

Mass Loss of Platinum-Rhodium Thermocouple Wires at 1324°C

Lower mass loss observed with enclosed wires

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It is known that platinum-rhodium thermocouples exhibit mass loss when in the presence of oxygen at high temperatures due to the formation of volatile oxides of platinum and rhodium. The mass losses of platinum, Pt-6%Rh and Pt-30%Rh wires, commonly used for thermocouples, were considered in this paper to characterise the mass loss of wires of the three compositions due to formation and evaporation of the oxides PtO₂ and RhO₂ under the conditions that would be seen by thermocouples used at high temperature. For the tests, the wires were placed in thin alumina tubes to emulate the thermocouple format, and the measurements were performed in air at a temperature of 1324°C, i.e. with oxygen partial pressure of 21.3 kPa. It was found that the mass loss of the three wires increases linearly with elapsed time, consistent with other investigations, up to an elapsed time of about 150 h, but after that, a marked acceleration of the mass loss is observed. Remarkably, previous high precision studies have shown that a crossover after about 150 h at 1324°C is also observed in the thermoelectric drift of a wide range of platinum-rhodium thermocouples, and the current results are compared with those studies. The mass loss was greatest for Pt-30%Rh, followed by Pt6%Rh, then platinum.

Introduction

Platinum-rhodium thermocouples are used widely as temperature sensors (1) and are often used

in industry where the accuracy and stability requirements are greater than those that can be provided by less expensive base metal thermocouples. Examples of such processes are iron and steel manufacturing (2), quartz glass manufacturing and aerospace heat treatment and casting. Platinum and rhodium are also important industrial catalysts, for example for the oxidation of ammonia to nitric oxide (3, 4).

At temperatures above about 1200°C, it is known that platinum-rhodium thermocouple wires form volatile oxides where the solid platinum or rhodium oxide films formed on the surface of the wires at lower temperatures evaporate (5). This causes the wires to lose mass (3, 6–8), which is the dominant cause of progressive instability and thermoelectric-inhomogeneity of the platinum-rhodium alloyed thermocouples. This instability arises because the vapour pressures and oxidation rates of platinum and rhodium are different. The overall behaviour also differs for each alloy (2, 6, 9). The departure of platinum and rhodium oxides from the wire at different rates causes a change in the composition of the thermoelements (4, 6) and hence calibration drift of the thermocouple.

An investigation conducted by Rubel *et al.* (4) studied the contribution of the volatile oxides to the mass loss of Pt-5%Rh and Pt-10%Rh alloy gauzes. The gauzes were exposed to oxygen over periods of 70 h to 300 h at 890°C and 1100°C. By using X-ray photoelectron spectroscopy (XPS), the type of volatile oxides produced were identified as platinum and rhodium oxides PtO₂ and RhO₂ respectively. It was also found that the rate of mass loss of rhodium oxide was greater with increasing rhodium content of the platinum-rhodium alloy.

Although the oxidation rates of platinum-rhodium alloys have not been investigated much in recent years, the effect of oxidation of the platinum group metals at high temperatures has been

widely studied. Phillips, in particular, studied the mass loss of the platinum group metals osmium, palladium, ruthenium, platinum, iridium and rhodium, and evaluated the time dependence of the mass loss by considering metal powders placed in 1" billets over the temperature range from 600°C to 1400°C (10). He concluded that all the platinum group metals lost mass when oxidised in air and that the rate of mass loss was greater at higher temperatures. Notably, the rate of mass loss increased with temperature, and for a given temperature the mass loss was linear with elapsed time, provided the volatile oxides are formed from the corresponding metal.

Another key experiment to determine the mass loss of platinum metals was conducted by Crookes (11). The two temperatures considered in that investigation were 900°C and 1300°C. The mass loss was investigated by using crucibles made of platinum and rhodium, where the original mass of platinum and rhodium was about 150 g and 33 g respectively. The mass loss was measured at time intervals of 2 h for a total period of 30 h. The significance of the results from this investigation was that at 900°C the mass loss of the platinum and rhodium crucibles was found to be negligible. However, at 1300°C it was found that the mass loss of both platinum and rhodium increased linearly with time. This measurement showed that volatile oxides are formed and vaporise at high temperatures, and that these are formed above some threshold temperature (3, 11).

Jehn (5) also observed a linear dependence of the mass loss with elapsed time, though it was noted in that study that in other experiments extended over "extremely long time periods" a marked increase in the mass loss rate had been observed for platinum at 1300°C after about 60 h (12) and 400 h (13); no explanation was given.

One difficulty with previous measurements of the rate of mass loss of platinum and platinum-rhodium alloys is the very wide dispersion of results, which vary by several orders of magnitude. This may be due in part to the wide variation of geometries of the test conditions, and the wide variation of environments (such as ambient gas or vacuum). Furthermore, none are applicable to typical thermocouple formats, which comprise thin noble metal wires inserted in narrow ceramic (typically alumina) bores. In addition, no attempt has been made to link the rate of mass loss of the wires to thermocouple drift performance. The aim of the current investigation was to perform such mass loss measurements in a manner that is directly

applicable to thermocouples, to better inform thermocouple drift models based on evaporation of platinum and rhodium oxides. Wires of Pt-30%Rh, Pt-6%Rh and platinum were investigated in ambient atmospheric conditions, within a typical alumina insulation tube used for thermocouples to make the test as realistic as possible in the context of thermocouple usage. A temperature of 1324°C was selected for the tests, because this is the melting temperature of the cobalt-carbon alloy, which is a well-established temperature reference point (a so-called 'fixed point') for calibrating thermocouples, and is used for *in situ* periodic calibration during long-term experimental thermoelectric drift tests.

In this article, the method is described, followed by a presentation of the results and an assessment of the associated uncertainties. The results are compared with thermocouple stability measurements where there are some intriguing qualitative similarities. Finally, some conclusions are drawn.

Method

Two identical wires were used for each type of wire to investigate the change of mass, where one wire was used as the control (kept at room temperature) and the other was the test wire exposed to high temperatures. This allows the change in mass to be calculated by comparing the masses of both wires. Measuring the mass change in this way reduces the influence of calibration drift and scale linearity of the mass balance. The wire diameter for all wires was 0.5 mm. The length of the platinum wire was 60 cm, while the Pt-6%Rh and Pt-30%Rh wires were 70 cm long.

Each of the wires was thoroughly cleaned using acetone and distilled water in order to remove any surface contamination prior to making mass measurements and heating. The wire masses were then measured using a Sartorius Supermicro S4 balance (Sartorius AG, Germany) with a resolution of 0.1 µg and a standard deviation of less than 1 µg. The measurement uncertainty of the mass comparison performed was approximately ±25 µg, largely due to random fluctuations in the readings. The balance was placed in a laboratory at a constant temperature (20°C ± 1°C), and the apparatus was kept in an isothermal enclosure to prevent the air from the surroundings from interfering with the measurements.

Prior measurements were made to determine how the surroundings affect the mass measurements using two scrap platinum wires. One wire was kept

as a control, where the scales were tared, and the other was the test wire (which in subsequent measurements would be the one exposed to high temperatures). The air conditioning in the laboratory caused short-term temperature fluctuations and air currents which manifested as long stabilisation times and noise in the mass measurements, so the thermal isolation of the balance was progressively improved until the stabilisation time and random fluctuations were both minimised.

To facilitate measurement on the balance pan, the wire was coiled around a plastic former to minimise contamination of the surface; the former was removed before weighing. Mass measurements of the test wires were made by comparison with the corresponding control wire, which was used to tare the balance. The mass of the control and test wires was measured three times to determine the average mass and to account for, and characterise, the random fluctuations in the test readings.

For each type of test wire used, three single alumina tubes of length 40 cm and diameter 3 mm, with bore diameter approximately 1 mm, were used. The wire was threaded into the bore to emulate the thermocouple format. The assembly was then placed in a thermal annealing furnace, which was maintained at 1324°C with stability of approximately $\pm 1^\circ\text{C}$. Before beginning the experiment, the alumina tubes were maintained at 1500°C in air for 6 h to drive off volatile impurities, in order to minimise contamination of the test wires.

The platinum and platinum-rhodium test wires were placed into the alumina tube bores by straightening the test wires (which are coiled for the mass measurements), while the control wires were kept coiled and stored in clean plastic bags.

The bores containing the test wires were placed in the furnace for designated intervals before being removed at the end of each interval and coiled again to perform the mass measurements.

Results

The uncertainty of the mass measurements was assessed by considering the individual contributions listed in **Table I**, which were summed in quadrature in a manner consistent with the International Organization for Standardization (ISO) Guide to the Expression of Uncertainty in Measurement (GUM) (14). The two statistical contributions, i.e. repeatability and reproducibility, were assessed by considering the standard deviation of repeated weighings *in situ* and of re-weighing the same item (i.e. removing from the balance and replacing) several times. The resolution, accuracy of the weights used to calibrate the balance, linearity and temperature of the balance reading were obtained from the manufacturer's specifications. For general applicability of the results, the mass loss was expressed per unit surface area (mg cm^{-2}); this was determined by dividing the mass loss values by the surface area of the wires. This yields

Table I Uncertainty Budget for Mass Measurements^a

Description	Estimate, mg	Probability distribution	Divisor, mg	Standard uncertainty, mg	Comments
Repeatability ^b	0.0064	Normal	1.0000	0.0064	Highest recorded value
Reproducibility ^c	0.0039	Normal	1.0000	0.0039	Highest recorded value
Resolution	0.0001	Rectangular	1.7321	0.0001	From specifications
Accuracy of calibration weights	0.0100	Normal	1.0000	0.0100	From specifications
Linearity	0.0003	Rectangular	1.7321	0.0002	From specifications
Temperature dependence	0.0002	Rectangular	1.7321	0.0001	From specifications ^d
Combined uncertainty	–	Normal	–	0.0125	Coverage factor $k = 1$ (67%)
Expanded uncertainty	–	Normal	–	0.0250	Coverage factor $k = 2$ (95%)

^a Standard uncertainty and expanded uncertainty correspond to normally distributed uncertainty with 67% (sometimes denoted one-sigma, or coverage factor $k = 1$) and 95% coverage probability ($k = 2$) respectively. Rectangular distributions correspond to the case where errors are equally likely across a range, such as resolution of the balance; the half-width of the distribution is divided by $\sqrt{3}$ as per the GUM guidance. Conversely, normal distributions generally correspond to cases where the errors are statistical in nature

^b Repeated weighings *in situ*

^c Re-weighing the same thing

^d Maximum ambient temperature variation of $\pm 1^\circ\text{C}$ assumed

an uncertainty ($k = 2$) of $\pm 0.0027 \text{ mg cm}^{-2}$ for the platinum wire and $\pm 0.0023 \text{ mg cm}^{-2}$ for the Pt-6%Rh and Pt-30%Rh wires.

It was found that all the wires progressively lost mass during high temperature exposure. **Figure 1** shows the mass loss per unit surface area as a

function of time of exposure to high temperature. It can be seen that the mass loss is a linear function of elapsed time, at least up to about 150 h. Beyond that, however, a marked departure from linearity is seen, which suggests an acceleration of the mass loss per unit surface area. Intriguingly, previously

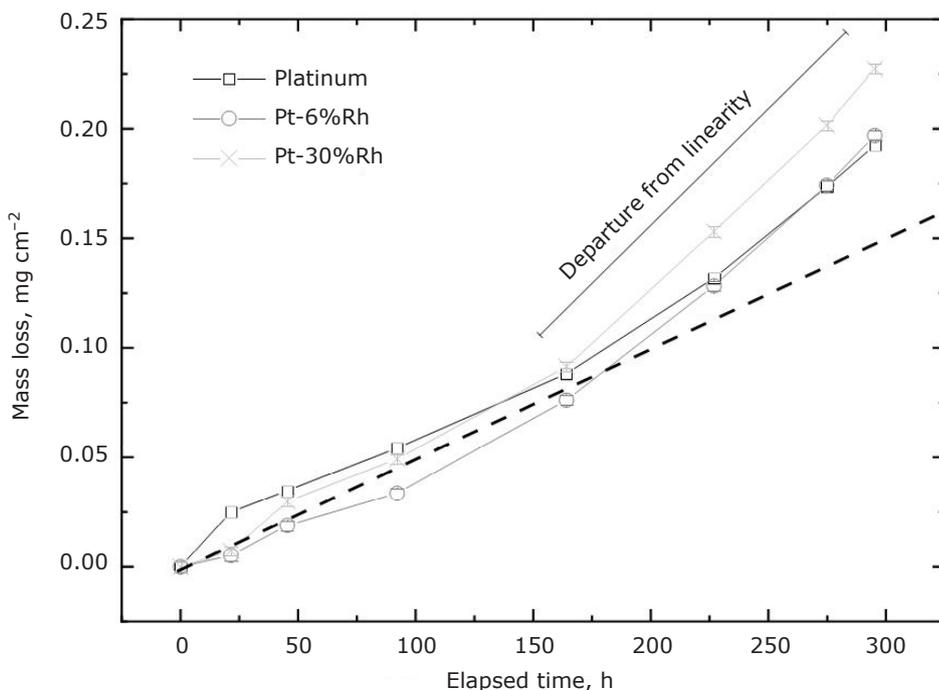


Fig. 1. Mass loss as a function of elapsed time at 1324°C for the three wires studied. Dashed line shows linear guide to the eye for data up to about 150 h; beyond that, there is a marked departure from linearity, where the mass loss appears to accelerate. The error bars (which are approximately the same size as the data points) correspond to the expanded uncertainty from **Table I**, converted to mass loss per unit area

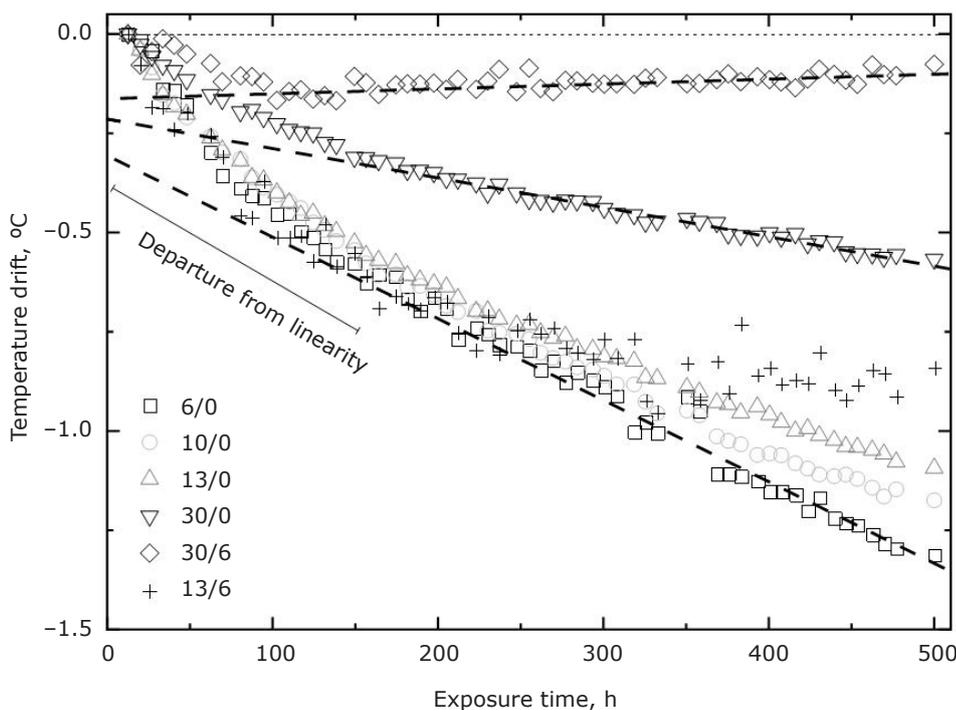


Fig. 2. Very high precision measurements of thermoelectric drift (in temperature terms) as a function of elapsed time at 1324°C for a variety of different thermocouples, after (14). Here the thermocouples are denoted by rhodium content. For instance, '6/0' corresponds to Pt-6%Rh versus platinum. It can be seen that the drift is non-linear up to about 150 h, beyond which there is a 'cross-over' to a linear regime (shown by the dashed 'guides to the eye')

reported very high precision drift tests of a set of different platinum-rhodium thermocouples (shown in **Figure 2**) show that they all exhibit a marked change in drift rate at about 150 h as well; beyond about 150 h the drift rate is constant for many hundreds of hours (15). The Pt-30%Rh appears to lose mass fastest, which is what might be expected since this wire contains more rhodium, and the vapour pressure of RhO_2 is higher than that of PtO_2 at this temperature (16).

The fact that the mass change up to about 150 h is linear for the reported measurements is in qualitative agreement with previous results (5, 10, 11). However, the rate of mass loss of platinum, using the data of Jehn (5) and Phillips (10), was about $0.0049 \text{ mg cm}^{-2} \text{ h}^{-1}$ and $0.0048 \text{ mg cm}^{-2} \text{ h}^{-1}$ respectively at 1350°C . In the current study, the rate of mass loss up to 150 h was about $0.0006 \text{ mg cm}^{-2} \text{ h}^{-1}$, which is about an order of magnitude lower. This may be because in the present study the wire is enclosed in quite tight-fitting bores to emulate their use in thermocouples, so the reduced rate of mass loss may be due to the establishment of saturated vapour pressure above the wire (inhibiting further evaporation), or reduced oxygen present as the surface oxidation proceeds, or deposition of the oxide vapour or all of these effects. This is in contrast to the previous studies cited, where the samples were bulk (for example, crucibles, meshes, coupons) and the surface was exposed to the surroundings rather than enclosed in tight-fitting bores.

Discussion

The mass losses of platinum, Pt-6%Rh and Pt-30%Rh wires, commonly used for thermocouples, were considered as a function of elapsed time at 1324°C . The wires were placed in thin alumina tubes to emulate the thermocouple format. It was found that the mass loss of the three wires increases linearly with elapsed time, consistent with other investigations, up to an elapsed time of about 150 h, but after that, a marked acceleration of the mass loss is observed.

In the latter case, it is thought that, because the whole length of the thermocouple which develops an output is exposed to the full range of temperatures from room temperature to the measurement junction temperature, the behaviour in the first 150 h (17) arises from early development of microscopic ordering in the platinum-rhodium alloys (during exposure to temperatures below 600°C). This is followed by a slow coating of the

platinum-rhodium leg by rhodium oxide (during exposure to temperatures between 600°C and 950°C) (18–22). This is difficult to apply directly to the mass measurements because the all of the wire was held at 1324°C so the oxidation effects at lower temperatures do not occur, but it is conceivable that comparable ordering and coating behaviour is taking place during the slow increase and decrease of the setpoint temperature of the furnace. It is also possible that the mass loss simply varies non-linearly over the whole duration: the motivation for expressing the data in terms of a discontinuity at about 150 h duration has been guided by the previously observed marked increase in the rate of mass for platinum at 1300°C after about 60 h (12) and 400 h (13); and also by the rapid change in thermocouple drift rate at about 150 h. To draw a definitive conclusion on this point, more detailed measurements would be needed, perhaps with the wire exposed to the entire temperature range from ambient to 1324°C .

Conclusion

The rate of mass loss was approximately an order of magnitude less than that observed in previous studies, and the enclosed nature of the wires in the alumina insulation tubes is thought to be a cause of this. Previous high precision studies have shown that a change in the drift rate after about 150 h at 1324°C is also observed in the thermoelectric drift of a wide range of platinum-rhodium thermocouples, and the current results were compared with those studies. The mass loss was greatest for Pt-30%Rh, followed by Pt-6%Rh, then platinum.

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