METHODS FOR EVALUATING THE CONDITION OF PLATINUM RESISTANCE THERMOMETERS

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Abstract – Standard platinum resistance thermometers (SPRTs) and secondary platinum resistance thermometers (PRTs) are fragile and are often inadvertently damaged by severe conditions or even routine use. It is very important for a user to know what kind of damaged has occurred, and whether it is possible to restore the thermometer to a nearly normal condition. In this paper, methods for evaluating the condition of SPRTs and PRTs are presented and discussed.

INTRODUCTION

Standard platinum resistance thermometers (SPRTs) and secondary platinum resistance thermometers (PRTs) are widely used as standard or reference thermometers to calibrate other thermometers and to measure temperature precisely in temperature laboratories. The thermometers are sent to upper level calibration laboratories for routine calibration. Often, the calibration interval for a reference thermometer is one year. Applications require PRTs or SPRTs to be sufficiently accurate and operating properly. Using thermometers that have unstable or uncharacteristic resistances produces unsatisfactory or invalid results, with possibly very costly consequences. PRTs are fragile and are often inadvertently damaged by severe conditions or even routine use. Unless there is a system in place for frequently evaluating the condition of PRTs, loss of accuracy, when it occurs, may be unrecognized. It is important for quality assurance that all thermometers be tested regularly. There are convenient methods available for this [1].

Upon investigation of re-calibration results of SPRTs and PRTs, along with the feedback provided by customer services, it was found that most SPRTs and PRTs that did not pass calibration were damaged physically during transportation, daily application, or handling. When a thermometer has been found to be damaged or is inaccurate, it is also important to be able to discern the cause so it can be avoided in the future, since it is expensive to replace and recalibrate PRTs, especially SPRTs. Knowing what kind of damaged has occurred, it might even be possible to restore the thermometer to a nearly normal condition. We have observed many SPRTs and PRTs pass calibration after adequate annealing.

Useful methods of evaluation tell when a PRT or SPRT has lost accuracy, indicate what kind of damage it has received, what the likely causes of the damage are, and what actions should be taken. Based on our research and experience, we propose some methods for evaluating PRTs and SPRTs, which will be presented in this paper. These involve a few simple measurements and analysis of these in comparison with previous measurements. Research and testing from which these methods originate will be explained. Interpretations of possible measurement results are discussed, and recommended actions based on the results are proposed. These methods are useful not only in the evaluation of SPRTs and PRTs, but may also be applied to industrial platinum resistance thermometers (IPRTs).

CONSTRUCTION OF SPRTS AND PRTS

SPRT sensor construction

The International Temperature Scale of 1990 (ITS-90) states that “an acceptable platinum resistance thermometer must be made from pure, strain-free platinum” [2]. The platinum wire used for sensors is obtained “hard drawn”, as it is somewhat easier to handle in this condition. It is annealed after the resistor is formed. For 2.5-ohm, 25-ohm, and 100-ohm SPRTs, the sensor wire is made into a coil first, and then carefully wound onto a fused quartz glass cross support. For 0.25-ohm SPRTs, the platinum wire is wound onto the support directly. The support is well designed to keep the sensor wire strain as low as possible during thermal expansion and contraction, vibration, and mechanical shock. After the SPRT is made, the sensor has to be fully annealed to remove strain.

PRT sensor construction

The sensor in a secondary PRT adopts a partial strain free design [3]. The sensor wire is first wound into a small-diameter coil. The coil is then wound onto the fused-quartz-glass cross support, alumina spool, or inserted into a four-bore alumina tubing. A special powder mixture is usually filled into the sensor capsule to support the element wire to protect the element from mechanical shock. A powder is chosen that will not contaminate the platinum and is specially mixed not only to protect the element from mechanical shock but also to enable the platinum sensor wire to expand and contract as freely as possible. Due to this compromise design, the stability of a PRT is somewhat poorer than that of an SPRT, but its ability to handle mild mechanical shock is much better.

CAUSES OF FAILURE

Mechanical shock

Upon investigation of service records of SPRTs and PRTs, the primary cause of drift observed in SPRTs and PRTs has been improper handling. Being fully annealed, the platinum wire is relatively soft. Particularly with SPRTs, the sensor coils can easily move and touch adjacent coils, causing a short circuit, as can be seen in the examples shown in Figure 1. Here, one sensor was damaged by mechanical shock during shipping and handling, and the other was damaged by vibration.

This sensor was damaged by shock during shipping and handling

This sensor was damaged by vibration. Notice shorting of coils.

Figure 1. Shorted sensors due to mishandling

In most cases where an SPRT experienced moderate mechanical shock, the sensor coils appear normal. But there is strain induced in the sensor wire that causes significant change in resistance. Mechanical shock can be incurred by even the slightest tap to an SPRT while inserting or removing it from an instrument. Vibration during transport can also be a cause of mechanical shock. Even when great care is taken, an SPRT may still be inadvertently subjected to some mechanical shock. Annealing the SPRT can eliminate most of the strain caused by minor shocks and restore the resistance close to its original value.

Contamination

It is well known that a fused-quartz-sheathed SPRT becomes contaminated in a metal block containing base metals (such as nickel, iron, or copper) when exposed to temperatures above 850°C [4] [5] [6]. Energetic atoms of metal migrate through the silica sheath and into the sensor, reducing the purity of the platinum wire. This causes an increase in the resistance of the sensor, as seen by its value at the triple point of water, R(tpw). It also decreases its sensitivity to temperature, observed as a lower ratio of resistance between the melting point of gallium and triple point of water, W(Ga). With excessive contamination, W(Ga) may be reduced to the point where it no longer satisfies the requirements of ITS-90, which specifies that W(Ga) be at least 1.11807. Contamination cannot be reversed.

In literature it is suggested that a fused-quartz-glass SPRT not be exposed to a base metal above 500°C. Our own research shows that a fused-quartz-glass SPRT is generally not susceptible to contamination from a base metal until about 660°C [4]. When it is necessary to anneal an SPRT or PRT at 660°C or higher, a graphite or alumina block should be used instead of metal to avoid contamination [5]. An alternative might be to use a platinum foil shield surrounding the thermometer in the metal block, but this can be expensive.

Oxidation

In the 1970s, Berry discovered platinum oxidation effects within the range of -40°C to 500°C [7] [8]. A three-dimensional (3d) form of PtO_2 will grow on a thermally cleaned Pt wire in as little as 5 kPa of O_2 in the temperature range from about 300 to 500°C, and a two-dimensional (2d) form of Pt oxide will grow in as little as 0.1kPa of O_2 in the range from about -40 to 300°C, approximately. The resistance of platinum wire increases as part of its cross-sectional area is replaced by a poorly conducting oxide film.

Resistance drift occurring at lower temperatures, in the absence of mechanical shock, is mainly caused by oxidation. Oxidation can be largely reversible as it tends to dissipate at temperatures above 500°C. The R(tpw) of an SPRT or PRT can increase or decrease as the platinum oxide grows or diminishes. The oxidation effect that occurs at certain temperatures is very repeatable with a fused-quartz-glass SPRT. Oxidation in a metal-sheathed SPRT or PRT is less repeatable and diminishes over time because oxidation of the sheath metal gradually removes oxygen from the gas around the sensor [9].

Devitrification of the fused-quartz glass sheath

Devitrification of the fused-quartz glass appears as milky white corrosion on parts the sheath, as shown in Figure 2. It is caused by the chemical reaction of contaminants eating away at the surface of the glass at higher temperatures, particularly above 500°C. Devitrification generally will not affect the resistance characteristics of an SPRT, but it can reduce the mechanical integrity and lifetime of the instrument, and in the least it is unsightly. Once it occurs, it cannot be eliminated. But it can be avoided with reasonable care. The SPRT must be kept clean. The sheath should never be touched by bare skin, which contaminates the surface with oils and salts that quickly lead to devitrification when heated. Gently cleanse the sheath of the thermometer regularly with pure ethanol alcohol and a clean soft towel, especially prior to operation at temperatures above 500°C.

Figure 2: Devitrification of a fused-quartz glass sheath

Gas leakage

An SPRT or PRT must remain well sealed, with the proper dry gas mixture inside the sheath to protect the sensor and supporting materials. If the sheath seal leaks, moisture from the outside air enters the sheath and reduces the resistance of the insulating materials. This results in lower apparent resistance of the sensor and significant measurement error, especially when operated at low temperatures [5].

Another problem with seal damage is that outside air, which contains a relatively high concentration of oxygen, enters the sheath. This causes excessive platinum oxidation and degraded stability. An SPRT that has a leaky seal might possibly be repaired by the manufacturer if the problem is recognized early.

Grain growth of platinum

If an SPRT or PRT is used at high temperatures or annealed for long periods of time, the grain size of the sensor platinum will increase. This causes the wire to gradually lose structural strength and its resistance to become less stable. The R(tpw) will continually decrease as grain sizes increases. This phenomenon is not reversible. It is best to avoid it by operating the thermometer at temperatures no higher and for no longer than is necessary.

ANNEALING

Annealing is a recommended procedure that usually can reverse effects of minor strain and oxidation in an SPRT or PRT and restore performance. It involves heating the thermometer to a high temperature and holding it there for a period of time. Because of susceptibility to further oxidation, performance of an SPRT or PRT may degrade if it is annealed at a temperature below about 450°C. The annealing temperature should be at the maximum operating temperature of the thermometer, preferably between 550°C to 660°C if possible. It is suggested that the initial annealing period should be four hours. The R(tpw) should be measured before and after annealing. If the annealing temperature is higher than 500°C, it is recommended to finish by gradually reducing the temperature to between 480°C and 500°C at a rate of 1.8°C per minute, and then remove the thermometer from the annealing furnace.

The block in the annealing furnace should be of a non-contaminating material such as graphite or alumina rather than a base metal. The thermometer sheath should be carefully cleaned with ethanol before it is inserted into the annealing furnace.

METHODS OF EVALUATION

SPRTs and PRTs should be regularly tested to check for damage or adverse effects that degrade accuracy. Evaluation can be based on comparison results from simple measurements. Required equipment includes a non-contaminating annealing furnace, a resistance measurement instrument such as a bridge or Hart Scientific model 1590 Super-Thermometer, a triple point of water cell and its maintenance bath, a melting point of gallium cell and its maintenance device, and/or other fixed-point cells.

The evaluation relies on observation of the thermometer's R(tpw). As part of the calibration quality assurance, the R(tpw) of an SPRT or a secondary PRT should be measured regularly and tracked [1]. If it is found to have drifted, further examination is needed. Ideally, the W(Ga) should then be measured. If the melting point of gallium is not available, other fixed-point cells, such as tin or zinc, may suffice.

With metal-sheathed SPRTs and PRTs, the insulation resistance can be checked by measuring the resistance between the sheath and any of the leads with a megohmmeter after the thermometer has been exposed to 0°C or lower for some time and then returned to room temperature. If the insulation resistance is lower than that specified by the manufacturer, the seal might be compromised and the thermometer should be repaired. With a fused-quartz-glass SPRT, insulation resistance cannot be measured directly. However, moisture can be detected by inserting the SPRT into a cold bath or container of crushed dry ice for a few hours and looking for condensation that appears inside the sheath.

Following are possible trends that might be observed, with interpretations given.

R(tpw) increases slightly, W changes little

This is common with SPRTs and PRTs. It is the result of platinum oxidization or slight mechanical shock. It is corrected by annealing. An example of this case is shown in figure 3. With an SPRT, it is recommended that R(tpw) be monitored and the thermometer annealed when it drifts over 2 mK.

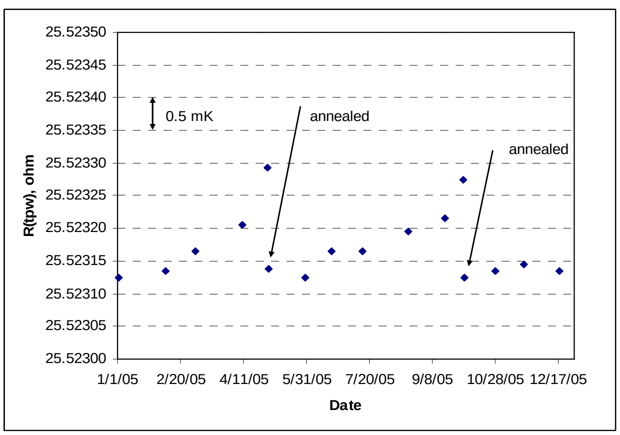

Figure 3: R(tpw) recovery through annealing

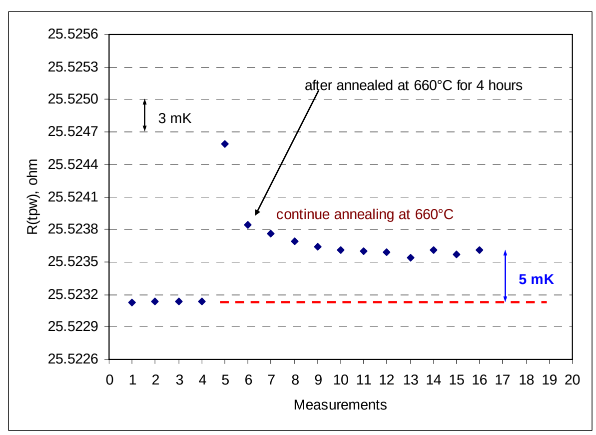

Figure 4: R(tpw) partial recovery through annealing

R(tpw) increases significantly, W changes little

The thermometer might have experienced severe oxidation, or the sensor wire has been physically damaged, probably by mechanical shock. If the R(tpw) is restored by adequate annealing, the cause was oxidation, and the thermometer can still be used. If the R(tpw) only increases more after annealing, the sensor is damaged and the thermometer should no longer be used, as it is likely to continue to be unstable.

R(tpw) increases slightly, W decreases slightly

This can be the result of mechanical shock or slight contamination. After annealing, if the R(tpw) is recovered, the cause is mechanical shock; otherwise, it is contamination. In the case of mechanical shock, the thermometer can continue to be used, but greater care sure be taken to avoid further mistreatment. In the case of contamination, the damage is irreversible. It is important to find the root cause of the contamination so it can be avoided in the future. A slightly contaminated thermometer might still be usable, but re-calibration is recommended.

R(tpw) increases significantly, W decreases slightly

This is usually caused by severe mechanical shock that has strained the sensor wire. The R(tpw) might be partially restored by annealing. An example is shown in figure 4. The thermometer should to be re-tested for stability. Even if it appears stable after annealing, it should be re-calibrated. It may be usable, but the accuracy might be slightly degraded. Take measures to prevent further mechanical shock.

R(tpw) increases significantly, W decreases significantly

The thermometer has probably received significant contamination. The R(tpw) will only shift more through annealing. Find the cause of the contamination and check if other thermometers have also been contaminated. Results of contamination are shown in Figure 5. If further contamination is avoided and the thermometer appears stable and the W(Ga) still meets the requirements of ITS-90 [2], the SPRT should still be usable, but re-calibration is necessary.

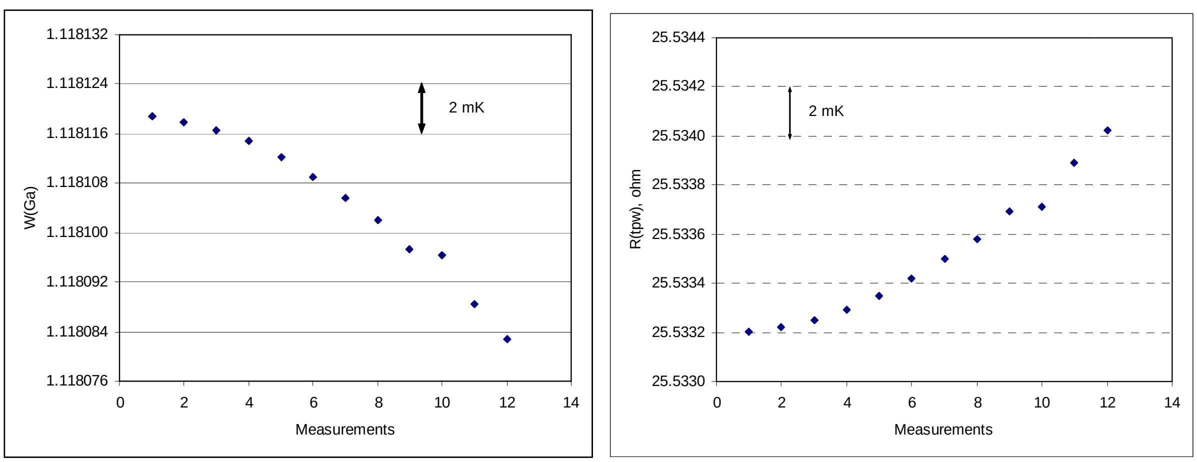

Figure 5: Contamination of an SPRT

R(tpw) decreases significantly, W increases

The sheath of the thermometer might not be properly sealed, allowing moisture to seep in. Check for reduced insulation resistance or condensation inside the sheath as explained previously. If the seal is questionable, the SPRT should be returned to the manufacturer for examination.

R(tpw) decreases significantly and is unstable

This is typical behavior when there is a short circuit between sensor coils caused by severe mechanical shock. With a fused-quartz glass SPRT, the damage might be visible with a magnifying glass, as seen in Figure 1, but it is often less visible. An SPRT in such condition is no longer usable.

R(tpw) decreases continuously with annealing

This is likely caused by grain growth of the sensor platinum. The thermometer might still be usable, but stability could be degraded and it will be more sensitive to mechanical shock. Avoid further use at high temperatures.

SUMMARY

When a thermometer has been found to be damaged or is inaccurate, it is also important to be able to discern the cause so it can be avoided in the future, since it is expensive to replace and recalibrate PRTs, especially SPRTs. Convenient evaluation methods were presented and discussed. Knowing what kind of damaged has occurred, it might even be possible to restore the thermometer to a nearly normal condition. Useful methods of evaluation tell when a PRT or SPRT has lost accuracy, indicate what kind of damage it has received, what the likely causes of the damage are, and what actions should be taken. These methods are useful not only in the evaluation of SPRTs and PRTs, but may also be applied to industrial platinum resistance thermometers (IPRTs).

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