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# Changes in Seebeck Coefficient of Pt and Pt 10% Rh after Use to 1700°C in High-Purity Polycrystalline Alumina

**R. E. Bentley**[1]

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A technique is presented that enables the effects of temperature on the Seebeck coefficient to be assessed for individual wires. The technique, involving a high-resolution thermoelectric scanning rig and a nonuniform conditioning furnace of known temperature profile, was applied to 0.5-mm-diameter wires of Pt and Pt 10% Rh. Changes were observed in Seebeck coefficient when these wires were used in high-purity twin-bore insulation for up to 200 h at temperatures over the range 500 to 1700°C. Contamination from the insulation was found to be transmitted by a vaporization process, having an activation energy of 3 eV. This caused changes of up to 0.14 $\mu V \cdot {}^{\circ}C^{-1}$ in Pt and 0.01 $\mu V \cdot {}^{\circ}C^{-1}$ in Pt 10% Rh. Rhodium transfer to the pure Pt wire changed its Seebeck coefficient by up to 5 $\mu V \cdot {}^{\circ}C^{-1}$. The consequences of both processes for thermocouple pyrometry are presented.

**KEY WORDS:** alumina; high temperature; platinum; Seebeck coefficient; thermocouple; thermoelectric scanning.

## 1. INTRODUCTION

This paper covers the first part of a two-part study into Pt-based thermocouple alloys at high temperatures. It deals with Pt and Pt 10% Rh that together form the type S thermocouple. The next part will deal with Pt 6% Rh and Pt 30% Rh, the wires of the type B thermocouple.

What little work has been done on Pt-based thermocouples above 1100°C has amounted to observations of *in situ* drift at a particular temperature or of calibration changes measured at one temperature after an earlier use at a higher temperature. *In situ* drift studies have been done at 1320°C [1] and at 1450°C [2], and Bedford [3] observed changes in

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[1] CSIRO Division of Applied Physics, P.O. Box 218, Lindfield 2070, Australia.

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calibration at 1554°C after using various alloys at 1700°C. Walker et al. [4] detected changes at 860°C produced by an earlier use at either 1380 or 1730°C and correlated the changes with the Fe content of various grades of insulation used to support the wires. Whereas the above studies give information of practical value, they are specific to particular situations, give little insight into the processes involved, and do not indicate the temperature dependence of the effects.

We used a thermoelectric scanning device [5] to obtain thermoelectric profiles, or signatures, of wire specimens by moving a steep temperature step along them. When used in conjunction with a conditioning furnace of known temperature profile, the subsequent changes in Seebeck coefficient can be obtained as a continuous function of temperature.

This technique was applied to wires conditioned for up to 200 h at temperatures in the range 500 to 1700°C. Conditioning involved being placed in high-purity twin-bore insulation of polycrystalline alumina. By using various insulator/wire configurations it was possible to distinguish among the effects from various processes.

## 2. MATERIALS

Twelve specimens of Pt (P1, P2,..., P12) and twelve of Pt 10% Rh (PR1, PR2,..., PR12) were studied, each being 0.5-mm-diameter wire from Johnson Matthey (Sydney, Australia). They were cleaned in a series of acid and distilled-water rinses and annealed electrically in air without insulation at 1450°C for 1 h [6]. The specimens were paired (P1 with PR1, etc.), placed in new 600-mm-long, 3-mm-OD, 0.8-mm-bore, twin-bore insulation of Haldenwanger ALSINT 99.7 and given an isothermal anneal for 1 h at 1100°C. They were removed rapidly from the 1100°C anneal, to avoid significant time in the rhodium oxide-producing zone (500 to 900°C), and given an overnight anneal at 450°C to establish a reproducible state of hysteresis [6].

The twin-bore insulators used in the conditioning furnace were of Haldenwanger ALSINT 99.7, 600 to 1050 mm long, 3 mm OD, and with 0.8-mm bores.

## 3. METHOD

Wire specimens were scanned thermoelectrically before and after placing them in a nonuniform temperature zone of known profile. The observed change as a function of position along each wire was then translated into a change in Seebeck coefficient as a function of the temperature that initiated the change.

The scanning rig has been described fully by Bentley and Jones [5]. It is a device for obtaining the thermoelectric "signatures" of up to two specimens simultaneously by scanning 560 mm of their lengths with a steep temperature step. This is done (Fig. 1) by moving the specimens at $18.6\ \mathrm{mm} \cdot \mathrm{min}^{-1}$ into a uniform-temperature cavity at 400°C having an especially steep temperature gradient (see Fig. 2) at its entrance port. The emf's developed by the wires were measured to better than $\pm 0.1\ \mu\mathrm{V}$ relative to matching reference wires that supplied stable signals for the interval 0 to 400°C and compensated for slight departures from 400°C at the hot ends of the specimens.

The Seebeck emf developed by a specimen is the product of Seebeck coefficient and temperature gradient integrated over its length. Hence at an immersion depth of $d$ mm (Fig. 2) the measured emf reltive to that of the reference wire, $e'(d)$, is

$$e(d) = \int S(x, T)(dT/dx)\,dx - e'(d)$$

where $S(x, T)$ is the Seebeck coefficient at position $x$ and temperature $T$, the dependence of $S$ on $x$ representing the chemical and physical inhomogeneities along the wire.

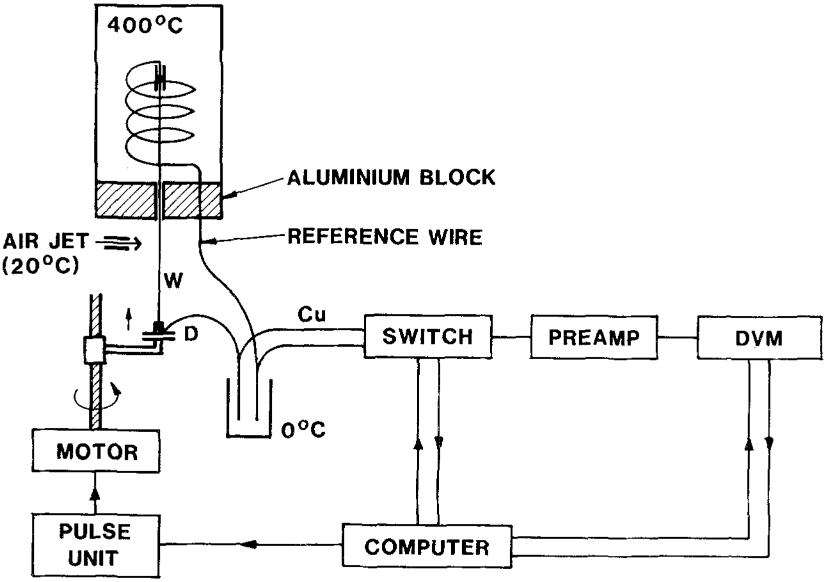

**Fig. 1.** Schematic diagram of the high-resolution scanning rig. The circuit for only one of the two wire specimens (W) is shown. The double disk arrangement, D, accommodates flexing in the driven insulator that contains the specimen.

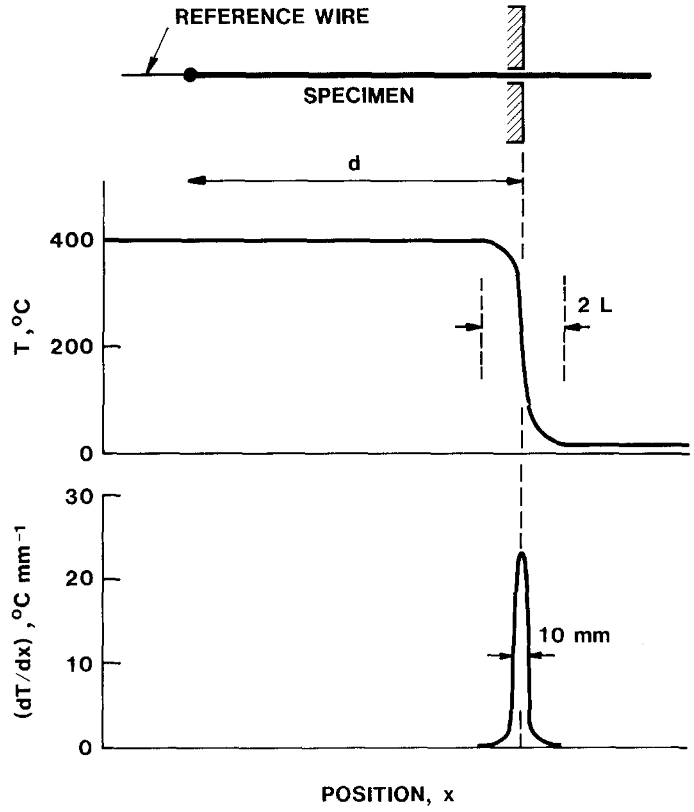

**Fig. 2.** Profiles of temperature and temperature gradient in the scanning rig.

Because that portion of $e(d)$ developed in the region of specimen between 0°C and ambient (20°C) is fixed, then if the ambient and cavity regions are assumed uniform in temperature, we have

$$e(d) = \text{cont} + \int_{T_{x=d-L}}^{T_{x=d+L}} S(x, T)\, dT - e'(d)$$

or

$$e(d) = \text{const} + \bar{S}(d)(T_{d+L} - T_{d-L}) \tag{1}$$

so defining the mean Seebeck coefficient $\bar{S}$ over the high-gradient region. Because the resolving power of the rig is $\sim$10 mm $\sim 2L$, we can safely ignore the explicit variation of $S$ with $x$ in the range $(d-L)$ to $(d+L)$ and take $\bar{S}$ as the temperature-averaged coefficient at $x = d$ for the interval 20 to 400°C.

If the specimen is scanned before and after a change in Seebeck coefficient is effected, the observed change in emf is a measure of the change in coefficient, from Eq. (1);

$$\delta\bar{S}(d) \simeq \delta e(d)/380 \tag{2}$$

In this study the Seebeck coefficient was changed by heating the wires in a known and reproducible temperature profile for various periods, while supported in twin-bore insulators of polycrystalline alumina. The temperature profile was developed in a conditioning furnace, which had a Mo heater wound on a 32-mm-ID alumina tube, 850 mm long. The winding, protected in nitrogen with 10% hydrogen, was in three zones and had a varying pitch to give for each specimen the longitudinal temperature profile shown in Fig. 3. Above 1100°C, $T_0$ was roughly linear with respect to immersion, ~2°C · mm$^{-1}$.

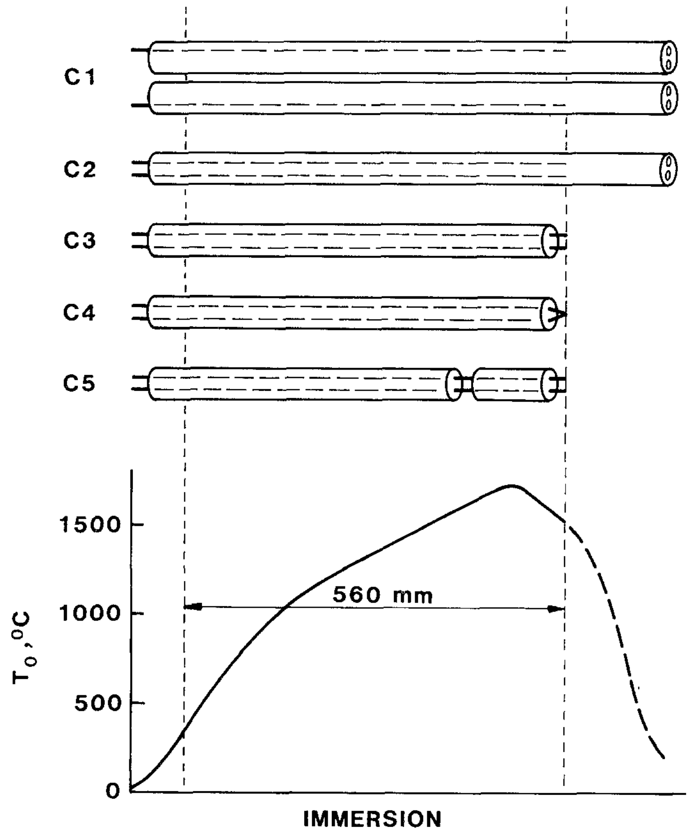

Fig. 3. Various insulator/wire positions in the conditioning furnace shown relative to the longitudinal temperature profile in the furnace.

Samples were conditioned using various wire/insulator configurations (C1 to C5, Fig. 3) to assess the relative significance of various processes such as contamination, diffusion, vaporization, and annealing.

After conditioning for a known period, $t_0$, specimens were withdrawn rapidly from the furnace to minimize time spent cooling through the oxide-producing zone (500 to 900°C) [5] and were then given an overnight anneal at 450°C to overcome quenching effects.

The effect of conditioning on the Seebeck coefficient, $\delta S(T_0, t_0, T)$, was studied in two parts. First, the scanning rig gave values of $\delta \bar{S}$ for various $t_0$, as a function of $T_0$, using Eq. (2) at $x = d$. Second, the dependence of $\delta S$ on $T$ was obtained by measuring the change in emf, $\delta E(T)$, over the range 0 to 1555°C, where

$$\delta E(T) = \int \delta S(T_0, t_0, T)\, dT \tag{3}$$

and $E(T)$ is the emf developed by a specimen with 0°C at one end and $T$°C at the other. For Eq. (3) to be valid, all the wire contributing to $E(T)$ was given the same use and the same values of $t_0$ and $T_0$. The equivalent of $t_0 = 35$ h and $T_0 = 1700$°C was achieved for specimen lengths of 400 mm by slowly moving the wires through the conditioning furnace.

Before and after conditioning, $E(T)$ was measured relative to the emf in Pt by welding the ends of the specimens to a Pt reference wire. It was measured from 0 to 1100°C to $\pm(1\,\mu\text{V} + 0.04\,\%E)$ [6] using an automatic calibration facility [7] and at the melting point of Pd (1555°C in argon) [8] to $\pm 2\,\mu$V with a potentiometer having 1-$\mu$V resolution.

All insolators used for conditioning and scanning were marked to allow control of their histories. For example, to avoid cross-contamination between Pt and Pt 10% Rh specimens, the bores of the insulators were marked and wires of one metal were not used in a bore previously used with the other in either the conditioning furnace or the scanning rig.

Since insulators used in conditioning the wires were often not the same as those used in scanning, specimens had to be moved from one to the other. In doing this, care was taken to avoid kinking and other forms of cold work, since cold working causes localized changes in $e(d)$ of up to $\sim 5\,\mu$V for each wire [9]. To minimize contamination, specimens were handled on a cleaned glass bench surface and, once assembled in insulators, were stored in clean glass tubes when not in use.

## 4. RESULTS

### 4.1. Scan Data

Figure 4 shows the thermoelectric signatures for P1 and PR3 obtained before and after conditioning. It refers to previously unused wires conditioned for $t_0 = 25$ h in new insulation and is typical of all the results obtained with configurations C1 and C2 (Fig. 3). For the other configurations the signatures had localized distortions, indicated by dotted lines in Fig. 4, corresponding to positions where wires were exposed to each other. Data for these configurations are given in Section 4.4.

In the fully annealed condition, initial inhomogeneities observed as variations in $e(d)$, of $\pm 0.05$ to $\pm 0.2\,\mu$V in Pt and $\pm 0.25$ to $\pm 0.6\,\mu$V in Pt 10% Rh, were noted. A change in $e(d)$ (Fig. 4), increasing with $T_0$ and $t_0$, was common to all runs. There was also a trough, centred on $T_0 = 800$°C, in the signatures of all Pt 10% Rh wires.

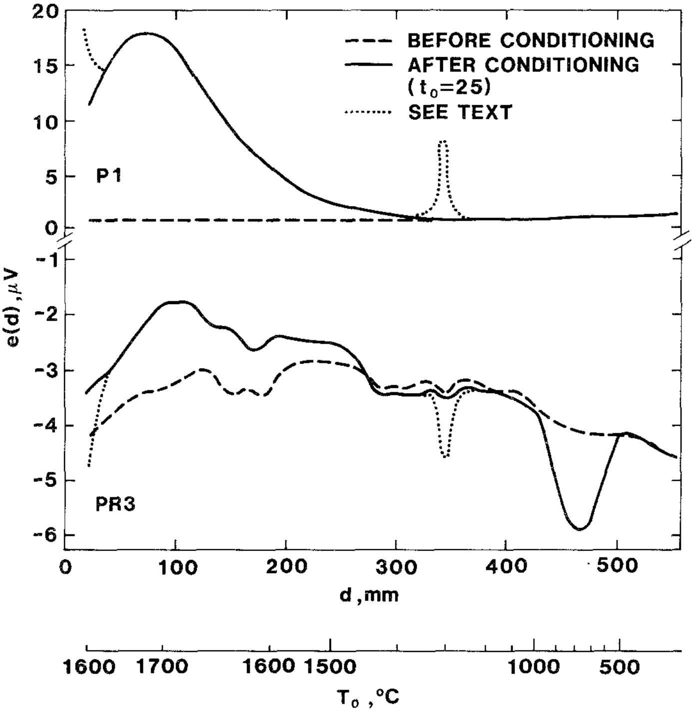

Fig. 4. Thermoelectric signatures of Pt and Pt 10% Rh before and after conditioning for 25 h.

At the largest value of $T_0$ (1700°C), the change in $e(d)$ amounted to 12 to 32 $\mu$V for Pt and 1.0 to 2.5 $\mu$V for Pt 10% Rh, when conditioned for 25 h in new insulation. The scatter in these values represents a variability in the batch of insulators used for conditioning, since repeated use of the same insulator gave consistent results.

The changes observed for Pt 10% Rh specimens after conditioning at $T_0 = 800$°C are shown in Fig. 5 as a function of $t_0$. Also shown are data from an earlier study [5] which are in excellent agreement.

### 4.2. Dependence of $\delta\bar{S}$ on $T_0$ and $t_0$

The effect of conditioning Pt and Pt 10% Rh in new insulation for 25 h is shown in Fig. 6 as a function of $T_0$.

In assessing the dependence on $t_0$ (Fig. 7), wires were removed from their conditioning insulators for scanning at various values of $t_0$. With four pairs (Pt, Pt 10% Rh) of specimens, conditioning began in new insulation and the wires were returned to the same insulation to continue conditioning until at least 120 h had been accumulated.

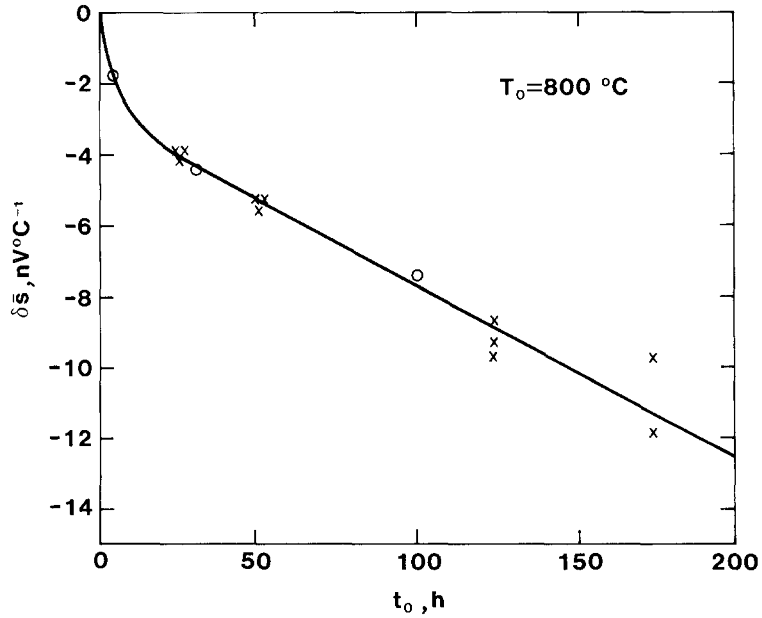

Fig. 5. Change in Seebeck coefficient of Pt 10% Rh caused by heating in air at 800°C for $t_0$ h. Data are for PR1, PR2, and PR3 (×) and from Bentley and Jones [5] (O).

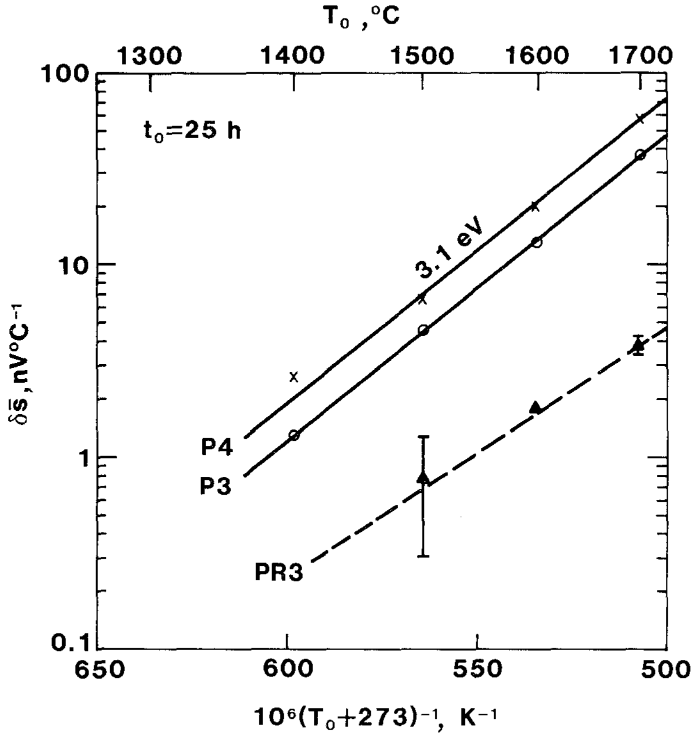

**Fig. 6.** Change in Seebeck coefficient of Pt (solid line) and Pt 10% Rh (dashed line) after heating in new insulation for 25 h at $T_0$.

In each of these four cases, $\delta\bar{S}$ showed a leveling off after $t_0 \sim 100$ h. The results for P1 (Fig. 7, up to 120 h) were typical for Pt and the effect in Pt 10% Rh was similar but an order of magnitude smaller. Possible reasons for this saturation/depletion process were sought by using insulators with varying surface conditions:

(a) In two cases the insulators were replaced by new ones after every 25 h of conditioning. The results for the Pt specimens, P1 and P5, are given in Fig. 7; for P1 the insulator replacement sequence began after 120 h, rather than at $t_0 = 0$ h, as was the case with P5.

(b) Two pairs of specimens were conditioned, for the first time, in insulators previously used in the same position for 120 h. One insulator during its earlier use had Pt and Pt 10% Rh wires in its bores and the other had no metallic contact. In both cases the results were the same (P8, P9 in Fig. 7), the change after 25 h at 1700°C being about four times smaller than for new insulators.

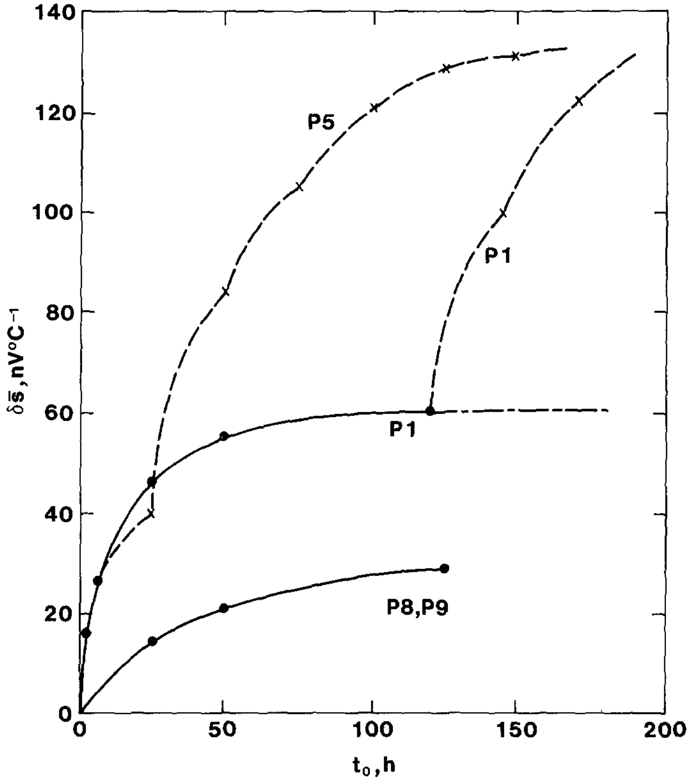

**Fig. 7.** Change in Seebeck coefficient for Pt after conditioning at 1700°C for $t_0$ h. Conditioning was done in the same insulator (solid curve), either new (P1) at $t_0 = 0$ or used (P8, P9), or by replacing with a new one every 25 h (×; dashed curve).

## 4.3. Dependence of $\delta S$ on $T$

The effects of conditioning 400-mm lengths of wire for 35 h at 1700°C in a new insulator can be seen in the observed change, $\delta E(T)$, given as a function of $T$ in Fig. 8. The curves are roughly linear and hence indicate little, if any, temperature dependence for the change in Seebeck coefficient. The mean slopes are $\delta S = 70\, nV \cdot {}^\circ\mathrm{C}^{-1}$ for Pt and $5\,\mathrm{nV} \cdot {}^\circ\mathrm{C}^{-1}$ for Pt 10% Rh.

## 4.4. Vapor Transfer

During conditioning, gaps of 2 mm in insulation (insulator/wire configuration C5, Fig. 3) allowed vapor transfer between the wires at various

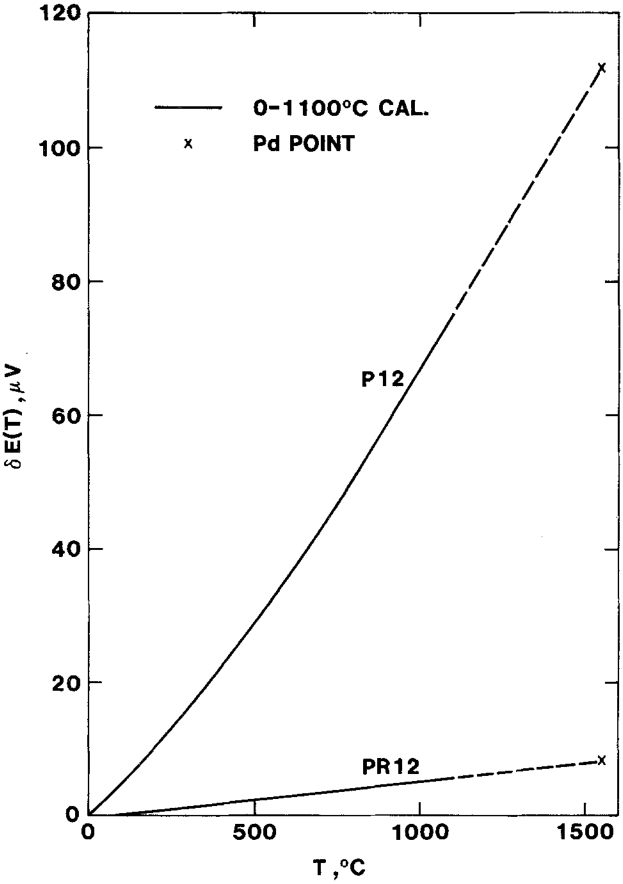

**Fig. 8.** Change in emf developed in Pt (P12) and Pt 10% Rh (PR12) wires after a 35-h conditioning at 1700°C in new insulation.

values of $T_0$ and led to peaks in the signatures for both Pt and Pt 10% Rh (Fig. 4). The height of these peaks, $\delta e_0$ (Table I), is approximately the product of peak temperature gradient (22°C · mm$^{-1}$) in the scanning rig, mean change ($\Delta \bar{S}$) in $S$ for the wire in the gap, and gap width (2 mm)

$$\Delta \bar{S} \simeq \delta e_0 / 44 \tag{4}$$

The dependence of $\Delta \bar{S}$ on $T_0$ is given in Fig. 9.

Vapor transfer effects were evident near the tips of the specimens conditioned in configurations C3, C4, and C5. The effect on signature was consistent in both direction and extent with the results for 2 mm gaps and welding specimens together at their tips (C4) made no noticeable difference.

**Table I.** The Change, $\delta e_0$, Caused by 2-mm Gaps in Insulation When Conditioned for 25 h at $T_0$

| Specimens | $T_0$ (°C) | $\delta e_0$ ($\mu$V)<br>Pt | <br>Pt 10% Rh |
|---|---|---|---|
| P2, PR2 | 1600 | 125 | −20 |
| P3, PR3 | 1100 | 1.2 | −0.7 |
| P3, PR3 | 1400 | 30 | −5.8 |
| P5, PR5 | 1200 | 2.6 | −0.5 |
| P7, PR7 | 1000 | 0.5 | −0.0 |
| P7, PR7 | 1550 | 68 | −10 |

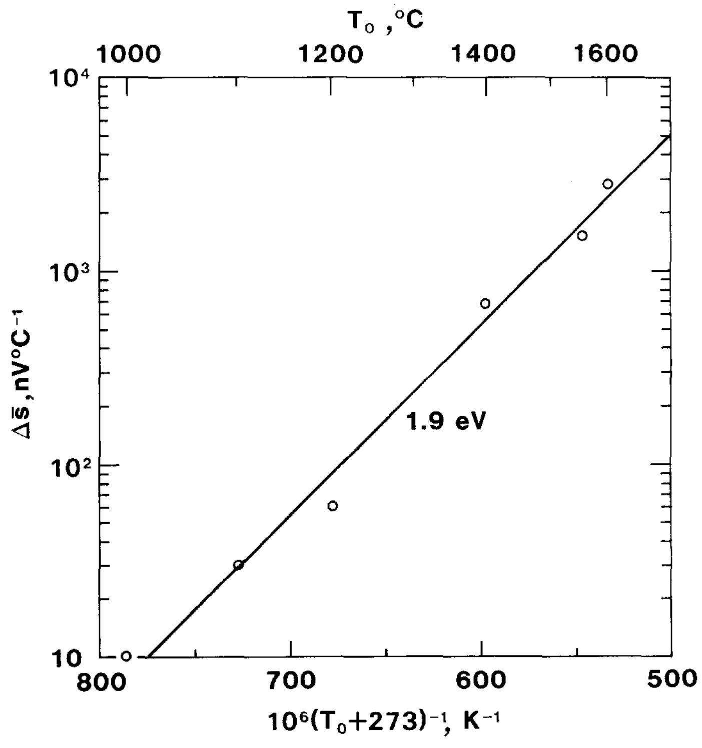

**Fig. 9.** The effect of a 2-mm gap, in the insulation separating Pt and Pt 10% Rh wires, on the Seebeck coefficient of Pt after 25 h of exposure at $T_0$.

## 5. DISCUSSION

Three effects were observed: the Seebeck coefficient of Pt 10% Rh was reduced when used near 800°C, the coefficient increased for both metals when used within alumina insulation, and a far greater change was noted where the wires were exposed to each other.

The change at 800°C has been attributed to rhodium oxide [5, 10] and the data in Fig. 5 show that, after about 30 h of exposure to air at this temperature, the drift in Seebeck coefficient is linear in time to at least 200 h, the linear rate being equivalent to $-18\,\text{nV} \cdot \text{h}^{-1}$ in $\delta e$.

The functional dependence of $\delta S(T_0, t_0, T)$ on $T_0$ (Fig. 6) indicates an activation energy of 3.1 eV for the conditioning process, and the dependence on $t_0$ (Fig. 7) shows that the process observed for all configurations (C1 to C5) was due mainly to contamination from the surface of the insulator. The drift in Seebeck coefficient levels off for a particular wire/insulator combination if they continue to be used together. It can be accelerated by replacing the insulator with a new one and lessened if replaced by one previously used. The leveling off in time was observed for P1, used in the same insulator, and for P5, which had its insulator replaced regularly. The results for P1 suggest a depletion in contaminant at the insulator surface, and those for P5, saturation in the metal.

The agreement between runs with P8 and runs with P9 (Fig. 7) in used insulators shows that the change in surface conditions on each insulator during its previous used did not require the presence of metal and hence could not have involved diffusion from insulator to wire. It could have been due to a loss of contaminant by vaporisation.

Walker et al. [4] compared the change in calibration at 860°C of various Pt allows after a 120-h use at 1380 or 1730°C in different grades of alumina ranging from 96 to 99.7% in nominal purity. The results correlated well with Fe but not with the other contaminants found in the wires. Whereas contamination by Fe, transferred as metallic vapor, may explain the large drifts they saw with insulators high in Fe, it does not follow that the far smaller drift observed with their best insulators was also due to Fe. Indeed they could not detect this metal in wires used with 99.6 and 99.7% pure insulation.

It is unlikely that Fe was the contaminant in the present case. The activation energy for its vaporization, calculated from vapor pressure data [11], is 4.27 eV, much higher than the 3.1 eV observed here.

Part of the change, $\delta S(T_0, t_0, T)$, could be due to the annealing effect of temperature, i.e., to lattice changes not involving the insulator. However, annealing could not have contributed more than the change seen in P8 and P9, i.e., in 25 h a change of 20 to 30% of that seen for new insulation

(Fig. 6). For example, at 1450°C its effect is less than 1 nV · °C$^{-1}$ in Pt. To measure the effects of annealing, annealing would need to be done in the absence of hot insulation, e.g., using electrical self-heating of bare wires. This was not tried because of the necking and stretching that occur at high temperatures, especially above ~1400°C. However, McLaren and Murdock [10] were able to examine the effect of up to 44 h of bare-wire annealing at 1300 and 1450°C on calibrations at the tin point (232°C), i.e., $\delta E(232)$ [see Eq. (3)]. Values of $\delta S$, calculated from their data for $T_0 = 1450$°C, are 4 nV · °C$^{-1}$ for Pt and 5 nV · °C$^{-1}$ for Pt 10% Rh, which suggest a far greater annealing effect than could have occurred in the present study. At 1300°C the discrepancy is greater.

These discrepancies could be explained by assuming a greater impurity level in McLaren and Murdock's wires, which were obtained (1969 to 1972) at about the time manufacturers began supplying materials of greater purity, in readiness for the revised thermocouple reference tables [12].

Figure 8 shows that the change in Seebeck coefficient produced by a use in alumina insulation is, to the first order, a constant independent of temperature. This is consistent with the work of Rhys and Taimsalu [13], who found that additions to Pt of up to 1000 ppm of various elements caused a change in Seebeck coefficient that was constant over the range 400 to 1100°C. Hence the change, $\delta S(T_0, t_0, T)$, can be expressed as $\delta S(T_0, t_0)$ and equated to $\delta \bar{S}$, the value calculated from measurement using Eq. (2).

The vapor pressures of Pt and Rh [14] are two to three orders of magnitude smaller than those of their oxides. Hence the interchange of metal between specimens exposed to each other by 2-mm gaps in insulation would probably occur via the oxide vapors. The activation energies for vaporization calculated from the vapor pressure data [14] are 1.71 eV for $PtO_2$ and 1.89 eV for $RhO_2$.

The change, $\Delta \bar{S}$, shown in Fig. 9 is too great to be accounted for by contamination from either the conditioning insulator or the surrounding alumina tube, which was equally, pure. Also, the change in Pt was opposite in sign to that in Pt 10% Rh. However, the results are consistent with rhodium transfer as the slope, 1.9 eV, for $\Delta \bar{S}$ of Pt agrees well with the activation energy for vaporization of $RhO_2$. Rhys and Taimsalu [13] found that each ppm by wt. addition of Rh to Pt produced an increase of 0.21 nV · °C$^{-1}$. Hence the observed increase in $\Delta \bar{S}$ (Fig. 9) at 1600°C, for example, corresponds to about 1% Rh. A loss of this amount from Pt 10% Rh would cause a decrease in Seebeck coefficient of 160 nV · °C$^{-1}$, calculated from the relative Seebeck coefficients of various PtRh alloys [12], and an even bigger change could be expected because not all the Rh lost by the alloy would be picked up by the Pt. The observed change in $\Delta \bar{S}$ for Pt 10% Rh, from Table I and Eq. (4), was −450 nV · °C$^{-1}$ and seems reasonable. However, this appears inconsistent with the suggestion by Selman [14] that evaporation from Pt 10% Rh would cause little change in Seebeck coefficient; the vapor pressure of $PtO_2$ is five times that of $RhO_2$ at these temperatures and the loss of both metals would maintain the nominal composition of the alloy. The fact that $\Delta\bar{S}$ for Pt 10% Rh did change can be accounted for by the presence of the Pt wire whose vaporization would effectively reduce the loss of Pt from the alloy. The vapor pressure data of Selman [14] refer to saturation levels in equilibrium with a Pt 10% Rh surface.

## 6. CONSEQUENCES FOR PYROMETRY

It is useful to regard 1300°C as a transition temperature for precision thermocouple pyrometry, especially if using Pt 10% Rh and Pt wires. Below this temperature the effects of cold work [9], hysteresis [6], and rhodium oxide can be reversed by annealing; the performance of a fully annealed Pt 10% Rh versus Pt thermocouple is then limit by its inherent inhomogeneity of ±0.01 to ±0.02% of net developed emf. Above 1300°C, two irreversible processes become significant, *viz.*, contamination from twin-bore insulation and a net transfer of Rh from the alloy to the Pt where the two wires are exposed to each other. Both processes cause a loss in emf for the Pt 10% Rh versus Pt thermocouple, due mainly to the Pt leg.

Assuming the insulators used in this study to be typical, the *in situ* drift to be expected in 25 h for a Pt 10% Rh versus Pt thermocouple in a single high-quality insulator of alumina is given in Table II (it was calculated by integrating under the curves of Fig. 6 from 0 to $T_0$°C). The subsequent effect of reducing the immersion, with the tip still at $T_0$ and the interval 0 to $T_0$°C lying within the wire fully affected by 25 h at $T_0$, is equal to $T_0 \cdot \delta S(T_0, t_0)$ (Table II). If, instead, this affected zone is used to span a smaller

**Table II.** *In Situ* Drift of Pt 10% Rh Versus Pt Thermocouples at a Tip Temperature, $T_0$, While in Alumina for 25 h and the Effect of a Subsequent Reduction in Immersion

| $T$ (°C) | *In situ* drift ($\mu$V) | $T_0 \cdot \delta S(T_0, t_0)$ ($\mu$V) | $\delta S/S(800)$ (%) |
|---|---|---|---|
| 1300 | −0.03 | −0.6 | −0.004 |
| 1400 | −0.14 | −2.7 | −0.017 |
| 1500 | −0.51 | −9.6 | −0.06 |
| 1600 | −1.7 | −30 | −0.17 |
| 1700 | −4.9 | −85 | −0.46 |

temperature interval, the emf developed by it will be changed by the amount shown in column 4 of Table II, using the Seebeck coefficient at 800°C as representative for the thermocouple.

When allowance is made for the observed variability among insulators and the effect of operating for longer than 25 h, changes of twice that shown in Table II could be expected, e.g., –0.1% at 1500°C and –1% at 1700°C. Greater changes in Seebeck coefficient will occur if the insulator is replaced by a fresh one, $\delta S$ could eventually level off, after repeated replacements, for example, at a value three times greater than that for single insulator. On the other hand, contamination effects can be reduced by a factor of four by first heat treating the insulation for 50 h or so at 1700°C, although this could cause unacceptable bending.

It is instructive to calculate some effects of using short lengths of twin-bore insulation rather than one long one. Consider a single 2-mm gap in insulation at 1500°C during measurements near the Pd point (1550°C), say. After 25 h, at least 2 mm of thermocouple would have its Seebeck coefficient reduced by $-1.2\,\mu\mathrm{V}\cdot{}^{\circ}\mathrm{C}^{-1}$ (Fig. 9). During this use the temperature gradient at the gap would be relatively small, $2\text{–}3^{\circ}\mathrm{C}\cdot\mathrm{mm}^{-1}$ say, being near the tip in temperature. The affected wire would therefore span 4–6°C and cause a gradual loss of 5–7 $\mu$V in the 25-h period. If the thermocouple were then used with its affected zone in a steep gradient of $20^{\circ}\mathrm{C}\cdot\mathrm{mm}^{-1}$, e.g., by reducing its immersion, thermocouple emf would be low by $\sim 50\,\mu\mathrm{V}$.

The effect would be compounded if many gaps occurred and would increase with the temperature of vapor transfer by 2.5 to 1 for each 100°C. Clearly, a single insulator should be used for accurate work, at least for that part of the thermocouple beyond 1100°C.

## 7. CONCLUSION

Contamination from even the best available twin-bore insulation of polycrystalline alumina is a problem in thermocouple pyrometry, a change of –3% in emf for type S thermocouples being possible. Contamination involves a process of vapor loss for the insulator; it has an activation energy of 3 eV and changes the Seebeck coefficient by an amount independent of subsequent temperature. Because it involves vapor loss, it is possible to reduce the effects in pyrometry by heat treating the insulator before inserting the wires. If the insulator is then kept with the thermocouple, changes in emf could be confined to about –0.2%.

It was found also that since large localized increases in Seebeck coefficient occur if thermocouple wires are exposed to each other at high temperatures, the use of a number of short insulators should be avoided. A single length of twin-bore insulation should be used to separate the wires, at least for that section above 1100°C, and rhodium transfer near the tip will usually be of little significance because of the small temperature gradients in the vicinity.

## ACKNOWLEDGMENTS

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