EFFECT OF PURITY OF THE PLATINUM WIRE OF HTPRTS ON THEIR CHARACTERISTICS

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ABSTRACT

High temperature platinum resistance thermometers (HTPRTs) were introduced in the International Temperature Scale of 1990, replacing thermocouples in the range 660.323 °C - 961.78 °C. That resulted in increasing the reproducibility of the scale by more than an order of magnitude. In the definition of ITS-90 there is a requirement on the quality of the platinum used in the platinum resistance thermometers in all the temperature sub-ranges above 0 °C. The resistance ratio, W(Ga), at the melting point of gallium must not be less than 1.11807. Experience in using HTPRTs showed that different long-term stability of the resistance might be obtained at different temperatures. The reasons for less stability at high temperatures are possibly due to changes in crystal structure of the platinum and mobility of impurities and defects. In this paper the work, carried out at VNIIM on the investigation of HTSPRTs with different values of W(Ga) is analyzed and summarized to discuss the influence of the purity of the platinum wire on the stability of the HTSPRTs. A suggestion is made to tighten the requirement on W(Ga) for platinum resistance thermometers used at high temperature as standard interpolation instruments of the ITS-90.

1. INTRODUCTION

VNIIM has a lot of experience in using HTPRTs. During the last ten years, dozens of HTPRTs have been stabilized and calibrated at the Thermodynamic Laboratory of VNIIM. Several papers on investigation of the characteristics of Russian HTPRTs have been published [1,2,3]. Some research was carried out at NIST [4]. The results confirmed good performance characteristics of the HTPRTs. The data led us to conclude that the best stability could be obtained at temperatures below 800 °C: at higher temperatures, the HTPRTs became less stable. It was noticed also that the HTPRTs that had a low value of W(Ga) are more unstable than those with a high value of W(Ga). It was suggested that the purity of the platinum wire of the sensitive element might have an effect on the stability of an HTPRT in the high-temperature range. In the ITS-90, two requirements are stated for the standard platinum resistance thermometers for the range 0 - 962 °C: W(Ga) $\geq$ 1.11807 and W(Ag) $\geq$ 4.2844. The first requirement defines a high purity and quality of the platinum wire. The same restriction on the W(Ga) value is stated both for middle-range SPRTs and for HTPRTs. It should be noted here that for metals of a very high purity the term 'chemical purity' is not an equivalent to the 'electrical purity'. The chemical purity is determined by the concentration of chemical impurities in the metal. The 'electrical purity' depends also on changes in the structure of the crystal lattice, creation of big crystals, grains, holes, vacancies, dislocations, and distribution of impurities in the platinum. W(Ga) is a characteristic of the electrical purity of the platinum.

Experience with HTPRTs has shown that in the range 0-662 °C, thermometers with W(Ga) less than 1.11807 could be as stable as Standard thermometers. This can be explained by a low mobility of impurities and lattice imperfections at low and middle temperatures. The main reason for instability of the resistance in the middle-temperature range is likely due to strains developed in the platinum wire during heating and cooling of the thermometers. At temperatures above 660 °C mobility of the lattice defects increases; at temperatures above 800 °C, metal impurities are capable of alloying with platinum, and the process of growing big grains goes faster. Stress introduced in the wire during heating and cooling of the thermometer, as well as accidental vibration during moving the hot thermometer between furnaces, may cause cracking of the structure, and creating holes and dislocations in the platinum. Impurities and dislocations move to the grains boundaries. The process goes very slowly and may cause a long-term increase of the resistance during high-temperature annealing. Conditions of the annealing, such as environment in the furnace, temperature distribution along the thermometer, and leakage currents between leads and ground, affect the processes in the platinum and may affect the shape of the stabilization curves. These phenomena are more observable for impure platinum. In paper [3], it was shown for a thermometer with a low W(Ga) that if a positive voltage were applied between the leads of the thermometer and ground, then what had been an increase of the resistance with time at 975 °C would become a decrease. In paper [1] some calibration data for three Russian HTPRTs at the fixed points of Ag and Au were given. The best reproducibility was observed for HTPRT N 0012, which had W(Ga) = 1.118125. Two of Russian HTPRTs were investigated at NIST in 1992 [4]. Better stability during the initial annealing was observed for HTPRT "I", which had a W(Ga) value greater than that of HTPRT "J".

In this paper some observations on the behavior at high temperatures of HTPRTs of different purity are presented. Two different furnaces were used for annealing the HTPRTs. All the thermometers are of Strelkov's design.

2. EXPERIMENTAL

In constructing Russian HTPRTs, high-pure platinum wire, type PL-0 from Ekaterenburg, is used. After construction, the thermometers receive an anneal at 1100 °C for 10 hours at the plant, and then they are sent to the Laboratory of VNIIM for further stabilization and calibration. Usually the value of W(Ga) of the thermometers after construction and anneal at the plant is between 1.11820 and 1.11850. It is a very rare case when an HTPRT has a W(Ga) less than 1.11810. In the Laboratory the HTPRTs are annealed in cycles each lasting from 5 to 20 hours. An HTPRT is considered to be stable and ready for calibration if the change of its resistance at the triple point of water after 20 h of anneal at 975 °C does not exceed the temperature equivalent of 2 mK. During the stabilization at the Laboratory, W(Ga) may decrease, and sometimes it approaches the value of 1.11809. For this study we have chosen several thermometers, with different W(Ga) values, from different groups of HTPRTs, manufactured in Russia during the last four years.

HTPRTs N322-N325 were stabilized in a furnace containing a graphite block at 975 °C. That high-temperature annealing furnace contains a ceramic tube with a ribbon heater wound on it. Inside the bottom part of this tube, there is a stainless steal cylinder connected to ground. Inside the ceramic 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 using the graphite block is to obtain an uniform temperature distribution in the furnace. The temperature gradient over the length of 10 cm from the bottom of the wells was about 1 K/cm. The thermometers were inserted into the annealing furnace when the temperature in the furnace was about 500 °C. Then the thermometers were heated slowly to 975 °C, exposed at that temperature for 15-20 hours, cooled to 500 °C over 3.5 hours and removed from the furnace. Each annealing cycle was followed by the measurements of the resistance at the triple point of water R(TPW). The stabilization curves are shown in Fig.1. The increase of the resistance might be caused by the contamination of the platinum wire by impurities coming through the quartz and graphite from the metal cylinder. However, the resistance stopped increasing after 200 hours of heat treatment. So, the impurities might come from the inner parts of the thermometer and redistribute in the platinum. The W(Ga) values decreased from about 1.118130 to values between 1.118109 and 1.11820. So, all the thermometers met the requirements of the ITS-90. HTPRT N 324 that had the largest W(Ga), was calibrated at the fixed points of Ag, Al, Zn, Sn. As can be seen from Fig.1, its R(TPW) value increased by the equivalent of 2 mK after the first measurement at the silver point. HTPRTs N330 - N335 were annealed in the furnace without a graphite block and metal cylinder. Thus, the source of outer contamination was excluded. The temperature gradient over the length of 10 cm from the bottom of the wells was about 3 K/cm. The curves R(TPW) are shown in

Fig. 2. We observed continual decrease of the resistance during 120-140 hours. The decrease can be explained by growth of big grains in the very pure platinum wire and oxidation of impurities on the surface of the wire. The W(Ga) was increasing concomitantly. The difference in the behaviour of the HTPRTs from the two groups might be related to the difference in the temperature distribution in the furnace. It happens very seldom that after the treatment at the plant an HTPRT has a W(Ga) value less than 1.11809 (this value, however, is still inside the requirements of the Scale). Such thermometers always show a large and fast increase of R(TPW) during stabilization. An example of such behaviour is given in Fig.3. After 100 h of annealing, the thermometer became more stable. The W(Ga) decreased from 1.118085 to 1.118073. As usual, the resistance of thermometers with a low W(Ga) increases in steps during long heat treatments. A fast change in R(TPW) is followed by a period of stability. The reason for the fast increase of the resistance is possibly due to redistribution of impurities in the platinum at high temperature. After a stable distribution is approached, the resistance stopped increasing. When the crystals of the platinum crack, the motion of the impurities starts again.

The concentration of impurities in the platinum might have an effect on the process of quenching the defects in the crystal lattice of the platinum during cooling an HTPRT from a high temperature. We carried out an experiment on quenching and cooling HTPRTs. Three HTPRTs were chosen. Two of them had a W(Ga) of 1.11809, one had a W(Ga) of 1.118145. The thermometers were quickly removed from the furnace at 975 °C, the R(TPW) was measured, then they were annealed and cooled according the procedure described above. The R(TPW) was measured again. The change in R(TPW) is presented in Fig. 4. As can be seen from the figure, the increase in R(TPW) after quenching is the smallest for the thermometer with the largest W(Ga). However, the annealing procedure proved to work well both for pure and for less pure platinum, and it was used in all our experiments with the thermometers.

For an investigation of the stability of HTPRTs in this work, several HTPRTs that had different values of W(Ga) were selected. Besides HTPRT N322 and N330, whose initial stabilisation was described above, we took HTPRTs N074 and N260 that were used in the work [2] and had been exposed to a temperature above 960 °C for more than 600 h. The W(Ga) of the thermometers decreased during the previous heat treatments from 1.118130 to about 1.118103. HTPRT N305 was used at the silver fixed point for a long time and it may have been slightly contaminated by silver. Its W(Ga) was about 1.11809. HTPRT N294 was an unique thermometer that had the W(Ga) of 1.118072 after the construction and initial stabilisation. HTPRT N329 had the largest W(Ga) (1.118150). It was annealed previously for 100 h at 1000 °C in the furnace without a block; a decrease of R(TPW) was observed. These six thermometers were simultaneously subjected to a heat treatment in the furnace without a block, at first at 975 °C, then at 1100 °C. The curves showing the change in R(TPW) are given in Fig.5. Values of W(Ga) shown in the figure were obtained at the beginning of the experiment. The R(TPW) of the thermometers with a low W(Ga) increased continuously. HTPRT N294 was found to be unstable in the sense that its R(TPW) increased for more than 10 mK after 50 h at 975 °C, W(Ga) decreased to 1.118065. The values of W(Ga) of HTPRTs N329, N330, N260, N074 did not noticeably change during the experiment. For HTPRT N 329, which had the largest W(Ga), we observed a decrease of R(TPW) by the equivalent of 3 mK over 68 hours. HTPRTs N260 and N074 appeared to be the most stable thermometers. The change of R(TPW) was within the equivalent of 1 mK. These thermometers were previously used at 975 °C for more than 600 h. However, during the experiments carried out at VNIIM and NIST [2], the R(TPW) of these HTPRTs behaved very differently upon annealing at VNIIM and NIST.

In the research [4], carried out at NIST in 1992, two Russian HTPRTs were calibrated in the range 0-1065 °C. Between calibrations the thermometers received anneals at temperatures above 1000 °C. The changes in the successive calibrations of the HTPRTs showed a continuous decrease of the resistance ratios at the fixed points. The change of W(Ag) was greater for the HTPRT with a lower W(Ga). It was decided in this work to analyse the calibrations of some other HTPRTs at the silver fixed point, to assess the possible relationship between the reproducibility of W(Ag) values and the purity of the platinum. In the Table 1 one can see the average values of W(Ga), W(Ag) and the temperature equivalent of the range of W(Ag) for three successive calibrations. The data are also plotted in Fig.6. All the thermometers showed a good reproducibility. Two HTPRTs with the smallest W(Ga) appeared to be less stable, however.

3. CONCLUSION

From our experience with HTPRTs, we have noticed that thermometers with a W(Ga) between 1.11807 and 1.11809 often have a worse reproducibility than such new instruments as gold-platinum or platinum-palladium thermocouples.

In the present work, we analysed some data on initial stabilisation of the HTPRTs. It was shown that R(TPW) and W(Ga) for the HTPRTs from different groups could show different changes, and that these differences might be explained by having different surroundings in the furnace, different temperature distribution over the sensitive element, and perhaps some difference in the construction of the HTPRTs. The processes proceeding in the platinum at high temperature depend on the impurity concentration. The data presented in this work show that the thermometers with W(Ga) less than 1.11809 were not stable at high temperature, a continues increases of R(TPW) was observed, and the reproducibility at the Ag fixed point was the worst of all the other thermometers.

For Russian HTPRTs, a W(Ga) less than 1.11810 is a very rare case. However, the W(Ga) may decrease during long heat treatments at high temperature. There are several companies in the world manufacturing HTPRTs. All the HTPRTs are very expensive instruments. In the characteristics of an HTPRT, the manufacturer states W(Ga) as being not less than 1.11807, thus meeting the requirements of the ITS-90. The stability is usually declared to be 10 mK per 100 h at 1000 °C. A customer may purchase a thermometer with the W(Ga) of about the lower limit for the scale, and, possibly his expectations of having an instrument of a higher accuracy than thermocouples would not come true. Other customers purchasing a HTPRT with a higher W(Ga) value will risk less. It should be added that the stability of the HTPRTs depends on many factors, not only the purity of the platinum wire. However, the purity always should be taken into consideration when choosing a HTPRT. Probably, a suggestion can, and should, be made to tighten the requirement on W(Ga) for the HTPRTs in the International Temperature Scale.

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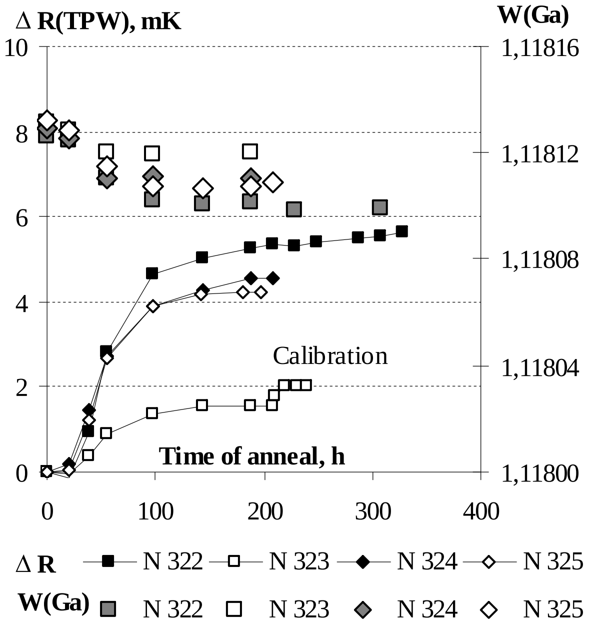

Figure 1: Change in R(TPW) during heat treatment in the furnace with a graphite block

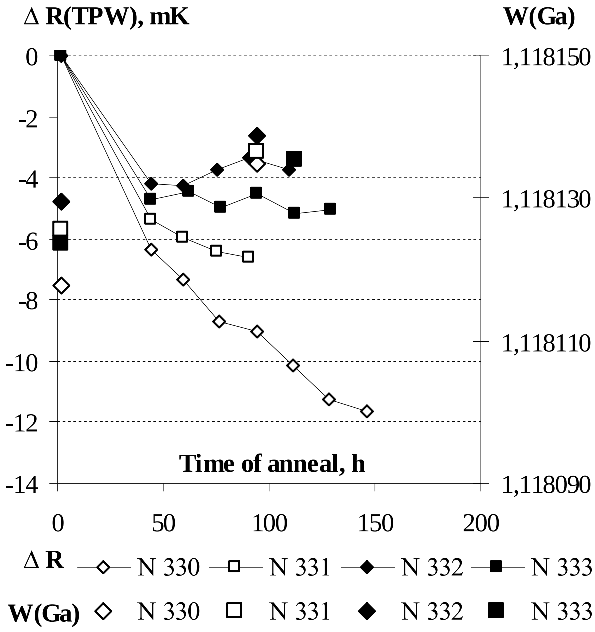

Figure 2: Change in R(TPW) during heat treatment in the furnace without a block

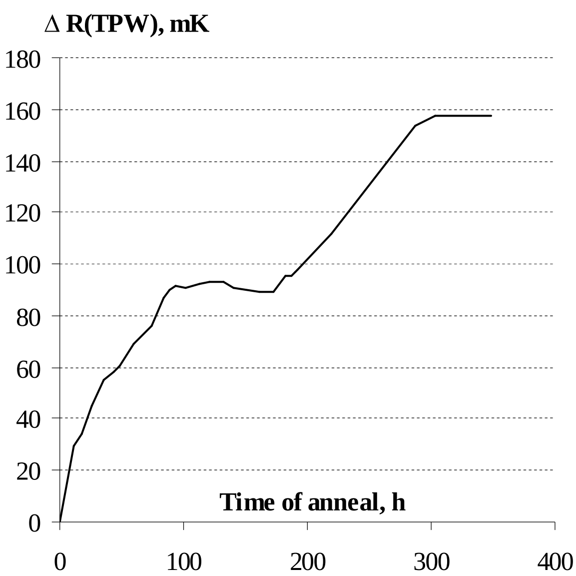

Figure 3: Change in R(TPW) during heat treatment of HTPRT N307, W(Ga)=1.118085

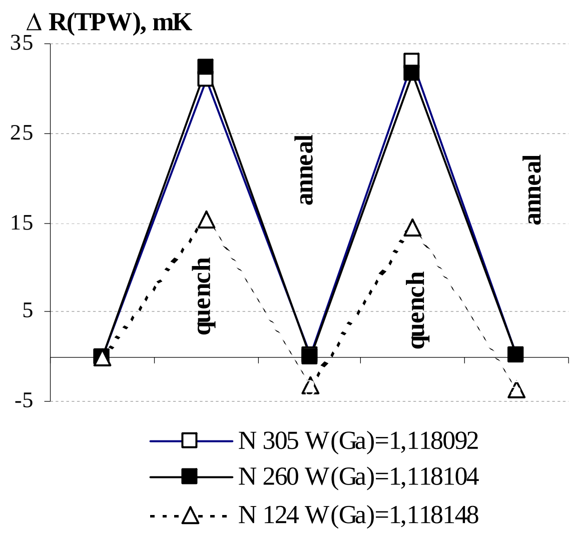

Figure 4: Change in R(TPW) during quench and anneal of HTPRTs

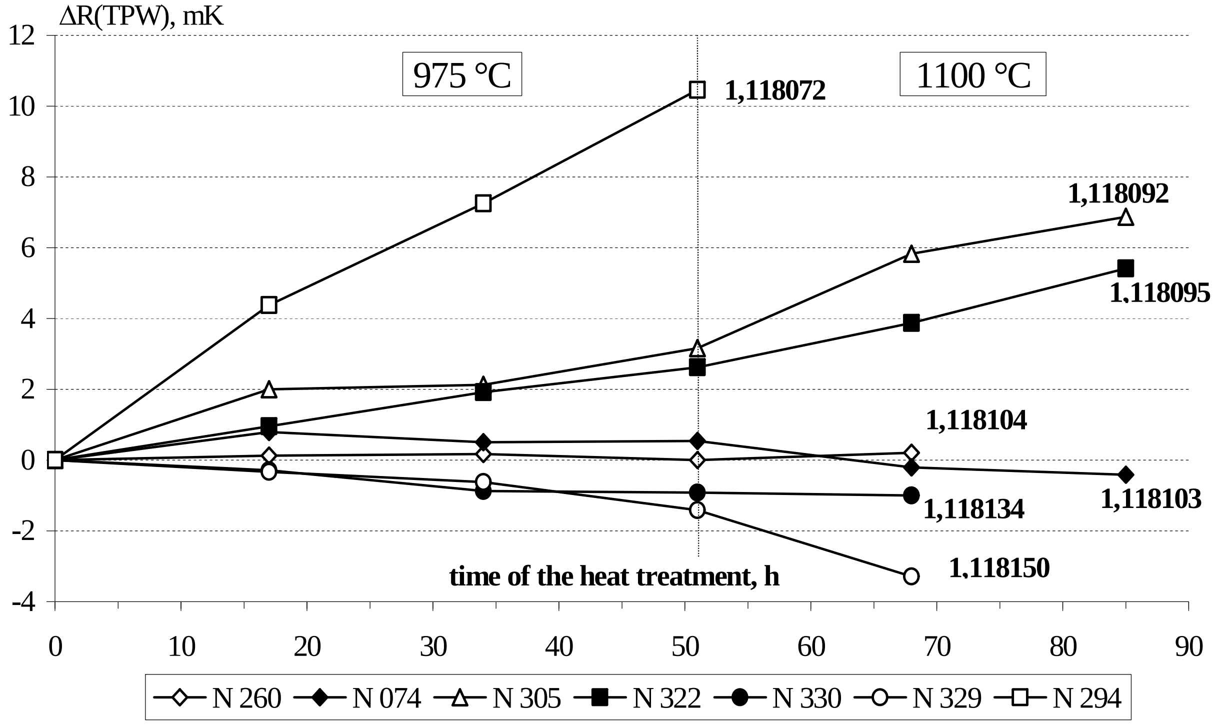

Figure 5: Change in R(TPW) during the simultaneous heat treatment of HTPRTs with different W(Ga) values.

Table 1: The values of W(Ga), W(Ag), and the range of W(Ag) during three calibrations at Ag point

N therm.	W(Ga)	W(Ag)	ΔW(Ag), mK
46	1,118094	4,284993	4,47
257	1,118091	4,285048	7,67
271	1,118108	4,285336	3,20
262	1,118108	4,285358	2,57
81	1,118110	4,285401	1,26
245	1,118111	4,285447	1,13
83	1,118112	4,285479	0,35
240	1,118113	4,285499	1,72
277	1,118114	4,285557	1,97
247	1,118114	4,285571	1,76
268	1,118116	4,285635	2,64
92	1,118124	4,285757	1,90
12	1,118125	4,285841	1,83

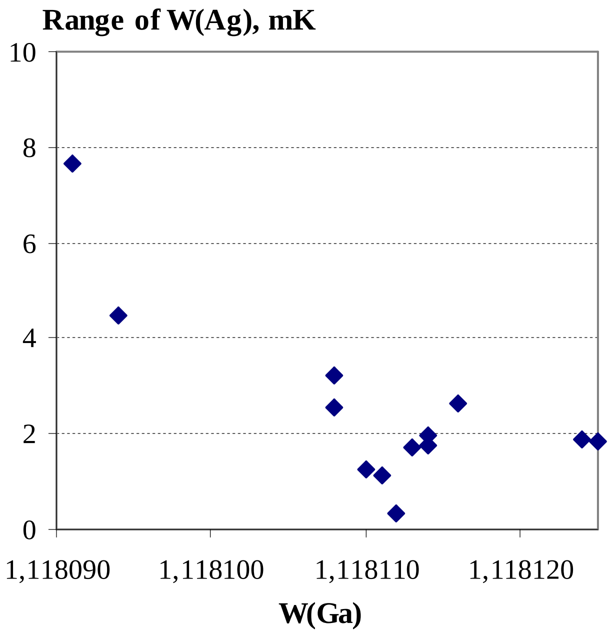

Figure 6: Range of W (Ag) in dependence on the value of W(Ga).