INVESTIGATION OF STABILITY OF HTPRTS AT HIGH TEMPERATURE

N. P. Moiseeva [1], A. I. Pokhodun [1], B. W. Mangum [2], G. F. Strouse [2]
[1] D. I. Medeleyev Research Institute of Metrology, St. Petersburg, Russia
[2] National Institute of Standards and Technology, Gaithersburg, USA

ABSTRACT

Reproducibility of measurements on, and non-uniqueness of, the ITS-90 depends to a great extent on the stability of the defining interpolation instruments of the Scale, such as the high temperature platinum resistance thermometers (HTPRTs). An investigation of the stability of HTPRTs was made on seven HTPRTs of VNIIM (0.59 Ω) design. The thermometers were given a long heat treatment at temperatures above 960 °C. A study was made of the influence of the heat treatment conditions on the stability of the resistance at the triple point of water and on the relative resistance *W*(Ga) of the HTPRTs. Different annealing furnaces with graphite and Inconel blocks were used in the study. It was shown that a change of annealing furnace, and a change of the temperature of heat treatment may cause instability of an HTPRT. The voltage between the thermometer leads and ground was found to have an influence on the change of the resistance of the HTPRT. The application of a positive voltage between the leads of an HTPRT and ground can result in decreasing the resistance of the HTPRT, a negative voltage can lead to increasing the resistance and deterioration of the quartz parts of the HTPRT. The thermometers that have large values of *W*(Ga) seems to be less sensitive to the change of conditions of heat treatments than HTPRTs with low value of *W*(Ga). The observed properties of the HTPRTs are considered to be related to certain processes in the platinum and the quartz.

1. INTRODUCTION

The platinum resistance thermometer (PRT) is the exclusive defining interpolation instrument of the ITS-90 in the temperature range from 24.5561 K to 961.78 °C and the high-temperature platinum resistance thermometer (HTPRT) is the appropriate PRT in the temperature range from 660.723 °C to 961.78 °C. Investigations carried out before the adoption of the ITS-90 confirmed the stability and reproducibility of the HTPRTs to be an order of magnitude better than the accuracy characteristics of thermocouples. However, the experience of using large numbers of HTPRTs in calibrations and in comparisons showed that some difficulties could appear in obtaining the desired long-term stability of the HTPRTs at high temperatures. The reasons for losing the stability are possibly due to the properties of platinum and quartz, materials used for constructing PRTs.

It is well known, and can be easily seen through a microscope, that large crystals grow in platinum wire during long-treatment times of an HTPRT at temperatures above 900 °C. Cracks between the platinum crystals and segregation of impurities at the boundaries of the grains will cause the HTPRT to be very sensitive to vibrations and may result in increases in its resistance. This process is considered to be non-reversible. To prevent the grain growth, special fibro-platinum is used in the PRTs. Design of the sensor may also have an effect on the speed of the growth of the crystals, due to differences in the strains in the wire when changing the temperature.

The increase of the PRT resistance caused by quenching vacancies in the crystal lattice of platinum by fast cooling from high temperature is reversible. The process was carefully investigated by Berry [1] and special methods of annealing were suggested to remove the strains and thus to decrease the resistance of the HTPRT to the previous unquenched value.

Marcarino [2] observed a large increase in the resistance of some HTPRTs during their heat treatment in an Inconel block at temperatures above 960 °C. Analyses of some platinum wires, sealed in silica capsules and exposed for a long time in an Inconel block at high temperature, showed that some metal impurities can diffuse through the quartz and contaminate the platinum. It was suggested to use special platinum tubes, SiC tubes, or to maintain a slow gas flow around the thermometers to protect the HTPRTs from the contamination [2, 3].

Hill [4] investigated the stability of HTPRTs at the silver fixed point and found that the polarity of the bias voltage applied between the leads of the thermometers and ground had an influence on the slope of the curves of *R*(Ag) and *W*(Ag) versus time of heating the thermometer in a Ag cell.

An investigation of the electrical leakage process in the quartz insulation of PRTs was carried out by Berry [5]. He studied the insulation battery effect in PRTs and found that a no-load equilibrium voltage produced by the insulation battery, depends on the temperature, on the thermometer insulation and on the furnace construction. He discovered that the insulation resistance of silica-insulated thermometers can be increased by orders of magnitude by applying a bias voltage of about +6.4 V between the thermometer leads and ground.

The purpose of the present work was to study the long-term stability of HTPRTs by heating at temperatures above 960 °C. In this study we investigated the influence of the following factors on the stability of the resistance at the triple-point of water and the *W*(Ga) of the HTPRTs:

- the change of the conditions of heat treatment by using three different annealing furnaces;
- the change of the temperature of heat treatment;
- the change of the voltage between thermometer leads and ground.

The influence of the resistance ratio of an HTPRT at the gallium fixed point *W*(Ga) on the sensitivity of the HTPRT to the above factors was studied by using HTPRTs with different values of *W*(Ga).

Seven HTPRTs of the VNIIM (0.59 Ohm) design were used in this research. The time of exposure of the HTPRTs at temperatures above 960 °C was from 150 h to 1100 h.

2. INITIAL STABILIZATION OF THE HTPRTS AT VNIIM AND NIST

After construction at VNIIM, each HTPRT is usually given the following annealing treatment at 1100 °C. The thermometer is inserted into the annealing furnace when the temperature in the furnace is about 500 °C. Then the thermometer is heated slowly to 1100 °C, exposed at that temperature for 5 h, cooled to 500 °C over 3.5 h and removed from the furnace. Each annealing cycle is followed by the measurements of the resistance at the triple point of water *R*(TPW). Usually it takes 100 h to 150 h for an HTPRT to achieve a stability at the *R*(TPW) corresponding to ±0.5 mK. The stabilization curves show that both an increase and a decrease of *R*(TPW) may be observed during the course of the initial stabilization.

For the present investigation, we chose three HTPRTs that showed different behavior during the initial stabilization at VNIIM. We observed an increase in *R*(TPW) for HTPRTs 014 and 249 and a decrease for HTPRT 074. The curves of the values of *R*(TPW) as a function of annealing time during the heat treatment of the HTPRTs are given in Fig. 1. A stability of about ±0.5 mK was obtained for the HTPRTs after 150 h of annealing at VNIIM. The high-temperature annealing furnace at VNIIM contains a ceramic tube with a ribbon heater wound on it. A stainless steel cylinder, inside the bottom part of the tube, is a connected to ground. Six quartz closed-end tubes for holding HTPRTs are located in the furnace. The ceramic tube is closed very tightly at the top with a block of insulation, which makes it possible to maintain the heads of the thermometers at a temperature of about 30 °C. Thus, in this annealing furnace HTPRTs are kept in an air atmosphere without direct contact with a metal block.

After the initial stabilization at VNIIM, HTPRTs 014, 249 and 074 were taken to NIST for further investigation. The first measurements on all the HTPRTs on arrival at NIST gave the same deviations from the previous VNIIM data of about the equivalent 0.5 mK. That could be explained by different reference resistors and by some influence of vibrations experienced during the transportation of the thermometers to NIST. At NIST the HTPRTs received a number of heat treatments of different duration, varying from 2 to 70 h, followed by slow cooling to 500 °C over 4.5 h. The annealing furnace at NIST contains an Inconel block and thermometer tubes that are three-layer protective tubes consisting of a platinum tube between two quartz tubes. The first short-time heat treatments at NIST resulted in an increase of *R*(TPW) for all the thermometers. The increase for HTPRT014 corresponded to 10 mK for 4 h at 975 °C and then 3.5 mK for another 5 h. HTPRT 074 increased *R*(TPW) by the equivalent of 0.7 mK and 3.3 mK, respectively, during the same heat treatment. Further long-time heat treatments at 975 °C resulted in an additional increase in *R*(TPW), the rate of increase being the same for the two HTPRTs after about 250 h of total exposure in the furnace (see Fig. 1). During the next heat treatments, the rate of increase of *R*(TPW) was smaller and after about 400 h, the thermometers showed rather good stability of 0.4 mK for HTPRT 074 and 1.3 mK for HTPRT 014 for 10 h at 975 °C. Five short annealing cycles for HTPRT 249 resulted in an increase of *R*(TPW) by the equivalent of about 6.6 mK, and the study of this thermometer at NIST was stopped. Measurements in the fixed point of gallium showed that *W*(Ga) decreased for all the HTPRTs during the work at NIST.

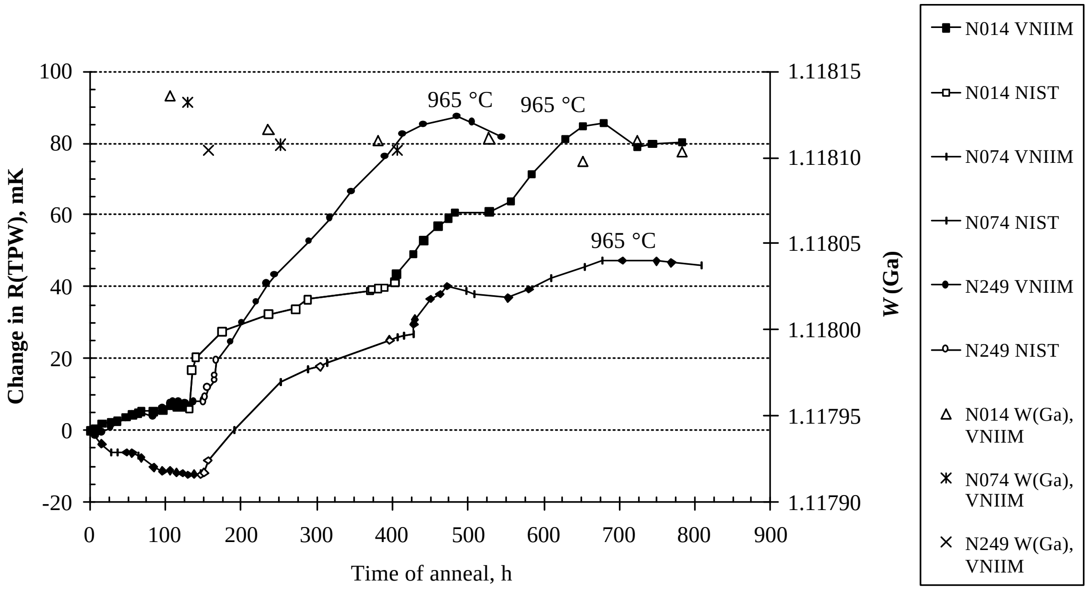

Figure 1. Change in *R*(TPW) and *W*(Ga). Initial stabilization at VNIIM and NIST.

The thermometer sensors were observed through a microscope at NIST and large crystals of platinum were clearly seen in the platinum wire. The creation of dislocations and cracks may have occurred in the big-grained platinum wire. The process of distribution of vacancies and impurities in the platinum with the new structure takes a long time and may result in a new stabilization structure. This process could be one of the possible reasons for the increase of *R*(TPW) during the heat treatment at NIST. If on the other hand, the diffusion of impurities and the contamination of the sensor wire depends on the electrical potential between the thermometer and its surroundings, then the change of annealing furnace and, as a result, the change of the electrical potential, would cause a change of *R*(TPW) and *W*(Ga). Also, a change of the temperature distribution in the a furnace might have an effect on the diffusion process in the platinum.

The thermometers were then taken back to VNIIM. The first treatments at 1100 °C caused an increase in *R*(TPW), with an approximately equal rate for all three HTPRTs. After 50 h, the temperature was set to 1020 °C and for the following 45 h we saw a decrease in *R*(TPW) for HTPRT 074 and a stabilization of *R*(TPW) for HTPRT 014. The *R*(TPW) for HTPRT 249 continued to increase with a slightly smaller rate. However, further treatments at temperatures from 1050 °C to 1070 °C showed an increase in *R*(TPW) for all of the HTPRTs. *W*(Ga) was decreasing during this treatment at VNIIM.

3. THE EFFECT OF THE CONDITIONS OF HEAT TREATMENT ON STABILITY OF THE HTPRTS

When the curves of *R*(TPW) showed an approximately constant rate of increase, the temperature of the furnace was set to 960 °C. The HTPRTs were raised 20 mm in the furnace from the position previously used in order to provide a better distribution of the temperature along the sensors. At this time, three more HTPRTs, numbers 319, 307, and 260, which had different values of *W*(Ga) were added to the experiments.. During previous anneals, the *R*(TPW) of the thermometers increased during heat treatment at 1050 °C. HTPRT 307 had the smallest *W*(Ga) [*W*(Ga) = 1.11805]. The behavior of *R*(TPW) from this experiment are shown in Fig. 2. As can be seen from the figure, the slopes of the curves become smaller when the heat-treatment temperature is reduced. After the first 20 h at 960 °C, HTPRT 074 approached a stability of ± 0.5 mK over the 20 h. The other HTPRTs showed a tendency toward a decreasing *R*(TPW). The maximum decrease of *R*(TPW) was observed for HTPRT307, which also had the lowest value of *W*(Ga).

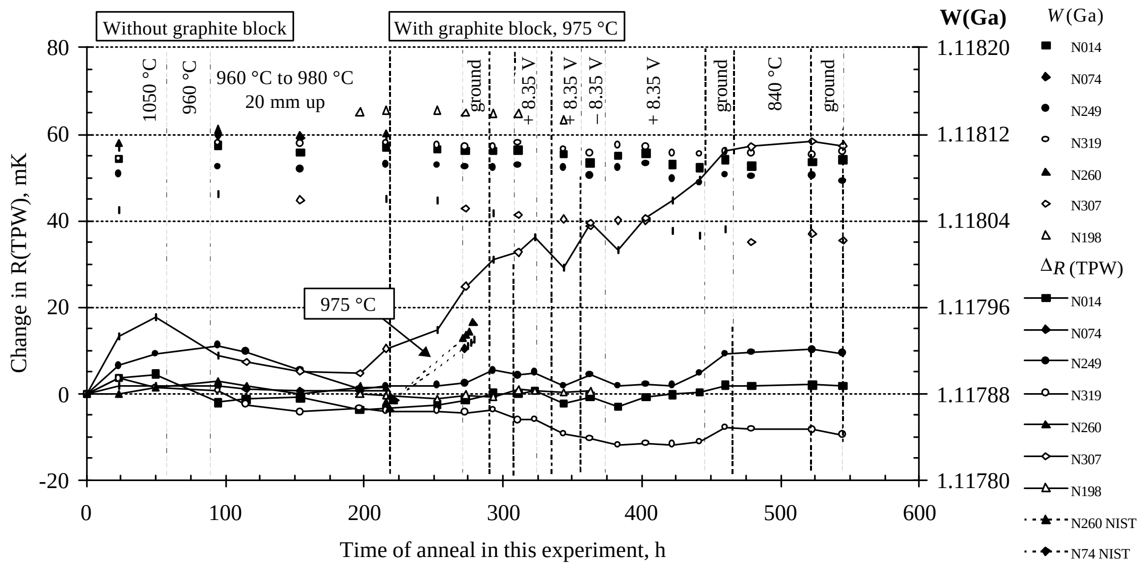

Figure 2. Change in R(TPW) and W(Ga) during the heat treatments.

After about 200 h of heat treatment in this experiment, the HTPRTs were moved to another furnace. The second furnace contains a ceramic tube with a heater wound on the tube. Inside the tube there is a closed-end quartz tube containing a graphite block. The block has six wells for quartz protective tubes for holding the HTPRTs. The purpose of the change of furnace was to obtain a more uniform temperature distribution and to change the thermometer surroundings. To study the effect of the purity of the platinum on the stability of HTPRTs, HTPRT198, with *W*(Ga) = 1.118140, was included in the experiments. During the first 50 h in the new furnace, the HTPRTs showed good stability. The equivalent temperature changes in *R*(TPW) were from 0.23 mK for HTPRT074 to 1.3 mK for HTPRT 014. Only for HTPRT 307 did the R (TPW) began increasing as soon as this thermometer had been moved into this second furnace with a graphite block. After obtaining a satisfactory stability for HTPRTs 074 and 260, they were sent to NIST.

The experiment on the effect on *R*(TPW) of an applied voltage between the leads of a thermometer and ground was conducted at VNIIM with five HTPRTs. The leads of the thermometers were grounded during 20 h of the treatment at 975 °C. As can be seen from Fig. 2, the curve for HTPRT 307 exhibited an increase in the slope. The next heat treatment resulted in an increase in the slopes for HTPRTs 249 and 014. Next a bias voltage of +8.35 V was applied between the leads of the HTPRTs and ground. The slopes of the curves for all of the HTPRTs, except HTPRT 198, changed. The resistance *R*(TPW) of HTPRTs 249, 014, and 249 decreased. Grounding the leads for the next heat treatment caused some increase of *R*(TPW) again. The experiment was repeated with a bias of +8.35 V. This resulted in a decrease of *R*(TPW) for all the HTPRTs. The decrease of *R*(TPW) was greatest for HTPRT 307, corresponding to about 7 mK. The next heat treatment was carried out with –8.35 V applied between the leads and ground. After this experiment, there was a change in the appearance of the HTPRTs. Short sections of white color were clearly seen on the thin quartz insulation tubes (for the leads), but the protective quartz sheaths of the HTPRTs remained transparent. The resistance *R*(TPW) for HTPRTs 014 and 249 increased by the equivalent of 3 to 4 mK and that for HTPRT 307 increased by the equivalent of 10 mK. *W*(Ga) for all the thermometers decreased. It can be seen from Fig. 2 that the resistance *R*(TPW) of HTPRT 198 was stable at the level of ±0.2 mK over all 170 h of the heat treatment with the different bias voltages applied. However, *W*(Ga) became smaller after the last treatment. Unfortunately, this thermometer was broken and was not available for further research. The heat treatment that followed with a positive voltage of +8.35 V applied resulted in a decrease of *R*(TPW) at first, but then those for HTPRTs 014 and 307 started increasing again. After grounding the leads in the next experiment, a change was observed in the slope of the *R*(TPW) versus time of heat treatment curves.

To study the influence of the temperature of heat treatment on the stability of the HTPRTs, we set the temperature of the furnace was set to 840 °C. As can be seen in Fig. 2, the HTPRTs showed very stable values of *R*(TPW), even HTPRT 307.

HTPRTs 260 and 074 were taken to NIST where they were exposed to a temperature of 975 °C in a furnace containing an Inconel block and platinum protective tubes. As one can see from Fig. 2, the thermometers showed a large increase in *R*(TPW) after the first short heat treatments.

4. DISCUSSION

From the experiments performed in this study, some interesting observations can be made about the effects of the heat treatment conditions at high temperature on the stability of HTPRTs:

- Changing the annealing furnace may cause a change of the shape of the stabilization curve of *R*(TPW) versus time of heat treatment – the HTPRTs that exhibited a good stability at VNIIM showed an increase of *R*(TPW) at NIST, and the *R*(TPW) of HTPRT 307 started increasing when it was placed in a different furnace at VNIIM.
- The curves of *R*(TPW) were sensitive to the temperature of heat treatment - a decrease of *R*(TPW) and an increase of *W*(Ga) were observed after lowering the heat treatment temperature from 1050 °C to 960 °C; stabilization was observed after lowering the temperature of the furnace from 975 °C to 840 °C.
- The voltage between the thermometer leads and ground appeared to have an effect on the *R*(TPW) of the HTPRT. After applying a positive voltage, *R*(TPW) decreased, a negative voltage caused an increase of *R*(TPW) and a decrease of *W*(Ga) and appeared to be very undesirable for the thermometers because of deterioration of the quartz parts.
- The effect of the applied voltage on an HTPRT is greater the smaller the value of its *W*(Ga).

What processes are responsible for an increase of *R*(TPW) and a decrease of *W*(Ga) of an HTPRT? The most probable cause is the contamination of the platinum wire by metal impurities. For the heat treatments at NIST, however, the source of such impurities cannot be impurities coming from the metal block, since platinum-quartz tubes, such as used at NIST, are known to provide protection for the HTPRTs. On the other hand, the impurities may be released from the quartz parts of the HTPRT at high temperature. A bias voltage between the thermometer leads and ground seems to have an effect on the process of contamination of the sensor. The temperature of heat treatment and the distribution of the temperature along the sensor also may have an effect on the change of *R*(TPW), since these influence the motion of impurities in the platinum. The NIST furnaces are set up such that a positive bias voltage exists between the thermometer leads and ground. The smaller the *W*(Ga), the more contaminated the HTPRT and the greater the influence of the bias voltage.

Observed deterioration of the quartz parts of the HTPRTs was seen only at the inner surface of the thin tubes, the outer surface remaining smooth. This process could possibly have been caused by the contamination of the platinum wire.

This work is not a contradiction to the previous successful investigations of stability of HTPRTs. This study showed that good stability of *R*(TPW) can be maintained for the HTPRT operating in the same furnace at the same conditions. The problems arise when it is necessary to work with an HTPRT under different conditions at high temperatures. The observed instability is greater for the HTPRTs with low values of *W*(Ga). The HTPRTs with *W*(Ga) greater than 1.11840 seem not to be sensitive to the change of the environments as long as the purity of the platinum is kept at the high level. Additional investigations are necessary to explain the results observed and reported in this paper.

REFERENCES

[1] Berry R. J. *The influence of crystal defects in platinum on platinum resistance thermometry,* TMCSI, 1972, v.4, Part 2, pp 937..949

[2] Marcarino P., Dematteis R., Gallorini M., and Rizzio E., *Contamination of Platinum Resistance Thermometers at High Temperature Through Their Silica Sheaths,* Metrologia, 1989, 26, pp 175..181

[3] Crovini L., Marcarino P., *Accurate contact temperature measurements for 420 to 1064 °C,* High Temperatures – High Pressures, 1991, 23, pp 231..240

[4] Hill K. D., *A method to prevent the contamination of platinum resistance thermometers by silver*, Proceedings of TEMPMEKO '96, edited by P. Marcarino, Levrotto & Bella, Torino, 1997

[5] Berry R. J., *Analysis and control of electrical insulation leakage in platinum resistance thermometers up to 1064 °C,* Metrologia, 1995, 32, pp 11..25