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Comparative Study of Pt/Pd and Pt–Rh/Pt Thermocouples

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Abstract The Pt/Pd thermocouple has demonstrated superior thermoelectric drift and homogeneity performance over conventional Pt–Rh/Pt thermocouples. Here, we present a systematic comparison of the drift and homogeneity performance of Pt/Pd and Type R thermocouples by ageing the thermocouples at 1350 °C for a total of 500 h and measuring the performance at regular intervals during this time. The thermocouples studied were one Pt/Pd thermocouple, one Type R thermocouple and one 'special' Type R thermocouple which was given the same preparatory annealing treatment as the Pt/Pd thermocouple prior to use. The thermoelectric stability of each thermocouple was measured at the freezing point of Ag (961.78 °C) and the melting point of Co–C eutectic (1324.29 °C). The thermoelectric homogeneity of the thermocouples was also measured. Two difference methods were used by withdrawing the thermocouple from the Ag cell and by moving a localized heat source along the thermocouple. The long-term drift of the Pt/Pd thermocouple was around 50 mK (Ag) and 65 mK (Co–C) after the first 100 h ageing at 1350 °C, followed by a further 25 mK (Ag) and 35 mK (Co–C) over the subsequent 400 h ageing. This drift performance and inhomogeneity were an order of magnitude lower than for the two Type R thermocou-

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ples. The Type R thermocouple which was given the 'special' preparatory treatment was about 50 % more stable than the conventional Type R thermocouple.

Keywords Ag fixed point · Co–C eutectic · Heat treatment · Pt/Pd · Pt–Rh/Pt · Thermocouple · Type R

1 Introduction

There is currently significant interest in the potential of Pt/Pd thermocouples to provide a thermoelectrically stable, homogeneous sensor for scale dissemination and industrial reference. Because a pure element is far more thermoelectrically homogeneous than an alloy, the pure elemental thermocouples such as Pt/Pd and Au/Pt are expected to provide higher performance than those consisting of alloys such as Pt–Rh/Pt [1]. A number of studies of Pt/Pd thermocouples have been published and have demonstrated that the stability and homogeneity of the Pt/Pd thermocouples are superior to Pt–Rh/Pt thermocouples [1–4]. However, to the authors' knowledge there has not, thus far, been a systematic comparative study of the drift and homogeneity performance of Pt/Pd and Pt–Rh/Pt thermocouples.

In this article, we present a comparative study of Pt/Pd and Pt–Rh/Pt (one conventional, one given same preparatory treatment as Pt/Pd) thermocouples. The preparatory heat treatment of Pt/Pd thermocouples involves substantially longer electrical annealing of the thermoelements, followed by a much longer (>100 h) furnace annealing. It is thus of significant interest to examine the effect of exposing a Type R thermocouple to such treatment, in comparison with the more conventional short preparatory treatment. The reproducibility of the three thermocouples under test at Ag and Co–C fixed points after exposure to 1350 °C at intervals over a period of 500 h are compared. In addition, the detailed homogeneity profile of all three thermocouples was determined and will be discussed. This article is arranged as follows. First, the construction of the thermocouples are described. Then the comparative measurement is described and finally the results of the stability and homogeneity are presented and discussed.

2 Construction of Thermocouples

2.1 Pt/Pd Thermocouple

The Pt/Pd thermocouple (NPL-PtPd04/09) was constructed using high-purity wires of 0.5 mm diameter and 2000 mm length. The purities of the Pt and Pd wires were 99.997 % and 99.97 %, respectively. The thermoelements were cleaned with ethyl alcohol and distilled water. The Pd wire was annealed electrically in air for 9.5 h at approximately 1300 °C and then 0.5 h at 450 °C. The Pt wire was electrically annealed for 9 h at the same temperature, followed by 0.5 h at 750 °C and then 0.5 h at 450 °C prior to cooling to ambient temperature by switching off the current [2]. The wires were then inserted into a twin-bore re-crystallized alumina insulator tube (Al_2O_3, 99.7 % purity, outer diameter of 4 mm, inner diameter of 1.2 mm, length of 710 mm) which was pre-cleaned by baking at 1500 °C, in air, for 24 h. The measuring junction of the

Pt/Pd thermocouple was prepared by bending the Pt arm into a U-shape, then welding the two thermoelements directly to each other [5,6]. The junction was then drawn around 10 mm into the bore containing the Pd leg. The thermoelements emerging from the alumina insulator were insulated with flexible Teflon tubes and connected to a pair of Cu wires of diameter 0.3 mm to form the reference junction. The thermocouple was inserted into a one-end closed alumina protection tube (outer diameter of 7 mm, inner diameter of 5 mm, length of 700 mm), and then the thermocouple 1000 mm from the measuring junction was annealed at 1100 °C in a horizontal furnace for a further 150 h.

2.2 Pt–Rh/Pt Thermocouples

Two Type R thermocouples (NPL-03/09 and NPL-04/09) were prepared using different methods to perform the comparative measurements along with the Pt/Pd thermocouple.

2.2.1 Normal Type R Thermocouple

The NPL-03/09 was fabricated using the wires of diameter 0.5 mm, length 2000 mm, with the following procedure: the Pt wire was electrically annealed in air for 0.5 h at approximately 1100 °C and the Pt alloy (Pt–13 %Rh) wire was electrically annealed at 1450 °C for 0.5 h prior to cooling to ambient temperature by switching off the current. All alumina components were of the same specification and dimensions as the Pt/Pd thermocouples above. The wires were inserted into the alumina insulator tube, and 1000 mm from the measuring junction of the thermocouple was annealed at 1100 °C in a horizontal furnace for a further 1 h. The measuring junction was formed by directly welding the two thermoelements together. The thermoelements emerging from the alumina insulator were insulated with flexible Teflon tubes and connected to a pair of Cu wires of diameter 0.3 mm to form the reference junction.

2.2.2 Special Type R Thermocouple

In order to improve the performance of the Type R thermocouple, a special Type R thermocouple, NPL-04/09, was constructed in the same way as for the normal Type R in Section 2.2.1, but subjected to the same heat treatment procedure as for the Pt/Pd thermocouple in Section 2.1, except that the electrically annealed temperatures of Pt and Pt alloy were 1100 °C and 1450 °C, respectively.

3 Measurements

3.1 Stability Measurement

The ageing temperature for the thermocouples was selected to be 1350 °C, and was applied using a horizontal single-zone tube furnace. When the thermocouples were

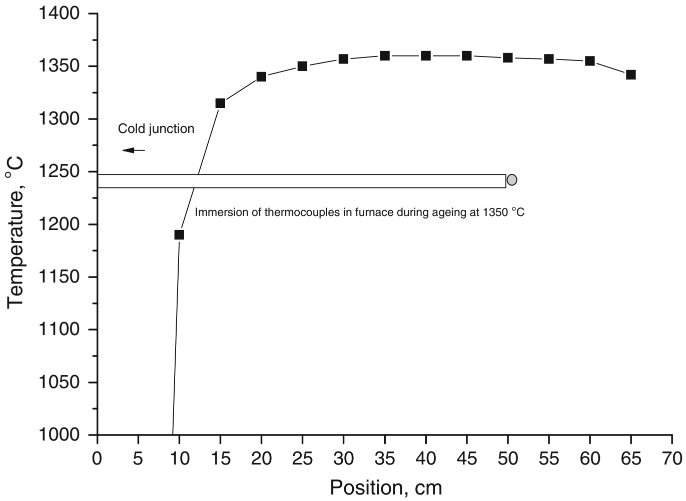

Fig. 1 Temperature profile of the ageing furnace showing the highest temperature gradient is located between 35 cm and 45 cm from the measuring junction of the thermocouples (during ageing, thermocouples were immersed in the furnace about 50 cm)

in the furnace, the most significant part of the temperature gradient along the thermocouples was located between 35 cm and 45 cm from the measuring junction of the thermocouples. Figure 1 shows the furnace temperature profile and the position of the thermocouple during ageing. The output of the three new thermocouples was measured at the freezing point of Ag and melting point of the Co–C eutectic prior to ageing, and again every 100 h during the ageing process. The uncertainty contributions, and combined uncertainty, of thermocouple measurements at the fixed points of Ag and Co–C are summarized in Table 1.

3.2 Homogeneity Measurement

The homogeneity measurements were performed in two ways: Firstly, the output of each thermocouple was measured by measuring the maximum emf deviation ($\Delta E_{\max}$) when the measuring junction is raised in 2 cm steps to 12 cm above the bottom of the thermowell of the Ag fixed point, where the temperature is assumed to be uniform. The maximum emf difference is taken to represent the inhomogeneity.

Secondly, the emf was measured using the moving temperature gradient method [7,8]. The experimental setup used is shown in Fig. 2 of [7]. A heat gun was used to produce a gradient-point source of heat (full width at half maximum of peak of ~20 mm, peak temperature of ~185 °C, while the measuring and reference junctions are both placed in a Fluke 9101 automatic ice point. Here, the scan rate was 4 mm/ min over a distance from 200 mm to 600 mm from the measuring junction. The maximum emf difference along the scan is taken to represent the inhomogeneity ($\Delta E_{\max}$).

Table 1 Summary of uncertainty contributions and the combined uncertainty ($k = 1$) of the measurement of the thermocouples at the fixed points of Ag and Co–C

Fixed point:	Co–C		Ag	
Uncertainty contributions	Type R	Pt/Pd	Type R	Pt/Pd
Type A				
Statistical standard uncertainty (μV)	0.10	0.10	0.10	0.10
Type B				
Ingot impurity (μV)	0.16	0.27	0.08	0.11
Heat flux (μV)	0.16	0.27	0.15	0.22
Immersion, inhomogeneity (μV)	0.96	1.29	0.64	0.75
Plateau determination (μV)	0.58	0.58	0.29	0.29
Voltmeter calibration (μV)	0.29	0.29	0.29	0.29
Spurious emf (μV)	0.29	0.29	0.29	0.29
Ice-point uncertainty (μV)	0.31	0.31	0.31	0.31
Combined uncertainty (μ*V*)	1.25	1.56	0.89	0.99
Temperature equivalent (mK)	90	70	70	55

The inhomogeneity, expressed as a percentage, is calculated by

$$\%\ \text{inhomogeneity} = \frac{\Delta E_{\text{max}}}{E_{\text{ref}}} \times 100\%$$

where E_{ref} is the reference emf at the test temperatures (i.e. 962 °C for the Ag immersion method or 185 °C for the moving temperature gradient method). The homogeneity profile was measured every 100 h during the ageing procedure. The calculated values are summarized in Table 2. The prime advantage of this method is that it allows a qualitative visualization of the homogeneity profile along the length of the thermocouple.

4 Results

4.1 Stability Evaluation

The stability of the Pt/Pd thermocouple, as measured at the freezing point of Ag, is shown in Fig. 2a. After the first ageing step of 100 h, a maximum drift of the emf of about 1 μV(52 mK) was observed. During further ageing, from 200 h to 500 h, the Pt/Pd thermocouple retained its stability within 0.5 μV(26 mK). These results are consistent with those reported by Burns and Ripple [1] in Fig. 2.

The stability of the Type R thermocouples is presented in Fig. 2b. After the first ageing step of 100 h, the 'normal' Type R NPL-03/09 and the 'special' Type R NPL-04/09 exhibit a decrease in emf of about 5 μV (385 mK) and 2 μV (154 mK), respectively. During further ageing, from 200 h to 500 h, the drift appears to decrease for both thermocouples. In this period, both thermocouples exhibit a further drift of about 2 μV (154 mK).

Table 2 Summary of thermocouple inhomogeneity results

Descriptions	Inhomogeneity (%)					
Method (Scan range, Temp.)	Immersion test at Ag cell (0 to 120 mm, 961.78 °C)			Moving heat source (200 mm to 600 mm, 185 °C)		
Ageing time (h)	Pt/Pd	Special R	R	Pt/Pd	Special R	R
0	0.01	0.02	0.02	0.04	0.03	0.01
100	0.01	0.02	0.02	0.05	0.07	0.10
200	0.01	0.02	0.02	0.05	0.11	0.10
300	0.02	0.02	0.02	0.05	0.07	0.15
400	0.01	0.02	0.02	0.05	0.10	0.15
500	0.02	0.01	0.01	0.04	0.07	0.14

The stability of the Pt/Pd thermocouple, as measured at the melting point of Co–C, is shown in Fig. 3a. After the first ageing step of 100 h, a maximum drift of the emf of about 1.5 μV (64 mK) was observed. During further ageing, from 200 h to 500 h, the Pt/Pd thermocouple retained its stability within about 0.8 μV (34 mK). These data at Co–C indicated that the stability of this Pt/Pd thermocouple is likely to be comparable to those reported by Edler et al. [2] in their Fig. 2.

The stability of the Type R thermocouples is presented in Fig. 3b. After the first ageing step of 100 h, the 'normal' Type R NPL-03/09 and the 'special' Type R NPL-04/09 exhibit a decrease in emf of about 10 μV (714 mK) and 4 μV (286 mK), respectively. Upon further ageing, from 200 h to 500 h, the 'normal' Type R drifted 3 μV (214 mK) and the 'special' Type R drifted 2 μV (143 mK).

4.2 Inhomogeneity Evaluation

4.2.1 Immersion Measurements at the Freezing Point of Ag

The maximum output deviation when the measuring junction is raised from 0 cm to 12 cm above the bottom of the thermowell of the Ag fixed point is presented, in temperature terms, in Fig. 4. Of particular interest is the fact that the Pt/Pd thermocouple and the 'special' Type R thermocouple give a maximum output variation of about 120 mK, whereas the maximum output variation of the 'normal' Type R is higher by a factor of two at 400 h. Table 2 shows calculated values of the thermocouple inhomogeneity in percentage plotted against the ageing time. The values calculated in this way, for the three thermocouples, are comparable, taking the values between 0.01 % and 0.02 %. Note that his value is the same as the suggested typical variation in emf due to inhomogeneity for a new platinum-based thermocouple by Bentley [9]. It is likely that the uniform temperature zone of this Ag fixed point (about 12 cm) is too short for a thorough characterization of the homogeneity after ageing of these thermocouples. In our view, the uncertainty of this type of measurement is too large to draw any firm

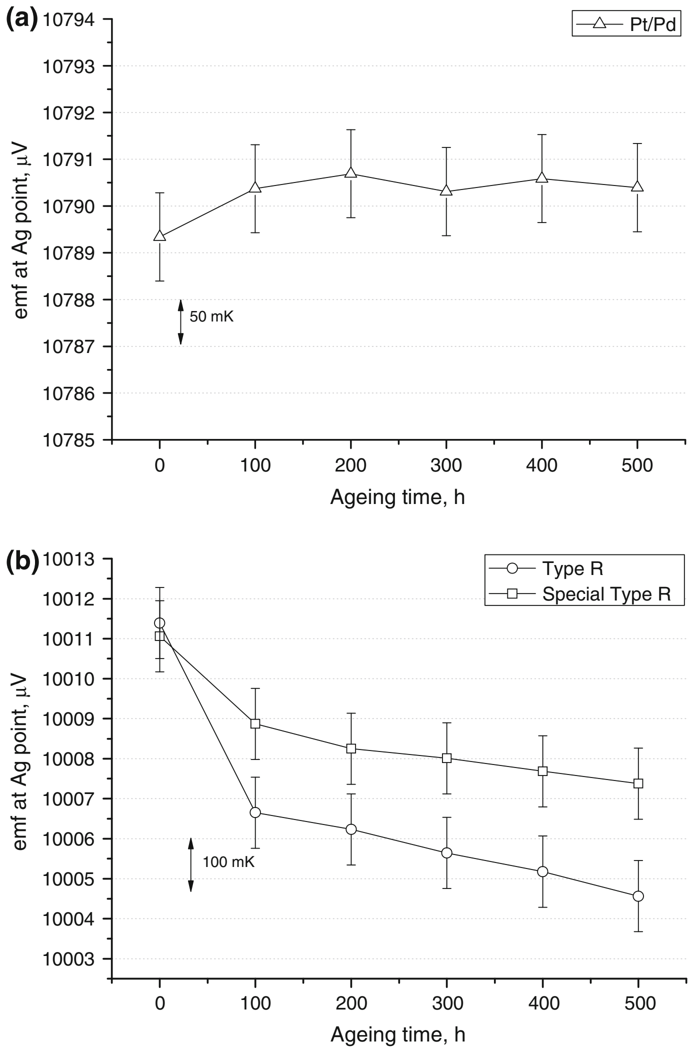

Fig. 2 Thermoelectric stability at the freezing point of Ag as a function of ageing time at 1350 °C, for (a) Pt/Pd thermocouple and (b) Type R thermocouples with measurement uncertainty ($k = 1$)

conclusions about the variation of homogeneity as a function of ageing time according to the manual increment and the limited length of Ag cells.

4.2.2 Inhomogeneity Measurement Using Moving Temperature Gradient

Because of the limitations of inhomogeneity measurements using immersion in a Ag fixed point, the detailed homogeneity profile of each thermocouple, measured with the moving temperature gradient method, when both measuring and reference junctions

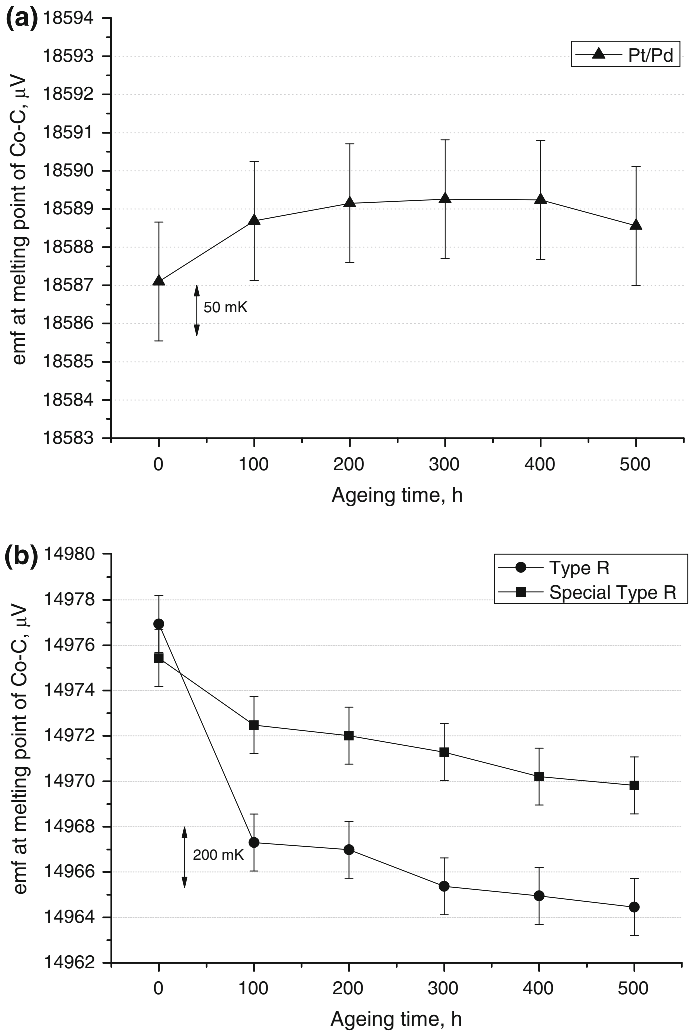

Fig. 3 Thermoelectric stability at the melting point of Co–C as a function of ageing time at 1350 °C, for (a) Pt/Pd thermocouple and (b) Type R thermocouples with measurement uncertainty ($k = 1$)

are at the temperature of melting ice, is shown in Fig. 5. The Pt/Pd thermocouple shows very little change in its homogeneity profile throughout the ageing sequence, while both Type R thermocouples exhibit continuing changes to their homogeneity profile. The Pt/Pd remains considerably more homogeneous than the Type R thermocouples, within about 0.05 %. With regards to the inhomogeneity profile, there appears to be a little significant difference in the behaviour of 'special' and 'normal' Type R thermocouples. According to calculated values shown in Table 2, it is seen that after 500 h ageing the inhomogeneity of the 'special' Type R thermocouple is 0.07 %, whereas 'normal' is about 0.14 %, which is about 50 % higher.

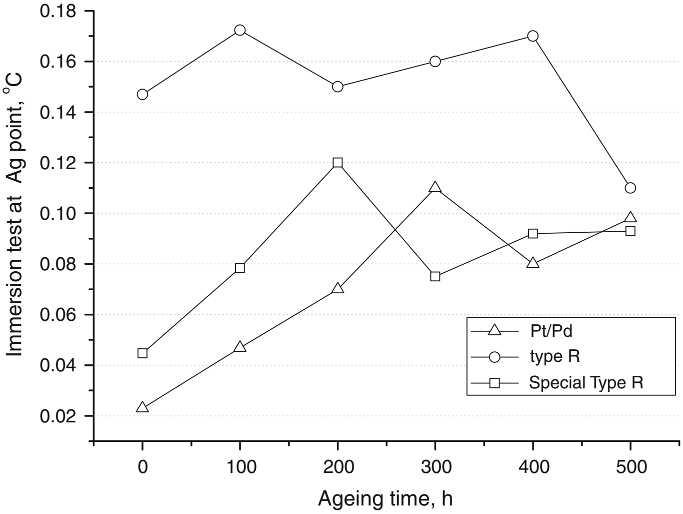

Fig. 4 Maximum output change, in temperature terms, during immersion measurements at the freezing point of Ag, for all three thermocouples

4.3 Discussion

Figure 6 shows a summary, in temperature terms, of the drift of each thermocouple at each fixed point. The stability measurements at the Ag point indicate that after the initial ageing period of 100 h all thermocouple output becomes more stable than when new. However, it is clear that the Pt/Pd thermocouple was substantially more stable at the Ag point than the Type R thermocouples, with the latter exhibiting a continual, regular, decline in output during the ageing process.

These results were repeated at the Co–C point. Again, after the initial ageing period of 100 h, the drift in the output of the thermocouples declined markedly. After initial ageing, the ‘special’ Type R thermocouple appeared to be a factor of two more stable than the ‘normal’ Type R. At both fixed points, the emfs of both Type R thermocouples exhibit a systematic downward trend as a function of ageing time, whereas the Pt/Pd thermocouple is completely stable within the measurement uncertainty.

The results obtained using a movable localized heat source indicate a correlation between the thermoelectric homogeneity profile and the thermocouple calibration drift.

5 Summary

A Pt/Pd thermocouple, a (‘special’) Type R thermocouple that was given the same preparatory treatment as the Pt/Pd thermocouple and a conventional (‘normal’) Type R thermocouple were constructed for a comparative study of their thermoelectric stability and homogeneity at regular intervals during a 500 h ageing program at 1350 °C. The stability was measured every 100 h at the Ag and Co–C fixed points. The thermoelectric homogeneity was measured by immersion measurements at the Ag fixed point

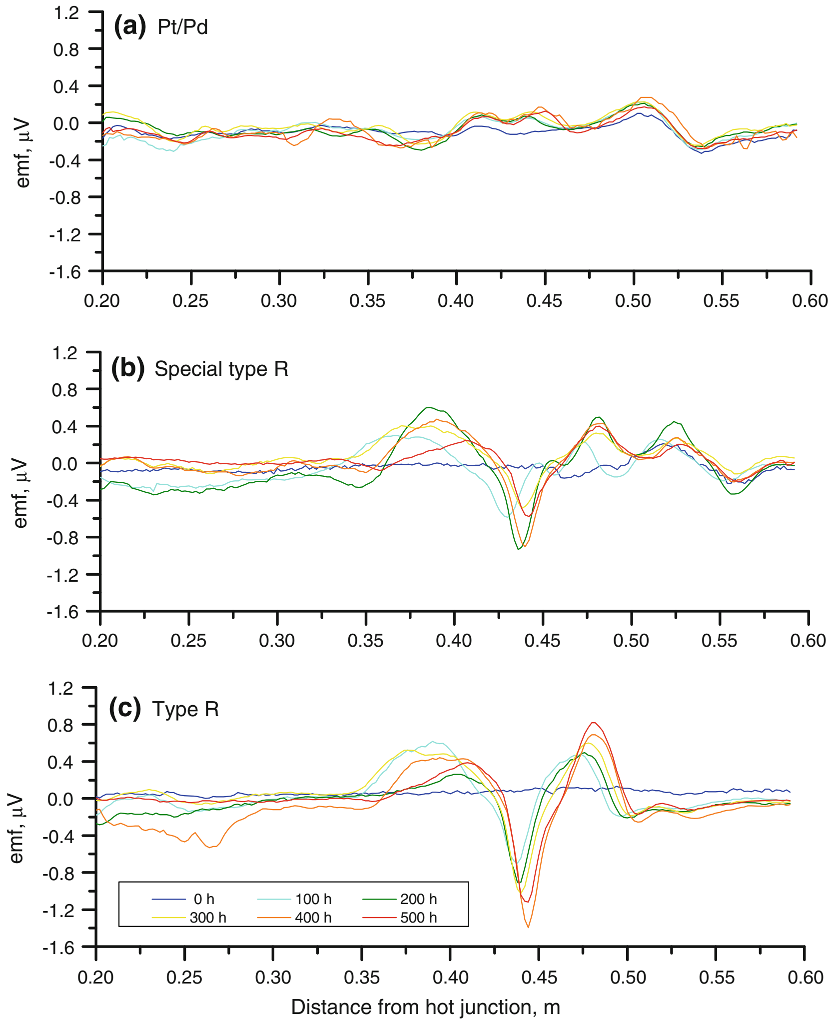

Fig. 5 Homogeneity profiles using moving temperature gradient method. Each trace represents the profile after a different ageing time: (a) Pt/Pd thermocouple, (b) 'Special' Type R thermocouple, and (c) 'normal' Type R thermocouple

and by the moving temperature gradient method. It is clear that if a detailed evaluation of inhomogeneity is required, the Ag immersion method should be used with caution.

We found that the Pt/Pd thermocouple shows substantially better stability and homogeneity performance than the two Type R thermocouples. These findings can demonstrate the superior performance of Pt/Pd thermocouples when compared directly to the alloy noble metal type thermocouples, and they are eminently suitable for use as reference standard thermocouples. The 'special' Type R thermocouple that was given the same preparatory treatment as the Pt/Pd thermocouple showed better stability and homogeneity than the'normal' Type R thermocouple.

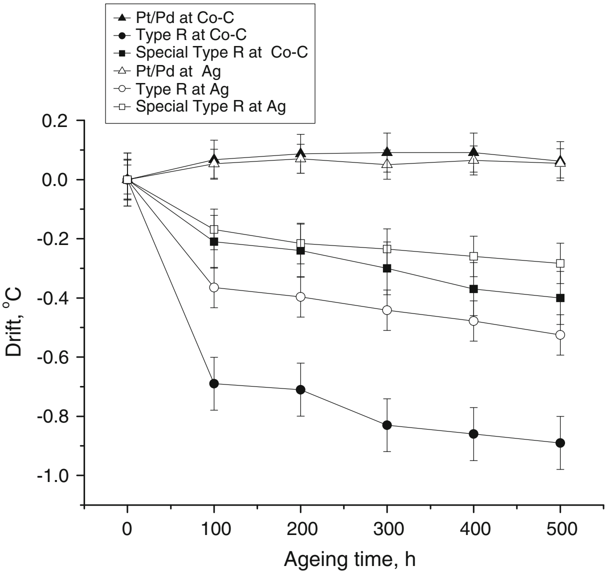

Fig. 6 Summary of the drift, in temperature terms, of all three thermocouples at Ag (*open symbols*) and Co–C (*closed symbols*) fixed points, as a function of ageing time with measurement uncertainty ($k = 1$)

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