Optimising Platinum-Rhodium Thermocouple Wire Composition to Minimise Composition Change Due to Evaporation of Oxides

Determining the optimal composition as a function of temperature

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Barring the presence of significant amounts of impurities, an important cause of thermoelectric inhomogeneity and therefore calibration drift of platinum-rhodium thermocouples at high temperatures is the vaporisation and transport of the oxides of Pt and Rh, which causes local changes in wire composition. By examining the vapour pressures of Pt and Rh oxides and their temperature dependence, it is shown that at a given temperature there is an optimal wire composition at which evaporation of the oxides has no effect on the wire composition, provided the vapour does not leave the vicinity of the wire. This may also have applications for Pt-Rh heater elements.

Introduction

Noble metal thermocouples based on Pt and Rh are widely used in industry for applications requiring high accuracy and good long-term stability. Thermocouples consist of two dissimilar metal wires joined together at one end (the measurement junction). Usually the other end of each wire is connected to a copper wire which is connected in turn to a high accuracy voltmeter to enable measurement of the voltage across the two wires. The two junctions between the thermocouple wires and the copper wires are held at a known temperature; this comprises the reference junction. Thermocouples rely on the thermoelectric principle (1–4) to generate an electromotive force (emf) in response to a temperature gradient along the metal wires, which, since the wires are dissimilar, manifests itself as a measurable voltage across the wires. As the temperature at the reference junction of the wires is known and the thermocouple provides a measure of the temperature gradient from the measurement junction to the reference junction, the thermocouple can be used as a temperature sensor. Thermocouples are calibrated by exposing the measurement junction to known temperatures; this enables the relationship between emf and temperature to be established.

However, above about 1300ºC, where many high-value manufacturing processes operate, most conventional Pt-Rh thermocouples exhibit thermoelectric instability (1, 5–7) which causes a progressive loss of information about the relationship between emf and temperature. This results in reduced process efficiency, increased environmental footprint and increased product rejection rates. The general trend of process control towards higher temperatures to increase efficiency places increasing demands on thermocouple stability. Furthermore, above about 1300ºC only thermocouples with Pt-Rh alloy thermoelements of substantial Rh content are recommended, due to the high sensitivity

of alloys of low Rh content to changing composition arising from the significant vapour pressure of Pt and Rh oxides (6, 8–10) and the resulting vapour transport (1, 5, 6, 8–14). For this temperature range, Pt-30%Rh/Pt-6%Rh (designated Type B) (15, 16) and Pt-40%Rh/Pt-20%Rh (Land-Jewell thermocouple) (17) are in widespread use. Above about 1500ºC the Land-Jewell thermocouple is preferred for long term use. In this report, it is shown how to optimise the Pt-Rh wire composition to minimise local composition changes at high temperature due to vapour transport and thereby maximise thermoelectric homogeneity (and therefore stability). This is also applicable to heater elements, where it is desirable to minimise the change in resistance associated with changing composition.

Local changes in composition of Pt-Rh wires are due to evaporation of the oxides of Pt and Rh. Only saturation vapour pressures are considered in this analysis. The vapour pressures of the pure metals Pt and Rh are several orders of magnitude smaller than those of their oxides; only the oxide vapours are considered in this analysis. The vapour pressure of platinum oxide (PtO_2) and rhodium oxide (RhO_2) have been well characterised and are well known as a function of temperature (8). If the vapour pressures of the two oxides PtO_2 and RhO_2 are in the same proportion as the molar amount of the two elements Pt and Rh, and there is no significant vapour transport away from the evaporation site, the amount of composition change should be minimised. As the temperature dependence of the oxide vapour pressure is monotonic, at a given temperature there is a unique Pt-Rh alloy which corresponds to the case where the oxide vapour pressures are in the same proportion as the molar ratio of the species in the wire. Thus, in this study the optimal composition is determined as a function of temperature.

This study is concerned with an isothermal wire in stagnant conditions. It should be pointed out that, in the case of a thermocouple in typical usage, only those parts of the wires in the temperature gradient generate the emf. Hence, for application to a real-world system, it is more plausible to base calculations on an intermediate location within the gradient, where the temperature gradient is large and where oxide vapour pressure is significant. Stagnant conditions are assumed: when a temperature gradient is present vapour pumping action occurs within the temperature gradient region. The oxide vapour will naturally diffuse to the low-temperature regions and either condense back to a solid form or disassociate

into solid metal. The high-temperature end will become depleted and the temperature gradient region enriched (1, 6). These limitations should be borne in mind when considering the analysis.

The Model

The vapour pressures of PtO_2 and RhO_2 are directly proportional to the partial pressure of oxygen in the atmosphere (8), so the following argument applies to Pt and Rh in air. In pure oxygen gas with partial pressure 100,000 Pa, it has been shown by Alcock and Hooper (8) that the vapour pressure (*P*) of PtO_2 is given by Equation (i):

$$\log P_{Pt} = -\frac{(8585 \pm 74)}{T} + (0.204 \pm 0.047) + 5 \qquad (i)$$

For RhO_2 it is given by Equation (ii):

$$\log P_{Rh} = -\frac{(9866 \pm 126)}{T} + (1.079 \pm 0.079) + 5 \qquad (ii)$$

The temperature range of validity is from 1000ºC to 1600ºC. Here, *P* has units of Pa and *T* has units of K. It is assumed that the uncertainties given in (8) represent expanded uncertainties (coverage factor *k* = 2) associated with a normal probability distribution. The vapour pressures are plotted in **Figure 1** together with their corresponding uncertainties. Also shown in
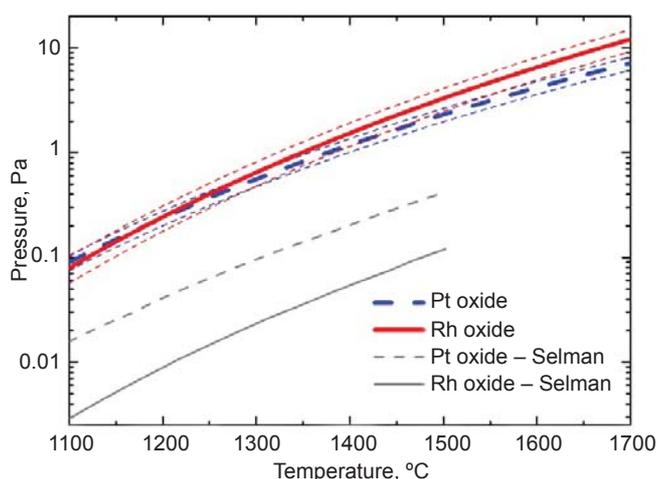

Fig. 1. Vapour pressure as a function of temperature for each oxide in isolation (1). Note the crossover where the Rh oxide vapour pressure exceeds that of the Pt oxide above about 1200ºC. Short dashed lines represent uncertainty arising from the parameters given in (8). Grey lines indicate data of Selman (6)

Figure 1 are the vapour pressure values of Selman (6) which extend to 1500ºC, though the values of Alcock and Hooper are used in preference in this study because Selman does not describe how the vapour pressures were derived.

It is assumed that the thermocouple wire is in a stagnant environment, i.e. vapour does not leave the system. In **Figure 2**, the molar ratio of Rh and Pt, f_{Rh}/f_{Pt}, in the wire is plotted as a function of Rh content in wt%. The ratio of vapour pressures of Rh and Pt, P_{Rh}/P_{Pt} at two temperatures are used to calculate the optimum Pt-Rh composition where the vaporisation leaves it unchanged. When the two curves intersect, the ratios are the same, i.e. Pt and Rh atoms leave the wire in the same proportion as their population in the wire. This means that vaporisation of the oxides leave the wire composition unchanged. It can be seen in **Figure 2** that this optimum composition, expressed in terms of wt% Rh, is dependent on temperature.

Rather than using graphical methods, it is of interest to develop an algorithm to locate the optimum f_{Rh} at a given temperature. It occurs when the ratio of oxide vapour pressures is equal to the ratio of molar amount of species in the wire (Equation (iii)):

$$\frac{P_{Rh}}{P_{Pt}} = \frac{f_{Rh}}{f_{Pt}} = \frac{f_{Rh}}{1 - f_{Rh}} \tag{iii}$$

Setting Equation (iv):

$$\chi = \frac{P_{Rh}}{P_{Pt}} \tag{iv}$$

It follows that the optimum $f_{Rh}(opt)$ takes the value (Equation (v)):

$$f_{Rh}(opt) = \frac{\chi}{1 + \chi} \tag{v}$$

It is then possible to plot the optimal wire composition (in terms of the more familiar wt% rather than molar fraction); this is done in **Figure 3**.

It can be shown with Monte Carlo techniques that the uncertainty of f_{Rh} is approximately represented by a normal distribution, regardless of the initial distribution of uncertainties in the original expressions for the vapour pressures (P) (8). The uncertainties of the parameters in (8) were propagated to estimate the resulting uncertainty in f_{Rh} using the Monte Carlo method (dashed lines in **Figure 3**).

Having found the optimum wire composition at a particular temperature (**Figure 3**), the remaining question is then what the composition of the other wire should be. It might be suggested that the other
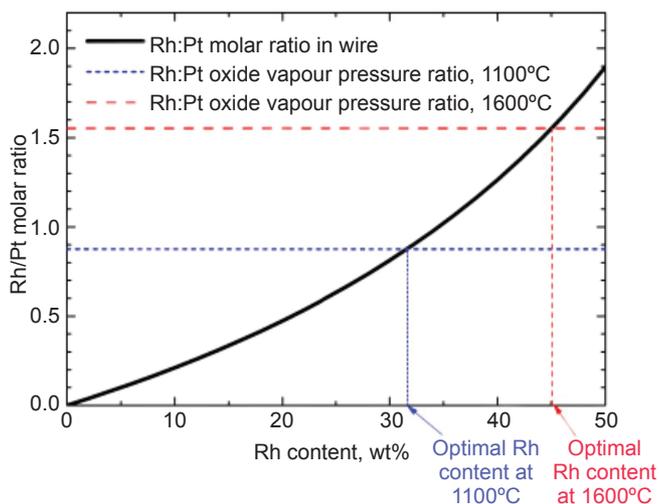

Fig. 2. Variation of the molar ratio of Rh and Pt in the wire and the ratio of Rh and Pt oxide vapour pressures, with wire Rh composition. Two temperatures are considered: 1100ºC (blue vapour pressure ratio) and 1600ºC (red vapour pressure ratio). At each temperature, the ratios are equal at the intersection of the two curves; at this point, there is no preferential volatilisation of Rh or Pt oxides. The Rh content of the wire corresponding to this point is optimal
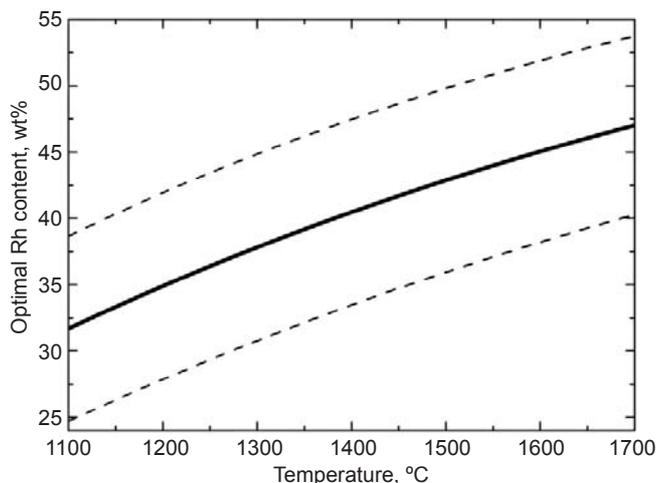

Fig. 3. Variation of optimal Rh composition (wt%), $f_{Rh}(opt)$ with temperature. This is the point of intersection of the two curves shown in Figure 2, determined at all temperatures. Dashed lines represent the propagated uncertainty, coverage factor $k = 2$

wire should have lower Rh content to avoid influencing the optimum wire with excess RhO_2 vapour. How much lower this should be depends on the acceptable sensitivity (μV ºC^{-1}).

However, given the magnitude of the uncertainties (**Figure 3**), it is proposed that the optimum strategy is to use a thermocouple having wires of compositions at

the extremes of the uncertainty limits applicable to the envisaged temperature range of use. For example, if the thermocouple is expected to be used up to 1500ºC, the upper bound on the optimum Rh composition is 50 wt%, while the lower bound is 35 wt%. In this case one may choose the Pt-50%Rh *vs.* Pt-35%Rh thermocouple, provided the sensitivity (about 1.5 µV ºC^{-1}) is high enough for useful measurements. Note that the above analysis suggests that the Land-Jewell (Pt-40%Rh *vs.* Pt-20%Rh) thermocouple is not a bad all-round choice for temperature measurements above 1100ºC.

This analysis ignores the fact that in use, the length of the thermocouple will experience the whole range of temperatures from that considered down to the temperature at the reference junction. This approximation is partly justified by the fact that the vapour pressures of both oxides and therefore the effect considered here, decrease exponentially with temperature, with correspondingly diminishing influence of oxide evaporation. The study is based on one set of measurements of the vapour pressure of Pt and Rh oxides which to the author's knowledge represents the only sufficiently complete data set; should further data come to light it may of course be necessary to review the findings.

Conclusion

By considering transport of Pt and Rh oxide vapour, it has been shown that there is an optimum Pt-Rh wire composition at a given temperature of use for which the evaporation of oxides has no effect on the wire composition, provided the vapour does not leave the vicinity of the wire. This analysis offers a range of suitable wire compositions to study in long-term thermocouple drift tests. The findings may also be of interest for heating applications, where changing Pt-Rh composition results in changing resistance; here the composition of the heating element could be tailored to minimise compositional change.

Acknowledgments

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