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VARIATIONS IN THE THERMOELECTRIC BEHAVIOR OF PALLADIUM FOLLOWING HEAT TREATMENT

G. W. Burns and D. C. Ripple

National Institute of Standards and Technology, Gaithersburg, Maryland, USA

ABSTRACT

In order to identify limitations on the use of Pt/Pd thermocouples as high-accuracy thermometers, we have studied the change in thermocouple emf at the Al and Ag freezing points following a series of heat treatments at various temperatures for several lots of Pd wire. Reversible changes in the thermocouple emf at the Ag point (962 °C) occur after heat treatments in the approximate temperature range 550 °C to 1000 °C, and slower, irreversible changes in emf occur after exposure to higher temperatures. Surprisingly, the sign of the reversible change was different for thermocouples fabricated from two lots of Pd of different purity. The magnitude of the changes in emf can be as high as the equivalent of 0.7 K per 200 h of heat treatment for the irreversible changes and 0.07 K per 200 h for the reversible changes. The consequences of these effects for metrology applications of Pt/Pd thermocouples are discussed.

1. INTRODUCTION

A thermocouple constructed from pure Au and Pt thermoelements can be remarkably stable in its thermoelectric behavior [1,2]. Although occasional annealing in a furnace is necessary to reduce quenched-in lattice vacancies following a rapid cooling from high temperature, this effect is both well understood and well characterized. With care, the thermocouple emf will be stable to within the equivalent of 15 mK at the Ag point for 1000 h. In contrast, the thermoelectric behavior of thermocouples fabricated from Pt and Pd depends significantly both on the source or purity of the Pd wire and on the thermal history of the thermocouple [3].

In this paper, we describe the changes in thermoelectric emf of Pt/Pd thermocouples at the Ag (961.78 °C on the International Temperature Scale of 1990) and Al (660.323 °C) freezing points following a series of heat treatments in a separate furnace. Because of the proven performance of Pt both as a thermoelectric reference and as part of the highly stable Au/Pt thermocouple combination, we ascribe these changes to changes in the thermoelectric properties of the Pd thermoelement. In contrast to the behavior of Au/Pt thermocouples, we find that [3]:

a. The emf values of Pt/Pd thermocouples at the Ag freezing point drift steadily upward following heat treatment at 1100 °C, at a rate that depends on the lot of Pd wire used.
b. Following heat treatment in the temperature range 550 °C to 1000 °C, the emf values of Pt/Pd thermocouples undergo reversible changes. Both positive and negative changes in emf have been observed, and the details of these reversible changes vary with the source of the Pd.
c. An electrical anneal of the Pd wire at 1300 °C, followed by a furnace heat treatment of the Pt/Pd thermocouple for approximately 50 h at 1100 °C is required to achieve optimum stability of the thermocouple emf with time.

Thermocouples fabricated from Pd from five different lots are described in this paper. One lot of wire (JM93) that produced thermocouples of the highest performance was used to fabricate all of the thermocouples used in a determination of a reference function for Pt/Pd thermocouples [4]. Data from the four other lots have not been previously presented. Recent studies [5,6] on Pd that give results different from that of JM93 have motivated us to publish and interpret our data for these other lots.

2. METHODS OF STUDY

Thermocouples were fabricated using the five lots of Pd wire listed in Table 1 and from a single lot of Pt wire, all of 0.5 mm diameter. Although several thermocouples were fabricated from each lot, we report only the results for one to three representative thermocouples from each lot. Differences in behavior were small for different thermocouples fabricated from the same lot of Pd and annealed electrically in the same manner. The thermocouples are designated by the Pd lot (E for wire supplied by Englehard-Clal, J for Johnson-Matthey, and SC for Sigmund Cohn*) followed by a suffix: for example E90-2 is the second thermocouple from the E90 lot of Pd wire. The annealing procedures, fabrication techniques, and the equipment and methods used to characterize the thermocouples have been documented elsewhere [3,4]. Here, we briefly summarize the experimental procedures.

Table 1. Lot designations, manufacturer's nominal total chemical purity, and levels of specific impurities, as measured by NRC-Canada, of the Pd wire used in this study. The stated impurity levels are equal to (mass fraction)$\times 10^6$, and only elements with $\geq 13 \text{x} 10^{-6}$ mass fraction are listed.

Lot	E90	JM92	JM93	SC89	SC90
Chemical purity (mass%, manufacturer)	99.95	99.997	99.997	99.98	99.98
Chemical purity (mass%, NRC)	99.98	99.996	99.991	99.6	99.94
O	5	5	23	50	5
Si	25	3	27	0.2	2
Mn	0.3	0.03	0.01	3200	6
Fe	50	5	5	86	70
Cu	4	0.09	0.3	6	110
Ru	5	1	<0.07	7	280
Rh	49	0.3	0.1	47	20
Sn	0.5	0.2	0.2	17	0.5
Ir	8	0.7	4	2	13
Pt	67	2	10	270	320
Au	2	2	<0.06	9	32
Pb	0.4	0.02	0.5	3	22

Prior to assembly, the thermocouple wires were annealed electrically in air for 10 h by direct passage of AC current through the wires, at a temperature of 1300 °C for Pt and at either 1100 °C, 1300 °C, or 1350 °C for Pd. The wires were then cut into 0.62 m long segments, and the segments annealed in the central region of a three-zone furnace, which was uniform in temperature to within ±2 °C. Pd segments were annealed in the furnace at temperatures of 1100 °C for 1 h, cooled quickly to room temperature, and then given an overnight anneal at 450 °C. Pt segments were annealed in the furnace at 1100 °C for 1 h, and then cooled slowly to 450 °C for an overnight anneal. The annealed segments were welded together and mounted in two-bore, high-purity alumina insulators, with an expansion coil connecting the two thermoelements at the measuring junction end. Following assembly, the thermocouples were given a series of furnace anneals by immersing 60 cm of the thermocouple assembly into the same three-zone furnace as used for the wire anneals. Note that the welded joints between segments occur only in sections of the thermocouple that are exposed to room temperature during use or annealing.

To characterize the effects of these different heat treatments, the thermoelectric emf of each thermocouple was measured at the freezing point of Al (660.323 °C) or Ag (961.78 °C). The variation of emf of a Pt/Pd thermocouple with temperature is 19 µV/K and 14 µV/K at the Ag and Al freezing points, respectively. Standard methods and equipment were used to realize the freezing points and to measure the thermocouple emf [4]. The standard uncertainty of the emf values are 0.055 µV at the Al freezing point and 0.09 µV at Ag, or the equivalent of 4 mK and 5 mK, respectively [4]. Immersion profiles, showing the emf reading as a function of depth of the thermocouple into the freezing-point cell, were obtained as in previous work [3]. At immersions greater than 6 cm, the thermocouple is in thermal equilibrium with the freezing metal, and any deviation from a constant value of emf is an indication of inhomogeneity or drift of the thermocouple. Other methods of determining the inhomogeneity of Pd wires are described in the literature [6,7].

3. IRREVERSIBLE CHANGES IN EMF

Pt/Pd thermocouples, when heated to temperatures of approximately 1100 °C or higher, will undergo irreversible thermoelectric changes, with a net result of an increase in emf at the Ag freezing point. Continued heat treatment at 1100 °C for periods of 50 h or more reduces the rate of change of the emf.

The magnitude of this change is reduced by electrically annealing the Pd wire prior to fabrication at a temperature of at least 1300 °C. Typical results for five different wire lots of Pd and three annealing temperatures are shown in Fig. 1. Thermocouples fabricated from Pd electrically annealed at 1100 °C have lower emf and higher drift rates than thermocouples with Pd electrically annealed at 1300 °C or higher, as seen by comparing JM92-3 to JM92-5, or SC89-9 to SC89-10. Annealing the Pd at 1350 °C gave results similar to those of the Pd annealed at 1300 °C, as seen by comparing JM93-2 to JM93-3.

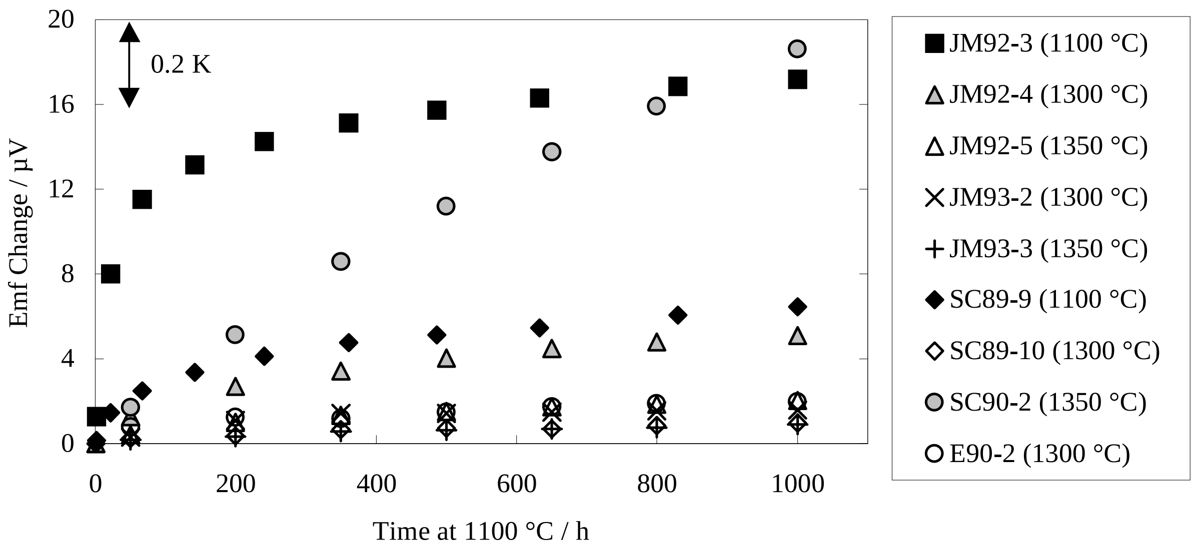

Fig. 1 The emf change at the Ag freezing point of nine Pt/Pd thermocouples as a function of time of heating at 1100 °C. Pd wires were annealed electrically at the temperatures listed in the legend.

Chemical analysis and nominal purity for the Pd wires referenced in Fig. 1 are given in Table 1. Comparison between the drift results of the various thermocouples annealed at 1300 °C or above reveals striking variations in drift rate for thermocouples fabricated from different lots of Pd of similar nominal purity. As examples of differences between lots, compare JM92-4 to JM93-3, and SC89-10 to SC90-2. There is no clear correlation of drift rate with level of a specific impurity. For example, E90-2 and JM93-2 both have excellent thermoelectric stability, relative to JM92-4, but a comparison of the E90 analysis to that of JM92 shows that E90 is higher in all impurities listed in Table 1.

4. REVERSIBLE CHANGES IN EMF

In Reference [3], we discussed changes in the emf of Pt/Pd thermocouples following short exposures to temperatures in the range 500 °C to 800 °C. It was found that these changes could be reversed by a suitable furnace anneal of the thermocouple. Here, we discuss these changes in greater detail.

To investigate the sensitivity of Pt/Pd thermocouples to exposure to various temperatures, immersion profiles were measured at the Ag freezing point following each of seven 200 h furnace anneals that were at temperatures ranging from 450 °C to 1100 °C. For each annealing cycle, the thermocouple was heated for 1 h at 1100 °C and then cooled in the annealing furnace to the temperature of the 200 h anneal. At the conclusion of each 200 h anneal, the thermocouple was cooled in the furnace to room temperature. After each furnace anneal, a full immersion curve was measured in the Ag freezing-point cell, and values of the hysteresis and emf at full immersion were obtained. Results for thermocouples constructed from two lots of Pd wire are shown in Fig. 2. The emf decreases for thermocouple JM93-2 in the approximate range 550 °C to 800 °C, but for SC89-10, there is only a small decrease at 650 °C and a substantial increase in the range 750 °C to 1000 °C. The results for lot JM93 are identical to those published in Reference [3].

An interpretation of these data is suggested by a careful study of the immersion curves of JM93-6 in the Ag and Al freezing-point cells during a freeze, following in-situ aging in these cells. (The irreversible changes in JM93-6 are virtually the same as for JM93-2.) These immersion curves are published in Reference [3], and are reproduced in part in Fig. 3. When a thermocouple is aged in a furnace at fixed immersion, different segments of the thermocouple are exposed to temperatures ranging from room temperature to the core furnace temperature. If, following aging, the thermocouple is partially withdrawn a sufficient distance, wire that was aged at the core furnace temperature is drawn into the region where there is a temperature gradient. Since thermoelements produce emf only in regions with a thermal gradient, changes in thermocouple emf at partial immersion of the thermocouple into the furnace are an indication of thermoelectric changes in that portion of the wire that has been drawn into the region of high thermal gradients.

Referring to Fig. 3, the emf of JM93-6 at the Al freezing point is depressed following exposure to core furnace temperatures of approximately 664 °C, both at partial and full immersion in the cell. We conclude that exposure of the wire to temperatures ≤660 °C results only in a decrease in emf.

At the Ag point, the emf of JM93-6 is depressed at full immersion following exposure to temperatures of approximately 962 °C, but at partial immersion of the thermocouple, there is a significant increase in thermocouple emf. This suggests that the Pd wire of JM93-6, when aged at 962 °C and drawn into the temperature gradient region, does result in an increase in thermocouple emf. Qualitatively, this is the same effect as observed in thermocouple SC89-10 in the uniform annealing experiment, but with Pd from the JM93 lot, the increase in emf at temperatures near 962 °C is much smaller than for SC89-10. We note that these immersion profiles are more sensitive than the results from uniform annealing shown in Fig. 2, since there is less interference from the irreversible drift and from irreproducibility associated with thermal cycling.

Results similar to that observed for thermocouple SC89-10 have been reported in the literature [5,6]. The techniques used in the work of Ref. [5] are similar to those employed here, but the nominal purity of the Pd wire studied was “99.99+%”. Following exposure to temperatures in the range 500 °C to 600 °C, there was a small decrease in emf, while exposure to temperatures from 600 °C to 1000 °C resulted in small changes in the emf at full immersion, but an increase in emf when the thermocouple was at partial immersion. The work of Ref. [6] used a gradient-anneal approach in which a single wire is exposed to a heat treatment temperature that varies along the wire length. Thermoelectric scanning of the wire can then be used to identify segments of the wire that have undergone thermoelectric changes, due to exposure to a particular temperature. In this work, significant changes in the Pd, corresponding to an increase in thermocouple emf, were observed following exposure of the Pd to temperatures in the range 550 °C to 850 °C for Pd of nominally 99.95% purity.

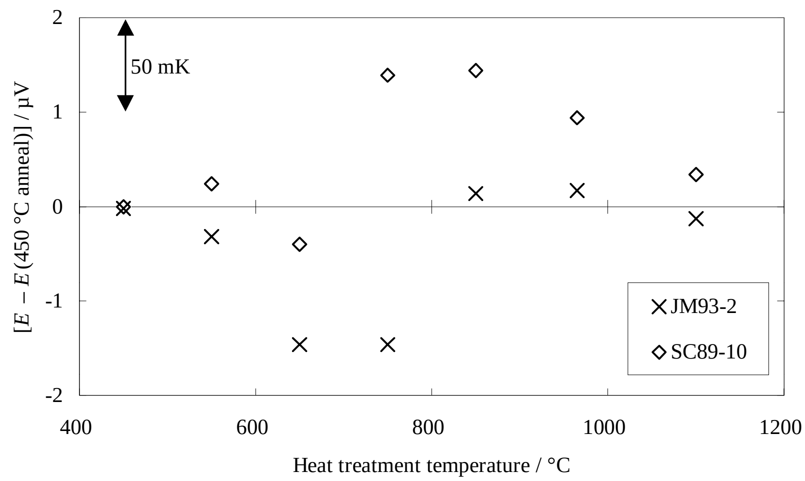

Fig. 2 Deviations of the emf value *E* at the freezing point of Ag of two Pt/Pd thermocouples, following 200 h heat treatments at the temperatures indicated. The value of *E* after the 450 °C heat treatment is used as a baseline.

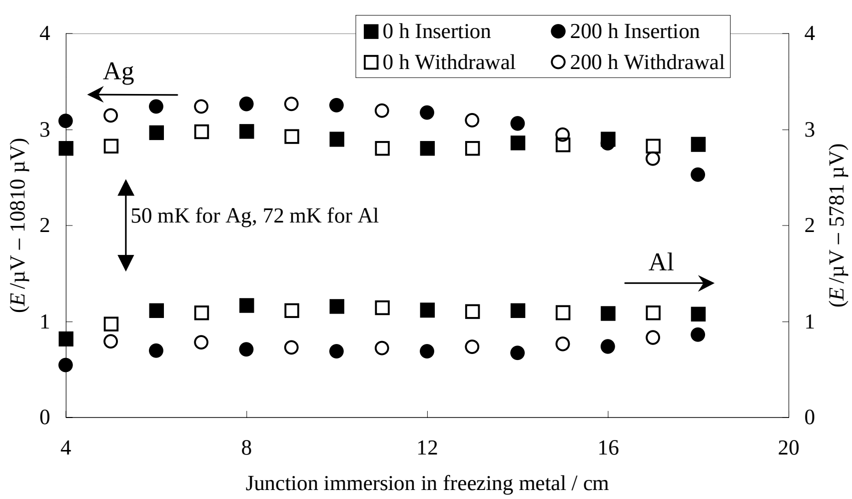

Fig. 3 Immersion profiles of thermocouple JM93-6 on insertion into and withdrawal from the Al and Ag freezing-point cells during a freeze, both before and after the thermocouple was heated at full immersion in the Ag cell for 200 h at 965 °C and in the Al cell for 200 h at 664 °C, respectively.

We suggest that there are two separate reversible effects of opposite signs: a reversible decrease in thermocouple emf following exposure to temperatures in the approximate range 550 °C to 800 °C, and a reversible increase following exposure to temperatures in the approximate range 750 °C to 950 °C. When the available data are studied as a whole, the magnitude of the reversible change in the range 750 °C to 1000 °C appears to be generally smaller for Pd of higher purity. At this time, we cannot identify unambiguously the source of the reversible changes. Our previous work attributed reversible decreases in emf to an oxidation effect, but it is not likely that oxidation of Pd is the source of the emf increase in the range 750 °C to 950 °C, which is generally above the approximate range 350 °C to 800 °C where Pd oxide is stable [3].

5. CONSEQUENCES FOR METROLOGY

The rate of irreversible changes in the thermoelectric properties of Pd limit the useful lifetime of Pt/Pd thermocouples as reference standards. Referring to Fig. 1, there are clear benefits to electrically annealing the Pd at 1300 °C and then heat treating the assembled thermocouple at maximal possible immersion at a temperature of 1100 °C for ≈50 h. A heat treatment at maximal immersion reduces the thermoelectric drift without increasing the inhomogeneity of the thermocouple. Because each lot of Pd wire has a characteristic drift rate that is not highly correlated to the purity specifications from the manufacturer, measurement of the thermocouple emf during the stabilization process, for at least one thermocouple from each lot of Pd, will give increased confidence in the stability of the thermocouple in subsequent use. We recommend that Pt/Pd thermocouples be heat treated at 1100 °C for ≥50 h, and that the emf be measured at least three times at the Al or Ag freezing point during this process.

The time scales for the irreversible changes in emf are quite long—hundreds of hours—even though the heat treatment temperatures are relatively close to the Pd melting point of 1555 °C. Because the drift depends on the wire origin but not the alumina insulator used [3], we believe that the source of drift is intrinsic to the Pd wire itself. The long time scale for irreversible changes suggests that the thermoelectric changes are not a result of localized annealing of the crystalline lattice or of oxidation or reduction of elements, both of which occur at shorter time scales.

It is clear that the reversible effects observed with Pd are complex and depend on the particular lot of Pd used. What is not clear is the identification of the impurity or other property responsible for the effect in the range 750 °C to 950 °C. Since high-purity Pd is difficult to obtain, such knowledge would enable screening of lots of low-purity Pd that have acceptable thermoelectric performance.

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REFERENCES

* Certain commercial materials are identified in this paper in order to specify adequately the experimental procedures. Such identification does not imply recommendation or endorsement by NIST, nor does it imply that the materials identified are necessarily the best available for the purpose.

1. McLaren E. H. and Murdock E. G., "The Pt/Au Thermocouple", Part I and Part II, NRCC/27703, National Research Council of Canada, Ottawa, 1987
2. Burns G. W., Strouse G. F., Liu B. M., and Mangum B. W., In *Temperature: Its Measurement and Control in Science and Industry*, Vol. 6, (Edited by J. F. Schooley), New York, American Institute of Physics, 1992, 531-536
3. Burns G. W. and Ripple D. C., In *Proceedings of TEMPMEKO `96, 6th International Symposium on Temperature and Thermal Measurements in Industry and Science*, (Edited by P. Marcarino) Turin, Levrotto & Bella, 1997, 171-176
4. Burns G. W., Ripple D. C., and Battuello M. *Metrologia* 1998, **35**, 761-780
5. Hill K. D., In Proceedings of EUROMET Workshop on Temperature, Paris, March 1998
6. Bentley R. E., *Meas. Sci. Technol.* 2000, **11**, 538-546
7. Kam Y.-G., Gam K. S., and Lee J. H., *Meas. Sci. Technol.* 1997, **8**, 317-321

Addresses of the Authors:

Dean Ripple, NIST; 100 Bureau Dr. Stop 8363; Gaithersburg, MD, 20899-8363; USA. E-mail: dripple@nist.gov