist of only two constituents: zinc oxide and sodium hydroxide. In addition, carbondioxide in the air dissolves and is contained in the baths in the form of carbonates. Zinc is present in the solution in the form of zincate ions—$Zn(OH)4^{2-}$ From the solution containing only the basic constituents, coarse deposits with no leveling

property can be obtained, and dendrites that have poor adherence property are deposited at the high current sections. To achieve the leveling and glossy external appearance, organic brightening agents are indispensible. In the early periods, zincate baths lacked the capability to prevent scorching of brightening agents at high current sections, and they were thus used primarily in barrel plating. Later on improvements were made to brightening agents, scorching was suppressed, and films flexible enough to withstand post-processing could be obtained. Currently, zincate baths are also used in place of zinc cyanide baths in static plating. Zincate baths exceed zinc cyanide baths in the volume of usage and have become the mainstream process in zinc plating. With further progress in the development of brightening agents, new-generation zincate baths that are far superior to traditional zincate baths in uniform electrodeposition property have begun to be used extensively.

Zinc chloride Baths

As shown in Table 8.4, zinc chloride baths include ammonium baths, potassium baths, and mixed ammonium-potassium baths, the usage of which depends on the type of conductive salts used. Ammonium baths have a relatively broad current density, which gives a level external appearance to the material being plated, and are in wide usage. However, there are problems with their usage. Ammonium salts and zinc form a stable ammine complex, which, in terms of effluent treatment, is poor in sedimentation property and results in the generation of metallic hydroxides. Ammonia is also one of the substances causing eutrophication, including red tides, in closed water systems, and is subject to regulations controlling nitrogen compound effluents. The effluents standard for nitrogen is 100mg/L, but in the electroplating industry, the regulations continue to be enforced with 500mg/ L as the interim standard.

Table 8.4 Composition of Zinc Chloride Bath

Type of bath	**Zinc Chloride bath (g/L)**		
Type of chemical	Ammonium	Potassium	Mixed bath
Zinc chloride	42	42	42
Ammonium chloride	210	-	45
Potassium chloride		220	180
Boric acid		30	
Ph	5.5		
Brightening agents	Moderate amount		
Bath temperature (Oc)	20-30	20-50	
Current density	0.5-5	0.5-3	0.5-4
Current efficiency %	95-98	95-98	95-98

Meanwhile potassium baths are extremely superior in effluent treatment property, but they are not widely used in Japan because the scope of their current density is narrow, their uniform electro-deposition property is poor, and their process management is complicated. In addition, they include boric acid as a buffering agent component, and now that regulations controlling boric acid effluents have been implemented, potassium baths are saddled with another problem. Due to reasons, plating baths in which ammonium and potassium are mixed have now become the mainstream process and are on the rise. In the mixed baths, ammonium salts serve as a buffering agent, making boric acid unnecessary. The technology behind the high temperature baths is being applied to the mixed baths and is producing results. In zinc chloride plating, the

bath voltage is low, current efficiency is high, and thedeposition speed is fast. In order words, zinc chloride plating is superior in energy utilization efficiency. High current efficiency indicates that there is very little hydrogen generation, and since hydrogen absorption is very small compared to alkaline baths, it is said that zinc chloride plating is also favourable with regard to hydrogen brittleness. In addition zinc chloride plating has excellent leveling property, the film luster is superior to that produced by alkaline baths, and it is possible to easily plate cast iron, high-carbon steel, and carbonitrided steel, for which plating cannot be done using alkaline zinc baths. Since zinc chloride plating baths have higher zinc concentration in the solution in comparison to alkaline baths, a high current efficiency of more than 95% can be achieved even when the current density exceeds 5A/dm. on the other hand despite its high current efficiency, zinc chloride plating has poor uniform electrodeposition property, which is a tradeoff relation with current efficiency, and it is also inferior to zincate baths with regard to covering property. Another shortcoming is the problem of corrosion of plating facilities and building due to the formation of chloride mists.

Zinc Alloy Plating Baths

In the 1980s, deterioration of the corrosion environment became marked due to changes in the atmospheric environment caused by acid rain and snow melting agents sprayed to prevent freezing of roads during the winter season. As a result, there arose strong calls primarily for raising the corrosion resistance of auto parts. In response, various plating processes using alloys that combined zinc with tin, nickel, and iron were developed for the purpose of improving corrosion resistance of zinc plating. However, alloy plating requires advanced management techniques and with development costs added to the price of chemicals and processing costs being very high, there has been limited usage of alloy plating. After 2000, trivalent chromium

chemical conversion films that were free of hexavalent chromium were adopted due to restrictions on the usage of harmful substances. However, corrosion resistance specification were not satisfied for some parts depending on the combination with zinc plating. Therefore, zinc alloy plating, which has superior corrosion resistance, has attracted renewed attention.

8.2.6 Zinc –Nickel Alloy Plating

Zinc-nickel alloy plating has corrosion resistance that is 3-4 times higher than that of zinc plating. Major steelmakers have traditionally used sulfate baths for surface-treated steel sheets. Plating baths used by plating specialists include weak acid ammonium chloride baths and alkaline zincate baths. Ammonium chloride baths have high current efficiency, allowing fast plating speed. They have characteristics that are similar to those of acid zinc plating baths. For example, plating of cast iron and high-carbon steel is possible, but the uniform electrodeposition property is also poor. Ammonium chloride baths are more suitable for barrel plating than static plating. The nickel co-deposition rate of these baths are normally 5- 10%, but the rate increases to more than 14% at a low current density of less than 1A/ dm^3. Alloy films with 13% nickel content have the most excellent corrosion resistance.

The codeposition rate of nickel in a zincate bath depends on the type and concentration of the nickel complexing agent and the metal concentration. However, it is said that plating temperature and current density have almost no effect . currently two types of plating baths are used-one in which the nickel codeposition rate is 6-8% and theother with a nickel codeposition rate of 12-16%. In addition zinc alloys with a 12-16% nickel content are very compatible with trivalent chromium chemical conversion films, and they are used extensively for parts inside an automobile engine room. They also have excellent paint adhesion property.

Tin –Zinc Alloy Plating

In tin zinc alloy plating, the codeposition rate of tin is high. This makes it favourable for preventing the occurrence of whiskers. It has also been considered for use in lead-free solder plating. By taking advantage of its conjugative property and corrosion resistance, tin-zinc plating has been used not only in auto parts, but also in electronic, electric, and precision processing components. Tin-zinc alloy plating is an alloy plating process that possesses corrosion resistance of the barrier-type plating film of tin plating and corrosion resistance resulting from sacrificial dissolution in zinc plating. In other words, the plating film of tin –zinc alloy plating is slightly nobler in potential than iron, contributing to preventing corrosion of iron, while its own corrosion progresses slowly and the film wears out very little. After the chemical conversion treatment, the corrosion resistance is the greatest with the tin co-deposition rate at 70-75%. The corrosion resistance is excellent within a wide range of 50-80%, but once the co-deposition rate exceeds 85%, the corrosion resistance drops sharply. In an acidic atmosphere, the corrosion resistance is not very good. Since the plating film has superior flexibility, tin-zinc alloy plating is used in parts that require secondary processing, such as bending, caulking, and deep drawing.

Among zinc alloy plating processes, tin –zinc alloy plating was developed at an early period. While many types of baths, such as cyanide baths, boride baths, fluoride baths, and organic acid baths, have been studied, neutral organic acid baths are commonly used today.

Zinc-Iron Alloy Plating

Zinc-iron alloy plating is a type of alloy plating in which small amounts of iron ions are dissolved into a zincate bath and a suitable complexing agent is used to codeposit 0.2- 0.5% iron into the zinc plating. The bare corrosion resistance of zinc-iron plating is not very much different from zinc plating, but the film with an iron codeposition rate of 0.4% that has undergone chromate treatment has excellent corrosion resistance, which is more than three times that of the film formed by zinc plating. In particular, black chromate treatment can be conducted without the addition of silver ions, and moreover, high corrosion resistance is a characteristic of the film. However, corrosion resistance becomes poor after the film has been heated

8.2.7 Management of Zinc Plating Baths

Preprocessing

In order to obtain a plating film with superior quality, it is natural to manage such aspects as the concentration of the plating solution constituents and their balance, brightening agents, and

impurities. At the same time, the plating pretreatment process is important. It is said that defective plating caused by preprocessing flaws amount to 31%. Press oil, rolling oil, and other impurities are securely adhered to parts to which zinc plating is applied. Thick oxide films such as surface altered layers and black scales also exist. Since plating specialists must treat various grease and different materials during the same process, this is prone to cause problems. Here, we will introduce issues and improvement cases during the following standard pretreatment process: alkaline immersion degreasing→acid wash (pickling) → electrolytic degreasing→ acid activation → plating.

Items tainted with high viscosity index oil or scorched grease may require preliminary degreasing. A combination of mechanical actions, such as agitation, oscillation, ultrasonic waves, and electrolysis will be effective in increasing the degreasing capacity. In an improvement case in which air agitation and weak anodic electrolysis were used in combination on a static plating line, the item was prevented from falling by placing an air pipe on the side of the tank, and oscillation was applied gently. To prevent anodic corrosion, the current density was regulated to remain below 0.5A/dm^3 on average. Removing welding scorch marks is one of the difficult problems in preprocessing. It is believed that in the field, the reality is that wire brushes are used to scrape off the scorch marks. In this case, using ultrasonic cleaning during the water washing stage after the final electrolysis stage is effective.

8.2.8 Effects of Impurities and relevant Countermeasures

Since Aoe et al have given a detailed explaination of plating defects due to impurity incorporation and countermeasures against them in the field, their explanation will be quoted here.

Classification of Impurities and their Paths

Table 8.5 Classification of impurities and their Effects

Type	Example of Impurity	Common harmful effects
Heavy metals	Copper, nickel, iron	Turns black after being immersed in nitric acid and undergoing chromate treatment (form eutectoid on the plating film)
	Chromium, lead	Poor electrodeposition, degradation of luster (causes substantial reduction of current efficiency)
Organic substances	Oil content, brightening agent, decomposition products, formulated products, etc	1. Poor luster and electrodeposition (hampers effect of brightening agents) 2. Poor adhesion 3. Greasiness
Inorganic salts	Carbonic acid root, chlorine root in alkaline bath	**1.** Degradation of leveling and luster **2.** Poor dissolution property of brightening agent

Excessive additives even if they are brightening agents that are essential ingredients, will turn into organic impurities and cause degradation of the films property. Impurities in zinc plating baths can be roughly classified into three types as shown in table 8.6. it is often a combined contamination involving several impurities.

The contamination path of impurities can be roughly classified into the following four types: (1) carried over from the previous process (oil, iron, etc) (2) dissolution of the material to be plated (iron, lead, etc, from products that have fallen from jigs), (3) dissolution from plating equipment (copper from bus bars, metals and resins from plating tanks and facilities) and (4) impurities in chemicals during construction of baths or replenishment. The first three contamination paths can be resolved through proper management of the facility and working conditions. (4) are chemical impurities, and sometimes there are cases in which their effects cannot be ignored. For example, there was a case in which six brands of sodium hydroxide were subjected to a hull cell test to determine the effects of impurities on zincate baths. Three brands were found to be unsuitable.

Since zincate baths are sensitive to impurities, it is necessary to pay attention to the brands being used even if they cause no problems in zinc cyanide baths

8.2.9 Confirmation of Impurities by Hull Cell Test and their Removal Methods

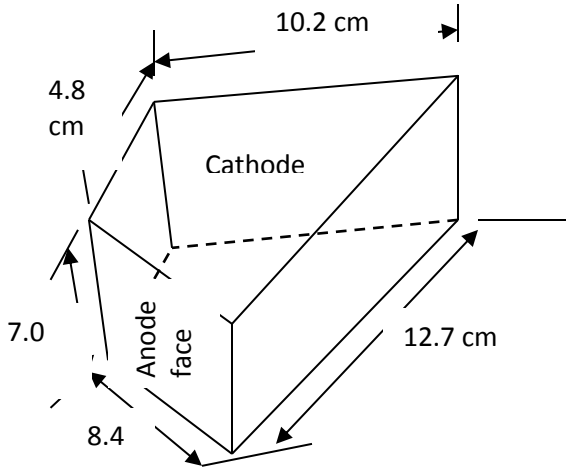


Fig.8.5 Hull Cell Test Tank

Although it is important to install analytical equipment and conduct regular analysis of impurities in plating solutions, plating specialists may not necessarily be able to do so. The Hull Cell test can be easily conducted and permits analysis to be carried out easily. Fig. 8.5 shows a Hull cell. In the Hull cell test, 267ml of plating solution is prepared and a polished steel plate measuring 65 x 100cm is used as the cathode test piece. Plating is conducted for 10 minutes with a 1A current. After the plating has been completed, the bottom half of the test piece is immersed in a 0.5% diluted nitric acid for 30- 120 seconds without agitating the solution, and changes in the colour are observed. In this case there are three observation points that should be noticed: 1) parts where the gas accumulates; 2) the right upper surface of the Hull cell test piece where the solution begins, and 3) the back part of the Hull cell test piece where the glossy plating is deposited. Representative Hull cell plating patterns formed in standard solutions into which such impurities as sodium carbonate, iron, hexavalent chromium, copper, lead and nickel have been added should be sets aside for making comparisons. The process is shown in fig.8.6.

Suspended particles in the plating solution are removed by filtration, while organic impurities are removed by activated carbon adsorption. After undergoing precoat filtration or treatment with activated charcoal in a separate tank, the solution is returned to the plating task after being passed through the filtering device. Such heavy metals as iron, copper, and nickel are subject to

zinc powder treatment and filtered as with activated carbon treatment, or subject to weak electrolysis treatment at 0.2 – 0.5A/ dm^3 for more than one whole day. Bivalent iron ions are turned into trivalent ions with hydrogen peroxide in a zinc chloride bath and removed by precipitation. In a cyanide bath, the ions are turned into sulphides by adding sodium sulphide and removed by precipitation. Likewise, there is a chemical treatment process in which sodium sulphide is added to reduce hexavalent chromium into trivalent chromium to reduce adverse effects.

Fig.8.6 Hull cell

8.3 Post-processing

Chemical Conversion Processing with Chromic Acid

Zinc and zinc alloy plating prevents corrosion of iron electrochemically. At the same time, under normal atmospheric conditions, a relatively stable film is formed around the iron, and although the corrosion speed is slow, the iron will corrode in the presence of chloride ions that break the film, as well as in a highly humid environment, generating a white corrosive formation (white rust). Therefore, in order to improve the corrosion resistance of zinc plating, chemical conversion treatment using chromic acid, etc. has been conducted as an after-treatment process.

Chromium compounds are formed by primarily using chromite ($FeO\text{-}Cr_2O_3$) as the basic raw material that is reduced in a furnace with carbon to produce metallic chromium, which is then melted and oxidized along with lime and soda ash to form sodium chromate. Various hexavalent chromium compounds and trivalent chromium compounds are produced via sodium chromate as an intermediate. Among the chromium compounds, hexavalent chromium compounds have a

wide range of applications, such as tannage, dye mordant, and oxidizing agent for manufacturing chemicals. However, in terms of volume, they are overwhelmingly used for surface processing. In Japan, 10,000 tons of chromium compounds are used annually in the form of chromic anhydride (CrO_2), of which 7,000 tons are used in chrome plating, with metallic chromium attached to various products. The remaining 3,000 tons are used as chemical conversion treatment chemicals for corrosion prevention, of which 2,500 tons are subject to effluent treatment and disposed as sludge after reduction neutralization treatment. The remaining 500 tons are apparently recovered and recycled via the ion-exchange resin method.

However, various harmful effects of hexavalent chromium on living organisms have been pointed out and the substance has been designated as a carcinogen under the PRTR (Published pollutant Release and Transfer Registry). Volvo's self-imposed curb in 1992 on the amount of elution of hexavalent chromium from its chromium films led to the inception of the ELV (End of life Vehicles) directive and the ROHS (Restriction of the use of certain hazardous substances in electrical and electronic equipment) directive, which regulates the use of hexavalent chromium and other hazardous substances for corrosion prevention in the EU. The use of chromate treatment has drastically declined, only remaining primarily in the processing of old spare parts. Fig.8.7 shows various conversion coatings.

Fig 8.7 Various Conversion Coatings

8.3.1 Alternative Chemical Conversion Treatment using Trivalent Chromium Compounds

Chemical conversion treatment using trivalent chromium compounds has been known from long ago. It is not particularly new in itself. In recent years, however, trivalent chromium chemical conversion films with excellent corrosion resistance have been developed, and attention has suddenly focused on this treatment method. There is no problem with trivalent chromium with regard to hazardous property. Instead, it is known as an element that is essential to living organisms in minute quantities. However, since it is possible for trivalent chromium to turn into hexavalent chromium as a result of oxidation, completely chrome-free films are sought in the future.

The specific composition of trivalentchromium chemical conversion solution that is in practical use has not been disclosed, but it is possible to get a glimpse of its general outline from parts of its patents that have been made public.

Table 8.6 Example of Composition of trivalent Chromium Chemical Conversion Treatment Solution and Film Performance

Example 1	**Example 2**	**Example 3**
100 g/ L $CrCl_3$. $6H_2O$ 100 g/ L $NaNO_3$ 15.75 g / L NaF 26.5 g / L Citric acid.$1H_2O$ Treatment temperature: boiling (approximately 100^oC) Treatment time: 30 secs Salt water spray corrosion resistance: 1000 hours Film thickness: approx 800nm	50g/ L $CrCl_3.6H_2O$ 100g/ L $NaNO_3$ 31.2g/L Malonic acid pH 2.0 Treatment Temperature: 60^oC Salt water spray corrosion resistance: 250 hours Film thickness: approx. 220-270nm	50g/L $CrCl_3.6H_2O$ 3g/L $Co(NO_3)_2$ 100g/L $NaNO_3$ 31.2 g/ L Malonic acid pH 2.0 Treatment time: 60 secs Salt water spray corrosion resistance: 350 hours Film thickness: Approx. 220-270nm

Table 8.6 shows two or three examples of the composition of solutions in actual use. Trivalent chromium chemical conversion treatment solutions consists of Cr^{3+} components, such as $CrCl_3$ and $Cr(NO_3)_3$, and catalytic components, such as nitrates, as the main ingredients, in combination with organic polyacids, such as oxalic acid, malonic acid, and citric acid, or silicate compounds, such as colloidal silica. The addition of cobalt salts, which have a marked effect on improving rust prevention strength, is also indispensable. For the sake of convenience, the treatment solutions are sometimes classified into organic acid and inorganic acid types, mixed types also exist.

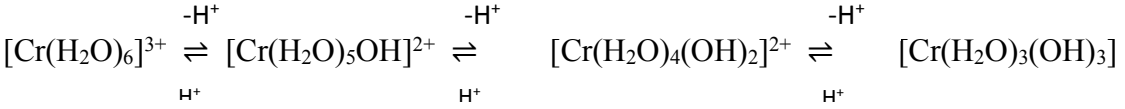
Compared to traditional treatment solutions, trivalent chromium chemical conversion treatment solutions have the following characteristics: high chemical concentration, generally higher treatment temperatures, rather high acidity of around pH 2 and long treatment time. However, chemical solutions with lower treatment temperature of around 30°C have also been made public. With the organic types, there reportedly are differences in corrosion resistance depending on the type of organic acid used, while with the inorganic acid types, the differences in corrosion resistance depend on the type and stock number of the silicate compounds, as well as on the manufacturing company. As such, this is indeed a world of competition for technical know-how, if sulphides are used the presence of sulphur is clearly detected in the plating films, and this is suspected to cause patchy discoloration that appears over time. As a result, sulphates are normally not used.

When trivalent chromium compounds are dissolved in water, Cr^{3+} are present as deep blue hexa-aquo ions with six water molecules coordinated to each ion. However, as shown in the following formulas, the ions gradually lose protons, forming mono, di-, and tri-hydroxo complexes. Moreover, they undergo olation and acquire the property to turn into dimmers, trimers, and polymers. At room temperature, the reactions are very slow, but in an equilibrium state, the solution turns green.

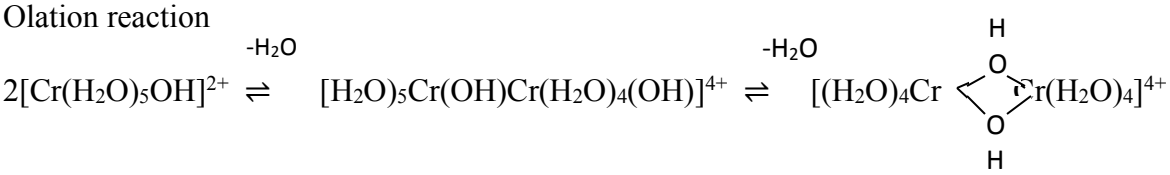
Cr^{3+} solutions turn into a gel when the pH value rises or when olation progresses as a result of desiccation-dehydration. Speaking qualitatively about the process of chemical conversion treatment, a zinc-plated surface dissolves when it is immersed in an acid treatment solution with a pH value of around 2. The pH value at the interface rises, resulting in the olation of chromium complex ions, and a semi-gelatinous film is deposited on zinc surface. During the subsequent drying stage, the olation progresses, resulting in the completion of a chemical conversion film

that has the three-dimensional $[Cr(OH)_3]n.mH_2O]$ as its basic framework. Since the amount of H_2O in this film is very small in comparison to the amount of H_2O present in films obtained from hexavalent chromium baths, the corrosion resistance does not fall even at temperatures exceeding 100°C.

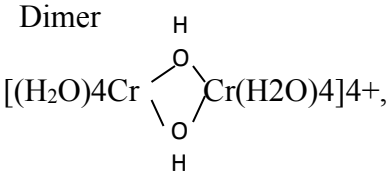
Hydroxo compound formation reaction



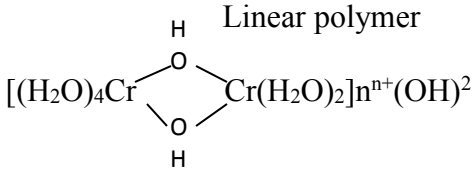
Olation reaction



Dimer



Linear polymer



Three –dimensional polymer

$[Cr(OH)_3]n.mH_2O$

Along with the formation of a trivalent chromium chemical conversion film, a dissolution reaction of the chemical conversion film also occurs at the same time, so the film does not grow thicker, remaining at around 50- 60nm. However, as a result of the effects of such additives as organic acid or silicate compounds, the thickness can be increased from several times to about 10 times. Thickening the film is believed to greatly contribute to improving corrosion resistance. Trivalent chromium chemical conversion treatment processes require a heating facility because the treatment temperatures are slightly high, as mentioned above. Moreover, although the immersion treatment time is somewhat long, the fact that existing facilities for conventional chromate treatment can be used without modification is a big advantage as an alternative

technology. It has been a requirement for trivalent chromium chemical conversion films to have the same film performance as chromate films, and the prime requirement is corrosion resistance. Table 8.7 shows a comparison between the characteristics of trivalent chromium chemical conversion treatment and those of hexavalent chromium chemical conversion treatment. Initially, there were cases in which overcoat layers or finishing agents were applied to reinforce corrosion resistance. Currently, however, the performance of trivalent chromium chemical conversion films has drastically improved, and corrosion resistance comparable to that of yellow chromate has been achieved. In other words, trivalent chromium chemical conversion films now satisfy corrosion resistance standards in actual products, and in the case of assessment using flat-plate test pieces, the films can withstand corrosion for more than 240 hours. However, depending on the type or on the brightening agents used in the same bath, the performance or the color tone reportedly differ. Therefore, thorough confirmation is necessary before deciding on introducing this treatment process. It is said that the zinc plating chemical conversion films obtained from zincate baths are generally superior to those obtained from cyanide baths or chloride baths. However, all of these films satisfy standards. Trivalent chromium chemical conversion films have excellent corrosion resistance under a heated environment as one characteristic that conventional chromate films lack. It is notable that their corrosion resistance does not drop at all even after they have been subjected to baking treatment for the purpose of countering hydrogen brittleness. However, as it now stands, changes need to be made in the treatment process schedule, so the common procedure is to carry out trivalent chromium chemical conversion treatment after the baking treatment stage. Although it is believed that trivalent chromium chemical conversion films do not have self – repairing features as chromate films do, their resistance to scratch corrosion, which becomes a problem in barrel plating, has been improved.

The colour tone of trivalent chromium chemical conversion films is generally pale. Organic acid type films have a primarily light yellowish glossy external appearance with a slightly reddish tinge, while inorganic acid type films have a light yellowish external appearance with a slightly bluish tinge. Meanwhile, progress has been made in putting to practical use black trivalent chromium chemical conversion films, for which there has been strong demand.

Table 8.7 Comparison of Trivalent Chromium and Hexavalent Chromium Chemical Conversion Treatments

Item	**Chemical conversion treatment of trivalent chromium series**	**Chemical conversion treatment of hexavalent chromium series**
Unit cost of chemical	1.5-2.5 times that of hexavalent chromium series	1
Treatment conditions Concentration (mL/L) Temperature ^{o}C Time (s)	 60-150 40-70 30-90	 10-20 Room temperature-30 15-25
Fine material property Corrosion resistance Heat resistance Color tone	 Good (depends on bath type) Good White, black film	 Good Poor White, yellow, green, black film
Clamping torque constant	Higher values than those of hexavalent chromium series exist	Set as the standard
Effluent treatment	Comparatively easy (excluding organic acids) nitrate-nitrogen	Hexavalent chromium reduction treatment.
Management of solutions	pH, temperature, immersion time, impurities	pH, control generally not administered

8.3.3 Management of Chemical Conversion Treatment Solution and Effluent Treatment

To obtain trivalent chromium chemical conversion films with stable quality, such as corrosion resistance, thorough management of the pH, temperature, etc of the solution is necessary. Because the films have a pale, monotonous color tone, management in the field by color cannot be done. Therefore, pH management is important. It is important to constantly measure the pH using a pH meter with a replenishment pump interlocked to maintain the pH in the optimum range by adding nitric acid or a replenishment solution. When applying the chemical conversion treatment, moderate air agitation or mechanical oscillation is required. In the case of barrel treatment, the pH value of the treatment solution within the barrel rises substantially, so consideration must be given to renewing the solution within the barrel.

Since a chemical conversion solution is depleted as a result of film formation and the solution's being pumped out, it is important to manage the concentration of the treatment solution. Depletion of the solution is mainly due to its being pumped out. When the concentration of Cr^{3+} in the solution is 10g/ L and the amount of solution pumped out is 1ml/dm^2, the depletion of the Cr^{3+} due to the pump out of the solution is 1g/m^2, while the amount of Cr^{3+} spent in film formation is about 0.12g/m^2. A constant rate pump automatically replenishes the chemical solution by an amount equal to the depleted amount. Meamwhile, the chemical conversion treatment solution becomes retrograded as zinc ions that elute along with the reaction accumulate as impurities. In comparison to conventional chromate solutions, this solution has little tolerance against metallic impurities. Although the tolerance level against impurities varies depending on the type of chemical agents used in the solution, the tolerance level against zinc is generally 15-20g/L. If this level is exceeded, the chemical conversion film takes on a whitish external appearance, and the corrosion resistance decreases. Generally, the

solution should be managed so that the elution amount and the pumped out volume balance out and it remain under the tolerance level. Although the tolerance level against iron ions is 100-200mg/L, the film takes on a whitish external appearance at 50mg/ L, and the corrosion resistance under a heat environment drops. When the iron ions exceed 300mg/L, the film takes on yellow external appearance, and the corrosion resistance under a non-heated environment also drops, so the material to be plated must be dropped into the treatment solution and made to reside. Copper ions inhibit the chemical conversion reaction, and the tolerance level of the solution against copper ions is even lower at 5-10mg/L.

The treatment temperature of trivalent chromium chemical conversion films has generally become lower than in the past. However, there is a substantial amount of evaporation of water when chemical conversion treatment is applied at 50-70^{o}C, and the concentration of the chemical solution could further increase as a result of replenishing the chemical. Therefore, replenishment of water may be necessary in order to maintain the solution level.

With regard to the material of the container used for chemical conversion treatment, an announcement has been made about a chemical solution that can be used with stainless material, but generally, it is apparently desirable not to let the material to be treated come in direct contact with the stainless material. In effluent treatment of inorganic type trivalent chromium chemical conversion treatment solutions, thorough heavy metal treatment can be carried out by conventional neutralizing coagulation and sedimentation. However, the nitrate-nitrogen component requires exercising caution. Meanwhile, in organic acid type and mixed type effluents, heavy metal ions form relatively stable metallic chelates, making the effluents difficult to treat. Moreover, the COD and BOD values are high due to organic acid components, in addition to the nitrate-nitrogen components. Normally, heavy metal ions are subject to

precipitation treatment with hydrated lime or calcined lime, but before that, it is necessary to adjust the pH of the effluent to 1-1.5 in order to separate the metallic ions from the chelate. Since the agglomerating property is improved by using a generous amount of aggregating agents, it is necessary to adjust the pH to the designed value when adding the agents. By doing so the chromium can reportedly be reduced to less than 2ppm and zinc to less than 0.1ppm when the initial chromium concentration is 100ppm. As another problem, cases have been reported that after effluent treatment has been carried out, chromium hydroxide sludge partially turns into hexavalent chromium in a few days. Therefore, care must be exercised in handling sludge after carrying out effluent treatment. It is believed that the cause of this is the effect of residue sodium bisulphite used in the treatment of hexavalent chromium effluent and cobalt ions present in trivalent chromium chemical conversion treatment solutions.

8.3.4 **Industrial Chromium Plating**

Chromium metal electrodeposited is extremely hard with bluish silver color. In addition, chromium forms the passive layer stable between the normal temperature atmospheres; therefore it is hard to be corroded. Industrial chromium plating is produced from chromic acid solutions, which contain one or more catalytic anions in proper proportion. Industrial chromium plating is also known as hard chromium plating, functional, or engineering chromium plating. Chromium ore is produced mainly in South Africa, Russia, Rhodesia, and used as steel alloy (stainless steel) / chemicals/ firebrick. It is only about 2% that is used for chromium plating. Normally industrial chromium is deposited to thicknesses ranging from 2.5µm to 500µm, while decorative chromium plating seldom exceed 1µm. industrial chromium plating is applied directly to the base metal, decorative chromium is applied over undercoats of nickel or of copper and nickel.

Principal Uses of Industrial Chromium Plating.

The major uses of industrial chromium plating are wear-resistance, low coefficient friction and/ or corrosion resistance applications such as automobile, motorcycle, construction machine, steel industry, etc. also industrial chromium plating is used for rebuilding mismachined or worn parts. Table 8.8 shows parts to which industrial chromium plating is applied and standard thickness.

Table 8.8 Application of Industrial Chromium Plating

Part	**Thickness (µm)**
Piston and Rings	50-100
Piston and piston rod	5-100
Shaft and journal	30-50
Roll	20-50
Mould	10-50
Cutting tool	3
Engine valve	5
Cylinder and liner	20-100
Shock absorber rod	10-25
Hydraulic cylinder shaft	30-50

Basic Reactions and Characteristics of Chromium Plating

The mechanism of reaction that hexavalent chromium ion is reduced to metal in plating bath is complicated compared with other metal reduction reaction. There is not an established theory yet, and the results of research about the reaction mechanism are announced currently. Hexavalent chromium ion is hazardous and needs to be treated with caution. Trivalent chromium ion is harmless but used only for decorative chromium field at this moment. Industrial trivalent

chromium plating technique is now under development. I must quickly add that some companies have perfected trivalent chromium plating but are not willing to make available details as per the method they are using. Fig.8.8 shows the basic reaction of chromium plating.

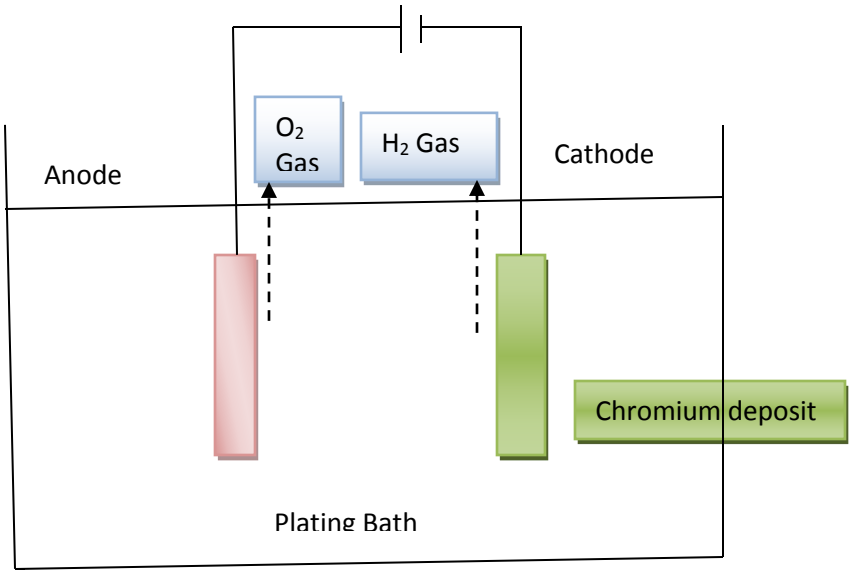


Fig.8.8 Reaction of Chromium Plating

Cathode

1. Chromium deposit: $CrO_4^{2+} + 8H^+ + 6e \rightarrow Cr + 4H_2O$

2. H_2 Gas: $2H^+ + 2e \rightarrow H_2$

3. Cr^{6+} Reduction: $CrO_4^{2-} + 8H^+ + 3e \rightarrow Cr^{3+} + 4H_2O$

Anode

1. Cr^{3+} Oxidation: $Cr^{3+} + 4H_2O - 3e \rightarrow CrO_4^{2-} + 8H^+$
2. O_2 gas: $4OH^- - 4e \rightarrow O_2 + 2H_2O$
3. Pb Oxidation: $Pb + 2H_2O - 4e \rightarrow PbO_2 + 4H^+$

There are many points where chromium plating is different from other metal plating (copper plating, zinc plating etc.) chromium plating has the following characteristics:

- Current efficiency is very low: most of the power is used for generation of hydrogen gas and heat is wasted. Chromic acid mist is generated and the temperature of the solution goes up.
- Metal ion concentration is very high
- Big electric current is needed (roughly 10 times of other metals). The electric contact gets heated easily.
- Throwing power is low: edge become thick (dog bone effect)
- Insoluble anode is used
- Main chemical (hexavalent chromium ion) is hazardous.

3) Plating Baths

Chromic acid is the source of metal in industrial chromium plating baths. But a chromic acid solution does not deposit chromium without catalyst. If there is either too much or too little catalyst, no chromium metal is deposited. Dr Sargent succeeded in practical chromium plating for the first time in 1920 by chromium acid solution including sulphuric acid as impurities, and built the basics of bath used currently. Bath which added fluoride or sulphonic acid to sulphuric acid as a catalyst ingredients were put to practical use afterwards.

History of chromium plating Bath (content = chromic acid + catalyst)

1925 conventional sulphate bath/ Sargent bath ($Cr_2O_3 + H_2SO_4$)

1950 Mixed catalyst bath ($CrO_3 + H_2SO_4 + SiF_6^{2+}$)

1989 Fluoride-free High Efficiency Bath / HEEF25R bath ($CrO_3 + H_2SO_4$ + Sulphonic acid)

Throwing power of conventional sulphate bath is optimum at ratios by weight of chromic acid to sulphate radical between 90 to 1 and 110 to1. Mixed catalyst baths can increase production rate 40 to 60% over that obtainable with conventional sulphate baths, because of their greater current

efficiency and ability to operate at higher current densities. One limitation of mixed catalyst baths is that they may cause etching of unplated surfaces at areas of low current density. This etching can be prevented by using HEEF25R bath.

Table 8.9 Industrial Chromium Plating Baths

Items		Conventional sulphate bath (Sargent Bath)	Mixed catalyst bath (Fluosilicate Bath)	Fluoride-free high efficiency bath (HEEF Bath)
Content	CrO_3 (g / l)	200-300	250-350	250-300
	SO_4^{2-} (g/l)	2-3	5-10	3-4
	SiF_6^{2-}	-	1.5	-
Condition	Temperature (^OC)	40-55	35-55	50-65
	Current density (A/dm^2)	10-60	10-60	10-100
	Current Efficiency (%)	13-17	25	25

1 Process Control

Chromium plating baths of all types need periodic chemical analyses for control of bath composition and should be brought into proper balance. All soils and passive films must be

removed from surfaces of substrate before chromium plated. Anodic etching of steel before plating is necessary to ensure adherence. A typical process of industrial chromium plating is as follows:

- grinding
- degreasing: remove soil and anti-rust oil
- reverse etching: anodic etching: remove passive layer for good adhesion and roughness
- chromium plating
- baking to avoid hydrogen embrittlement (if necessary)
- buffing or polishing: for good roughness and corrosion resistance.

Characteristic of chromium plating layer such as surface state, hardness, crack number varies with a plating condition (in particular, liquid temperature and current density). Cathode current efficiency varies with current density and temperature of the plating bath. Efficiency increases with increasing current density and decreasing temperature. A high bath temperature results in a semi-bright, dull and softer deposit at lower current efficiencies. Raising current density produces good results usually.

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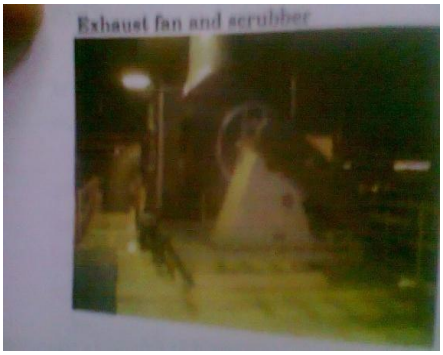
Industrial chromium plating equipment

Chromium plating equipment

Exhaust ducts

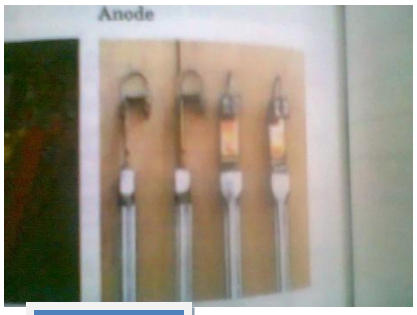


Exhaust fan and Scrubber

Circulating pump

Rectifier

Electrical contact



Anode

Circulating pump and heat exchanger

Heat Exchanger

Fig. 8.9 Industrial chromium plating equipment

8.4 COPPER PLATING

Cyanide Bath

Copper cyanide plating is mainly used as a strike and to a lesser extent for thick deposits. In dealing with the copper cyanide bath distinction must be made between total cyanide and free cyanide. Cuprous cyanide must be complexed with either potassium or sodium cyanide to form soluble copper compounds in aqueous solutions. The major complex is considered to be $Cu(CN)_3^{2+}$. The sum of that required for the complexation of copper cyanide plus the amount of cyanide required for the proper functioning of the bath (free cyanide) is the total cyanide. The total cyanide required by weight is given in the following equation

Total KCN = CuCN required x 1.45 + Free KCN required

Total NaCN = CuCN required x 1.1 + Free NaCN required.

Anodes for the baths should be high purity copper that is oxide-free. They can be bagged copper slabs or bagged steel baskets containing copper nuggets. Anode/ cathode ratio should be 1:1 to 2:1. General purpose strike: the general-purpose strike is used for improved adhesion activation

of passive substrates, or as an insurance step in the cleaning cycle. When used for zinc die-castings, the hydroxide concentration should be kept at a maximum of 3.75g/ l. Deposits are usually in the range of 0.5 to 2.0 μm in thickness.

Table 8.10 Bath Composition

	Potassium	**Sodium**
CuCN g/ l	30.0	30.0
Total KCN g/l	58.5	
Total NaCN g / l		48.0
KOH g/ l	3.75-7.5	
NaOH g/ l		3.75-7.5
K_2CO_3 g / l	15.0	
Na_2CO_3 g/l		15.0
Rochelle salt g/l	30.0	30.0
Free KCN by analysis g/l	11.25-15.0	
Free NaCN by analysis g/l		11.25 – 15
Temperature ^oC	24-66	
Current density	0.5-4 A/dm^2	
Time	30 secs to 2 min or until fully covered	
Current efficiency %	30-60	
Agitation	None or mechanical	

Strike plate Bath: the strike plate bath is the one most used for the plating of zincates aluminium. It is also used for zinc diecastings and other metals that are subject to attack by

subsequent plating baths or finishing operations that require more than a strike deposit for protection. This formulation eliminates the need for two baths, a strike followed by a plate in a high efficiency bath. Deposits range from 3.0 to 5.0μm in thickness for the parameters given in the formulation.

Table 8.11 Strike Plate Bath Composition

	Potassium	**Sodium**
CuCN g/l	42.0	42.0
Total KCN g/l	66.6	
Total NaCN g/l		51.9
K_2CO_3 g/l	30.0	
Na_2CO_3 g/l		30.0
Rochelle salt g/ l	60.0	60.0
Free KCN by analysis g/ l	5.7	
Free NaCN by analysis g/l		5.7
pH	10.2-10.5	
Temperature ^oC	40-50	
Current density and Time	Initial (strike) 2.5-3.0 A/dm^2, 2 min. Final (plate) 1.0- 1.5 A/dm^2, 3-5 min.	
Current efficiency %	30-50	
Agitation	None or mechanical	

High Efficiency Bath

High efficiency bath is used when a rapid build-up of a significant copper thickness is required. The copper cyanide can be as high as 120 g/l for applications such as wire plating. Although the brightness and grain refinement of the deposit can be improved by the use of periodic reverse current interruption, the best results are obtained by using suitable additives.

Table 8.12 High Efficiency Bath

	Potassium	**Sodium**
CuCN g/l	60.0	75.0
Total KCN g/l	102.0	
Total NaCN g/l		97.5
K_2CO_3 g/l	15.0	
Na_2CO_3 g/l		15.0
KOH g/l	15.0	
NaOH g/l		15.0
Rochelle salt g/ l	45.0	45.0
Free KCN by analysis g/ l	15.0	
Free NaCN by analysis g/l		15.0
pH	-	
Temperature ^oC	60-71	
Current density	Up to 8 A/dm^2	
Current efficiency %	90-99	
Agitation	Mechanical	

8.4.1 Bath Preparation

Dissolve K- or NaCN in cold water. In a separate container mix copper cyanide with water to form thin slurry and slowly add to the K- or NaCN solution while mixing. The dissolving reaction is exothermic and the solution should not be allowed to overheat, as this may decompose some of the free cyanide. Add the rest of the required materials after dissolving the copper cyanide. Carbon treatment of the bath is before use is recommended. All salts should be sulphur-free to prevent dull, red deposits in low current density plating areas.

8.4.2 Maintenance and Control

Constituents

It is recommended that all constituents in the formulation be controlled to within 10% of their nominal values, especially the free cyanide. The copper cyanide concentration controls the allowable plating current density in combination with agitation. The free cyanide concentration controls efficiency, plating range, throwing-power and anode polarization. The hydroxide concentration controls conductivity and throwing power. Carbonates buffer the solution and reduce anode polarization. Although high concentration of 90.0 g/l to 120 g/l decreases the plating range, it is added to new baths to stabilize their initial operation. Rochelle salt enhances anode corrosion and provides some grain refinement. Potassium formulations have a broader plating range than sodium formulations.

Temperature

Temperature above $71^{O}C$ in the high efficiency formulations promotes the breakdown of cyanide and the rapid build-up of carbonates.

Agitation

Mechanical and/or solution agitation is recommended. Use air agitation only when required since air agitation promotes carbonate build-up.

Contamination

Organic contamination causes non-uniform, dull, rough or pitted deposits. In severe cases of organic contamination, the anodes may polarize. Carbon treatment will remove organic contamination. A copper strike should not be considered to be a cleaner and should carbon treated periodically to prevent organic contamination from spreading to other plating baths. Hexavalent chromium contamination causes skip plate in the low current density area, blisters and non-uniform deposits. Zinc contamination causes non-uniform or brass-coloured deposits and can be remove by dummying the bath at 0.2 to 0.4 A/dm^2. Sulfur and its compounds cause dull, red deposits in the low current density plating areas and usually appears from new baths because of impure cyanides or leaching from tank linings. Most other common types of metallic contamination cause deposit roughness and can usually be removed by dummying and filtration.

Carbonate

Excessive sodium carbonate can be removed by freezing out at a low temperature because of its limited solubility below -3^{o}C. Both Potassium and Sodium carbonate can be removed by precipitation with calcium oxide, calcium hydroxide or calcium sulfate.

Deposition Mechanism

$Cu(CN)_3^{2-} \rightleftharpoons CuCN + 2CN^-$

$CuCN + e^- \rightleftharpoons Cu + CN^-$

$Cu(CN)_2^- + e^- = Cu + 2CN^-$ -0.43V vs. NHE

Pyrophosphate bath

Copper Pyrophosphate plating baths require more control and maintenance than cyanide baths. However, the solutions are relatively non-toxic. The main uses of copper pyrophosphate baths have been printed circuits, plating on plastics and electroforming. The chemistry involved in copper pyrophosphate plating is the formation of the potassium copper pyrophosphate complex ($K_6Cu(P_2O_7)_26H_2O$) from copper pyrophosphate ($CuP_2O_73H_2O$) and potassium pyrophosphate ($K_4P_2O_7$). The ratio of pyrophosphate ($P_2O_7^{4-}$) to copper (Cu^{2+}) in the compound is 5.48 to 1. Any pyrophosphate in excess of this ratio is called 'Free' or 'excess' pyrophosphate. Free or excess pyrophosphate is essential for the operation of the bath in providing conductivity and anode corrosion. This is done by running a pyrophosphate to copper (P_2O_7 / Cu) ratio (P ratio) of 7 to 8: 1 in the plating bath. A strike bath may have a higher ratio. Potassium pyrophosphate baths are recommended over sodium formulations for better conductivity and higher solubility of the potassium copper complex. Anodes baths should be high purity copper that is oxide free. Anodes can be copper slabs or copper nuggets in titanium baskets. Anode bags are not recommended. Anodes to cathode ratio should be 2:1. Copper pyrophosphate baths tends to build orthophosphate (HPO_4^{2-}) concentrate by the hydrolysis of pyrophosphate. Small amount of orthophosphate are not harmful. However, higher concentration in excess of 100.0 g/l may cause banded deposits with decreased plating range and conductivity in the standard plating baths. In the printed circuit bath, the orthophosphate concentration should be allowed to exceed 40.0 to 60.0 g/l because, beyond this point, there is a decrease in the throwing power of the solution and ductility of the deposit. Orthophosphate concentration is lowered by dilution or replacement of the bath. The anode and cathode efficiencies of copper pyrophosphate baths are essentially 100%. Maximum agitation is require for best results.

Typical pyrophosphate bath

Copper pyrophosphate bath can form immersion coatings, similar to acid coppers, on steel and zinc die-castings and cause poor adhesion. The following copper pyrophosphate plating bath formulation can be used for all plating applications except printed circuits. Current interruption or periodic reverse current can further refine the grain structure.

$Cu_2P_2O_73H_2O$	52.5-84.0 g/l
$K_4P_20_7$	201.1- 349.1 g/l
KNO_3	3.0-6.0 g/l
Conc. NH_4OH	3.75- 11.0 ml/l
pH	8.0-8.7
Temperature	43-60^OC
Current Density	1.0- 8.0 A/dm^2
Agitation	mechanical and air
Filtration	continuous

Printed Circuit Bath

The use of non-proprietary additives that improve the throwing power and ductility of deposit it recommended for printed circuit application.

$Cu_2P_2O_73H_2O$	57.8- 73.3 g/l
$K_4P_20_7$	231.0- 316.5 g/l
KNO_3	8.2- 15.8 g/l
Conc. NH_4OH	2.7- 7.5 ml/l
Addition agent	As required
pH	8.0-8.4

Temperature 49-54 ^{O}C

Current Density 2.5- 6.0 A/dm^2

Agitation Mechanical and air

Copper pyrophosphate baths are sensitive to contamination, especially organic contamination, and are made from purified liquid concentrates.

8.4.3 Maintenance and Control

Constituents

Ammonia aids in anode corrosion and as a grain refiner. Ammonia is replenished daily because of evaporation loss. Nitrate increases the high current density plating range and is a cathode depolarizer. The pH is controlled by using pyrophosphoric acid or KOH as required.

Temperature

Operating the baths above 60^{o}C causes the rapid hydrolysis of pyrophosphate to orthophosphate.

Agitation

Copper pyrophosphate baths need vigorous agitation for a normal operating current density plating range. The most common form used is air agitation by itself or in combination with mechanical agitation. Ultrasonic and solution jet agitation can be used.

Contaminants

Copper pyrophosphate baths are sensitive to organic contamination such as oil or breakdown products of organic addition agents. Organic cyanide and lead contamination can cause dull, non-uniform deposits with a narrow plating range. Carbon treatment will remove organic contamination and treating with hydrogen peroxide or potassium permanganate before carbon treatment will remove cyanide and severe organic contamination. Lead can be removed by dummying.

Orthophosphate

In addition to high temperature, localized overheating or too low a pH can cause the rapid build-up or orthophosphate.

Deposition Mechanism

$Cu(P_2O_7)_2^{-6} \rightleftharpoons CuP_2O_7^{2-} + P_2O_7^{-4}$

$CuP_2O_7^{-2} + 2e^- \rightarrow Cu + P_2O_7^{-4}$

Sulphate Bath

Copper sulphate baths are economical to prepare, operate and waste treat. They are used in printed circuits, electronics, rotogravure, electroforming, decorative and plating on plastics applications. The chemistry of the solution is simple, and bath is highly conductive. Previous problems with the throwing power have been overcome with the advent of the modern high throw formulations and additives. Steel parts must be cyanide copper or nickel-plated in strike formulations to prevent immersion coatings and poor adhesion. Zinc die-castings and other acid sensitive metals must have sufficient deposit to prevent attack by the sulphuric acid. The baths are operated at room temperature. Anodes should be phosphorised (0.02 to 0.08% by wt. phosphorous). Oxide-free, high purity rolled copper. Copper anode nuggets in titanium baskets can be used. Anodes should be bagged. The anode to cathode ratio should be 2:1. Anode and cathode efficiencies are essentially 100%. Since copper sulphate plating has become of major importance to the industry, a troubleshooting guide is given.

8.4.4 Standard Acid Copper Plating

The following are the standard formulations for copper sulphate bath. Air agitation with or without mechanical agitation, is recommended.

General formulation.

Copper Sulphate	195- 248 g/ l
Sulphuric Acid	30-75 g /l
Chloride	50- 120 ppm
Current density	2 - 10 A / dm^2
Semi-bright Plating	
Copper Sulphate	248 g/ l
Sulphuric Acid	11 g /l
Chloride	50- 120 ppm
Thiourea	0.00075 g/l
Wetting agent	0.2 g/ l
Bright Plating	
Copper Sulphate	210 g/ l
Sulphuric Acid	60 g /l
Chloride	50- 120 ppm
Thiourea	0.1 g/l
dextrin	0.01 g/ l
Bright Plating	
Copper Sulphate	199 g/ l
Sulphuric Acid	30 g /l
Chloride	50- 120 ppm
Thiourea	0.375 g/l
Molasses	0.75 g/ l

High Throw Bath

The following formulation is used in printed circuit, barrel plating and other applications, where high throwing power is required.

Copper Sulphate	40.0-90.0 g/ l
Sulphuric Acid	172-217 g /l
Chloride	50- 100 ppm

Proprietary additive

8.4.5 Maintenance and Control

Constituents

Copper sulphate is the source of copper ions in solution. Since the anode and cathode efficiencies are normally close to 100%, the anodes replenish the copper ions so that the copper concentration remains fairly stable in solution. The sulphuric acid increases the conductivity of the solution and reduces the anode and cathode polarization. It prevents precipitation of basic salts and improves throwing power. In high throw formulations the weight ratio of copper metal to sulphuric acid should be maintained at approximately 1:10. Copper sulphate is reduced in concentration in high throw formulations to prevent common ion precipitation effects as the sulphuric acid is increased. Sulphuric acid concentrations above 11% by volume begin to reduce cathode efficiency. Chloride ion, in bright and high throw baths, reduces anode polarization and eliminates striated deposits in the high current density areas.

Temperature

These baths are operated at room temperature for the majority of applications. If temperature is too low, cathode efficiency and plating range will be reduced. Baths used where bright deposits

are not required may be operated at temperatures as high as 50°C to increase the plating range in electroforming, printed circuit or rotogravure applications.

Agitation

Air, mechanical solution jet or rotating work agitation can be used. The more vigorous the agitation needs the broader the allowable plating current density.

Contaminants

Organic contaminants are the most commonly dealt with in acid copper plating. Major sources are decomposition products of brighteners, tank liners, un-leached anode bags, stop-offs, resists and impure salts or acid. Contaminants will adversely affect the appearance salts or acid. Contaminants will adversely affect the appearance and the physical properties of the deposit. A green coloration of the bath indicates significant organic contamination. Organic impurities are removed by treatment with activated carbon. In case of severe contamination, hydrogen peroxide, or potassium permanganate, may be necessary to break down the organics so that the carbon can effectively remove them. Some common metallic contaminants and their effects are as follows:

Iron (> 1000 ppm): reduces bath conductivity and throwing power

Nickel (> 1000 ppm): same as iron

Table 8.13 Troubleshooting Guide

Problem	**Cause**	**Corrective Action**
High current density burning	Low copper Low temperature Insufficient agitation Organic contamination Low chloride (bright baths)	Analyze and adjust Heat bath Lower current, unless agitation can be improved Carbon treat Analyze and adjust
Loss of brightness (in bright formulations)	Low additive Organic contaminants Low chloride High temperature Low copper	Determine addition by Hull cell Carbon treat Analyze and adjust Cool the bath Analyze and adjust
Rough deposit	Particles in solution Torn anode bags Improper anodes (bright baths) Low chloride (bright baths)	Filter bath Replace torn bag Use phosphorized copper anodes for bright baths Analyze and adjust
Pitting	Organic contamination Anode slough Low chloride (bright baths)	Carbon treat Bag anode Analyze and adjust
Low current	Organic contamination Low sulphuric acid	Carbon treat Analyse and adjust

	Low additive	Determine addition by Hull cell
	High chloride	Precipitate with silver nitrate and filter
	Current density too low	Increase current
	High temperature	Cool bath
Anode polarization	Tin, gold contamination	Dummy with a copper foil (no current)
	Low temperature	Heat bath
	Improper anodes	Bright baths require phosphorized anodes
	High chloride	Precipitate with silver nitrate and filter
	High sulphuric acid	Analyze and dilute bath
	Low copper sulphate	Analyze and adjust

8.5 Nickel Plating

Nickel and nickel alloy plating via the electro-less route can be applied to various substrates for various reasons. Some of the reasons include corrosion resistance, abrasion resistance, decoration purpose, and others. E.g. brake pistons require abrasion resistance they are applied with electroless Ni plating, and heat treated at 300OC for 1 hour to give a hardness value of 700Hv. The procedure for nickel plating is illustrated below in fig.8.17.

The nickel bath of the composition below will give a thickness coating of 4µm after 20 minutes of plating time.

Composition: nickel sulphate = 150mL/L

Sodium acetate = 45 mL/L

Sodium citric acid = 45 mL/L

Sodium hypophosphate = 3mL/L

pH = 4.6

Thickness of coating after 20 minutes: 4µm

Baths for Electroplating

1. Watts Bath

Nickel sulphate	200-380 g/l
Nickel chloride	30 – 60 g/l
Boric Acid	30-40 g/l
pH	1.5- 5.0
Temperature	40 -70^{O} C
Current density	0.5- 10 A/ dm^2

1. Anode

Electrolytic Ni, Sulphur-containing Ni, Carbonized Ni and Depolarized Ni.

Table 8.14 Mechanical Properties

	Hardness (HV)	**Elongation (%)**	**Tensile strength (MPa)**	**Internal stress (MPa)**
Rolled Ni	90-140	40-	>38	-
Plated Ni Watts	130-200	23-30	410	150(Tensile)
Plated Ni Sulfamate	160-200	18	410-	14 (Tensile)

(MPa x 0.102 = kgf/ mm^2)

2 The Role of Bath Ingredients

Nickel Sulphate: to supply Ni ions.

Nickel chloride: to improve anode dissolution and increase conductivity

Boric Acid: to maintain bath pH constant as a buffer.

Wetting agent: to protect pitting due to hydrogen evolution.

2. Cold Bath

Nickel sulphate	120-150 g/l
Ammonium chloride	15 g/l
Boric Acid	15 g/l
pH	5- 6.0
Temperature	Room temperature
Current density	0.5- 1.0 A/ dm^2

3. All Chloride Bath

Nickel chloride	300 g/l
Anti pitting agent	-
Boric Acid	30 g/l
pH	2- 4.0
Temperature	55-70^{o}C
Current density	2- 20 A/ dm^2

Wood Bath

Nickel chloride	240 g/l
Hydrochloric Acid	120 mL/ L
Temperature	Room temperature
Current density	2- 20 A/ dm^2

4. All Sulphate Bath

Nickel Sulphate	300 g/l
Anti pitting agent	-
Boric Acid	40 g/l
pH	2.5- 4.5
Temperature	50-55^{o}C
Current density	1- 10 A/ dm^2

5. Sulfamate Bath

Conventional Type

Nickel Sulfamate	300 -450 g/l
Nickel chloride	0-15 g/ l

Boric Acid	30- 45 g/l
pH	3- 5
Temperature	30-60^{o}C
Current density	2- 15 A/ dm^2

Concentrated Type

Nickel Sulfamate	550 - 650 g/l
Nickel chloride	5-15 g/ l
Boric Acid	30- 40 g/l
pH	4
Temperature	60- 70^{o}C
Current density	5- 85 A/ dm^2

6) Barrel Plating

Nickel Sulphate	270 g/l
Nickel chloride	70 g/ l
Boric Acid	40 g/l
Magnesium sulphate	225 g/ l
pH	4 – 5.6
Temperature	50- 55^{o}C
Voltage	8-12 V

7) Black Ni Plating

Nickel Sulphate	60-80 g/l
Nickel Ammonium Sulphate	35- 50 g/ l
Zinc sulphate	30.9 g/ l

Sodium Thiocyanate (NaSCN)	18-25 g/ l
pH	4 – 6
Temperature	50- 60^{o}C
Current density	0.5 – 1.5 A/ dm^2

For Solar Collector (Bath Improved by NASA)

Nickel Sulphate	53.9 g/l
Nickel Ammonium Sulphate	76.7 g/ l
Zinc sulphate	30.9 g/ l
Sodium Thiocyanate (NaSCN)	6 g/ l
pH	6
Temperature	22.2^{o}C
Current density	0.6 A/ dm^2
Duration of plating time	40 sec

2 **Decorative Ni Plating**

1.) Bright nickel Plating

- Brighteners

1ST Class Brighteners: to assist brightening action of 2nd class brighteners and to reduce tensile stress, but within leveling action.

2nd Class Brighteners: Adsorptive compounds and having brightening and leveling actions, but when used singly, to give deposits with high tensile stress

8.5.1 Operating Conditions

Bath Temperatures

Usually operated at 45-60^{o}C. at low bath temperature solution resistance increases and at high current density burnt deposits tend to appear.

pH

In normal operating conditions Ph tends to increase because of hydrogen evolution at the cathode. pH of the solution should be adjusted to the predetermined value in every 2-4 hours. To increase pH nickel carbonate is used and to decrease it 10% sulphur acid is used.

Cathode Current Density (CCD)

Generally 3-5 A/ dm^2. Factors to increase CCD are strong air agitation, increasing Ni concentration, increasing bath temperature, increasing boric acid concentration up to 50-60 g/ l, maintaining pH values 3-4, and protecting burning at high current density (CD) area by increasing first class brighteners concentration.

Anodic Current Density (ACD)

ACD is desirable to be half CCD. If ACD increase nobler than Ep (passivation potential), the anode will be passivated and will not dissolve. When passivated, oxygen and chlorine gas evolve from the anode, brighteners are broken down, and bath Ph decrease, and the deposit quality is lowered. Ideal ACD is 1-3 A/ dm^2.

Agitation

The purpose of agitation is to enable high CD operation by reducing concentration polarization at cathode-solution interface, to prevent pitting, and to make bath temperature uniform. Usually air agitation is employed.

Filtration

The purpose of filtration is to prevent rough deposits by removing floating objects on the solution and to remove organic impurities through the continuous filtration using activated carbon.

Anode bag and Anode Basket

There are 4 kinds of anodes, electrolytic, carbonized, depolarized and sulphur nickels. When operated at high CD, sulphur and depolarized nickels are suitable. An anode bag made of polypropylene is used to prevent anode slime and sludge from entering into the plating solution.

8.5.2 Properties of Deposits

Internal Stress (IS)

IS is important for plating on plastics and electroforming. High IS causes cracks in the deposits, peeling, and deformation of the substrate. IS is closely related to the brighteners added.

Hardness and Ductility

Hardness changes depending on several causes, such as hydrogen codeposition and C and S inclusion from the brighteners. Brittle deposits are obtained at high solution Ph and high concentration of brighteners. Ductility of the deposits becomes important when the work is mechanically deformed after plating. Hardness is inversely proportionate to ductility in many cases.

8.5.3 Plating Solution Control and Waste Water Treatment

Control Components and Brighteners

The basic bath components concentrations should be analyzed periodically and maintained to the proper value because they are drag out. Brighteners are consumed by electrolysis; drag out, adsorption on activated carbon, incorporation in the deposits breaking down, and so on. Usually the brighteners concentration is controlled by Hull Cell Test. In plating shops a constant volume

of brightener solution is replenished at constant Ah, namely constant volume of electrolysis. The consumption of brighteners is strongly dependent on the CD employed. The consumed quantity of brighteners at 1A/ dm^2 is nearly 2 times that at 4 A/ dm^2 is nearly 2 times that at 4 A/dm^2. Plating should be operated at high CD.

Purification of Plating Solution

Activated carbon treatments, oxidizing agent treatment, dummy plating, and so are the methods of purification. Activated carbon treatment is used to remove organic impurities through the continuous or transfer filtration. Dummy plating at low current density (CD) removes metallic impurities, such as Cu, and Zn.

Waste Water Treatment

Ni waste water from the rinsing tank is combined with acid and alkaline waste water and Ni is precipitated as $Ni(OH)_2$ with alkaline solution.

8.5.4 Bright Nickel Plating Without Leveling

In usual bright Ni plating, good leveling is required to smooth the surface and to give mirror bright finish. But recent demand of various decorative finishes required a bright finish without leveling. In this decorative finish, hairline and satin like pattern are maintained after bright Ni plating. This type of finish is accomplished by using a second class brightener without leveling action.

8.5.5 Satin Ni Plating

A bright surface is not permitted on certain internal components of motorcars because its very dangerous for the driver to be dazzled by reflection from bright trim. A lustrous but satin finish provides a pleasing appearance on a wide range of articles. Two examples of these articles are camera components and door furniture. A satin finish can be achieved by two methods. One is a

composite plating method and the other is an emulsion method. A uniform satin finish by composite plating method is obtained by incorporating inert particles, such as barium sulphate, silica, alumina of 1-5 μm in size into Ni layers. Features of satin Ni obtained by composite plating method are as follows: 1. By employing proper particles and brighteners, various surface appearance can be obtained 2. If conventional Cr is plated on the composite Ni layer, this means highly corrosion resistant system, microporous Cr (MPC). Another method to obtain satin Ni finish is to utilize a nonionic surfactant. The surfactant is fully soluble when cold, but above a critical temperature, this temperature is called cloud point, it precipitates in fine droplet. Such fine droplets absorb on the cathode and then desorbed. Such repetition of adsorption and adsorptions gives a homogeneous satin like finish.

8.5.6 High Corrosion Resistant Ni Plating

-Double and Triple Ni Plating

1. Constitution of plated layers and corrosion protection mechanism
2. Plating methods

Semi –bright Ni Plating

Performance to be needs: plated films having no sulphate, low internal stress, stable additives and easy solution control, and semi-bright appearance and having leveling action

8.5.7 Coumarin and Non-coumarin

Nickel Strike with High Sulphur Content

Performances to be needed: plated films having no sulphur, low internal stress, stable additives and easy solution control, and semi-bright appearance and having leveling action

8.5.8 Coumarin and Non-coumarin

Ni strike with High Sulphur Content

Performances to be needed: constant codeposition of Sulphur (0.1-0.25 wt.%),

Good adhesive to both semi-bright and bright Ni, stable additives and easy solution control.

Bright Ni Plating

3.notes when operating

-Removal of metallic impurities

- exclusion of bipolar phenomenon

-pretreatment

4. notes on Retaining of Corrosion Resistance

- thickness distribution

-Thickness ratio of each plated layer

-STEP (Simultaneous Thickness and Electrode Potential) Test

8.5.9 Micro discontinuous (MDC) Cr Plating

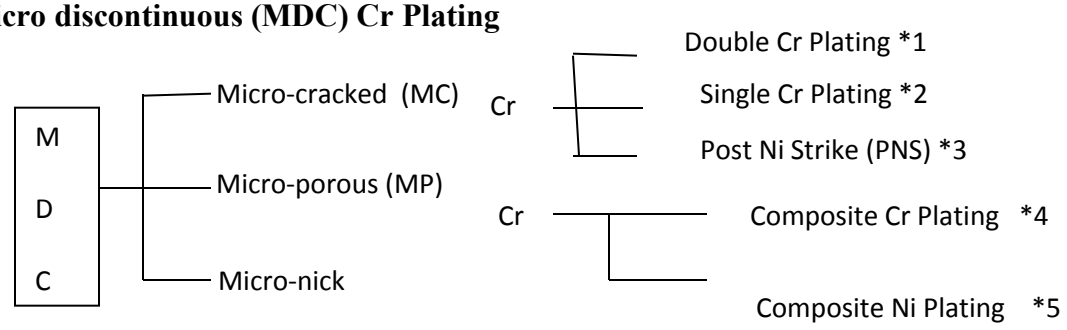


Table 8.15 Double Cr Plating (*1)

	1ST Layer	**2nd Layer**
CrO_3 g/ l	300	195
H_2SO4 g/ l	3	
$K_2Cr_2O_7$ g / l		36.5
$SrCrO_4$ g/ l		4.5
K_2SiFe g/ l		10.5
$SrSO_4$ g/ l		6.0
Temperature ^oC	49	49
Time (Min)	5-6	>6
Cathode current Density A/dm^2	15	13.5
Thickness µm	>0.375µm Sargebt Bath	>0.375µm SRHS Bath

Table8.16 Single Cr Plating (*2)

Items	Values
CrO_3 g/ l	180 -220
H_2SO4 g/ l	1.0-1.7
$Na_2Cr_2O_7$ g / l	1.5-3.5
Temperature ^oC	45-50
Time (Min)	8-12
Cathode current Density A/dm^2	10-20
Thickness µm	>0.375µm Sargent Bath

Table 8.17 Post Ni Strike (PNS)*3

$NiCl_26H_2O$ g/ l	250
$CH_3COONa_3H_2O$ g/ l	100
Saccharin g / l	1.5-3.5
Temperature ^oC	25
Ph	4
Cathode current Density A/dm^2	5 -10

Table 8.18 Composite Cr Plating *4

CrO_3 g/ l	275
H_2SO_4 g/ l	1.7
Graphite g / l	15
Temperature ^oC	43.3
K_2SiO_6 g/ l	3
Cathode current Density A/dm^2	16

Table 8.19 Composite Ni Plating*5

Nickel Sulphate g/ l	250
Nickel Chloride g/ l	60
Boric Acid g / l	40
Temperature ^{o}C	60
Saccharin g/ l	2
Cathode Current Density A/dm^2	5
2-butyne-1, 4-diol	0.15
Sodium lauryl sulphate g/ l	0.3
SiO_2 (Ø 0.2µm)	100
Time (min)	1 (1µm)

Table 8.20 Brighteners

1st Class brighteners	**Example of 1st class brighteners**	**2nd Class brighteners**
Aromatic sulphonic acids	Benzene sulphonic acid 1,3,6 naphthalene sulphonic acid	Aldehydes (Formaldehyde)
Aromatic Sulphonamides	p-toluene sulphonamide	Chloro and bromo substituted aldehyde (chloral hydrate)
Aromatic sulphonimides	o-benzoic sulphonimide (saccharin)	Alkyl and vinyl compounds (alkyl sulphonic acid)
Heterocyclic sulphonic acids	Thiphen-2-sulphonic acid	1,2 benzo pyrones (coumarin)
Aromatic sulphonic acids	Benzene sulphonic acid	Acetylene compounds (2-butyne-1-4-diol)
Ethylenic aliphatic sulphonic acids	Alkyl sulphonic acid CH2=CH-CH_2-SO_3H	Azo dyes (p-amino azo benzene)

8.6 Composite Coating

Often material for engineering application is chosen to meet requirements of strength. However it may not possess satisfactory surface properties such as wear resistance, corrosion resistance, abrasion resistance, etc. Coating can be used to impact specific surface properties. Electroplating and electroless plating are commonly used to apply coatings as these

are economical, versatile and easy to reproduce. Electroplating can produce a combination of desired surface properties with suitable reinforcements.

A composite material is heterogeneous mixture of two or more homogeneous phases bonded together, each component imparting its assets and suppressing the shortcomings. Thus composite material is more useful than any of its components. Any complex shape can be produced by electroforming composites. Electrolytic co-deposition process can coat to close tolerances, bond strength of coating is high, no pressure of heating is required during the process, and uniform coating is possible even on complex contours, wide range of metal particle decompositions can be applied, and process can be easily automated. Thus electrocomposites offer the designer an ability to tailor a material to meet any requirement.

Electrocomposites can be classified into five categories:

(i) **Particle dispersed metal composites.** Insoluble materials in fine powder form are added to electroplating bath and particles are held in suspension by any type of stirring. The metals which can be plated with particles are cobalt, copper, gold, chromium, iron, cadmium, lead, nickel, zinc, and their alloys. This process can be used to increase wear resistance, creep resistance, corrosion resistance, impart dry self-lubricating coating, and increase strength at elevated temperature, offer heat-treatable alloys.

(ii) **Fibre-reinforced metal composites.** Fibre-reinforced metal matrix composites with polymers produce strong, stiff material with low density. These can be electroformed either by simultaneously winding and plating or by alternately winding and plating. Several techniques like liquid metal infiltration, compaction and sintering of powder, vapour deposition, spraying, and electroplating can be used for fabricating fibre-reinforced metal matrix composites. Two methods of fabrication used are filament

winding and compaction. Filament winding is limited to shapes that are solids of revolution. Hot-pressed warp sheet (electroformed monolayer fibre composite) can be used when a shape can't be formed by winding. Electroformed fibre-reinforced metal matrix obeys the mixture rule. These composites can't be used a higher temperature because of tendency to delaminate, and have poor resistance to corrosion.

(iii) **Electroless metal composite.** Electroless nickel is used in this process and particles like SiC, diamond, and PTFE are embedded. Such metal composites are used for applications like wear resistance, obtaining a surface with a desired friction coefficient, obtaining hard surface for machining and finishing tools.

(iv) **Layered or laminated composites.** These consist of laminated structures in which the constituent materials integrate their properties from layer to layer. The examples are plywoods, bimetallic elements, clad metals for corrosion protection, metal honeycomb sandwich panels, etc. Electrodeposited laminated composites with enhanced magnetic and electrical properties have been produced.

(v) **Optical composites.** These find application for coloured finishes for decorative application and other engineering applications like selective black coating on solar collector to improve their efficiency. Optical properties of composites are enhanced by particles. Black nickel and black chromium have been used as antireflection coatings on components of optical instruments as well as on certain parts of printing machinery.

8.6.1 Electroless Nickel-Phosporus Alloy Plating

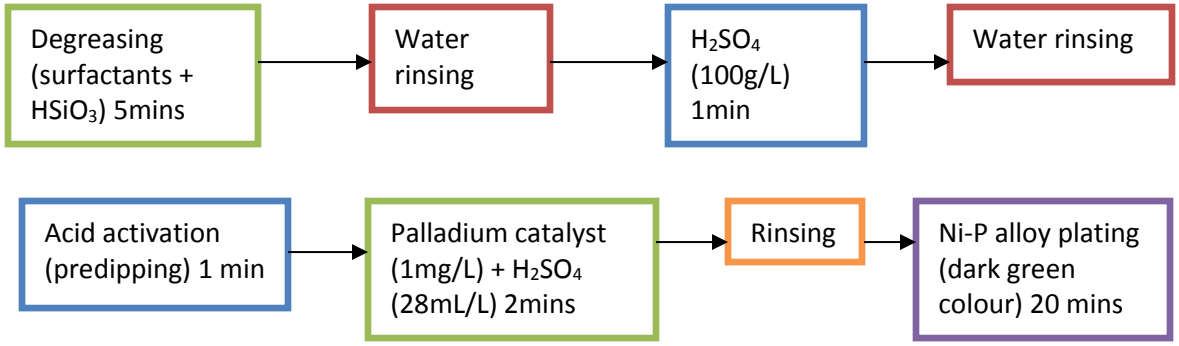
The plate below shows three plating lines for electroless plating. The lines can be used for nickel-phosphorus plating, Teflon composite electroless nickel-phosphorus alloy plating, amorphous plating, Ni-P-B Plating and others. In electroless plating process an initial strike is

normally necessary for a smooth and uniform plating to take place. After the strike the plating can go on without the supply of electricity to the electrodes.

Fig.8.10 Electro-less Nickel-phosphorus Alloy

Electroless Nickel-Phosphorus (Ni-P) Plating

This process is normally applied on brake piston and other vehicle parts. The procedure is illustrated below.



The predipping and catalyst baths are only needed for copper and brass matrices. They are needed for nucleation. These two steps can be replaced by using steel to make contact with the brass work piece. In this way the electro-potential of brass is reduced. The plating is initiated immediately and once initiated, the steel is removed. Oscillating the work pieces is done to remove the oxygen bubbles. Striking can be used also in place of palladium catalyst. For striking

with stainless steel plate, bath needs to contain NiCl and HOCl. Small steel balls are included in barrel for initiating the plating. Nitric acid (30-40% conc) treatment is made to stainless steel tank to create passive film during maintenance of the bath.

8.6.2 Nickel-Phosphorus / PTFE Compound Plating

PTFE (Teflon) particle is dispersed in a matrix of Ni-P alloy during electro-less plating. The function of Teflon is to provide self-lubrication with very low coefficient of friction μ. The figure below illustrates the plating process for Ni-P/ PTFE. The plating process is divided into two parts; the pretreatment and the plating parts. The pretreatment involves; first, the workpiece is given alkali degreasing in the alkali tank, it is then transferred to cathode electrolysis degreasing tank, then to acid emulsion tank from where it is taken to anode electrolysis degreasing tank, then to acid pickling tank. Nickel strike is carried out on the work piece in the Ni strike tank to ensure adhesion during the final plating stage. The last part is the plating of Ni-P / PTFE on the work piece in the Ni-P / PTFE plating tank. The compound plating formulation is made up of the plating solution with PTFE particle of sizes 0.2-0.4 μm dispersed in the solution. After the plating process the work piece is heat treated in the furnace for the hardening of the Ni-P phase. The coating has a high hardness of between 600- 1000Hv as a result of the deposition of N_3P during the heat treatment of the work piece. The process is used for the treatment of D-4 fuel pump plunger of an automobile.

Fig.8.11 Ni-P/ PTFE Compound Plating process

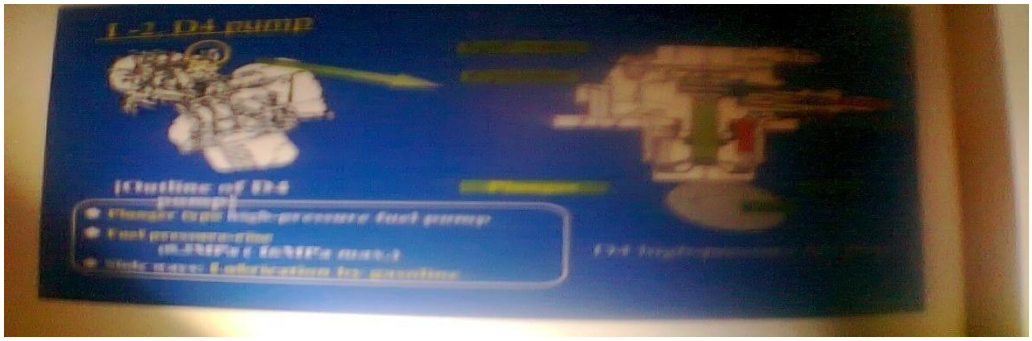
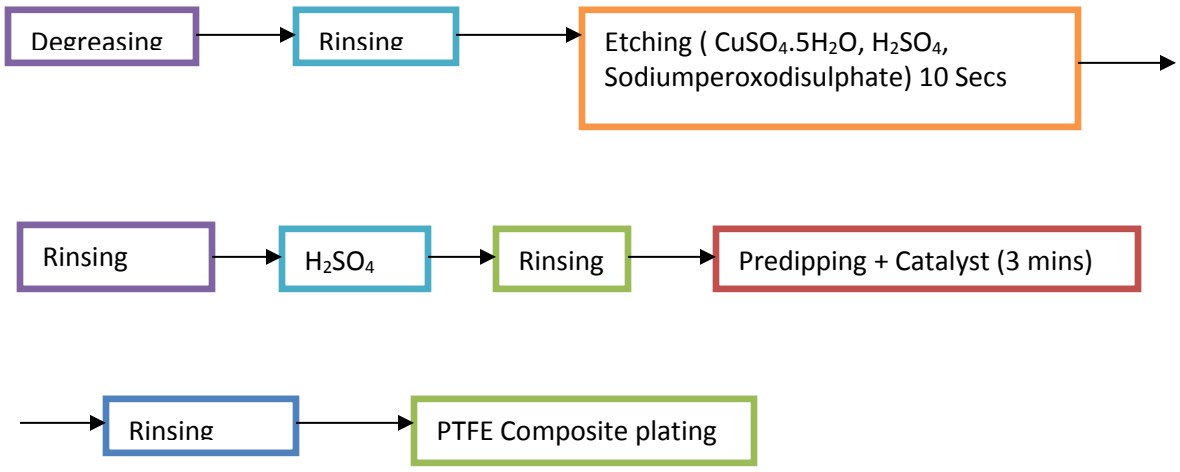


Fig. 8.12 D4 plunger pump

Ni-PTFE Composite Plating

Washers of gears can be applied with Teflon composite plating. The process is as indicated below.



Bath Composition Conditions

Temp: 88°C

Bath Load: 0.5 dm^2/ L

Ni concentration: 4.5g/L

pH: 4.9

Stir: mild

Principal ingredients in the bath are reducing agents, complexing agents, stabilizers, Ni agent, addition agent, and PTFE dispersing agent. Quality control is normally very important in plating automatic potentiometric titrator AT510 instrument is used for solution analysis. SEM is used for the analysis of the coatings and XRF coating thickness gauge SFT 9550 is used for coating thickness.

8.6.3 Nickel Ceramic Composite Coat

The coating is a composite and is achieved through composite dispersed nickel-phoshorus (Ni-P) alloy plating. It is an electrolytic plating process in which new ceramic particles (silicon carbide (SiC)) are dispersed and eutectoid precipitated in the matrices of Ni-P alloys, thereby primarily giving abrasion resistance to the plated material. The composition of the plating is Ni: 96 wt.%, P: 1wt.%, SiC 3wt.%. the hardness of the coatings is Ni-P: 600Hv, with SiC addition the hardness becomes 2500Hv. Thickness of plating: $130 \pm 30\mu m$. Area of application of the technology include components of snow mobile motorcycle, 2-cycle, 4 cycle, single cylinder, multicylinder, water-cooled and air cooled engine. The material is normally aluminium.

8.6.4 Newly Developed Pretreatment Process for Ornament Plating on Resin

Examples of ornament plating include plating on doors of car, door handles, aluminum wheel, emblem, door mirror, and radiator grill. See fig.8.13 below. Ornament plating requires high durability because of its exposure to adverse environment. Decorative plating is multilayered in composition and the various layers all have a role to play. You have the material or substrate the pretreatment which is for securing of conductivity and Copper layer which is for flexibility. The semi-glossy nickel, glossy nickel and the porous nickel layers are for corrosion resistance. The final-outer layer is the chromium layer and is for appearance and corrosion resistance. This multilayer plating is for durability.

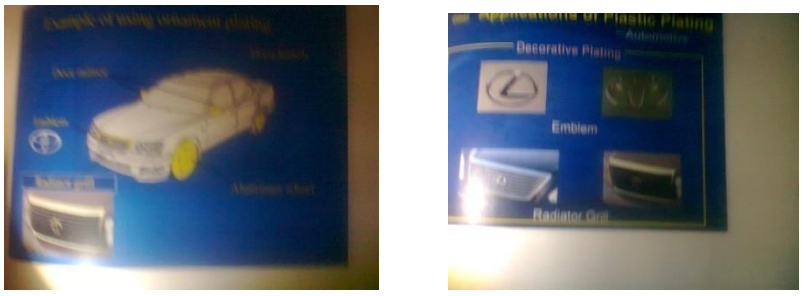


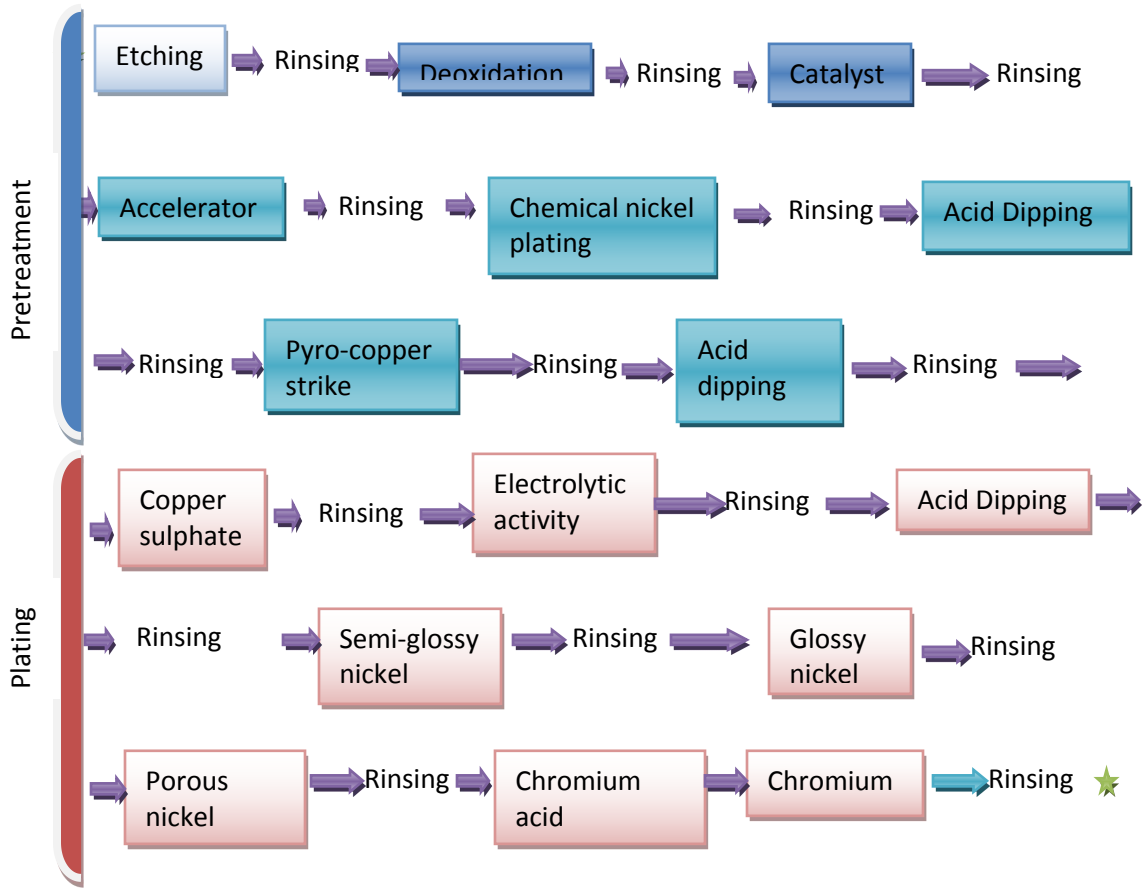
Fig.8.13 Ornament Plating on Resin

Ornament Cr Plating

The composition of ornament Cr Plating: is the substrate which is plated with copper, then followed by semi-glossy nickel, then glossy nickel, and then joule nickel, before finally plating with Cr on the outer surface.

The Newly Developed Ornament Plating Process on Resin

The plating process is made up of pretreatment and plating. The stages under pretreatment are 26 and plating has about 29 stages making a total of 55 processes. This is for the conventional process. In the newly developed process; the stages have been shortened as shown in fig.8.14a and b.



(3 hours required)

Fig.8. 14a Ornament Plating Process on Resin

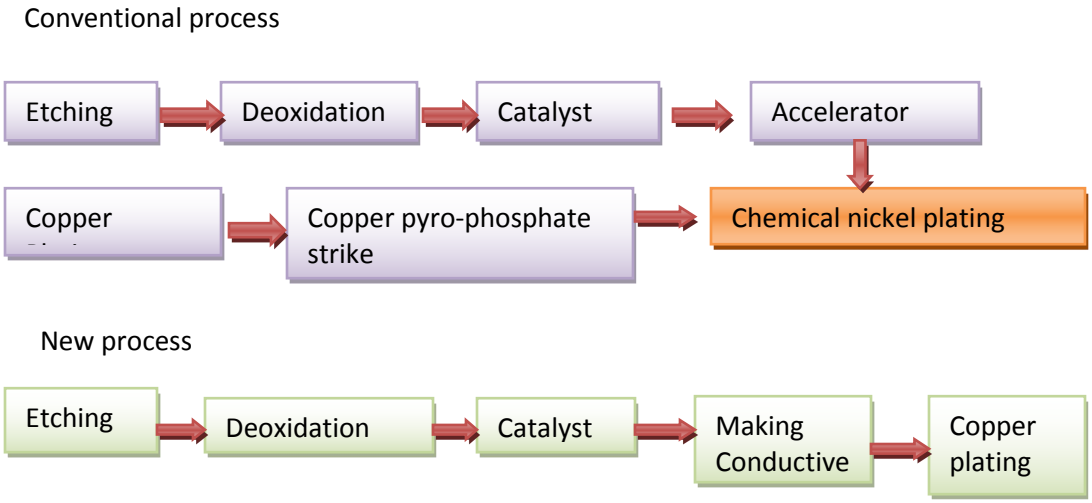


Fig.8.14b Benchmark: Process Shortening Technology. (process shortening resulting in cost reduction. Omission of chemical nickel plating resulting in reduction of environmental load substance)

8.6.5 Kaniboron (Ni-P-B) Plating: this is a high –performance plating with low phosphorus and boron content that possesses the properties of both electroless Ni-P and electroless Ni-B and has multiple functions exceeding conventional plating.

Features

Very compatible with aluminum and has superior sliding characteristics

1. Abrasion resistance: has a superior property that is three times that of electroless Ni-P.
2. High hardness: reaches Hv 700 with the plating as is and attains approximately Hv 1000 through heat treatment.
3. Heat resistance: superior to electroless Ni-P in terms of heat resistance and fully adaptable to usage under high heat conditions.
4. Impact resistance: the coating is very tough and even if the hardness is high it will not crack or become brittle

5. Lubricity: as the friction coefficient is superior at2/3 of electroless Ni-P, it is effective in preventing the fusing of sliding or rotating
6. High precision: high at $\pm$ 10% enabling uniformity of coating thickness.
7. Luster : unlike electroless Ni-P, it has bright luster

   Example of application of treatment include; variable speed clutch, valves, gears, engine parts, automatic transmission, flanges,slides, printed circuit boards, tools, camshaft, spherical bearings, exhaust pipes etc.

8.6.6 Leveling During Plating

Several expressions have been suggested as a means of evaluating the extent of leveling. Some of these depend on measurements of the depth of notch and the thickness of the coating, while others rely solely on measurements of surface roughness. Since leveling is dependent on the size of notch, the former procedure is more satisfactory but it is destructive and involves the preparation of a polished cross-section.

a) Percentage leveling= $\frac{T_N - T_S}{D_N} \times 100$

   Where T_N is the deposit thickness in the notch, T_S is the deposit thickness on the surface and D_N is the depth of the notch. Leveling is therefore shown as being 100% when the profile is completely leveled and 0% when the original profile is retained (perfect micro throwing power). If the leveling value is negative the micro throwing power is obviously poor since the surface roughness has increased.

b) Leveling = $\frac{T_N - T_S}{D_N}$

This expression shows the leveling to have a value of 1 when the profile is completely leveled. It also takes notch depth into account.

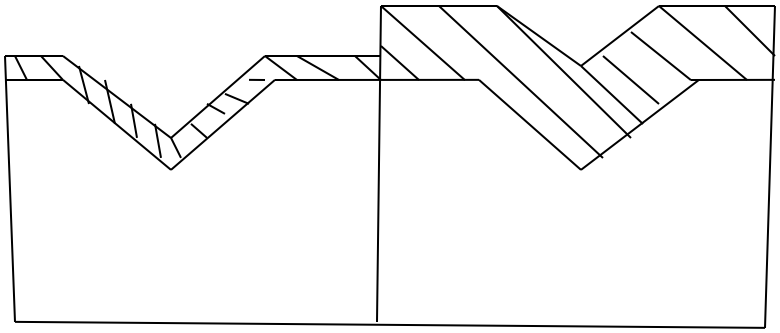


Fig.8.15 Geometrical leveling, the diagram illustrates that on a v-notch the geometrical leveling increases as the coating thickness increases.

Table 8.21 Plating Difficulties and Corrections in Nickel Plating

Difficulty	**Cause**	**Suggested Correction**
Pitting	Insufficient anti-pitting agent	Check surface tension and adjust concentration
	Metal content low	Analyse for metal content and adjust accordingly
	Boric acid low	Analyse for boric acid and adjust concentration
	Acidity too low	Check pH and adjust to proper value with nickel carbonate additions
	Inadequate agitation	Increase agitation
	Organic and/ or inorganic impurities	Chemical analyses, the properties and appearance of the deposits may indicate this type of contamination. Carbon and/ or high pH treatments followed by 'dummying' may be required.
Poor throwing	Metal content low	Analyse for metal content and adjust

power	Bath temperature low	Increase temperature
	Excessive anti-pitting agents or hydrogen peroxide	Check surface tension and peroxide additions. Carbon treats and purify electrolytically.
	Too low a current density in low pH bath	Increase current density or increase pH.
	Too high a current density in high pH bath	Lower current density or decrease pH
Low cathode efficiency	Metal content low	Analyse for metal content and adjust
	Current density too low	Increase current density
	Limiting current density has been exceeded	reduce current density or increase nickel content, temperature and agitation. Check pH and adjust to optimum value.
	Temperature low	Increase temperature
	Too much anti-pitting agent	Check surface tension and carbon treat to remove excess.
	pH too low	Adjust pH to optimum value by addition of nickel carbonate
Contamination (poorly adherent, brittle or burnt deposits)	Poor cleaning of the basis metal	Use standard methods of pre-cleaning metals and plastics. Inspect parts to check cleanliness before entering plating bath.
	Metallic	Use high pH treatment and the electrolytic purification.

	Organics	Use carbon treatment.

8.6.7Analysis of Nickel Plating Solution

1 Nickel chloride ($NiCl_26H_2O$)

1) Pipette 5ml plating solution. Add 50ml water and 1ml of 5% potassium chromate solution
2) Titrate with 0.1N $AgNO_3$ solution until the last one drop tinges the white precipitate with reddish brown.
3) Calculation:

   $NiCl_26H_2O$ (g/ l) = 0.01189 x (ml) x f x1000/ 5 = 2.38 x (ml) x f

   Nickel Sulphate ($NiSO_46H_2O$)

   1. Pipette 10ml of plating solution into a 100ml volumetric flask and dilute to the mark with water. Pipette 10ml aliquot.
   2. Add 150ml water and 10ml aqueous NH_4OH
   3. Add a small amount of MX indicator. Titrate with 0.05M EDTA solution, until the color changes from orange to reddish violet
   4. Calculation:

      $NiSO_46H_2O$ (g/ l) = 2.935 x (ml) x f- ($NiCl_26H_2O$ g/ l) x 0.247 x 4.48

   3.Boric Acid (H_3BO_3)

   1. Pipette 2ml of plating solution. Add 10ml water and 4g mannite. Stir to dissolve the mannite.
   2. After the addition of 5-6 drops of bromocresol purple indicator, titrate with 0.2 N NaOH solution until the color changes from greenish yellow to bluish violet

   8.6.8 Anodizing:

it is an oxidizing process used for aluminum and magnesium articles. The article to be anodized is made anode and sulphuric, oxalic and chromic acids are used as electrolyte. The coating is produced entirely by the oxidizing process and not by plating. The coating so produced is hard and at the same time It is porous enough and hence advantageous from decorative point of view. Such oxide coatings enable organic coating and dyes to be successfully used on aluminum article surfaces. Modern aluminum glasses and pitchers are examples of this class.

8.7 Phosphating and Chromating Processes in View

Definition of Conversion Coating

Conversion Coating: Formation of stable coating film on metal surface with chemical reaction.

- Phosphating : (Zinc phosphate, Manganese phosphate, iron phosphate, calcium phosphate etc.)
- Chromating: (Chromate chrome, Chromate phosphate, Non Chromate)
- Anodizing
- etc

Historical Development

- Found from archaeological excavation of Romans (1880s)—Corrosion –resistant blue film ----Vivianite ($Fe_3PO_4.8H_2O$) was formed on iron work.
- Conversion Coating process was used by Romans
- Phosphorus from bone and mud (contained alkali) made conversion coating.
- 1906 (T.W.Coslett) original patent of iron phosphate process (120-150 min, at boiling temperature)

- 1909 (T.W.Coslett) Zinc phosphate
- 1911 (Richards) Manganese Phosphate 60 min
- 1914 In commercial base in USA
- 1929 Addition of Cu into Zinc Phosphate bath 10 min
- 1931 Addition of oxidizing agent 5 min
- 1934 (Dr.F. Singer) Application for cold forming

  spraying system is employed 1-1.5 min
- 1943 (Jernstadt) Discover Titanium colloid surface conditioner
- Application for different field, shorter process time, lower process temperature and higher quality have been set target.

8.7.1 Basic Theory of Phosphating

(1) **Phosphate Coating on Steel**

The steel plate or work piece is dipped in phosphate solution tank and the reactions that take place are shown below. The steel has micro-anode areas and micro-cathode areas. The anode goes into solution releasing electrons, while at the cathode areas phosphate coating is deposited.

- Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ (Etching)

  Cathode: $3Me(H_2PO_4)_2 \rightarrow Me_3(Po_4)_2 + 4H_3PO_4$ (coating Formation)

Phosphate Coating on Zinc Plate

The same mechanism of coating deposition occurs here. Micro-anode areas on zinc substrate go into solution releasing Zn ions and electrons whereas on the microcathode areas of the substrate; phosphate coating deposition proceeds.

Anode: $Zn \rightarrow Zn^{2+} + 2e^-$ (Etching)

Cathode: $3Me\ (H_2PO_4)_2 \rightarrow Me_3(PO_4)_2 + 4H_3PO_4$ (Coating formation)

Phosphate Coating on Aluminium Substrate

The reactions are as below:

Anode: $Al \rightarrow Al^{3+} + 3e^-$ (Etching)

Cathode: $3Me(H_2PO_4)_2 \rightarrow Me_3(PO_4)_2 + 4H_3PO_4$ (Coating formation)

Chromate Coating for Zinc Substrate

The zinc substrate has microanode and microcathode areas when in the chromating solution the anode areas go into solution releasing zinc ions and electrons into the solution. At the cathode micro areas, deposition of chromate coating takes place. The following reactions take place.

Anode: $Zn \rightarrow Zn^{2+} + 2e^-$ (Etching)

Cathode: $2Cr(OH)_3 + CrO_4^{2-} + 2H^+ \rightarrow Cr(OH)_3 + Cr(OH)CrO_4 + 2H_2O$ (Coating formation)

The chromate coating is amorphous in nature.

Chromium Chromate on Aluminium Substrate

The substrate which is dipped in chromate solution has micro anode and cathode areas. The micro anode areas go into solution releasing Al ions and electrons into the solution. The chromium chromate coating is deposited on the micro cathode areas. The reaction is as follows:

Anode: $Al \rightarrow Al^{3+} + 3e^-$ (Etching)

Cathode: $2Cr(OH)_3 + CrO_4^{2-} + 2H^+ \rightarrow Cr(OH)_3 + Cr(OH)CrO_4 + 2H_2O$ (Coating formation)

Chromium Phosphate Aluminium Substrate

Substrate dipped in chromate solution with Cr^{4+}, Cr^{3+}, PO_4^{3-}, F^-..

Anode: $Al \rightarrow Al^{3+} + 3e^-$ (Etching)

Cathode: $HCr_2O_7 + 2H_3PO_4 + 7H^+ \rightarrow 2CrPO_4 + 7H_2O$ (Coating formation)

The coating $CrPO_4$ is amorphous.

Non Chromate Coating on Aluminium Substrate

Substrate dipped in non chromate solution with zirconium, titanium and other ions

Anode: $Al \rightarrow Al^{3+} + 3e^-$ (Etching)

Cathode: $ZrF_6^{2-} + 2H_2O \rightarrow ZrO_2 + 6F^- + 4H^+$ (Coating formation)

8.7.2 Basic Theory of Phosphating Reaction

1. Dissociation of phosphoric acid

Phosphate reaction

Using the dissociation of phosphoric acid, insoluble coating (phosphate coating) is deposited on metal surface.

Value of dissociation constant at 25°C

$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+ \quad K_1 = 7.5 \times 10^{-3}$ (1)

$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+ \quad K_2 = 6.2 \times 10^{-8}$ (2)

$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+ \quad K_3 = 4.8 \times 10^{-13}$ (3)

Primary phosphate: $Me(H_2PO_4)_2$

Secondary phosphate: $MeHPO_4$

Tertiary phosphate: $Me_3(PO_4)_2$

Reaction rate in phosphate reaction is guided by Arrhenius equation and Fick's law of mass transfer

Arrehenius Equation $k = Ae^{-E/RT}$

Where, E = Activation energy, A = Frequency constant, R = gas constant, T = Temperature

Fick's law of mass transfer $dn = - Dq (dc / dz) dt$

Where, dn = amount of mass transferred in dt time, q = surface area, D = diffusion coefficient, Z = transferred distance, c = concentration

Table 8.22 Composition of Various Phosphate Coating

Metals in phosphate solutions	No addition (alkali)	Substrates	
		Fe	Zn
		$Fe_3PO_4.8H_2O$ (Vivianite)	$Zn_3(PO_4)_2.4H_2O$ (Hopeite)
	Zn	$Zn_2(PO_4)_2.4H_2O$ $Zn_2Fe(PO_4)_2.4H_2O$ (Phosphophyllite)	$Zn_3(PO_4)_2.4H_2O$
	Mn	$Mn_nFe_yH_2(PO_4)_4.4H_2O$ (n +y= 5) (Hureaulite)	$Zn_3(PO_4)_2.4H_2O$ $Mn_5H_2(PO_4)_4.4H_2O$ (Mn. Hureaulite)
	Ca + Zn	$Zn_2Ca(PO_4)_2.2H_2O$ (Scholzite) $Zn_3(PO_4)_2.4H_2O$ $Zn_2Fe(PO_4)_2.4H_2O$	$Zn_2Ca(PO_4)_2.2H_2O$ $Zn_3(PO_4)_2.4H_2O$

Application of Conversion Coatings

- It is applied as a paint base for automobiles
- It is applied for rust prevention
- It is applied to increase lubrication and wear resistance of parts or work piece. The plate below shows various conversion coatings.

Conversion coating under the paint acts or serve as

- Barrier coating

- Improve adherence between substrate and paint
- Passivate substrate
- Non-conductive layer
- Self healing performance (chromium chromate)
- Neutralization in conversion atmosphere with coating dissolution under the paint.

8.7.3 Zinc Phosphating Process

The process of zinc phosphating starts with degreasing followed by rinsing, then surface conditioning, then the zinc phosphating proper and then water rinsing and drying. The flow-sheet is as below

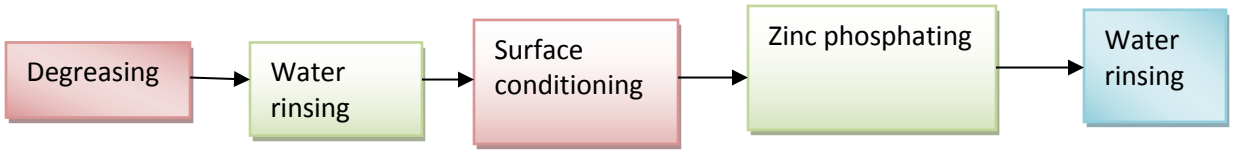


Fig. 8.16 Phosphating flowsheet

Components of the degreasing tank include alkali builder (phosphate, silicate etc), surface active agent and deformer. The purpose of the degreasing is to remove rust preventive oils, lubrication oil, dirts, iron particles, foreign matter etc. control parameters in the tank are usually total alkalinity, free alkalinity, oil concentration, and temperature.

The rinsing tank contains industrial water and deionised water after phosphating. The rinsing process removes oils, degreasing chemical, phosphate chemicals to prevent the contamination of E-coat bath. The control parameters of the tank are electro-conductivity, pH, and amount of water supply.

Surface conditioning process is to make phosphate coating uniform and make phosphate crystal denser and finer. The components in the tank are titanium colloid, condensed phosphate and alkali builder. The control parameters are total alkalinity, pH and the amount of water supply.

The phosphating process is to form phosphate coating and the components of the solution in the phosphating tank are phosphoric acid, nitric acid, fluoric acid, zinc, nickel, manganese and accelerator. The control parameters are usually free acidity, total acidity, accelerator, concentration and temperature.

Zinc phosphating Process

The steps in the zinc phosphating process are same as above. The difference is the composition of the zinc phosphating tank.

Electro-less Plating Process: Nickel, and Gold Plating in View

This review is part of a seminar paper delivered by the author on the 30th April, 2009 at an in-house at National Metallurgical Development Centre, Jos –Nigeria. The topic underscores the importance of nickel and gold plating to surface finishing technology. Nickel and nickel alloy plating via the electro-less route can be applied to various substrates for various reasons. Some of the reasons include corrosion resistance, abrasion resistance, decoration purpose, and others. E.g. brake pistons require abrasion resistance they are applied with electroless Ni plating, and heat treated at 300OC for 1 hour to give a hardness value of 700Hv.

Gold plating using copper substrate normally starts with nickel plating, this is to prevent gold from diffusing into the substrate.

Fundamental Procedures in Plating

Fundamental procedures in plating are normally degreasing, rust removing and then plating. This is illustrated below.

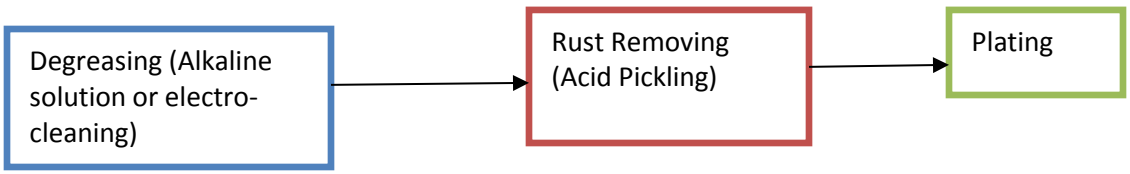


Fig. 8.17 Fundamental procedure in plating

There may be conditioning before plating which all depend on the plating nature. The procedure for electro-less nickel plating is shown below:

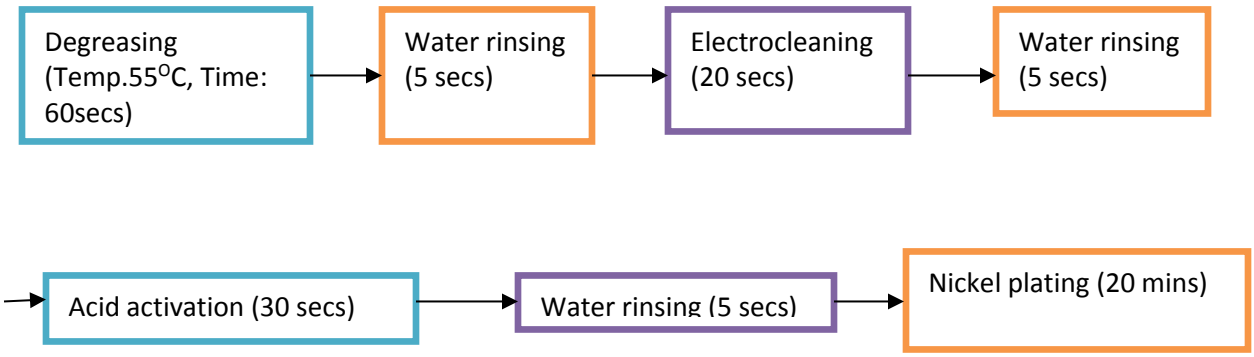


Fig.8.18 procedure for nickel electroless plating.

Strike Plating

Striking is an operation in electro-less plating. The striking plate is connected to the rectifier; it is used to strike the cathode. The strike initiates the deposition of the nickel on the substrate immediately. It is however, worthy of note that even without the striking, deposition can still take place; striking fastens the deposition rate.

Gold Plating

Gold plating procedure is as illustrated in fig. 8.17 below. It involves the cleaning of the substrate to remove dirts and activation and conditioning of the substrate before nickel plating.

The nickel forms the base for the gold plating and prevents the gold from diffusing into the copper substrate.

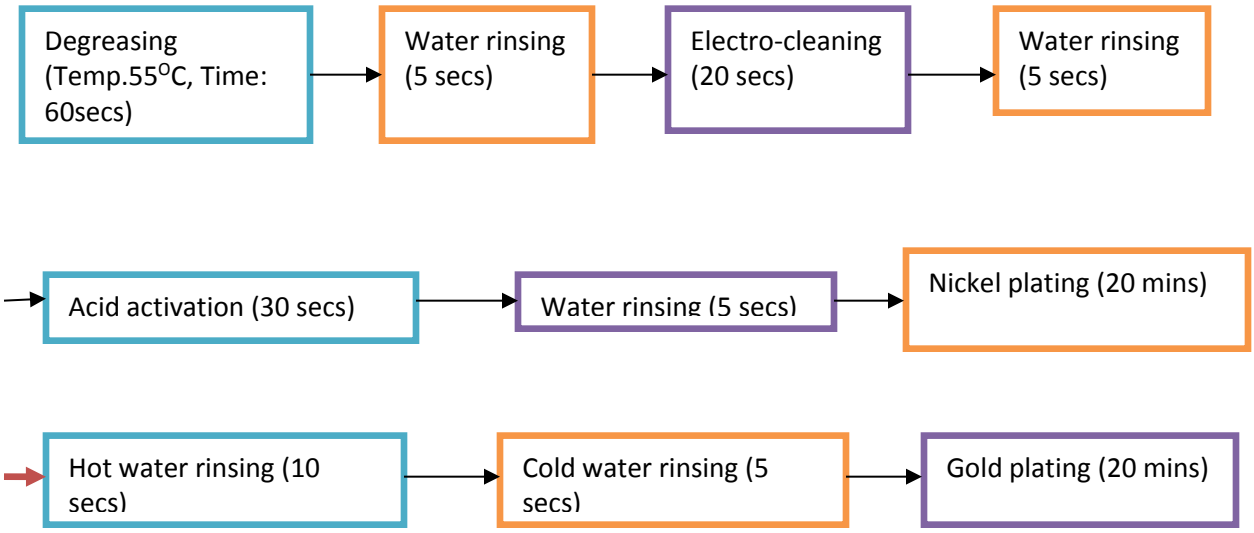


Fig.8.19 Gold plating procedure

Composition and Temperature of Gold Plating Bath

The temperature of the bath during operation is normally 85oc-90oc. The purity is normally 99.9% and thickness of the plating after 20 mins is 0.06µm. the composition of the plating bath is as below

Composition

- $KAu(CN)_2$ + KCN
- $KAu(CN)_2$ = 147 g/L
- Chelating agents (complexing agents)
- KCN = 0.5g/L
- pH = 4.6

Appendix A gives additional information on gold plating, TiN plating is gradually replacing gold plating in many applications

Fig. 8.20 Laboratory Plating Equipment

8.8 Testing and Analysis

Plating tests cells

The Hull cell proposed by R.O. Hull is one of the plating tests cells used for development, evaluation and control of plating bath. The size of Hull cells, common use today, is the 267mL trapezoidal shaped container, designed to test a small volume of solution with a 10x6.5cm test panel, inclined at 38^{o} to anode. Using the same cell, a solution volume can be selected among 250, 267, 320mL at the level height of 45, 48, 53mm respectively. It's convenient to control the additives or components in the solution. E.g. 2g/267mL = 1ounce/US gallon

2g/320 mL = 1 ounce/ British gallon

A plating range test is in essence a qualitative procedure that provides a qualitative answer. By visual examination, a series of cell tests will reveal the amount of substances to add to, or remove from, the bath in order to adjust it for continuing production.

Several researcher derived formula for the current densities along the cathode, e.g.

$P(x) = I(4.08 – 3.96\text{Log}(x))$ by Watson for 267 mL cell at 1960

$P(x) = I(5.10- 5.24\text{Log}(x))$ $0.6<x<8.3$ by DIN 50957 for 250 mL at 1958

$P(x) = I(4.38- 4.06\text{Log}(x)$ $0.9<x<4.0$ by Terakado et al for 267 mL at 1978

$P(x) = I(4.88-4.86\text{Log}(x))$ $4.0<x<9.0$

Approximation

$P(x) = I(4.44- 4.25\text{Log}(x)$ $0.5<x<8.0$

P(x) is primary current density at x point

I is the total current applied to the panel

X is the length (cm) along the panel from high current edge.

See fig. 8.5 For Hull cell

Other cell

Rectangular plating cell, Harring-Blum cell, Half-Box cell, open Hull cell, Slot cell

8.8.1 pH Determination

The term ``pH'' is used to express the degree of acidity or alkalinity of a solution. The pH, the logarithmic function of the hydrogen ion concentration, defined as $pH= -\text{Log}[H^+]$

The pH can be determined calorimetrically or electrometrically.

8.8.2 Calorimetric Method

For a visual indication of the pH, a weak organic acid (or base), having the special feature that it change in color within a definite pH range, is employed. Commonly used calorimetric method is the pH paper. The indicator is impregnated on an absorbent paper strip. A color chart with appropriate pH values is printed on the strip or a card. After immersion in the solution, the strip is compared with the standard color. Reliable pH papers area accurate ±0.3

units from the electrometric value. In the case of a strong oxidizing or reducing solution, the pH papers are not reliable.

8.8.3 Electrometric Method

Electrometric determination of pH depends on the fact that certain electrodes, e.g. glass electrode or Sb electrode, immersed in a solution containing hydrogen ions acquire a potential. The potential value depends on the activity (concentration) of hydrogen ion present. Standard pH meter is equipped with a glass electrode as for indicator electrode and a reference electrode sometimes, the two electrodes are united in one `combination electrode' The electrode are immersed in a known buffer solution, and the meter is adjusted. Typical buffer solutions are shown in Table 8.23

Table 8.23 Typical Buffer Solution

Ph	**Components**	**Concentration**
2.08	Hydrochloric acid Potassium chloride	0.365g/L 6.7 g/L 1:1 mixture
3.57	Potassium hydrogen tartrate	5.64g/L
4.00	Potassium hydrogen phthalate	10.2g/L
6.9	Acetic acid Sodium acetate	6.0 g/L 8.2 g/L 1:1 mixture
9.2	Boric acid	19.06g/L

8.8.4 Methods of Thickness Test for Metallic Coating

a) Microscopic method for cross-sectional thickness test

b) Calorimetric method

c) Eddy current method

d) Magnetic method

e) X-ray spectrometric method

f) β – back scatter method

g) Micrometric method

h) Mass instrumentation method for deposit quantity test.

8.8.5 Method of Corrosion Resistance Test

a) Neutral salt spray test

b) Acetic acid salt spray test

c) CASS test (copper accelerated salt spray test)

d) Corrodekote test

e) Sulphurdioxide test

8.8.6 Methods of wear resistance test

a) Sand-falling wear resistance test

b) Jet wear resistance test

c) Reciprocating motion wear resistance test

d) Flat disk revolution wear resistance test (Taber's wear resistance test)

e) Double ring driving wear resistance test (Amsler's wear resistance test)

8.8.7 Methods of Adhesion Test for Metallic Coating

a) Cathodic electrolysis test method

b) Push-out test method

c) Scratch mark test method

d) Grinding test method

*Grind test method

*filing test method

e) chiseling test method

f) thermal test method

*heating test method

* thermal shock test method

g) Barrel jostling test method

*taping test method

*soldering test method

h) peeling test method

i) tensile test method

j) bending test method

k) coiling test method

8.8.8 **Leveling**

a) Macro-throwing power

b) Micro-throwing power

c) Covering power

8.8.9 Calculation of Plating Times

Table 8.24 shows some vital calculations used in plating shops as a guide.

Table 8.24 calculation of plating Times

Metal	Symbol for element	Valence	Density	Grams deposited per ampere hour (η= 100%) (g/AH)	Thickness per 1 minute at 1A/dm^2 (η= 100%) (μm/minute)	Typical current density (A/dm^2)	Typical efficiency (η) (%)	Thickness per 1 minute at typical condition (μm/minute)
Chromium	Cr	6	6.95	0.323	0.074	50	22	0.814
Nickel	Ni	2	8.90	1.095	0.206	4	90	0.742
Electroless Nickel	Ni-P	2	8.90	-	-	-	-	0.300
Copper	Cu	1	8.93	2.372	0.442	2	90	0.796
Copper	Cu	2	8.93	1.186	0.221	4	100	0.884
Zinc	Zn	2	7.13	1.219	0.285	3	80	0.684
Tin	Sn	2	7.28	2.213	0.506	2	95	0.961

Notes) 1. Surface area: 1dm^2= 100cm^2 (= surface area of plate 10 cm square)

2. Thickness: 1μm = 1/1000 mm

3. Current Efficiency: η

Examples

Example 1

Target of chromium plating thickness: 20μm at current density of 50A/dm^2

a) What is the Plating time? (in minutes at η = 22%)

b) What is the Plating time? (in minutes at η = 14%)

Solution

a) From the table 8.24: 20/ 0.814 = 24.6 (minutes)

b) Rate of deposit: 0.074x50x14/ 100 = 0.518 μm/minute

Example 2

Chromium plating at following condition, target thickness =30μm, plating time? Work surface area: 2000cm^2, ampere: 1000A, η = 24%.

Solution

Current density = 1000/20 = 50A/dm^2

Rate of deposition = 0.074 x 50 x 24/100 = 0.888 μm/minute

Plating time = 30/ 0.888 = 33.78 minutes.

Example 3

Decide the capacity (ampere) of rectifier under following conditions; rectifier covers one (1) carrier bar 30 pieces piston rod loaded for each carrier bar. Current density: 50A/dm^2, piston rod size: diameter 20mm, plating length 315mm, (max).

Solution

1 rectifier covers 1 carrier bar, 1 carrier bar contains 30 pieces of piston rod, current density = 50A/dm^2, piston size: diameter = 20mm = 2.0cm, plating length= 315mm = 31.5cm

Surface area of piston rod= Length x Breadth

The length= πD = 3.14 x 20 = 62.8mm = 6.28cm

Surface area of one piston= 31.5x6.28 = 197.82cm^2

Total surface area of plated work pieces = 30x197.82 = 5934.6cm^2 = 59.35dm^2

50A - 1dm^2,

? - 59.35dm^2

Total Ampere required = 59.35 x 50 = 2967.3 A

Example 4

Calculate the current efficiency under following condition: average thickness= 22.1µm, plating time = 24.3 minutes, current density = 52 A/dm^2

Solution

Given: average thickness= 22.1µm, plating time = 24.3 minutes, current density = 52 A/dm^2

Average thickness (from table8.24) = 0.074x24.3x52xη = 22.1

Current efficiency η from above = $\frac{22.1}{0.074 \times 24.3 \times 52} = 0.2364 = 23.64\%$

Example 5

Calculate the total chromic acid (CrO_3) consumption per one month. Average thickness = 13.6µm, plating surface area = 0.63dm^2/ 1pieces, production quantity per one month: 250,000 pieces, atomic weight: Cr = 52, O = 16.

Solution

Given: average thickness = 13.6µm = 0.000136dm, plated surface area= 0.63dm^2/ 1piece,

Production quantity per month = 250,000 pieces, atomic weight = Cr = 52, O = 16

Total Surface of work pieces for one month = 0.63 x 250,000 = 157,500dm^2

Volume of coating on one work piece = 0.000136 x 0.63 = 0.00008568dm^3 = 0.08568cm^3

Density of coating from the Table 8.24 = 6.95g/cm^3

The mass of coating for one piece = 6.95 x 0.08568 = 0.595476g

One mole of CrO_3 contains Cr: 52, O: 48 = 100 molecular weight

Total chromium used for 250,000 pieces = $\frac{100 \times 0.595476 \times 250000}{52} = 286286.54g$

Plating Practical using Hull Cell Test (zinc plating continues)

Introduction

The place that is closer to the anode of the hull cell will be plated faster because of proximity to high current. The color will also be different likewise the thickness, this is undesirable. The solution therefore has to be developed to avoid this when certain solutions are added to the solution you can achieve a uniform thickness. Hull cell also helps you to determine which constituent was consumed. The anode is made of zinc plate, while the cathode is made of steel sheet. Bath solution is contaminated if impurities are included, Hull cell test will help in the determination of the impurities. For commercial purpose suppliers include all necessary additives in the bath chemicals.

The chloride bath is not widely used for commercial purpose. For practical purpose two baths compositions will be prepared according to tables 8. - 8.

Table 8.25 Potassium chloride bath (pH= 5.5)

P1	P2	P3	P4
$ZnCl_2$ 60g/l KCl 200g/l H_3BO_3 30g/l	ditto	Ditto	Ditto
Additive free	Surfactant*[1] 5g/l	Surfactant*[1] 5g/l Benzal acetone 0.4g/l (benzylideneacetone)	Ditto Nicotinic acid 0.2g/l

*1 Surfactant: polyoxyethylene octylphenyl ether

Table 8.26 Potassium chloride-acetic acid bath (pH= 4.0)

A1	A2	A3	A4
$ZnCl_2$ 40g/l KCl 200g/l CH_3COOH 30g/l	Ditto	Ditto	ditto
Additive free	Surfactant*[1] 5g/l	Surfactant*[1] 5g/l Benzal acetone 0.4g/l (benzylideneacetone)	ditto Nicotinic acid 0.2g/l

Note that P1- P4 and A1-A4 represent various plating solutions in which the plating experiment is to be conducted.

Surfactant: produce a white colour and give a better appearance in combination with other additives. It helps to achieve levelness. The volume of solution to be used in the work will be 500ml

Hull Cell Test Process

The following steps are involved in the Hull cell test process

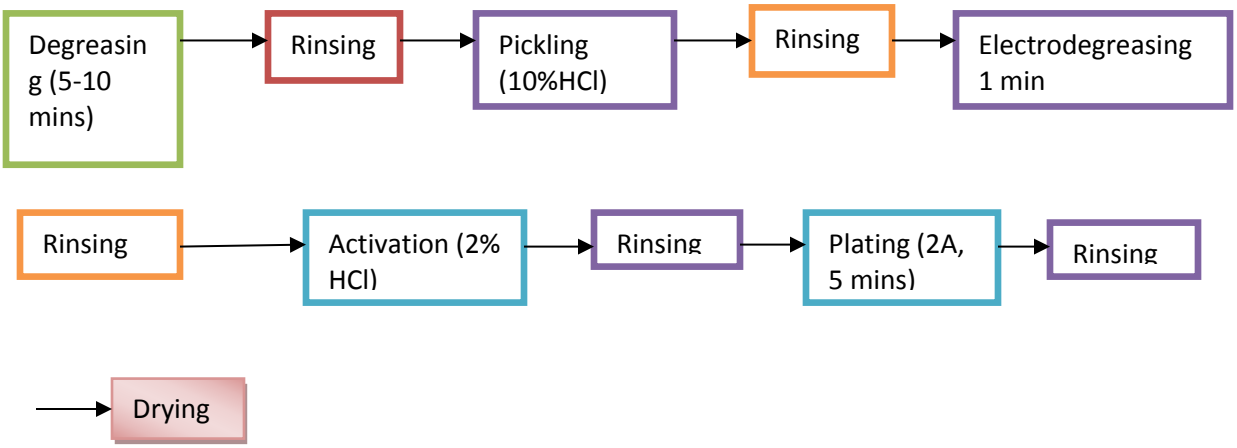


Fig.8.21 Hull Cell Test Process

How to prepare plating solution

The solution of $ZnCl_2$ and boric acid is transferred to the hull cell. Note $ZnCl_2$ is a dangerous substance and should be handled with care. Connect the anode to the positive terminal of the DC current regulator. The negative terminal of the DC regulator is connected to amperemeter and the cathode is then connected to the ampere meter. The supply current is then set to 2A. The specimen is pickled, rinsed and connected in the cell for 5 minutes. It is removed and taken for drying in the oven. The fig. 8. Shows how the hull cell is connected.

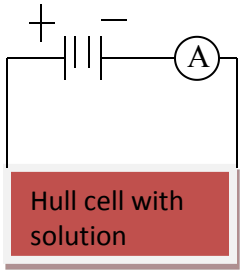


Fig.8.22 Connected Hull Cell for Test

- Weigh 30g of ZnCl2 into 500ml beaker
- Weigh 100g of KCl into the beaker
- Weigh 15g of boric acid into the beaker
- Make the solution to 500ml with distilled water and stir with magnetic stirrer heater and allow it to dissolve
- Then adjust the pH
- The pH can be adjusted with either acid or alkali depending on the as dissolved solution Ph. When as-dissolved pH is 5.18 then adjust to pH5.5 using 5%KOH under magnetic stirring. Where the electrolyte requires surfactant; the surfactant is dissolved to 40ml using distilled water and 20ml is taken using a pipette and added to the electrolyte, no heating of the solution is required only stirring. It is then poured to the Hull Cell. The specimen is pickled using 10HCl, it is then rinsed and mounted for plating for 5 minutes at 2A, as explained earlier. The electrolyte is returned to the beaker and 0.2 g of benzalacetone is added and stirred using magnetic stirrer. It must be ensured that it dissolves completely. The specimen is pickled, washed and mounted on the Hull Cell for 5minutes. It is then removed washed and dried. This is done as specified in table 8., for the 4^{th} experiment of the same table 8... nicotin 5ml is added to the solution and stirred using magnetic stirrer and then poured into the Hull Cell. The

specimen to be coated is pickled rinsed and then inserted in the Hull Cell at the cathode end. The stop watch is set to run for 5 minutes. The current is switched on and the watch stopped after 5 minutes. The sample is then removed rinsed and dried in the oven.

Note that for commercial purpose plating chemicals are supplied with all the necessary chemicals included such that you need not formulated the bath. Hull cell test is just for investigation.

Evaluation

The evaluation test is normally set at the middle of the workpiece with a paper guide see the results of the experiments for tables 8. And 8.

Corrosion tests can be carried out by using the combination of 0.17g $FeCl_3$, 10ml NH_4Cl, 7ml $CuNO_3$ and 30g kaolin, however, less of this test is carried out since the salt spray test is effective.

Zinc plating and conversion coatings.

Auken company chemicals are used for degreasing

Pickling: can be skipped when test pieces did not have rust.

Test Piece Dimension: $2.5cm^2$

Number of specimens on the rack: 18

Calculate how much current is needed for electroplating of 18 work pieces?

$1.5 \text{ X } 2.5 \text{ x } 2 \text{ x } 18 = 225cm^2$

$1\ dm^2 = 100cm^2$

$5A/dm^2 = 0.05\ A/cm^2$

$3A/dm^2 = 0.03A/cm^2$

225 x 0.05 = 11.25 A

225 x 0.03 = 6.75 A

i). **Zinc Plating**

Pretreatment

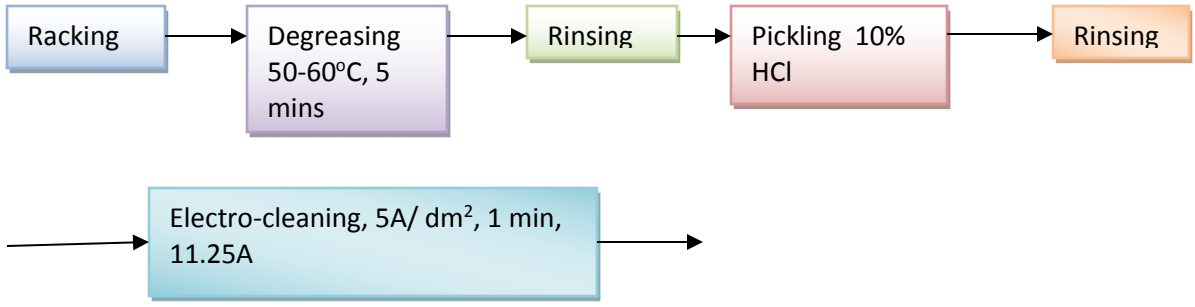


Fig.8.23 Pretreatment Process

Composition of Degreasing Bath (one example)

NaOH	30 g/L	(Sodium hydroxide)
$2Na_2O.SiO_2$	30	(Tetrasodium monosilicate)
Na_2CO_3	20	(Sodium carbonate)
ABS	1	(Sodium alkyl benzene sulfonate)

ii) **Plating**

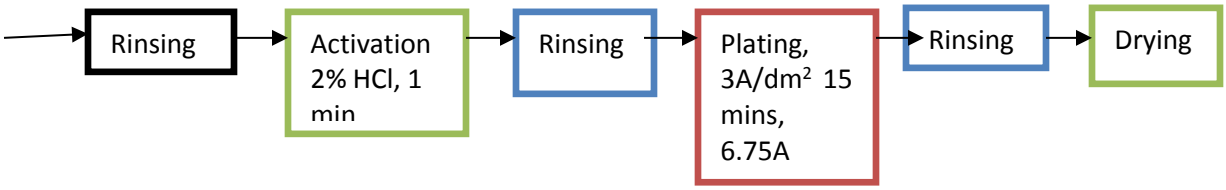


Fig. 8.24 Plating process

Composition of Zincate Bath

ZnO	10g/L
NaOH	120g/L

Brighteners

iii) Conversion Coating

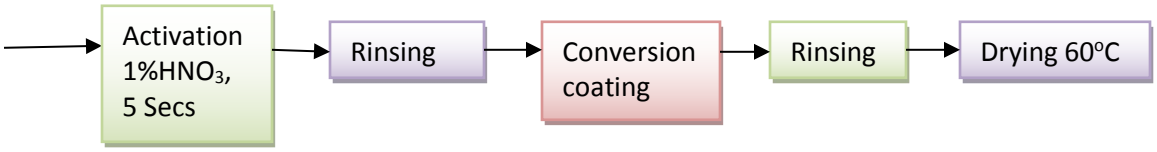


Fig. 8.25 conversion coating process

Conventional chromate conversion coating

A typical chromating conversion experiment is shown below

a). coloured chromate

CrO_3 5 g/L

H_2SO_4 (97%) 0.8 mL/L

HNO_3 (61%) 2 mL/L

Solution pH: 0.7 1.6 2.0 2.4

Dip Time (secs): group A 15, group B 30

Temperature: room temperature ^oC

b). green chromate

CrO3 10g/L

H_2SO_4 (97%) 1mL/L

H_3PO_4 2mL/L

HNO_3 (61%) 1mL/L

Solution pH: 0.8 1.0 1.2 1.4

Dip Time (secs): group A 60, group B 30

Temperature: room temperature ^oC

c). hexavalent chromium- free conversion coating (trivalent chromium)

i). oxalic acid type

40% $Cr(NO_3)_3$ 40mL/L

$NaNO_3$ 100g/L

Oxalic acid 10g/L

CoCl (g/L): 0+1, 1+2, 3+2, 5

Temp.: 60°C Solution pH: 2.0 dip.Time: group A: 30 secs group B: 60 secs

ii) silica hybrid type

40% $Cr(NO_3)_3$: 40mL/L

$NaNO_3$ 100g/L

Citric acid 20g/L

Colloidal silica 30mL

CoCl (g/L): 0, 1, 3, 5

Temp.: 60°C Solution pH: 2.0 dip.Time: group A: 60 secs group B: 30 secs

The bath for electro-cleaning has anode at both ends the anodes are made up of stainless steel back up with PVC plate. The test pieces are hanged in the middle as the cathode and connected to the cathode terminal of the DC converter. The anodes are connected to the anode terminal. The same arrangement holds for the zinc plating with the difference being the use of zinc anodes at the anode terminal. Conversion coating starts with the preparation of the solution according to the various pHs required as shown above. The specimen is dipped in 1% HNO_3 for 5 secs for activation rinsed and then dipped in the conversion coating and rinsed or dried. The coated specimens can be evaluated as below.

Salt Spray Test

The temperature is set normally at 35°C after placing the test pieces in the chamber. Spraying of salt solution with $CuCl_2$ is then carried out.

After salt spray test on coloured chromate specimen and trivalent chromic acid without $CuCl_3$; the coloured chromate specimen did not corrode after 24 hours but the trivalent chromic acid specimen did.

Analysis of Result of Conversion Coating.

High pH results in low plating of chromium. When the coating is too thick it peels-off. The resistance of the material too reduces when the coating is low. Chromating can be done on Al, and iron without pretreatment. The longer the time of treatment in the chromating solution the thicker the coating.

Electroless Nickel Plating

(Effect of bath composition on deposition rate)

Table 8.27 Composition of Electroless Nickel Bath

	Group A	Group B
Ni- P	Gly-Ace	Gly-Cit
NiSO4.6H2O	26g/L	26g/L
Sodium phosphinate	30g/L	30g/L
Sodium citrate	-	30 g/L
Glycine	15g/L	8g/L
Sodium Acetate	8 g/L	-
Pb(NO3)2 (4g/L Pb(NO3)2 solution 0.5mL/L)	2mg/L	2mg/L
Temperature	80^{o}C	80^{O}C

pH: 4.5, 5.5, 6.5, 7

i) Make 1L solution and divide into 4 baths (250mL each)

ii) set the bath pH by using H2SO4 or NaOH solution)

Process

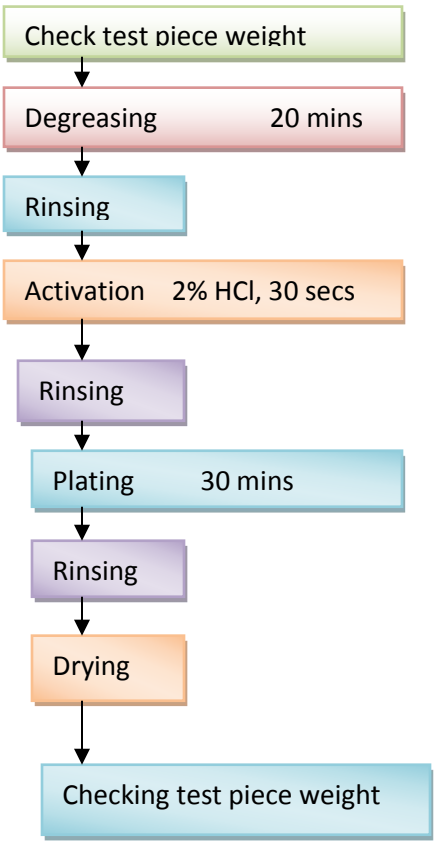


Fig. 8.26 Process of electroless nickel plating experiment.

For materials other than iron after activation catalyst is required. $SnCl_2$ is used in the bath, after that $PdCl_2$ is used. Rinsing comes in after dipping in each bath for a few secs. Alternatively Pd colloid can be used in place of the two baths.

20-40g/L $SnCl_2$ + 10mL- 20mL HCl

0.1- 0.3g/L $PdCl_2$ + 1-5mL HCl

8.9 Waste Water Treatment

Nigeria is yet to attain economic growth. High economic growth normally comes with serious water pollution problems and therefore the need for countermeasures technologies. Pollution is a global issue hence most nations have guidelines on wastewater treatment in plating shops. These guidelines are simply specifications and standards for wastewater treatment and disposal. Here in Nigeria, National Environmental Standards and Regulations Enforcement Agency (NESREA) has such specifications clearly spelt out in the National Environmental (base metals, iron and steel manufacturing/recycling industry sector) Regulations 2010. See Tables 8.25 and 8.26 Below.

Table 8.25 Effluent Limitations for Metal Manufacturing (metallurgical) Industries

S/N	Parameter	Unit	Guideline value
1	**pH**	S.I	6 – 9
2	COD	mg/l	250
3	TSS	mg/l	50 25 (electroplating)
4	Oil and grease	mg/l	10
5	Aluminium	mg/l	3.0
6	Arsenic	mg/l	0.1
7	Cadmium	mg/l	0.1
8	Chromium (total)	mg/l	0.1
9	Chromium (hexavalent)	mg/l	0.5
10	Copper	mg/l	0.1
11	Iron	mg/l	3.0
12	Lead	mg/l	0.2
13	Mercury	mg/l	0.01
14	Nickel	mg/l	0.5
15	Silver	mg/l	0.2
16	Tin	mg/l	2.0
17	Zinc	mg/l	2.0
18	Cyanides (total)	mg/l	1.0
19	Cyanides (free)	mg/l	0.2
20	Ammonia	mg/l	10.0 20.0 (electroplating)
21	Flourides	mg/l	20.0
22	Phenols	mg/l	0.5
23	Total Nitrogen	mg/l	15.0
24	Total Phosphorus	mg/l	5.0
25	Sulphides	mg/l	1.0
26	VOX	mg/l	0.1
27	Toxicity	To be determined on a case specific basis	
28	Temperature increase	°C	<3a*

***a** At the edge of a scientifically established mixing zone which takes into account ambient water quality, receiving water use, potential receptors and assimilative capacity. The effluent should result in a temperature increase of not more than 3°C at the edge of the zone where initial mixing and dilution takes place. Where the zone is not defined, use 0 -500 meters from the point of discharge.

Table 8.26 Sludge Disposal Permissible Limit

DRY SLUDGE (DS) GENERATION FROM WASTEWATER TREATMENT	
Parameters	Sludge Production Kg DS/tonne
Sludge (total)	200
Primary Treatment	
Mixing- sedimentation	80
Mixing-Chemical treatment+ sedimentation	150-200
Mixing chemical treatment+ Flotation	150-200

Source: NESREA [1]

Effluents from plating shops must be treated to standard specification before discharge into flowing streams. Most plants after treatment of the effluents recycle the water back to the plating tanks. The sludge is however sent to the smelters for recovery of valuable metals, and the residue is finally disposed in waste dumps using standard disposal methods.

Some processes used in wastewater chemical treatment include oxidation and decomposition of wastewater using electrolytic oxidation for cyanides, reduction process using sodium bisulphate to reduce hexavalent chromium to trivalent chromium, precipitation of metal ion, solubility, ion exchange and filtration.

Fundamentally wastewater treatment is to remove harmful substances from factory effluent. And the kinds of harmful substances include heavy metals, organic matter, nitrogen compounds, and phosphous compounds. The kinds of treatment methods available include physical treatment, chemical treatment, biological treatment and their combination. Wastewater treatment targets regulated substances like cadmium and cadmium compounds, cyanides and cyanide compounds, Pb, Sn, COD, hexavalent chromium and the compounds, and others. The fig.8.18 below shows a typical waste water treatment system.

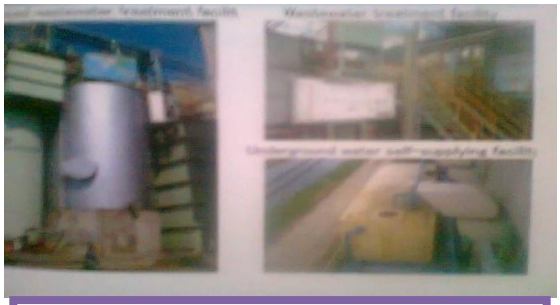


Fig. 8.18 Typical Waste Water Treatment System

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9.0 CHAPTER NINE
PACKAGING

9.1 Introduction

In the modern world, most of the goods are available in packages. The packaging protects and preserves the goods and offers convenience in transport, handling and sales also the goods in packaging should retain their original form, shape and properties. The packages should be convenient and attractive. A primary package is the one which comes in contact with the product. Therefore, the selection of material plays a vital role and it should be compatible with the product to be packed. The main function of a transport package is to give the required protection to the packaged commodity against incidental hazards during transportation, handling and storage.

The fundamental factors affecting the design of a package are:

- Product characteristics
- Modes of distribution; and
- Marketing considerations

Technical considerations which influence the package design are:

- Hazards during transportation, such as shocks and vibrations transmitted to the product during transportation by rail, road, sea, and air;
- Hazards during handling, such as impact due to drop, compression and puncture;
- Hazards during storage, for example, the greater the stacking height in a warehouse, the more the need for a strong and rigid package to withstand compression; and
- Hazards due to climatic changes.

The packaging should be best quality and be produced at competitive costs. Various materials used for packaging are plastics, metals, glass, wood and paper, including corrugated packaging. New mechanical packaging lines are employed and fully automated high-speed production systems are being introduced.

The traditional packaging materials like tin and glass are being forced to give way to plastics and paper. The whole concept is to give the consumer the most economical packaging material.

Traditional packaging materials like paper, wood and tin are increasingly becoming scarce and attempts are being made to substitute them by others. Plastics are now being used on a large scale for packaging due to their inherent advantages, such as light weight, strength, chemical resistance, flexibility, excellent barrier properties and aesthetic appeal. The use of plastics for packaging is increasing both in quantum and variety. A number of plastic raw materials are consequently available in various forms, such as films, sheets, pouches, bottles, jars, jerry cans, sachets and containers (rigid and flexible) of all shapes and sizes. These products are normally based on a single plastic material. For special applications more than one plastic raw material may be used co-extruded or laminated films, sheets and bottles based on two or more plastic materials extruded together are examples of such types.

The major drawback with plastics is migration of chemical constituents in the packaging material to the packed material due to intimate contact. Since there is always a possibility of transfer of a part of the plastic package to the contents, care should be taken to select so as to ensure that such transfer is at a minimum and the substances which do migrate from the package to the packed material are within limits and cause no toxic hazards, when consumed.

The ministry of health and family welfare has adopted under the Prevention of Adulteration Act (PAA) the standards on polyethylene, styrene polymers, polyvinyl chloride, polypropylene and monomers and have stipulated that plastics packaging for foodstuff should conform to the specifications. Similarly, standard have been formulated for finished containers namely blow-moulded HDPE containers (IS 10840:1986), flexible peaks for packaging vanaspati (IS 11355:1985), polyethylene pouches for liquid milk (IS 11805:1986), flexible packaging material for packaging of refined edible oils (IS 12724:1989).

9.11 Other I.S. Specifications

Plastic containers for reserve fuel (IS 7394:1984), polyethylene containers for transport of materials (IS 6312:1980), blow-moulded polyolefin containers up to 30 litres (IS 7408), plastic containers for pharmaceuticals (IS 7803), HDPE containers for liquid pesticides (IS 9754:1981), HDPE woven fabric for packaging of textile (IS 6899:1973), high density polyethylene (HDPE) woven sacks for packaging fertilizers (IS 9755:1985), polypropylene (PP) woven sacks for packaging cement (IS 11653:1086).

9.2 Plastic Fabric Packs

Fabric made from weaving of monoaxially oriented types of HDPE or PP is finding increased use vis-à-vis jute in a number of industries. This is primarily because of the superior chemical resistance and good strength of such fabrics. While fabric made from PP is commonly used in the world over, in India HDPE fabric is more popular. HDPE woven sacks are finding use in the packaging of a variety of products, such as fertilizers, food grains, pesticides, cement, wheat, flour milk powder and sugar. The same situation is obtainable here in Nigeria, a great use is made of HDPE woven sacks.

9.3 Metal Containers

The main metals used in packaging are mild steel sheet, tinplate, terne plate (mild steel coated with a tin or lead alloy), galvanized mild steel sheet, stainless steel, aluminium alloys and aluminium. Tin plate is the principal material for metal boxes and cans. Aluminium and its alloys have long been used for the manufacture of rigid containers, although not to the same extent as tin plate. Aluminium is also used in the form of foil (both alone and laminated to other materials) and for collapsible tubes. Metal containers, specially tin plate and aluminium are non-toxic and possesses excellent barrier properties and due to their basic strength they afford good protection to the contents.

Round open-top sanitary can (OTS) is a rigid metal container which can be hermetically sealed for packaging of thermally and non-thermally processed foods and drinks like fruit and vegetable products, synthetic beverages, meat and fish products, dairy products, instant coffee and instant tea. The

container withstands the temperature, pressure, vacuum, during processing and prevent entry of micro-organisms, (IS 2043 and 9396).

9.4 Glass Containers

Glass in spite of its fragility still holds its place as a choice material for packaging of variety of products. Glass is inert and does not react with most products. It is economical and can be readily formed into desired sizes and it is excellent for merchandizing and display purposes. The biggest users of glass containers are the manufacturers and processors of food, beverages, drugs, cosmetics, household products and industrial chemicals. The major drawback with glass containers is that they are not shock resistant.

9.5 Others

Jute and wood are the earliest packaging materials and are being used extensively in many applications. Here in Nigeria wide used was made of the two materials for packaging of harvested crops in the 50s to late 1980s particularly the jute bags which were produced in several cities in Nigeria including Jos – Plateau State were NASCO group of companies was producing them. They were widely used for packaging of grains. Wood containers are mainly used as transport containers, particularly for heavy machinery and engineering goods. Public awareness regarding conservation of forest is making consumer industry to go for alternate materials like, corrugated packaging, fibre board containers made from agricultural residues. Jute is mainly used for packaging grains, fertilizers and cement. Jute has been facing serious competition from plastics and multi wall paper sacks. The use of multi-wall paper sacks is however becoming less popular in Nigeria as was formally patronized by the cement companies most of whom are using HDPE bags today. Now improved jute bags with paper or plastic lamination are being increasingly used for packaging of milk powder and fertilizers.

“A package should save more than its costs”, is a simple but profound philosophy. Aseptic packaging is rapidly generating fundamental changes in the handling of many perishable foods like milk, juice and

other products. Aseptic packaging works on three fundamental principles: sterilization of packaging material, creation of a sterile environment while filling the product and production of packaging material which is hermetically sealed to prevent reinfection with aseptic packaging, distribution and storage are possible without refrigeration and the packs have a shelf-life of several weeks, during which vitamins and other nutrient values are maintained.

The long storage period at room temperature is made possible through Ultra High Temperature (UHT) treatment. In the case of milk, for instance UTH imparts a brief heat shock – about 140 degree Celsius – for – two to four seconds, killing bacteria and thereby maintaining sterility. Pasteurised milk needs to be refrigerated continuously, at not more than 8 degrees Celsius. This way it remains fresh for a few days. With UTH treatment and aseptic packaging, milk can be stored for several weeks at room temperature with flavour and quality maintained.

9.6 New Concepts in Packaging

Plastics are penetrating and invading in all directions, be it automobiles, agriculture, pharmaceuticals, fertilizers and processed foods. These have emerged as a means of substitution and complementation particularly in packaging. Plastics as a means of packaging are replacing all conventional materials. During the last decade newer concepts based on plastics packaging have appeared in the developed countries. A number of these have already entered the Nigerian market in certain applications. However, an array of these concepts has yet to come. It will be worthwhile to evaluate as to what extent these concepts would have relevance in Nigeria in promoting domestic and export packaging.

Plastics have become a dominating and dynamic means of packaging for the strength they possess. And hitherto their disadvantages, if any, are largely being controlled and diluted by the development of basic polymers or the blending of other materials.

The research work and development work of this type have made plastics as the most economical and prospective contender as the packaging means of tomorrow. These are the versatile properties of

plastics which have made them a universal means of packaging consumers have like them; producers and packers have opted for them since these are economical, lighter, formable, stackable, recyclable, mouldable, easily accepted on the filling, production and distribution lines, possessing conveniences in terms of opening, closing, disposal, easily and excellently printable, efficiently sealable and storable.

Further, the relative consumption of energy in cases of plastics is far less than glass, metal and other containers. It has been found that the relative cost differentials in case of plastics packaging are much lower when compared with corrugated boxes, tinplate containers, glass bottles etc.

Viewing from other perspectives the developments in plastics packaging have also taken place from the view-point of its structure and flexibility. Initially, the containers were rigid. Currently, the developments are towards lighter, transparent, see-through and multi-layers, with an emphasis on reduced use of materials with increased strength and improved packaging functions.

Plastics, copolymer of propylene, orientation of polyvinyl chloride, polyester, polypropylene; or very low density polyethylene, medium density polyethylene, nitrile resins, BAREX, etc. have made the plastics the most sought materials for packaging application. It will not be an exaggeration to say that the developments in plastics packaging have gone to multi-dimensional heights in terms of shapes of containers and closures, functions printing facility; reusability etc. Among the bioplastics, polyglycolic acid (PGA) has excellent barrier properties thus it’s one of the most promising new commercially available barrier polymers. Its precursor, glycolic acid, can now be produced via a natural metabolic route, the glyoxylate cycle.

Plastics have accepted the challenges faced by the production engineers, marketing professionals and environmentalist. Only recently, in countries like Sweden and Germany, there are certain controlled checks on the growth of plastics since these have reached the point of social and environmental threats. However, it must be conceded that the faults lie not with the plastics but to the level and rate of plastics consumption in packaging.

Horizontal development in plastics could be summarized as follows:

1. LDPE is used for the packaging of milk, soaps, detergent sealant and wrapping material. It is also used for packaging of textiles, meats, frozen foods, and horticulture products.
2. High density polyethylene finds applications made with the help of injection moulding, pallets, transport containers, bottle crates, other crates, flexible bulk containers, drums, blow moulded containers, films, sheets etc. Almost any products could be packed in the packages made of high density polyethylene.
3. Linear low density polyethylene, which possesses improved packaging properties finds applications almost in those lines where LDPE has been.
4. High molecular high density polyethylene is used for the packaging of flowers, foodstuffs, metal, fish, dairy products, cloths, books etc.
5. Polypropylene, which possesses more or less the same packaging properties in relation to HDPE, is used for the making of corrugated boxes, sacks containers, films, laminates etc. for the packaging of chemicals, foods, fruits and vegetables etc.
6. Plastics, especially polystyrene and ethylene in expended forms like cups, moulded structures etc. are used for the packaging of Ice-creams, processed foods, electronics etc.

Notable vertical development in plastics packaging could also be summarizes as follows:

1. PVC during the initial period was applied for the packaging of non-food product, basically for the reason it contained vinyl chloride monomer – a suspected cause for the cancer. Because of intensive research and development work, food grades PVC have been now developed, and these are now being used for the packaging of foods within acceptable rules. Further, orientation of polyvinyl chloride also enables PVC to be used for the packaging of liquid foods.

2. Newer plastics like Alathon have been developed. It is basically a high density polyethylene polymer, is an improved version which offers higher polymer properties, and at the same time reduced consumption of materials.
3. Barrier materials like ethyl vinyl alcohol, nylon modified, ethylene vinyl acetate etc. in the presence and in some cases without the presence of the layers are being used to make multi-layer films, laminates and bottles to improve their barrier properties as compared to that of glass.

9.6.1 Biopolymers

This review describes some of the most studied biopolymers which may have a great importance in the future packaging business. The aim is to cover recent developments with respect to their potential for use in the sustainable and green packaging industry. Especially the barrier properties are identified as key issues for effective utilization of bio-based materials.

Pectin

Pectin is a structural heteropolysaccharide found in the primary cell walls of terrestrial plants such as sugar beet. From a physico-chemical point of view pectin is an anionic polyelectrolyte, thus ionic interactions have a great impact on its film forming properties and behaviour in dispersions with e.g. nanoclays. Pectin films plasticized with glycerol and further incorporated with nanoclay (>98% montmorillonite) were prepared by casting onto Petri dishes. In order to ensure the sufficient delamination and nanosized structure of the nanoclay platelets, the powder was first dispersed in water using either ultrasonic treatment or high pressure fluidization. The model surfaces were prepared by spin coating onto silica surfaces from the aqueous dispersions after both pre-treatments. The high pressure fluidizer treatment produced an even and more homogenous layer of paralleled oriented nanoclay platelets with the narrower size distribution as compared to particles after ultrasonic

treatment. Thus, high pressure fluidizer treatment was selected as an efficient and easily up-scalable method to produce bio-hybrid nanocomposite dispersions. The resulting bio-hybrid nanocomposite films were totally greaseproof and also showed improved barrier properties against oxygen and water vapour . Recently, pectin solutions have been roll-to-roll flexo-coated with semi-industrial pilot-line onto argon/nitrogen plasma-activated oriented polypropylene (OPP) film. Plasma-activation was carried out in line to increase the surface energy of OPP film prior the coating with water-based pectin solution. Pectin was easily spread onto activated surface forming an even and smooth dry coating. Also other biopolymers, such as various starch grades and wood-derived xylan can be coated in a similar manner.

Starch

Starch films can be produced either by extrusion or casting. Plasticizers, such as glycerol, sorbitol or xylitol, are typically used for reducing the brittleness. At low glycerol concentrations both strain and strength decreased but above 20% glycerol concentration the elongation reached larger values. Effects of glycerol, sorbitol or xylitol on physical and mechanical properties of starch films are largest for glycerol and smallest for sorbitol. High contents of xylitol and sorbitol results in changes in physical and mechanical properties of films probably due to phase separation and crystallization. Crystallization can be prevented by using binary polyol mixtures as plasticizers. Water sorption and water vapour permeability are lower for the films plasticized with xylitol-sorbitol mixture compared to the films plasticized with glycerol-xylitol and glycerol-sorbitol mixtures at constant plasticizer contents. Oxygen permeability of the films is strongly dependent on the water content. At low humidity conditions the films are typically excellent barriers against oxygen transmission, but when the water content rises above 20% the barrier is mostly lost. The increased permeability was most likely due to increased polymer chain mobility, which facilitated the transport process. Oxygen permeability of starch films can be decreased by using below 21% of sorbitol. This behaviour was related to changes in secondary relaxations which are hindered because of the connections established between starch and sorbitol,

leading to decreased diffusion of oxygen molecules. For sorbitol contents above 21%, oxygen permeability increased slightly. Water produced a classic plasticising effect (an increase of oxygen permeability), but at low sorbitol content this is only moderate due to the effect of sorbitol itself. Compounding starch and glycerol with PCL (polycaprolactone) decreased the water vapour permeability of extruded films. Oxygen barrier properties however are impaired above 20% PCL concentration.

Chitosan

Chitosan, the β-1-4-linked polymer of 2-amino-2-deoxy-β-d-glucose, is prepared by the N-deacetylation of chitin, the second most abundant natural biopolymer after cellulose. Chitosan is soluble in dilute aqueous acid solutions and has been widely studied due to its good film forming properties. Chitosan can be used as such in cast-free standing film or it can be applied as a coating onto paper/board or plastic films. Chitosan dissolved in 1% acetic acid was applied onto copy paper by lab-scale bar coater and dried at 105˚C. Chitosan coatings clearly improved both the gloss and oxygen barrier properties of paper. The gloss value in the machine direction was increased as a function of added chitosan. Oxygen transmission rate at 0% relative humidity was decreased from >10,000 cc/m^2/day to 1.1 cc/m^2/day with 6.9 g/m^2 chitosan coating. In addition, the effects on the mechanical properties were positive, but not significant. The water vapour permeability of the paper increased as a result of the chitosan coating. Chitosan can also be immobilized onto NH_3- or CO_2-plasma activated polypropylene films by exploiting either carbodiimide or glutaraldehyde chemistries. Chitosan coatings made film surfaces hydrophilic and prevent clearly oxygen, carbon dioxide and ethylene transmission. Oxygen transmission rate at 0% RH decreased from 1500 cc/m^2/day to 27 cc/m^2/day with 1.8 g/m^2 chitosan coating. Barrier properties can be further improved by using nanoclays incorporated into chitosan. Nano-clay is mixed with chitosan and further dispersed using ultrasonic treatment and coatings are applied onto plasma-activated LDPE-coated paper by lab-scale coater. Also free-standing films are cast onto Petri dishes.

Bio-hybrid nanocomposite films and multilayer coatings had improved barrier properties against oxygen, water vapour, grease, and UV-light transmission. Oxygen transmission is significantly reduced under all humidity conditions. In dry conditions, >99% reduction and at 80% relative humidity almost 75% reduction in oxygen transmission rates is obtained. Hydrophilic chitosan lacks the capability of preventing water vapour transmission, thus total barrier effect of nanoclay containing films is not more than 15% as compared to pure chitosan.

Xylan

Xylan is alkali extracted from kraft hardwood pulp. It is almost as ubiquitous as cellulose in plant cell walls and contains predominantly β-D-xylose units linked as in cellulose. Xylan as such is not suitable for film formation due to its high internal cohesion, which results in fragile and fragmented films. Thus, xylan needs to be plasticized externally or internally. It can be further hydroxypropylated resulting in water soluble derivative with improved film forming properties. The inner plasticization with hydroxypropyl groups can be combined with external plasticization using glycerol or sorbitol. The biodegradability, high degree of bio-based raw materials, and non-food origin of hydroxypropylatedxylan (HPX) coatings and films make them an interesting option for food packaging. Coatings of aqueous HPX solutions containing glycerol and sorbitol were applied with a lab-scale bar coater onto a pigment coated board. 5% citric acid was used as a bio-based crosslinker to enhance the barrier properties. A crosslinked HPX coating demonstrated a good grease and mineral oil barrier as well as low oxygen transmission rate of 200 cm^3/m^2/day at 50% relative humidity. Water vapour permeabilities of the xylan coatings were slightly below that measured for the commercial biopolymer, polylactic acid (PLA), coating. Also the free standing HPX films plasticized with 10% and 20% of sorbitol had relatively low oxygen permeabilities at <75% relative humidity. In addition, fatty acid esters of hemicelluloses and cellulose have been coated successfully on paper/board. The coatings were hydrophobic and provided good grease and moisture barrier properties. The best water and water

vapour barrier was achieved with the cellulose derivatives esterified with the longest fatty acid. Benzyl ether derivatives of birch xylan with varying degree of substitution have recently been prepared. These derivatives are also hydrophobic and thermoplastic capable of forming free standing films from organic solvents. The paper sheets prepared from the esterified cellulose fibers showed high hydrophobicity. The barrier properties of xylan may be further improved through nanoclay reinforcement in aqueous medium. The nanoclay dispersions are mixed with the plasticized (glycerol) xylan, resulting in homogeneous and viscous coating solutions. Xylan-nanoclay dispersion is further coated onto paper by lab-scale bar coater. The coatings significantly enhance water vapour barrier properties.

Galactoglucomannan

The main hemicellulose in softwood is O-acetyl-galactoglucomannan (AcGGM). AcGGM has a main chain of 712 β-(1→4)-linked D-mannose and D-glucose with α-(1→6)-linked D-galactose moieties in various amounts. AcGGM is soluble in water and organic solvents. The solubility properties can be attributed to a high degree of acetylation in combination with a low molecular weight. Cast films have been produced with plasticizers such as glycerol, sorbitol and xylitol, and the bio-based polymers such as alginate and carboxymethylcellulose (CMC). The addition of plasticizers resulted in increased film flexibility and moisture sensitivity. With other bio-based polymers, the mechanical strength and resistance towards humidity increased.

Lignin

Lignin is one of the most abundant natural polymers, together with cellulose and hemicellulose. Softwood lignin has been esterified with tall oil fatty acid (TOFA) and applied with a lab-scale bar coater onto paperboard. The WVTR of the paperboard was reduced by 70% with a TOFA lignin ester double coating of 3.9 g/m^2. Also a decrease in oxygen transmission was observed for the TOFA lignin ester as well as the TOFA coated paperboard samples. The coating material did not affect the tensile strength of the paperboard. Esterification with palmitic and lauric acid chloride resulted in coatings with improved

moisture barrier properties. A significant decrease in water vapour transmission was observed, for example, 40 g/m^2/day for a paperboard coated with 10.4 g/m^2 hardwood kraft lignin palmitate. For all paperboard samples coated with lignin esters, a significant decrease in oxygen transmission rate was observed.

Cellulose Nanofibrils (CNF)

Cellulose nanofibrils (CNF), also referred to as nanocellulose are typically generated by mechanical grinding or high pressure fluidisation. CNF consists of very thin (~20 nm) and long (several μm) fibrils and in low concentrations of <2%, it forms a gel-like, transparent material which can be used for producing biodegradable and environmentally safe, homogenous and dense films. CNF can be produced from various raw materials.

Recently CNF films have been prepared from banana, sugar beet, hemp, softwood and hardwood pulps. Films were plasticized with 30% of sorbitol and they had some promising technical properties including grease proofness and high barrier against oxygen transmission especially at dry conditions. Lab-scale nanocomposite films of CNF, polyvinyl alcohol (PVA), and montmorillonite nanoclay were prepared via casting onto Petri-dishes. PVA matrices were further crosslinked with polyacrylic acid. Nanoclay provided an improved barrier properties against both water and oxygen transmission through the films. Permeability and adsorption were further reduced by crosslinking, while oxygen barrier properties were remarkably enhanced also at high humidity conditions. Recently, a semi-industrial roll-to-roll pilot-line has been utilized in production of high quality CNF films with excellent technical properties. The developed method is easily up-scalable and brings CNF film production a step closer to commercialization.

Modification towards Better Properties

In addition to incorporation of nanoclays, the barrier properties of biopolymers may be improved by chemical and physical crosslinking, or with surface treatments, such as grafting and coating. For example,

the plasma or heat induced oxidation/degradation can promote chain scission and crosslinking on surfaces. By heating the coatings over melting point and cooling them slowly back to room temperature, the coating density, morphology, crystallinity and spherulite size can be modified towards better barrier properties. Heat treatment at 200˚C induced irreversible hydrogen bonding to cellulose which improved both barrier properties and mechanical strength of CNF films. Chitosan-nanoclay bio-hybrid films have been successfully crosslinked with glutaraldehyde, genipin and glyoxal. Moisture sensitivity of films decreased as a result of crosslinking which led to improved barrier properties against water vapour and oxygen transmission at high humidity. Enzymatically crosslinked casein coatings have been applied onto co- 713 rona-treated PE film and board for improving the packaging related surface properties. Recently, the aqueous crosslinked PLA dispersions were coated onto board at pilot-scale. For decreasing the moisture sensitivity, the hydrophobic softwood galactoglucomannan films have been prepared by benzylation. Also styrene grafting of films based on unmodified AcGGM by plasma and vapour-phase treatments have been performed. Finally, lamination of an unmodified AcGGM film with benzylated AcGGM was also investigated in terms of water tolerance and oxygen permeability. Both surface grafting and especially the lamination method decreased the moisture sensitivity and improved the barrier properties. Recently, the enzymatically treated cellulose has been dissolved in a NaOH/ZnO solvent system and mixed together with poly (ethylene-co-acrylic acid) or poly (acrylamide-co-acrylic acid) polymers, in order to improve the properties and prepare homogeneous cellulose-based blends for films and coatings. Dissolved cellulose/acrylic acid copolymer-based blends performed well as coating materials on paperboard. All blends showed a good resistance against grease with 2 µm coating layer. In addition, cellulose/poly (ethylene-co-acrylic acid) coating showed improved water vapour and oxygen barrier properties as compared with neat dissolved cellulose coated paperboard. Plasma-activated biaxially oriented polypropylene (BOPP) films and paper substrates have been coated with hydrophobically modified chitosan solutions. Enzyme-catalysed grafting of octyl gallate and dodecyl

gallate to amino groups of chitosan increased surface hydrophobicity and improved oxygen barrier properties. Also CNF films have been enzymatically grafted with dodecyl gallate resulting in less hydrophilic coatings on paper. An easy method to improve hydrophobicity and oxygen barrier properties of CNF films at very high humidity is to use simple paraffin wax coating. The films were dipped into the melted wax and the excess wax was removed from the surface resulting in both improved water vapour and oxygen barrier as well as the high surface hydrophobicity.

Multilayer coatings of CNF and shellac have been deposited on the fibre based substrates using a lab-scale bar coater or a spray coating technique. Multi-layer system with CNF as a first layer and shellac as the top layer decreased both oxygen and water vapour transmission rates. Hydrophobization of the CNF film surface can also be achieved by chemical modification through silylation chemistry. After modification, the wettability of the film surface was drastically reduced. The hydrophobicity of the film did not only occur on the surface, but it was extended through the whole film, as verified by its significantly higher dimensional stability when submerged in water. Chemically surface-modified CNF has been used as reinforcement in cast polyvinyl alcohol (PVA) films. CNF was allylated and further epoxidised with hydrogen peroxide. The addition of 1 wt% epoxy-CNF enhanced the modulus, strength and crystallinity of the pure PVA film. In addition, the modified O-acetyl galactoglucomannans (GGM) have been recently utilized in modification of CNF film surfaces. Four GGM-block-structured, amphiphilic derivatives were synthesized using either fatty acids or polydimethylsiloxane as hydrophobic tails. It was found that the hydrophobic tails did not hinder adsorption of the GGM derivatives to cellulose, which was concluded to be due to the presence of the native GGM-block with high affinity to

cellulose. CNF films were further prepared and coated with the GGM derivatives, but only slight improvements in oxygen barrier properties at high humidity were obtained.

Thin Film Coatings and Multilayers

As single layer biopolymer films rarely can meet the industrial requirements set for packaging, the thin film coatings or integrated multilayer structures are necessary.

Sol-Gel

Sol-gel coatings are ceramic or organically modified hybrid materials formed from a colloidal solution (sol) that acts as a precursor. Typical process involves the hydrolysis of alkoxysilanes to produce hydroxyl groups, followed by polycondensation among these groups and residual alkoxy groups to form a three-dimensional polymeric network (or gel). The sol-gel coatings have been applied onto base paper by spraying resulting in the coating amount of 2 - 5 g/m^2. Coatings with a longer alkyl chain were found to decrease the wettability and absorption of base paper more efficiently. Sol-gel hybrid coatings applied with roll-to-roll pilot-line onto PLA laminated paperboard improved also other barrier properties. In addition, the atmospheric plasma pretreatment has been used to activate PE-coated paper prior to applying the sol-gel coatings. Sol-gels functionalised with long-chain hydrocarbon groups or amino groups were sprayed and cured by drying at 110˚C. Hydrophobic coatings containing long hydrocarbon chains were effective barriers against grease penetration whereas hydrophilic coatings with amino groups reduced oxygen transmission rates especially at low relative humidity.

Plasma activation clearly improved adhesion and performance of both coatings. Also hexamethyldisiloxane has been utilized as a siloxane precursor for the atmospheric plasma deposition of hydrophobic siloxane coatings on LDPE-coated paper and board. However, only minor improvements were obtained in water vapour barrier properties.

Atomic Layer Deposition (ALD)

Atomic layer deposition (ALD) technique is a surface-controlled layer-by-layer deposition process based on self-limiting gas-solid reactions. It is well suited to produce inorganic barrier coatings, such as Al_2O_3, SiO_2 and ZnO on various materials including synthetic and bio-based plastics and biopolymers such as PLA, PHB, pectin, galactoglucomannan and cellulose nanofibrils. Atomic layer deposited Al_2O_3 has

proven to be effective in enhancing the moisture and gas barrier properties of various films and coatings. With ALD ZnO coatings both barrier and antimicrobial properties of BOPLA and BOPP films were improved. PLA films were coated with 20 nm polyelectrolyte multilayer film made from sodium alginate and chitosan and additionally with 25 nm ALD Al_2O_3 layer. The double-coating was found to significantly enhance the water vapour barrier properties of the PLA film due to increased surface hydrophobicity. ALD, electron beam evaporation, magnetron sputtering and a sol-gel method have been used to deposit thin aluminum oxide coatings onto LDPE- and PLA-coated board. Increased barrier performance against moisture and oxygen permeation rates were observed with each technique. However, among the techniques tested ALD was found to be most suitable. Typically ALD coatings have been produced with slow batch processes. Recently, 30 - 40 nm Al_2O_3 barrier coatings were deposited onto cellophane, PLA and polyimide films with continuous roll-to-roll technique.

Multilayers

Based on the LCA analysis, the bio-based multilayer coating consisting of starch, nanoclay and inorganic nanolayer has been found favourable in terms of CO_2 emissions as compared to PET/aluminium coatings. In some cases the individual biopolymer layers may even be attached to each other using bio-based adhesives. As single layer CNF films have relatively weak moisture resistance, flexibility and zero sealability, the multilayer structures have been recently produced. CNF was first dispersion coated onto PET film and further extrusion coated with LDPE resulting in a 3-layer structure. PET/CNF/LDPE film had excellent technical properties which fulfilled both oxygen and water vapour barrier as well as sealability requirements of modified atmosphere food packaging. Demonstrator pouches filled with nitrogen were produced with the packaging machine and the oxygen concentration inside the packages was monitored as a function of time. As a result, CNF containing multilayer films performed better as compared to commercial 3-layer multilayer films containing EVOH barrier layer. The developed films could be used as

a packaging material for dry or low moisture content food products such as dry snacks, dried fruits, nuts, spices etc.

9.7 Packaging Systems

There are three major elements in any packaging operations and these include:

i) The Package: It should protect the product from environment, transportation and handling hazards. It should also preserve the product without deterioration during the expected shelf life. And most important it should convey necessary information such as quality, quantity, price, date of packaging and brand name to take full advantage of ''brand loyalty''.

ii) The Packaging Machinery: These machines should pack the product in required dosages without extensive variations, give the required output and be flexible enough to accommodate different pack sizes without major modifications.

iii) The Operating and Maintenance Personnel: People making the packaging machine, should have sufficient skills to operate and maintain the machinery at rated outputs, within normal allowable spoilage. There are problems of compatibility of the above three components especially in the case of mass produced items required high speed operations it becomes difficult to pinpoint responsibility in the case of a malfunction in the packaging line on either the packaging material or the machine or the personnel system packaging overcomes this problem because of a single supplier of packaging material and packaging machinery, with training being provided to the operators and maintenance personnel. The single supplier ensures compatibility of the above three elements by extensive trails at his end as well as that of the manufacturer-cum-packer.

9.7.1 Cekatainer Lined Carton System

The lined Carton-cekatainer-consist of a duplex board carton printed with the required designed and an inner heat-sealable liner glued to the carton provides mechanical strength and make the peak easy to

handle and distribute. It also provides excellent scope for decoration and multicolour printing. The heat-sealable liner provides physical, chemical and biological protection i.e it protects the contents from losing or absorbing moisture, from loss of aroma or odour pick-up, from oxidation and from the effect of light. Cekatainrs are characterised by flexibility and economy. They are also hygienic and pilfer proof. There is flexibility in varying the carton and liner material independently of each other. There is flexibility of formal i.e cartons length , width and height can be varied within wide limits. There is also flexibility in carton construction.

9.7.2 Vacuum Packaging

A vacuum package offers a very special kind of protection to the product. This protection is due to the fact that the product is hermetically sealed in a vacuum in a film pouch. The decisive factor here is that there is no more oxygen inside the package. For foodstuffs this means that the growth of microorganisms is greatly inhibited, and this in return increases a products shelf life considerably. Vacuum package products are safely protected from spoilage, dehydration, changes in flavour, contact and loss in weight. They are presented hygienically and attractively in self-serve packages. Pure vacuum packs are pressed together by the outside air pressure.

9.7.3 Paper Conversion

Paper conversion is the process of converting paper into useful products which have various end uses especially packaging. Packaging is a multi-dimensional, multi-disciplinary, dynamic art, Science and technology, to protect, preserve and present the product. Paper conversion machinery is suitable to produce paper cores, paper tubes, paper cores, composite containers etc. Paper core is a vital packaging material in the textile industry and is used in winding of yarns paper tube and cores have various end uses such as filament yarn winding, BOPP film winding, paper red winding etc., composite containers are used for the packaging of innumerable products like spices, pharmaceuticals, food products, motor oils etc.

9.7.4 Uncasers and Case Packers

Fully automatic uncasers and case packers can handle speeds of up to 480 bottles per minute, with half depth cases. Uncasers can handle case patterns up to 4 wide in 4 * 3, 4 * 4, and 4 * 6 configurations. They operate by the principle of continuous moving V-belts, which are guided to firmly hold the bottle and lift them from the case, before delivering them on a moving conveyor, to the bottle washer. The entire lifting mechanism is mounted on two supporting structures.

The new ranges of uncasers have several advanced and innovative features over the uncasers available ealier in the markek. The most remarkable development has been the quick belt change. In the older machines in the event of a belt snapping, the replacement took a quarter of a shift to change, this can now be done in minutes.

To accommodate the differences of height from one bottle to another in product change, all which is required to be done is the loosening of 8 bolts and jacking. This is accomplished conveniently through a gear box in a few minutes. Safety has been incorporated into the design. In the event of a down the lines hold up, a micro switch activates a timer, that stops the machine after a fixed time interval, and a pneumatically operated roller prevents any more cases from entering. In the event of a bottle being stuck in the case there are rollers that holds the case down, and further vertical hanging plates that remove the bottle out of the case. The in feed rubber conveyor runs on spring mounted rollers that prevent locking of the case. Case packer places the bottle back in the case, after filling and capping. They work with the same class end bottle configuration and perform exactly the opposite function of the un-casers, and operate between 18 and 21 cases a minute.

This machine consist of four min parts, the bottle in-feed conveyor and shuffler, the bottle stopper and drop mechanism, these two being on the top. Below is the case in-feed conveyor and stop mechanism, and finally the case elevating system. This is a complex and highly sophisticated machine that is user-friendly, and easy to handle. The bottles arrive on four chins and are diverted with a S profile guide to

prevent excessive bottle pressure build-up of the shuffler. Shuffling is done by an eccentric can and a pneumatic system that arranges bottles in four rows. Besides driving the monotony out of the job and employing several people, these machines require just the normal maintenance.

9.8 Packaging Machinery

Packaging machinery can be broadly classified into five categories:

a) Conversion machinery for production of packaging such as a tin can manufacturing line.

b) Usage machinery for carrying out the operation of actually packing the product in the pack.

c) Testing equipment for testing various properties of packing raw materials as well as out-line quality control during packaging.

d) Auxiliary equipment for packaging accessories such as labelling machines for glass bottles or gum tape dispenser for corrugated boxes, collators for unitising retail packs; and

e) Package handling equipment such as conveyors and elevators.

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