Experimental Study of Different Filling Gases on the Stability of Metal-Sheathed Standard Platinum Resistance Thermometers

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Abstract. There is a trade-off between the oxidation effect and element contamination in metal-sheathed standard platinum resistance thermometers (MSPRTs). Excessively high O_2 partial pressure causes the platinum sensor to oxidize, and excessively low O_2 leads to sensor contamination. The oxygen content in a thermometer may become unknown after a period of operation due to slow oxidation of the metal sheath and consequent loss of oxygen in the MSPRT. This can significantly affect the thermometer's performance. Our recent research has shown that a thermometer may eventually become contaminated due to a deficiency of oxygen surrounding its element. In order to research this phenomenon and improve the stability of MSPRTs, ten MSPRTs were specially manufactured for testing. In this paper, the construction of these MSPRTs is described. A series of experiments and their results are presented. Based on the experimental results, a feasible solution (having the element sealed separately from its sheath) is put forward. This solution can resolve the conflict between the oxidation effect and element contamination and improve the long-term stability of MSPRTs. The R_{tp} and W(Al) stabilities of the MSPRTs with this new design can be as good as 1 mK and 2 mK respectively after operation at high temperature over 1000 h.

INTRODUCTION

Metal-sheathed standard platinum resistance thermometers (MSPRTs) are widely used as references to calibrate various temperature probes, particularly in secondary calibration laboratories. In some cases, MSPRTs are chosen over fused silica SPRTs because of their apparent ruggedness. However, our research found that there are more factors that affect the stability of MSPRTs than affect the stability of fused silica SPRTs. One of the most important factors was loss of oxygen in the thermometer's sheath due to slow oxidation of the metal. The thermometers may eventually become contaminated after long-term operation at high temperatures. The resistance at the triple point of water (R_{tp}) drifted as much as the equivalent of 10 mK after every 100 h of operation at 675°C when the thermometers began to be contaminated.

Research done by Berry (NRC) shows that the O_2 component in the filling gas is very important to the stability of an MSPRT [1,2]. The magnitude of spurious resistance changes caused by platinum oxidation is seen to vary widely among MSPRTs. At the same time, contamination of the element can occur when the oxygen partial pressure is too low. Usually, the element of an MSPRT is not sealed separately from the metal sheath [2,3]. The oxygen partial pressure in the element can increase or decrease with the change of the oxygen content in the metal sheath. In order to obtain good resistance stability in an MSPRT in the range 0 °C to 500 °C, the oxygen partial pressure should be kept low to reduce oxidation of the platinum sensor. At the same time, the oxygen partial pressure should not be allowed to fall below 0.1 kPa if the thermometer is to be used near or above 630 °C, since there is evidence that contamination of the platinum sensor can occur at the higher temperatures. However, there is the possibility of significant O_2 loss during annealing of these thermometers at 660 °C after being sealed, and this loss can vary among thermometers. The oxygen content in a thermometer may be unknown after a

period of operation. This limits the resistance stability of the thermometer over the full range from 0 °C to 660 °C. Berry gave a method to solve this problem [2] by suggesting that a valve be installed on the thermometer to allow the oxygen to be replenished periodically. However, this would be very difficult for most users to do.

To improve the stabilities of Hart MSPRTs, we have to resolve the conflict between the *lower* oxygen partial pressure needed to reduce the oxidation effect below 500 °C and the *higher* oxygen partial pressure needed to protect the sensor from contamination near or above 630 °C. Recently, a series of investigations to improve the stabilities of Hart MSPRTs has been in progress in our primary standards laboratory. Ten special MSPRTs were made for this investigation—all constructed using the same design. The elements of eight of the MSPRTs were not sealed from the metal sheaths, to allow the filling-gas mixture to flow in and out of the elements within the sealed sheaths. Four different filling-gas mixtures with different oxygen contents were put into these eight MSPRTs. The elements of the remaining two MSPRTs were sealed from the metal sheaths so that changes in the oxygen content in the sheaths would not cause changes to the oxygen partial pressure in the elements.

Each of the ten MSPRTs was tested for stability at the triple point of water and occasionally at the freezing point of aluminum. The operation time of several of the MSPRTs was nearly 2000 h at 675 °C. During this period, the oxidation effect at the temperature of the freezing point of tin (231.78 °C) was measured after every 100 h exposure at 675 °C. In these tests, we tried to measure the effect of the oxygen content on the stabilities of the MSPRTs when the elements were not sealed from the sheaths versus the stabilities of the MSPRTs with sealed elements. The primary aim of these tests was to determine whether or not using the sealed element design can resolve the conflict between the different requirements for oxygen contents below 500 °C and above 630 °C and ultimately improve the stability of MSPRTs.

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 300 to 500 °C approximately, and a two-dimensional (2d) form of Pt oxide will grow in as little as 0.1 kPa of O_2 in the range from –40 to 300 °C approximately [2]. As found in our calibrations, Hart MSPRTs showed 2d oxidation effects were more significant than 3d. The reason is that the oxygen partial pressure in the Hart MSPRT was controlled at a relatively low level. Therefore, for the purpose of comparing oxidation effects, we chose a test temperature of 232 °C. Two MSPRTs with sealed elements were also tested at 232 °C, 350 °C, and 420 °C to verify the thermometers' performance.

THERMOMETER STRUCTURE

Ten special MSPRTs were manufactured for this investigation. The structure of the element of the thermometer is shown in Fig.1. All parts used in the thermometer were carefully cleaned and fired before assembly. Each thermometer has a resistance of 25.5±0.5 Ω at 0.01 °C. The sensor wire was first wound into a small-diameter coil. The coil was then wound bifilarly onto the alumina spool support and the coil ends were welded to the 0.3-mm-diameter lead wires. The thermometer utilizes a four-terminal construction to eliminate lead resistance errors. A platinum protection capsule is used to shield and hold the resistance element. A thin insulation tube between the sensor spool support and the platinum capsule protects the sensor wire from shorting to the platinum capsule. For research purposes, the elements of eight of the thermometers were not sealed, thus allowing the filling-gas mixture to flow in and out of the element capsule. The elements of two thermometers were sealed permanently using a special coating glass. Before the element was sealed, a mixture of pure gases, including oxygen, was put into the element at high temperature. The element was hermetically sealed under a known pressure. The thermal expansion coefficient of the seal of the element is close to that of platinum to prevent the seal from cracking after thermal cycling.

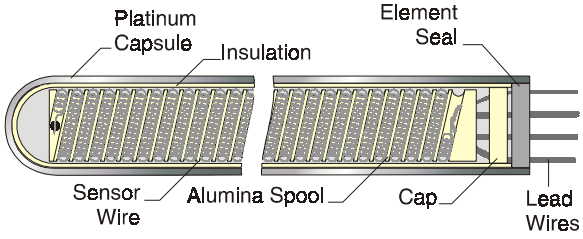

FIGURE 1. Structure of the element

A 5.5-mm outside-diameter Inconel sheath encases the element and leads with a gas mixture atmosphere (Fig. 2). In order to obtain more reliable test results for the oxidation effect, the Inconel sheath was pre-oxidized for a long time. For the two sealed elements, the gas mixture includes 9% O_2. For the eight open elements, four kinds of filling-gas mixtures, including 6% O_2, 9% O_2, 12% O_2, and dry air, were put into the sheath at high temperature. The sheaths were

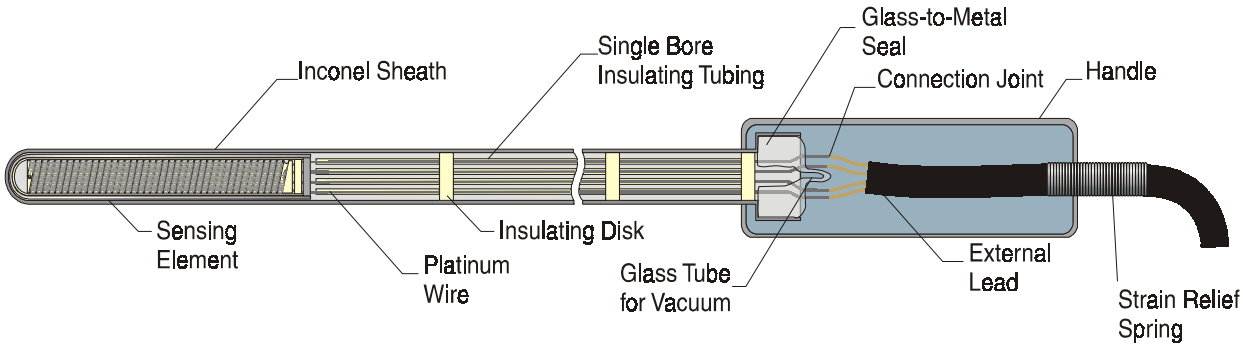

FIGURE 2. Structure of the thermometer

hermetically sealed using a glass-to-metal seal under a known pressure. The temperature non-uniformity of the furnace within 100 mm above its bottom is less than 1 °C at 660 °C. The furnace temperature decreased along the MSPRT stem to about room temperature. A piece of glass tubing extended from the glass-to-metal seal for pumping and filling with the gas mixture. This glass tube can easily be re-opened and re-sealed. By connecting this glass tube to a vacuum and filling system, the MSPRTs could be filled and the gas mixture changed.

The four thermometer leads were insulated by thin-walled single-bore alumina tubing separated by alumina disks. The junctions between the platinum leads and the external copper leads were designed to minimize thermal EMFs generated by the temperature differences.

EXPERIMENT RESULTS AND DISCUSSION

All ten MSPRTs were tested at the triple point of water after every 100 h of annealing at 675 °C until the MSPRTs showed that they were stable enough to satisfy the experiment. Whenever the oxygen contents in the MSPRTs decreased after the thermometers were operated at 675 °C, the MSPRTs were opened and the proper gas mixture replaced before the next experiment was started. This was to guarantee that the MSPRTs had the right oxygen contents in the filling-gas mixture before the experiments, especially for the MSPRTs with open elements. The R_{tp} drifts of the MSPRTs were less than the equivalent of 0.5 mK after 100 h annealing at 675 °C. After annealing or operation at 675 °C, the MSPRTs were cooled down to 480 °C at a rate of 1.9 °C/min first, and then they were taken out of the furnace. All of these MSPRTs met the ITS-90 ratio criteria.

All resistances were measured using a Guildline DC automatic bridge (Model 6675). The expanded uncertainty for the measurement of the ratio of two resistances was less than 2×10^{-7}.

Stability Tests in MSPRTs with Different Filling-Gas Mixtures

MSPRTs were made with four different filling-gas mixtures with O_2 contents as follows: thermometers S/N 60 and S/N 61, 6 % O_2; S/N 62 and S/N 81, 9 % O_2; S/N 68 and S/N 69, 12 % O_2; S/N 67 and S/N 70, dry air. The elements of these MSPRTs were not sealed

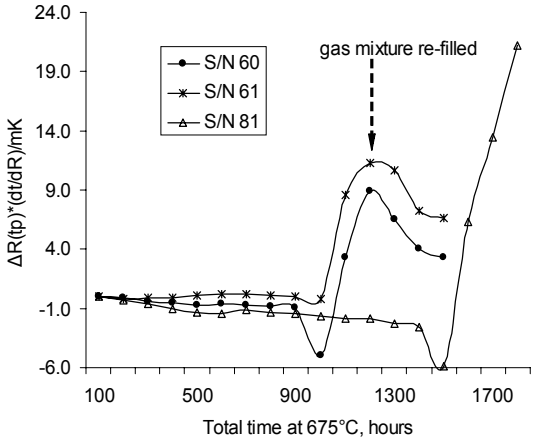

FIGURE 3. Stability test of MSPRTs with open elements and different filling-gas mixtures.

The R_{tp} drift of all MSPRTs was less than the equivalent of 2 mK after 900 h at 675 °C. However, the R_{tp} of thermometers S/N 60 and S/N 61 (6 % O_2) went up suddenly after 1000 h at 675 °C, as shown in Fig. 3. After we checked the resistance ratios at the freezing point of aluminum, W(Al), we found W(Al) decreased significantly. Further exposure at 675 °C caused the R_{tp} to increase more. This phenomenon indicated that the elements of thermometers S/N 60

and S/N 61 were contaminated significantly after 1000 h exposure at 675 °C. The cause of the contamination was that the oxygen partial pressure in the MSPRTs dropped too low as a consequence of the oxidation of the Inconel sheath at high temperature. In order to verify this cause, thermometers S/N 60 and S/N 61 were opened and re-filled with the original gas mixture. The R_{tp}'s started to recover toward their original values. The reason why the R_{tp} of the thermometers first went down and then went up after the MSPRTs started to become contaminated is not known (Fig.3).

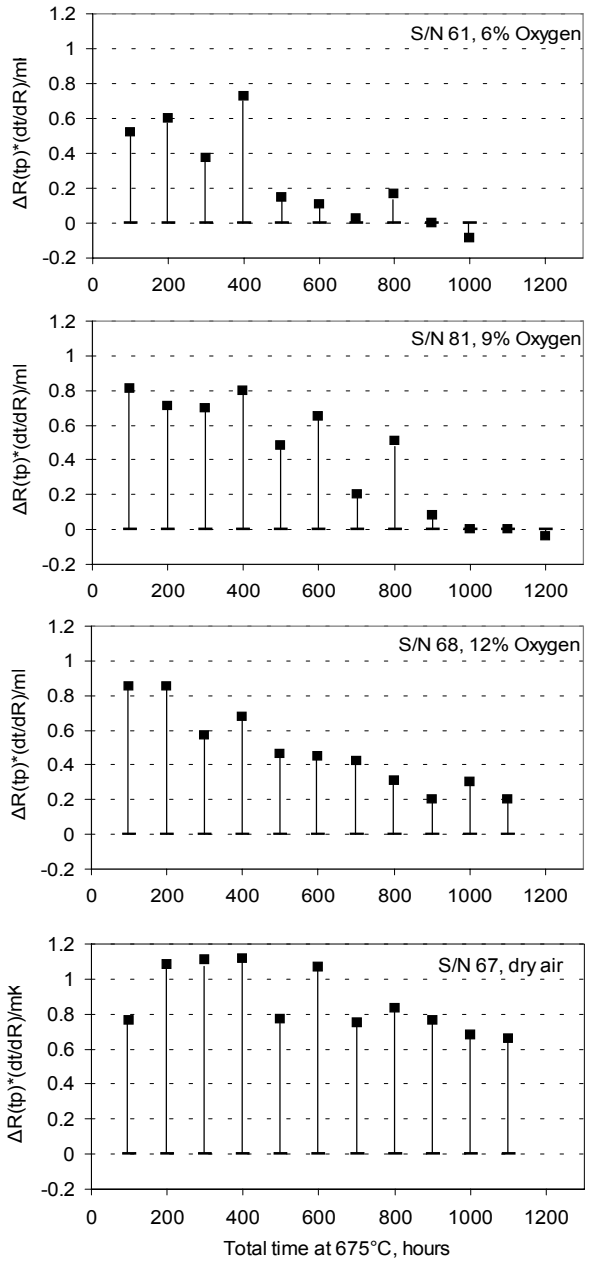

FIGURE 4. R_{tp} changes after exposure to 232 °C for 16 h during long-term operation at 675 °C

Thermometers S/N 62 and S/N 81 (9 % O_2) exhibited the same results. The only difference was that thermometer S/N 81 showed contamination after 1500 h at 675 °C, and thermometer S/N 62 showed contamination after 1600 h, due to the loss of oxygen. The test result for thermometer S/N 81 is shown in Fig. 3. Presumably, since thermometers S/N 62 and S/N 81 had more original oxygen content than thermometers S/N 60 and S/N 61, it took longer for their oxygen levels to fall below a certain pressure, above which the MSPRTs are protected from contamination. Thermometers S/N 68, S/N 69 (12 % O_2) and S/N 67, S/N 70 (dry air) have not been contaminated even after 1900 h at 675 °C. We assume that these thermometers would eventually become contaminated after a long enough exposure to high temperature. This test has been continuing in our lab, so we might observe when these thermometers become contaminated.

Part of the platinum oxidation test results from these thermometers is shown in Fig. 4. Since the oxygen contents in the MSPRTs decrease after exposure at 675 °C, we tried to determine the oxidation effects on the MSPRTs with different filling-gas mixtures after long-term operation at high temperature. For comparison purposes, the sensors of the thermometers were always thermally cleaned to remove any oxide before the oxidation effect tests. After every 100 h at 675 °C, the thermometers were exposed to 232 °C for 16 h. The R_{tp}s of the thermometers were measured before and after they were exposed to 232 °C. The changes of the R_{tp}s reflected the platinum oxidation effect at that time. Since the oxygen partial pressure in the MSPRTs had been decreasing while the MSPRTs were exposed to high temperature, the platinum oxidation effects were also decreasing. For example, the oxidation effect for thermometer S/N 68 changed from 0.8 mK to 0.2 mK after 1000 h at 675 °C. It is also seen in Fig. 4 that the oxidation effect is larger for thermometers with greater oxygen content than those with lower oxygen content.

There is a conflict between the contamination effect and the oxidation effect. Excessively high O_2 partial pressure causes the platinum sensor to oxidize, and excessively low O_2 leads to sensor contamination. It is more difficult to resolve this conflict with MSPRTs than with fused silica sheath SPRTs because the metal sheaths, themselves, oxidize and create a loss of oxygen in the MSPRTs. After a period of operation, the oxygen content in an MSPRT may be unknown and may significantly affect the performance of an

MSPRT. Thermometers may be contaminated quickly if no oxidation effect is detected (for example, thermometer S/N 61 and S/N 81).

Stability Tests for MSPRTs with Sealed Elements

In order to resolve the conflict explained above and improve the stabilities of MSPRTs, the elements of two MSPRTs were sealed permanently into platinum capsules using a special glass coating. This structure was described in a previous section. With this design, a change of the oxygen content in the sheath due to the sheath oxidation should not affect the element.

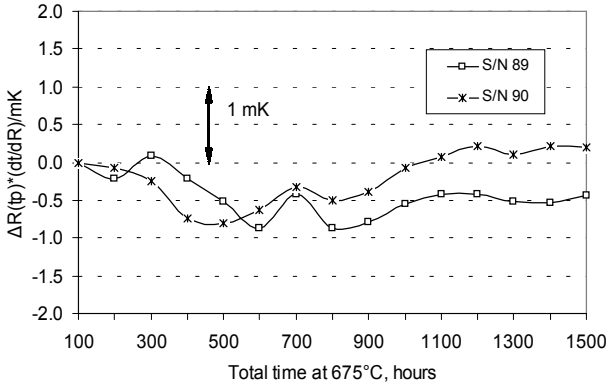

FIGURE 5. Long-term stability test at the triple point of water for MSPRTs with sealed elements.

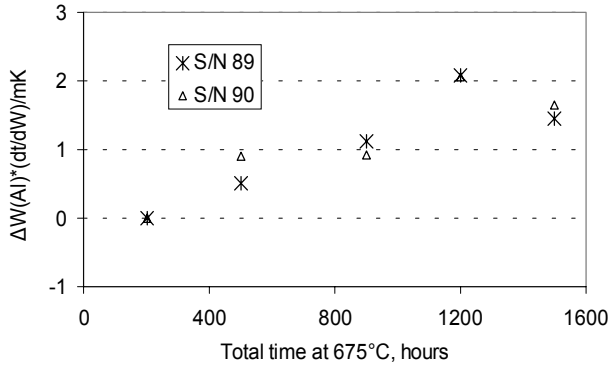

FIGURE 6. Long-term stability test at the freezing point of aluminum for MSPRTs with sealed elements.

The stabilities of these two thermometers (S/N 89 and S/N 90) were tested and the results are shown in Fig. 5. The R_{tp}s of the thermometers were measured every 100 h during operation at 675 °C. Their W(Al) were also measured occasionally. The test results indicate that the R_{tp} drift of both MSPRTs is less than the equivalent of 1 mK, and the W(Al) changes less than the equivalent of 2 mK after 1000 h at 675 °C. Compared to MSPRTs with open elements, thermometers S/N 89 and S/N 90 were more stable. The reason is presumably that stable oxygen content in elements helps to stabilize the resistance. The MSPRTs with sealed elements can be kept free from contamination after long-term exposure to high temperature.

Platinum Oxidation Test for MSPRTs with Sealed Elements

Platinum oxidation will significantly affect a thermometer's stability between 150 °C and 450 °C. A sealed element will not be affected by the consequent loss of oxygen in the sheath of an MSPRT. Therefore, the platinum oxidation effect should be constant, even after long-term exposure to high temperatures. The test procedure for the platinum oxidation effect was described in the previous section. Fig. 7 shows that the platinum oxidation effects for thermometers S/N 89 and S/N 90 stay the same after long-term exposure at 675 °C. The changes of R_{tp} due to platinum oxidation after the MSPRTs were exposed to 232 °C for 16 h were always less than 0.6 mK during the tests. This oxidation effect could be made even smaller by reducing the oxygen content in the elements. Comparing these results to the results shown in Fig. 4, the R_{tp} changes of the MSPRTs with open elements due to platinum oxidation varied between 0.2 mK and 1.5 mK equivalently, depending on the exposure time at high temperature and the original oxygen content.

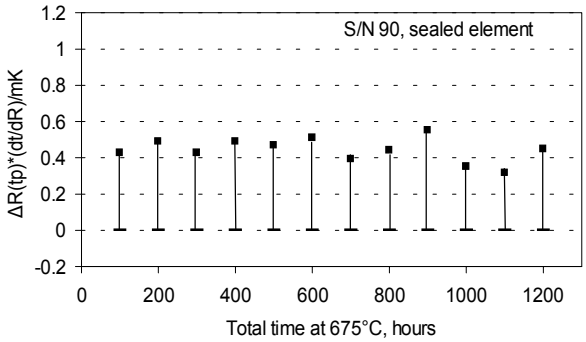

FIGURE 7. R_{tp} changes after exposure to 232 °C for 16 h during long-term operation at 675 °C.

At this point, it has been clearly shown that the conflict between contamination and platinum oxidation can be solved by sealing the element separately from the sheath. In order to investigate the platinum oxidation effect of the sealed element over a wider temperature range, thermometer S/N 90 was tested at 232 °C, 350 °C, and 420 °C, in that order. Thermometer S/N 89 was tested in reverse order at 420 °C, 350 °C, and 232 °C. Fig. 8 and Fig. 9 indicate

that the two thermometers showed only two dimensional (2d) platinum oxide, and no three dimensional (3d) oxide was detected. The 2d oxidation may become stable after 50 h exposure to 232 °C. The R_{tp}s changed less than the equivalent of 0.7 mK due to 2d oxide. The 2d oxide would be decomposed at 350 °C.

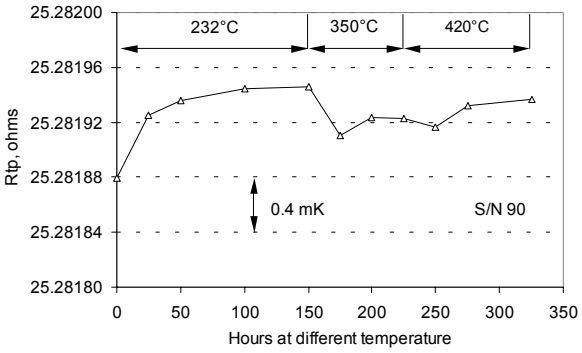

FIGURE 8. R_{tp} changes after exposure at different temperatures from 232 °C to 420 °C.

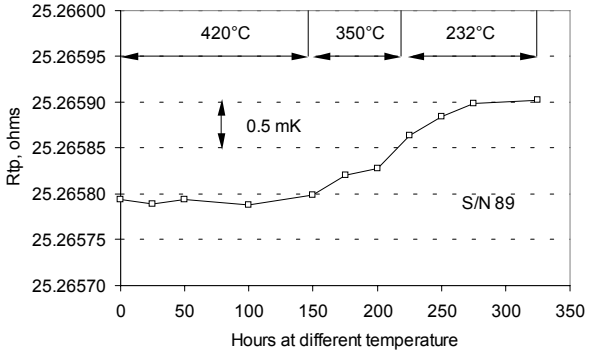

FIGURE 9. R_{tp} changes after exposure to different temperatures from 420 °C to 232 °C.

CONCLUSION

The oxygen consumption and subsequent drift rate significantly depends on thermometer design, materials, and the manufacturing process. The performance of the Hart MSPRT can be improved by using a sealed element design.

Because of slow oxidation of its metal sheath and the consequent loss of oxygen in an MSPRT, the oxygen content of an MSPRT element can significantly affect the performance of an MSPRT if its element is not sealed separately from its metal sheath. It is very difficult to maintain a balance between the oxidation effect and element contamination in the MSPRT, since the oxygen content in the thermometer can vary after a period of operation. A thermometer would show an oxidation effect after it was made, but no contamination problem. However, when no oxidation effect was detected, the thermometer was likely to become contaminated if it continued to be exposed to high temperature.

An MSPRT with an open element should have the gas mixture replaced when necessary, depending on its practical usage. The adoption of the sealed element in an MSPRT can resolve the conflict between platinum oxidation and element contamination and improve the resistance stability.

Our research confirms that a proper gas mixture (with a particular certain oxygen content) can be found that reaches a balance between the oxidation effect and element contamination. The oxygen content in the gas mixture can be high enough to protect the sensor from contamination but low enough to minimize the oxidation effect. Because the sealed element can maintain its oxygen content for a long time, it becomes possible to build an MSPRT with excellent performance at temperatures up to 675 °C.

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