Effects of Different Surroundings on the Stability of Standard Platinum Resistance Thermometers from 650°C through 1000°C

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Abstract

It was reported that standard platinum resistance thermometers (SPRTs) are contaminated when their sensors are close to base metals or alloys above 980°C. The Ni, Cr, and Fe ions seem to be able to permeate fused silica sheaths at high temperatures. In order to know if similar contamination occurs below 980°C, many SPRTs with different nominal resistances at 0.01°C (25.5, 2.5, and 0.25 ohms) were annealed in blocks of different materials (graphite, alumina, Inconel, and aluminum-bronze) from 500°C to 1000°C for more than 1000 hours. Our results showed no contamination at 660°C for any of the block materials investigated. There was no contamination discovered in the graphite and alumina blocks up to 1100°C. However, contamination began near 800°C in an Inconel block. The drift rates of Rtp of three SPRTs in an Inconel block were measured from 750°C to 1000°C.

Introduction

About twenty five years ago, Xumo discovered that the stability of high temperature standard platinum resistance thermometers (HTSPRTs) annealed in a Ni-Cr alloy block at about 1100°C was much worse than when annealed in a graphite block [1, 2]. The changes in Rtp (the resistance at the triple point of water) of HTSPRTs after annealing in a graphite block at about 1100°C for 100 hours were less than the equivalent of 1 mK. Similar changes when annealed in a Ni-Cr alloy block were more than ten times larger than when annealed in a graphite block. Later, Marcarino's work demonstrated that Ni, Cr, and Fe ions can permeate fused silica at temperatures above about 980°C. Consequently, we understand that SPRTs with fused-silica sheaths exposed at high temperatures in furnaces with a base metal block can be easily contaminated by metal vapor [3]. The temperature range in Marcarino's investigation was between 980°C and 1080°C. The temperature ranges of most SPRTs are below 980°C. So it is interesting to know whether similar contaminations through fused-silica sheaths occur below 980°C. If there are such contaminations below 980°C, at which temperature do they begin? In order to answer this question, we started an investigation in the temperature range from 500°C to 1000°C. It is well known that when a pure metal is contaminated its resistivity at any temperature will increase and its temperature coefficient of resistance will decrease. So the stability of an SPRT is closely related to the contamination of its platinum sensor. When the platinum sensor of an SPRT is contaminated, its resistance at the triple point of water, Rtp (or the resistance at any fixed point) will increase, and the resistance ratio W(t) = R(t)/Rtp at any fixed point above 0.01°C will decrease. As the first step of the project, we started an investigation on stabilities of SPRTs when their fused silica sheaths are close to different materials (graphite, alumina, Inconel, and aluminum-bronze) in the temperature range from 500°C to 1000°C. No direct chemical analysis on the platinum sensor has been made in the investigation. The results obtained are reported here.

SPRTs and Test Equipments

Three types of SPRTs with different nominal resistance values of 25.5 ohms, 2.5 ohms, and 0.25 ohms at the triple of water were tested in the investigation. The 25.5-ohm SPRT is the "workhorse of the ITS-90." It was tested up to about 660°C. Both 2.5-ohm and 0.25-ohm SPRTs were tested up to 1085°C. The diameters of the platinum wires used to form the sensor elements are about 0.07 mm for the 25.5-ohm SPRT, 0.2 mm for the 2.5-ohm SPRT and 0.4 mm for the 0.25-ohm SPRT. The details of their designs were reported earlier [4].

Four different block materials were used in the investigation. 1) A graphite block with five wells was sealed in a fused-silica vessel in a pure argon atmosphere. Several graphite disks and fiber ceramic disks were placed on the top of the graphite block alternately. Five fused-silica tubes with their bottom ends sealed were inserted into the five wells of the graphite block. Their top ends were sealed by the fused-silica lid of the vessel. 2) An alumina block containing five fused-silica tubes, each with their bottom ends sealed, was placed into a large fused silica vessel. Several alumina disks and fiber ceramic disks were placed on the top of the alumina block alternately. The fused silica vessel was not sealed on the top. 3) An Inconel block was placed into the furnace directly. It contained five fused-silica tubes with sealed bottom ends. Several Inconel disks and fiber ceramic disks were placed alternately on the top of the Inconel block. 4) An aluminum-bronze block was also placed directly into a furnace. SPRTs were inserted into the wells of the aluminum bronze block directly. The aluminum-bronze block was used up to about 660°C, and all other blocks were used up to 1100°C.

Two bridges were used in the investigation: a Model 6675A DC Bridge and a Model F18 AC Bridge. The nonlinearities of the bridges are better than 0.02 ppm according to the manufacturers' specifications**.** The reference resistances used with the bridges were maintained in baths at 25°C ± 0.01°C. The stabilities of these reference resistances were better than 2 ppm per year. The triple point of water was used throughout the investigation. The melting point of gallium and the freezing point of tin were used occasionally. The realization and equipment of these fixed points in the lab were reported in detail earlier [4-6]. The expanded uncertainties (k=2) for both the triple point of water and the melting point of gallium are 0.1 mK, and 0.6 mK for the freezing point of tin. The triple point of water is one of the most stable fixed points and is easy to use. So the resistance of an SPRT at the triple point of water, Rtp, is used as the main indicator to monitor the stabilities of SPRTs.

Test and Results

The behaviors of SPRTs when annealed in a graphite block and in an alumina block are very similar. Fig. 1 shows a typical curve of a 25.5-ohm SPRT annealed in a graphite block in the temperature range from 675°C to 720°C. Fig. 2 shows a typical curve of a 0.25-ohm SPRT annealed in an alumina block at 1085°C. Rtp decreased sharply during the first 200 – 300 hours of annealing at high temperatures because strains in the platinum sensor were released. Afterwards, the Rtp was stable during the continued annealing at the same temperature within a certain range. It is believed that no contamination occurs during annealing in either block. The data obtained from these blocks were taken as reference data to isolate contamination effects from SPRT drift when analyzing data from the other experiments. Fig. 1 and Fig. 2 provide a rough idea of how SPRTs behave during annealing at high temperatures when there is no contamination.

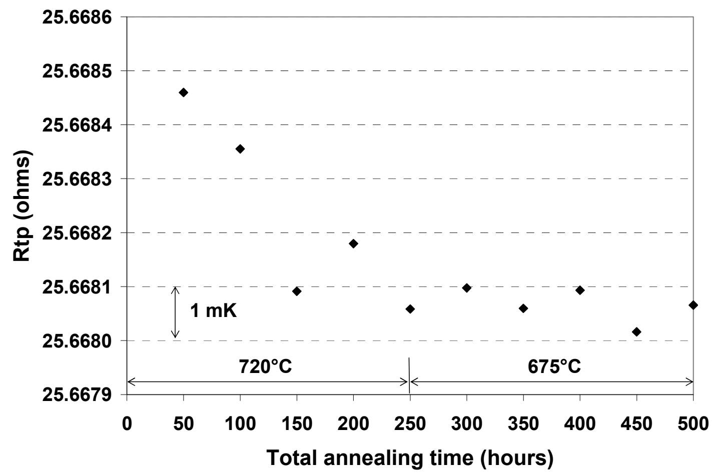

Figure 1. A typical Rtp curve of a 25.5-ohm SPRT annealed in a graphite block in the temperature range from 675°C to 720°C

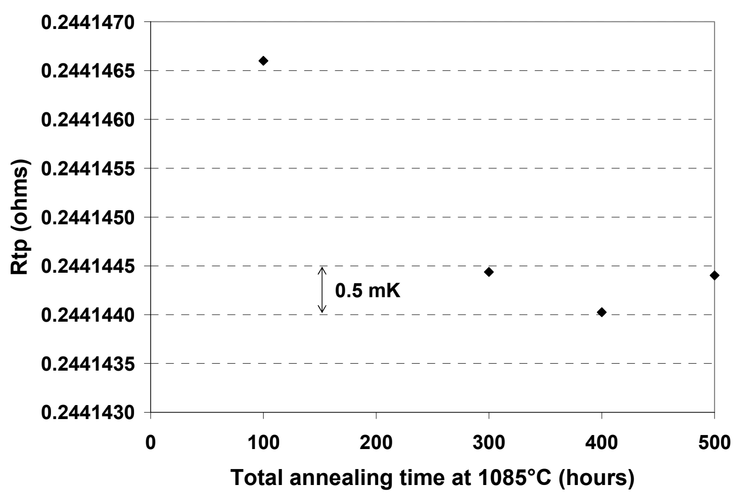

Figure 2. A typical Rtp curve of a 0.25-ohm SPRT annealed in an alumina block at 1085°C

25.5-ohm SPRTs were tested up to about 660°C in different blocks. The Model 6675A Bridge was used in the test. SPRT #1116 and SPRT # 1117 were first annealed in a graphite block at 660°C for 40 hours, and then they were annealed at the same temperature for 200 hours in an aluminum-bronze block (#1116) and in an Inconel block (#1117). The data are shown in Fig. 3 and Fig. 4. The maximum changes in Rtp during 200 hours of annealing at 660°C in both blocks (aluminum bronze and Inconel) were within 1 mK equivalently, which were very similar to the results from annealing in a graphite block (also see Fig. 1). We conclude from the Rtp curves that is no contamination occurred during annealing at 660°C in an aluminum-bronze block or in an Inconel block. Another way to distinguish whether there is any contamination is to check the change in W(t) at a fixed point as mentioned above. W(Sn) was checked before and after the 240-hour annealing at 660°C. The data are shown in Fig. 5. The W(Sn) of #1117 rose, and the W(Sn) of #1116 remained almost unchanged (within the equivalent of 0.2 mK). The results of the changes in W(Sn) after the annealing show no contamination during the annealing. As mentioned above, if contamination occurs, W(Sn) would decrease.

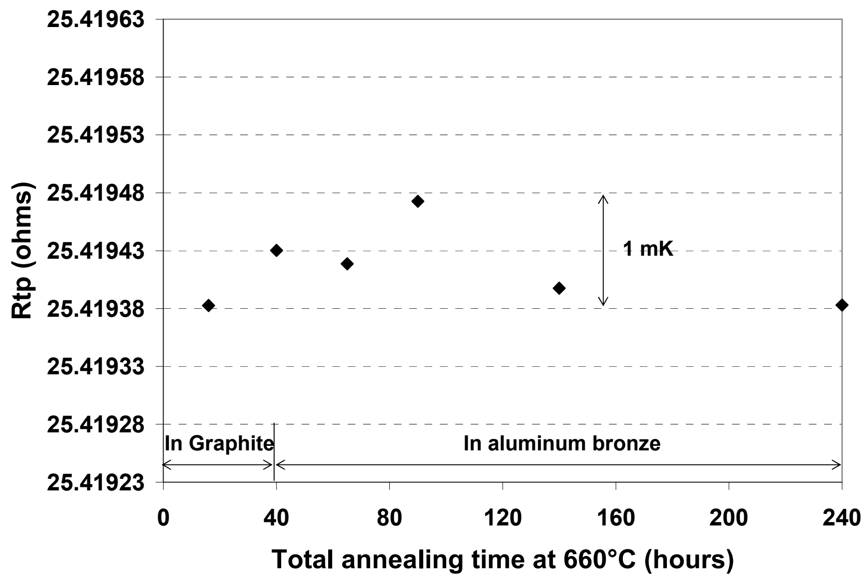

Figure 3. The Rtp curve of SPRT # 1116 during annealing at 660°C in a graphite block and in an aluminum-bronze block

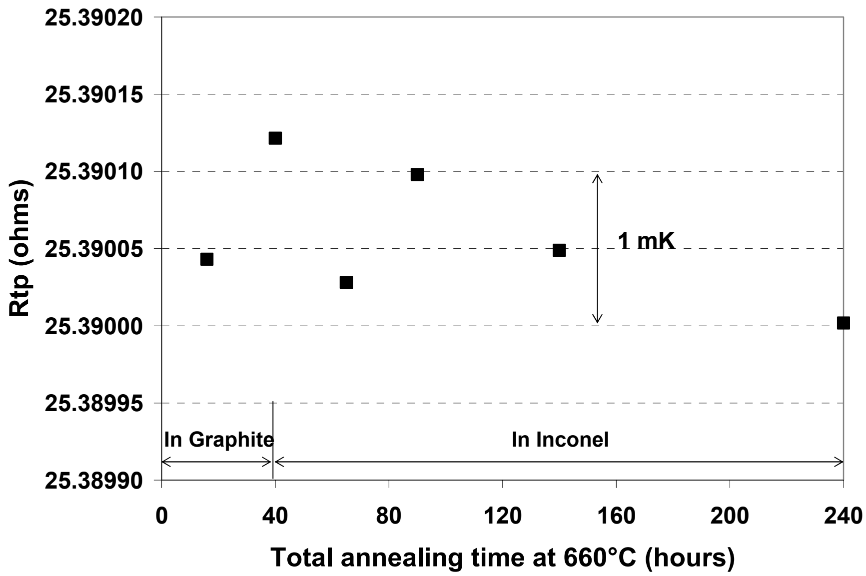

Figure 4. The Rtp curve of SPRT #1117 during annealing at 660°C in a graphite block and in an Inconel block

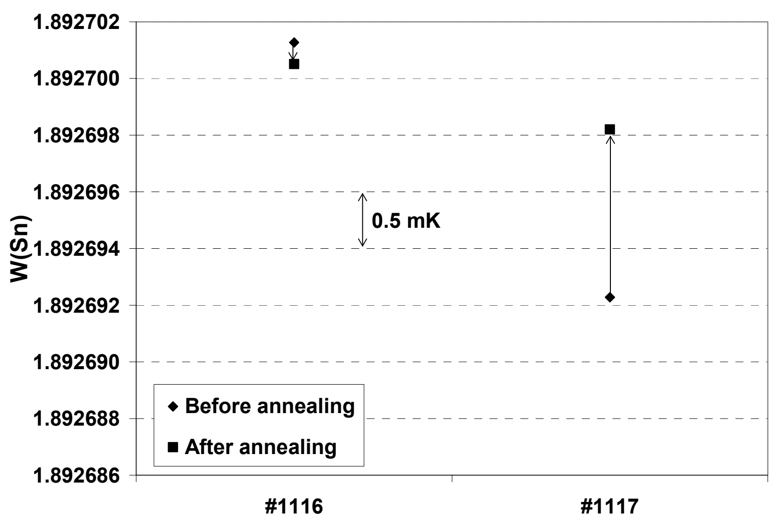

Figure 5. The changes in W(Sn) of two SPRTs after 240 hours of annealing at 660°C

In 2000, three 2.5-ohm SPRTs and a 0.25-ohm SPRT were tested at 750°C in a graphite block and in an Inconel block using the 6675A Bridge. All the SPRTs were first annealed at 750°C in a graphite block for 100 hours. Then they were annealed in an Inconel block at the same temperature for 50 hours. Finally they were annealed at 800°C in a graphite block for 50 hours as a check. The data for two of them are shown in Fig. 6 and in Fig. 7. The Rtp of the 0.25-ohm SPRT (#3040) was stable within the equivalent of 0.5 mK during the 200-hour annealing at 750°C and 800°C in both blocks. The excellent stability of Rtp during this annealing in both blocks showed that there was not any contamination to the 0.25-ohm SPRT at this temperature. The Rtp of the 2.5-ohm SPRT somehow showed a slow rising drift at 750°C even in the graphite block. The drifts in both blocks were close to each other, so it seems there was no contamination at 750°C in an Inconel block for the 2.5-ohm SPRT also.

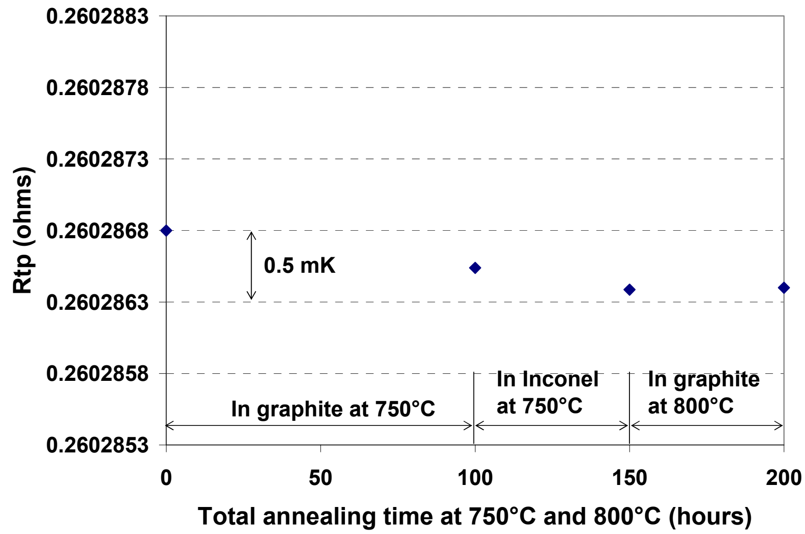

Figure 6. The Rtp values of SPRT #3040 during annealing at 750°C and 800°C in different blocks as indicated in the figure

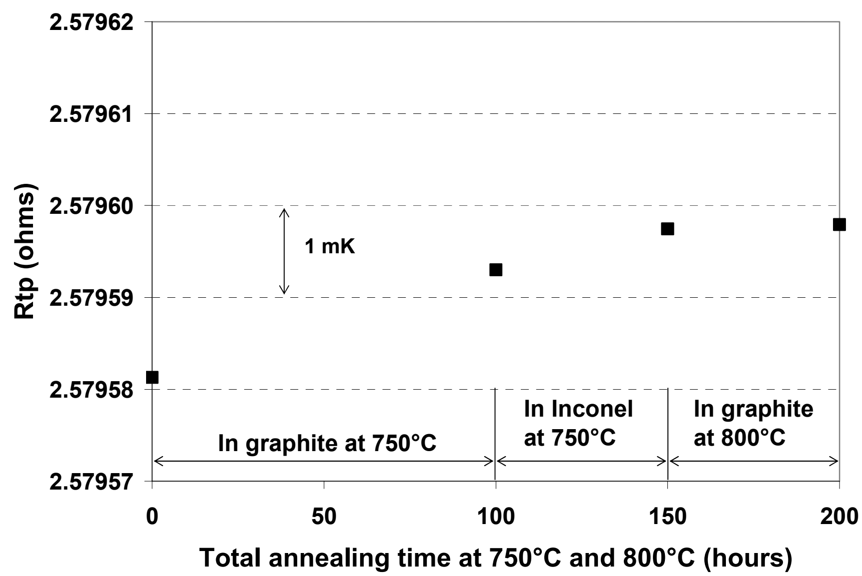

Figure 7. The Rtp values of SPRT #1045 during annealing at 750°C and 800°C in different blocks as indicated in the figure

In 2002 the investigation was continued up to 1000°C. Three 2.5-ohm SPRTs and a 0.25-ohm SPRT were heated from 800°C to 1000°C for a total of 1250 hours. An alumina block and an Inconel block were used alternatingly during the annealing. The F18 Bridge was used to measure the resistances of the SPRTs. A 2.5-ohm SPRT developed a short circuit in the middle of the investigation, and another 2.5-ohm SPRT experienced a similar problem near the end of the tests. The very long test procedures were as follows: R(Ga), Rtp, R(Ga), Rtp, 50 hours at 800°C in alumina, Rtp, 50 hours at 800°C in Inconel, Rtp, 50 hours at 850°C in alumina, Rtp, 50 hours at 850°C in Inconel, Rtp, 50 hours at 850°C in Inconel, Rtp, 50 hours at 900°C in alumina, Rtp, 50 hours at 900°C in Inconel, Rtp, 50 hours at 900°C in Inconel, Rtp, 50 hours at 930°C in alumina, Rtp, 50 hours at 930°C in Inconel, Rtp, 50 hours at 930°C in Inconel, Rtp, 100 hours at 930°C in Inconel, Rtp, 100 hours at 970°C in alumina, Rtp, 100 hours at 970°C in Inconel, Rtp, 100 hours at 970°C in Inconel, Rtp, 100 hours at 1000°C in alumina, R(Ga), Rtp, 100 hours at 1000°C in Inconel, Rtp, 1000°C in Inconel, and Rtp. Here "Rtp" means a measurement at the triple point of water, "R(Ga)" means a measurement at the melting point of gallium, and "50 hours at xxx°C in Alumina (or Inconel)" means SPRTs were annealed at xxx°C in an alumina block (or an Inconel block) for 50 hours. It took more than eight months to complete the tests. The Rtp values of two SPRTs during the tests are shown in Fig. 8 and Fig. 9. The Rtp of a 0.25-ohm SPRT (#3040) was very stable when annealed in an alumina block in the temperature range from 800°C to 1000°C (Fig. 8). The average drift rates of the Rtp of three SPRTs in both blocks at different temperatures were calculated according to the data and shown in Fig. 10. For evidence and convenience, the equivalent temperature drift rates (DRt) were used instead of resistance drift rates (DRr). The equivalent temperature drift rates can be calculated as in the following equation:

$$DRt = DRr/Rtp/0.0039885\ K^{-1} \qquad (1)$$

The value 0.0039885 K^{-1} is the approximate temperature coefficient of resistance of pure platinum at 0.01°C. The drift rates of a 0.25-ohm SPRT (#3040) in an alumina block up to 1000°C were very close to zero and were not shown in Fig. 10. The drift rates of two 2.5-ohm SPRTs were close to each other. The drift rates in an Inconel block were within 0.02 mK/hour below 850°C, within 0.03 mK/hour at 900°C, and rose to above 0.3 mK/hour at 1000°C for both 2.5-ohm SPRTs. The drift rates of the 0.25-ohm SPRT in an Inconel block were much lower than that of the 2.5-ohm SPRTs, by at least 40% at 970°C and 1000°C.

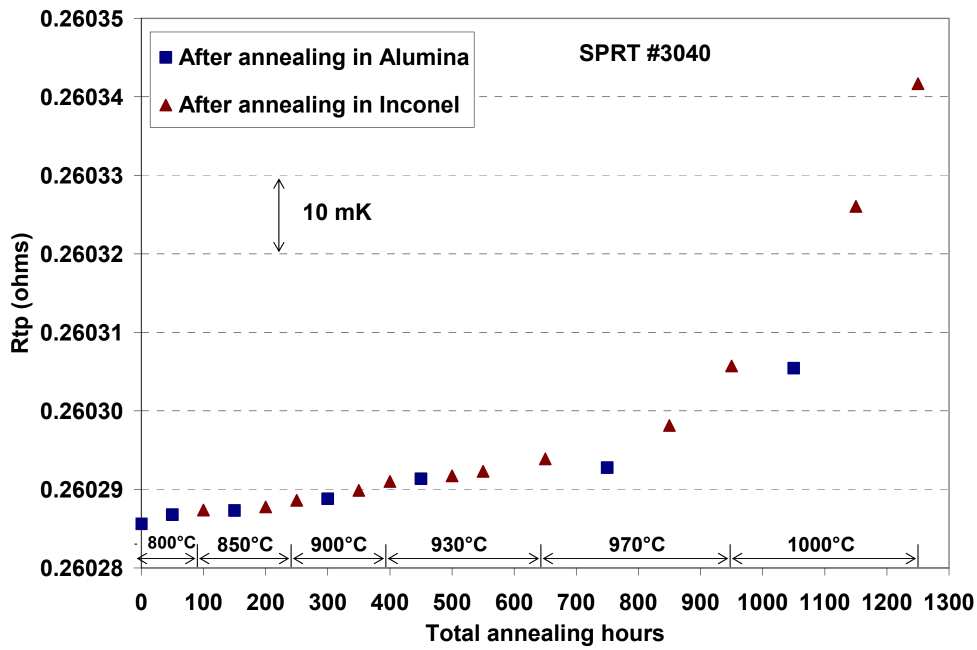

Figure 8. The Rtp values of SPRT #3040 during annealing between 800°C and 1000°C in different blocks for 1250 hours

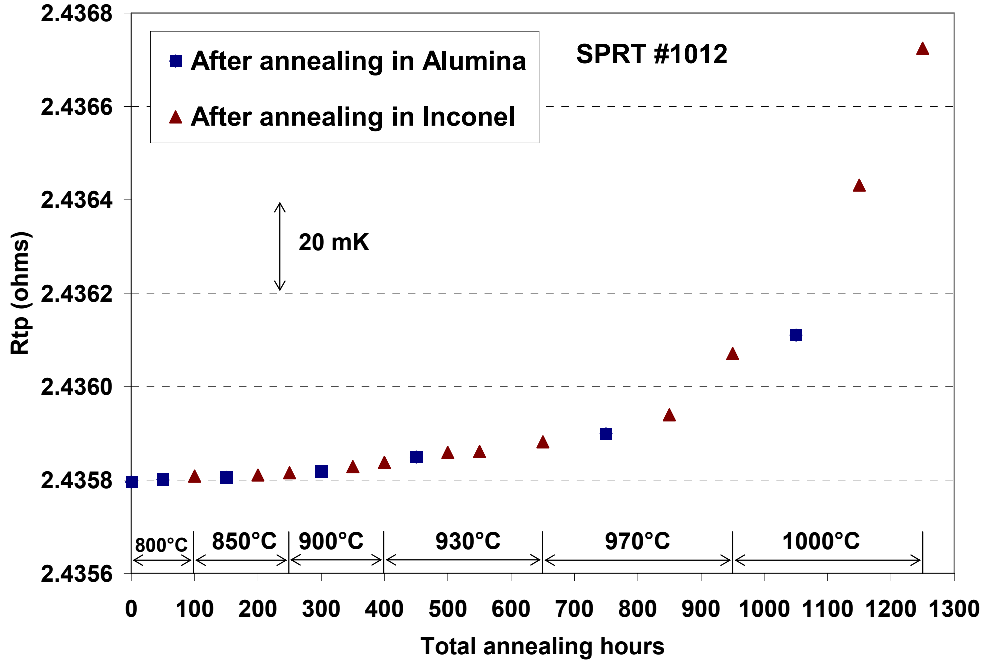

Figure 9. The Rtp values of SPRT #1012 during annealing between 800°C and 1000°C in different blocks for 1250 hours

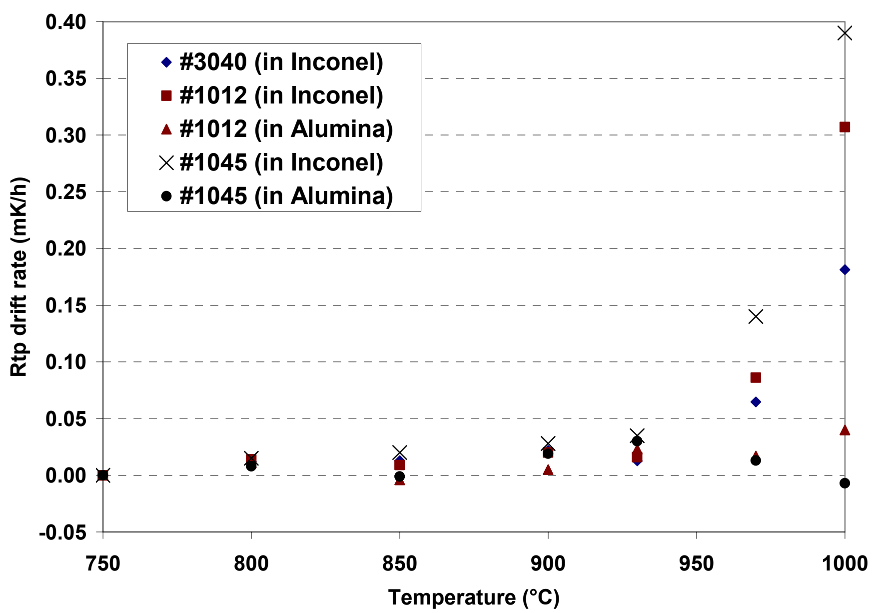

Figure 10. The Rtp drift rates of three SPRTs heated between 750°C and 1000°C in different blocks

W(Ga) of three SPRTs was measured before and after a total annealing of 950 hours in the range from 800°C to 970°C. The data are shown in Fig. 11. The change in W(Ga) was –0.002214 for SPRT #3040 (0.25-ohm), –0.003060 for SPRT #1012 (2.5-ohm), and –0.004560 for SPRT #1045 (2.5-ohm). In thermometry and the platinum industry, people often use the mean temperature coefficient of resistance from 0°C to 100°C, α, to represent the purity of platinum. For example, the IPTS-68 required a minimum purity of platinum for an SPRT with an α value of 0.003925. The α values can be calculated according to W(Ga) by using the following approximate equation:

$$\alpha = 0.034692774 \times W(Ga) - 0.034863056 \qquad (2)$$

The α values of all three SPRTs decreased after annealing in an Inconel block in the range from 800°C to 970°C. It was again evident that the platinum was contaminated through the fused-silica sheaths when the platinum sensor was close to an Inconel block in the temperatures above 800°C. Supposing that the changes of α are proportional to the changes of Rtp, α values were calculated after annealing at each temperature. Fig. 12 shows how the values of α changed during the process. The drift rates of α were quite low below 900°C and became much faster above 930°C. The draft rates of α for the 0.25-ohm SPRTs were much lower than that for the 2.5-ohm SPRTs, about 40% lower.

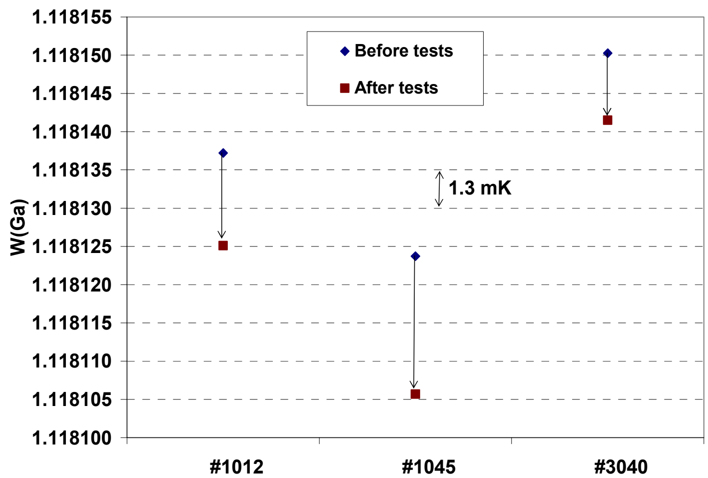

Figure 11. W(Ga) values of three SPRTs before and after annealing in the range from 800°C to 970°C for about 1000 hours in two blocks (alumina and Inconel)

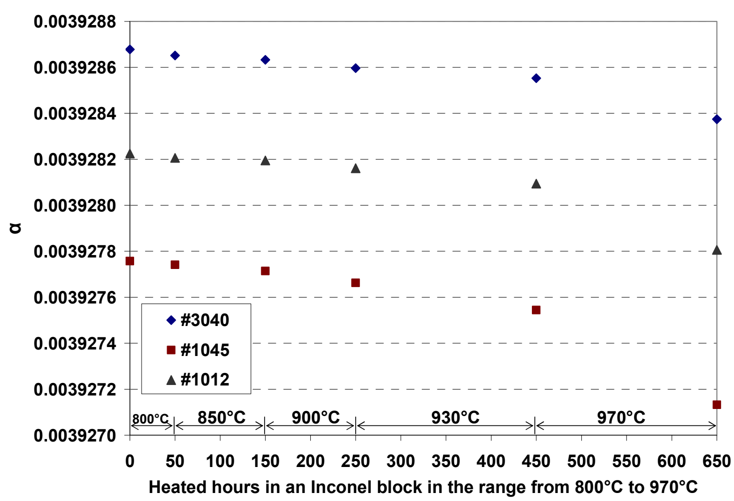

Figure 12. α values of three SPRTs during annealing in the range from 800°C to 970°C in Inconel block

Final Remarks and Conclusion

1. The various materials tested during our study have no effect on the stability of SPRTs up to 660°C when their fused silica sheaths are close to these materials. Base metals cannot diffuse through fused silica to contaminate platinum below about 660°C. SPRTs may be annealed in any block up to 660°C.
2. Neither pure graphite nor alumina will contaminate platinum at temperatures below 1100°C. They are advisable as block materials in which to anneal SPRTs and for other SPRT applications above 660°C.
3. The contamination of platinum from base metals through fused silica begins to happen at about 800°C. The drift rates of Rtp are within the equivalent of 0.02 mK/hour up to 850°C in an Inconel block, and rise with temperature. They rise sharply above about 970°C. The drift rates of Rtp of two 2.5-ohm SPRTs are above the equivalent of 0.3 mK/hour at 1000°C.
4. The drift rates of Rtp depend on the diameter of the platinum wire, which forms the sensor. The 0.25-ohm SPRTs with 0.4 mm platinum wire sensors have drift rates about 60% of that for the 2.5-ohm SPRTs with 0.2 mm platinum wire sensors.

Acknowledgements

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