

# Stability assessment of a new high strength, high temperature Type R and Type S thermocouple

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## Abstract

Platinum–rhodium Type R and S thermocouples fail in service because of two main reasons: excessive grain growth in the platinum limb at high temperatures (causing wire breakage) and temperature drift, i.e. deviation of electromotive force (emf) generated over time because of deposition of rhodium oxide on the platinum limb, out of accepted industry tolerances. Finding a solution to the problem is challenging because of the contradictory requirements of strength and narrow permissible emf range: emf is extremely sensitive to any dopants or alloying elements that can be used to improve strength at high temperatures. Johnson Matthey has developed a new thermocouple wire (platinum limb) called ‘HTX<sup>TM</sup>’, by doping platinum with a small quantity of zirconium which is oxidised during processing to electrically neutral zirconium oxide. Zirconium oxide improves the high temperature strength of platinum wire by restricting the grain growth but does not significantly affect the emf. The result is a wire which has the potential to last many times longer at high temperatures (>1200 °C) than standard platinum wire, whilst still achieving Class 1 tolerance (i.e.  $\pm 1$  °C at 1000 °C). It also improves the thermoelectric drift characteristics of the thermocouple by counteracting any reduction in emf due to rhodium contamination by an increase in emf as any remaining zirconium is converted to zirconium oxide. We describe an impartial long-term assessment (up to 1500 h) of the thermoelectric stability of the HTX<sup>TM</sup> wire by exposure to high temperature with periodic *in situ* calibration using a Co–C (1324 °C) high temperature fixed point. This yields stability measurements with very high precision.

Keywords: thermocouple, thermoelectric stability, oxide dispersion strengthening, high temperature fixed point

(Some figures may appear in colour only in the online journal)

## 1. Introduction

Noble metal thermocouples based on alloys of Pt and Rh are in widespread use, and are heavily relied upon for applications including heat treatment, casting, metal processing, power generation, and transfer of measurement standards. Their chief advantage is their excellent thermoelectric stability and robustness at high temperatures. In the long term, however, some calibration drift is inevitable. A key thermoelectric drift

mechanism involves local depletion and enrichment of Pt and Rh; this is due to transport of Pt and Rh oxides in the vapour phase [1–4]. Recently, using new information and techniques such as high temperature fixed points (HTFP) based on metal–carbon eutectic alloys, extensive studies have been performed on the stability of these thermocouples [1, 5–7] to accurately characterize the drift performance and to enable the identification of optimal alloy combinations.

One problem associated with the commonly used thermocouples Type R (Pt versus Pt-13%Rh) and S (Pt versus Pt-10%Rh) is the embrittlement of the Pt thermoelement after

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prolonged exposure to high temperature. This is due to growth of the crystal grains to macroscopic sizes; if a grain boundary spans the entire diameter of the wire, the wire becomes very weak and breakage soon follows. To overcome this difficulty, Johnson Matthey have developed a Pt wire doped with zirconium oxide to create an oxide dispersion stabilized (ODS) alloy. Because the zirconium oxide particles congregate at grain boundaries, growth of the grains is inhibited, and the wire should retain its strength during high temperature exposure.

The addition of dopants to inhibit grain growth is not new; in 1974 Selman and colleagues at Johnson Matthey added zirconium oxide to platinum [8] and, shortly after, platinum–rhodium alloys [9] to improve the strength. Later on the approach was applied to thermocouples; Wu and Liu added yttrium to platinum in solid solution to form an alloy for use in Type S thermocouples [10], although the yttrium resulted in a reduced emf, necessitating the further addition of gold, which has an opposing Seebeck coefficient to that of yttrium [11], to bring the emf back within the tolerance bands. Fischer *et al* explored dispersion hardening with zirconium–yttrium oxide particles for stabilization of platinum and platinum–rhodium alloys, and showed via microscopy that the grain growth was restricted and also that the creep rate of the material was reduced by a factor of ten [12]. More recently Hamada *et al* reported a Type R thermocouple with improved high temperature creep strength attained by ODS by dispersion of zirconium oxide [13], which also met the Class 1 tolerance specification [14]. Some members of that group also developed a ODS palladium wire for Pt/Pd thermocouples [15].

The novelty of the new Johnson Matthey HTX™ Pt wire is that it is doped with between 10 mg kg<sup>-1</sup> and 1000 mg kg<sup>-1</sup> zirconium, yttrium or samarium, rather than the corresponding oxides [16], for the purpose of both strengthening and controlling thermoelectric drift. When Type R or S thermocouples constructed with this Pt wire are exposed to high temperatures in air the zirconium is slowly converted to zirconium oxide, with a corresponding positive drift of the emf. The amount of positive drift is governed by the amount of dopant present. In other words, as providing additional mechanical strength by inhibiting growth of grain boundaries, the HTX™ wire is doped so that the upward drift of the emf corresponding to zirconium oxidation balances the generally observed downward drift of the emf, keeping the thermocouple within the Class 1 tolerance for longer.

The object of this paper is to describe the HTX™ wire, how it works, and to provide an impartial demonstration that the use of HTX™ wire does not adversely affect the thermoelectric performance of the thermocouple by making very precise measurements of the thermoelectric drift at around 1324 °C. This does not constitute or imply an endorsement of the product by NPL. Section 2 describes the grain growth mechanism, and the HTX™ wire and how it inhibits grain growth by ‘pinning’ the grain boundaries is described in section 3. The drift measurements are described in section 4, and the results presented in section 5. Section 6 concludes with a discussion.

## 2. Grain growth

The motivation for developing HTX™ wire originated with industry, where the mechanical failure (breakage) of pure Pt wire in Type R and S thermocouples is a common problem. The principal cause of this is embrittlement due to grain growth, whereby during prolonged exposure at high temperature crystalline grains grow to macroscopic sizes and give rise to a brittle ‘bamboo’ structure to the wire. In this case, individual grains occupy the entire wire diameter and the wire becomes a chain of grains linked by transverse grain boundaries. These boundaries are a point of weakness and are easily displaced or separated, causing a circuit break and loss of the temperature reading.

A key reference for this subject is the study of Undisz *et al* [17], who looked at grain growth with zirconium oxide doped Pt. Internal oxidation of alloys is a well-known process commonly used for generating ‘oxide dispersion strengthened’ materials. The main focus of research has been to establish ways of finely dispersing non-metallic precipitates for dispersion strengthening [18, 19]. The main advantage for platinum alloys is to improve high temperature mechanical properties and this is used in a number of applications.

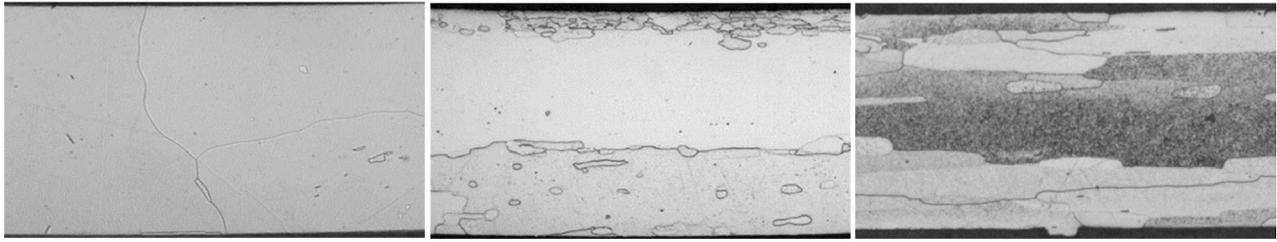
Internal oxidation of the zirconium has been described by Wagner in 1959 [20] who presented a basic model, and characterised the relationship between internal oxidation and the formation of external zirconium oxide layers as a function of composition, solubility and diffusion coefficients of the alloy constituents; importantly, he also introduced time dependence to the model. Others have since expanded on the model [21, 22].

The interface between the particles and the matrix can be important [23] and can itself influence the diffusion rate of oxygen [24, 25]. In the 1970s Reinacher [26], and later Fischer [27] described a preferred oxidation of zirconium along the grain boundaries of the material. The low solubility of oxygen in the platinum matrix prevents the formation of zirconium oxide particles inside the grains themselves. Cold working and heat treatment may help to promote migration of zirconium oxide particles into the grains [27, 28]. However, until the work of Undisz *et al* [17] the formation and distribution of zirconium oxide particles was poorly understood.

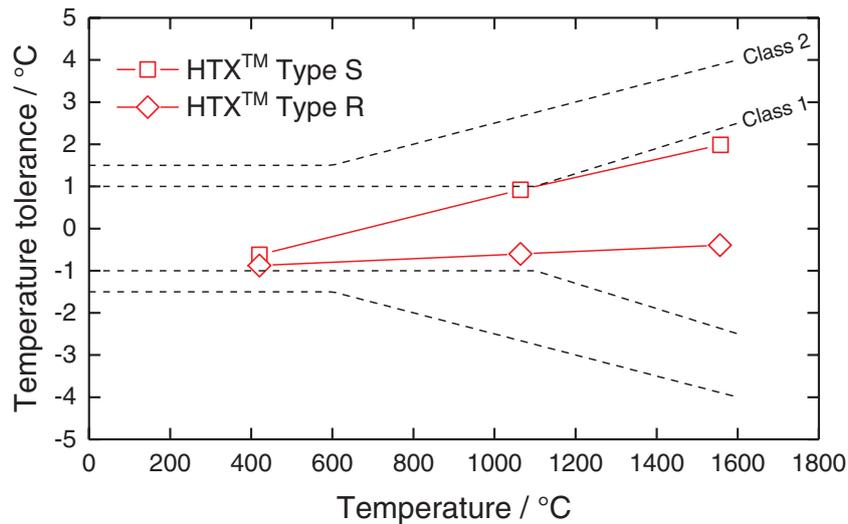
Undisz *et al* [17] investigated Pt-10%Rh/0.16%Zr alloy in the form of 100 μm thick foils. Oxidation was facilitated by heat treatment in air at 900 °C and at 1400 °C, for durations between 10h and 80h. It was found that external oxidation occurred at both temperatures after heat treatment. On the surface of the 900 °C samples, rhodium oxide formed (rhodium oxide is known to dissociate above about 1140 °C [29–36]); neither rhodium oxide nor zirconium oxide formed a dense protective layer on the surface.

## 3. HTX™ wire

For practical thermocouple wire, there are a number of approaches that can be taken to mitigate against the effect of



**Figure 1.** Electron microscope images of 0.5 mm diameter wire. Left: grain structure of regular Pt wire after 4 h at 1200 °C; a single grain occupies the full wire diameter with a grain boundary running all the way across. Middle: grain structure of HTX™ wire after 140 h at 1200 °C, showing elongated grains and inhibited grain growth. Right: HTX™ wire after 2450 h at 1400 °C with 2.76 MPa tensile loading; the structure is still stable with no evidence of creep processes.



**Figure 2.** Compliance of the Type R and S thermocouples constructed with HTX™ wire with the Class 1 and Class 2 tolerance bands.

grain growth: incorporating smaller grains to start with by, for example, working the material; alloying with substitute elements such as Rh, Ir, etc; doping with interstitial elements such as C, N, etc; and making a composite by adding oxides to restrict grain boundaries. There are two key considerations: it must work at high temperatures, ideally up to about 1700 °C, and it must not significantly change the electrical properties (emf versus temperature) of pure Pt. Taking these restrictions into account, Johnson Matthey have developed a material which incorporates barriers to grain boundary movement and has been shown to retain multiple grains across the wire diameter even during prolonged exposure to high temperatures.

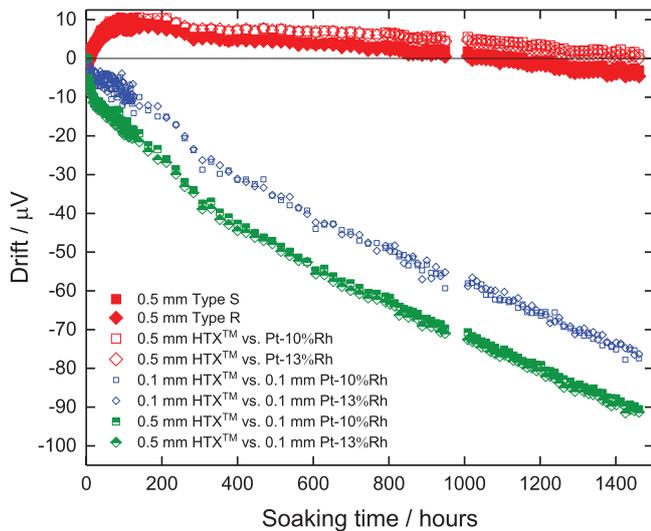
The solution adopted by Johnson Matthey is to micro-alloy Pt within the range from 10 mg kg<sup>-1</sup> to 1000 mg kg<sup>-1</sup> Zr [16]. The Zr is then subjected to *in situ* oxidation during exposure to high temperature. Importantly, the ZrO<sub>2</sub> particles do not participate in the thermoelectric behaviour and do not affect the emf. The particles enhance the mechanical properties of the Pt by increasing the yield stress, and restricting the grain growth by pinning grain boundaries at high temperatures. The effect can be seen in figure 1 which shows electron microscope images of the grains following exposure to high temperature and the application of axial strain.

Figure 2 shows the results of calibrations of Type R and Type S thermocouples at the zinc (419.527 °C), gold (1064.18 °C) and palladium (1554.8 °C when oxygen is not present), which

demonstrates their compliance with the Class 1 and Class 2 tolerance bands [14].

#### 4. Thermoelectric stability measurements

Seven wires of two different diameters (Pt 0.5 mm, Pt-10%Rh 0.5 mm and 0.1 mm, Pt-13%Rh 0.5 mm and 0.1 mm, Pt ‘HTX™’, 0.5 mm and 0.1 mm) were used to construct a multi-wire thermocouple, having a common measurement junction. All wires were supplied by Johnson Matthey. Because of the fragility of the 0.1 mm wire, the variability of annealing processes across the user community, and the need for comparability of the results to other drift studies, no electrical or furnace annealing was performed. This will give rise to a small error in the thermoelectric drift rate because the residual cold work changes the Seebeck coefficient, but since the relative performance of each wire is the parameter of interest this should not be a significant problem. Each wire was inserted in a separate bore of an eight-bore recrystallized alumina insulation tube, bore diameter 0.8 mm, outer diameter 4 mm, length 700 mm, which had been baked at 1500 °C for 24 h. The wires were welded together at one end. The thermoelements emerging from the alumina insulator were sleeved with PTFE tubing. The exposed ends were twisted together with individual copper wires to form seven reference junctions which were inserted into glass tubes. The copper wires were



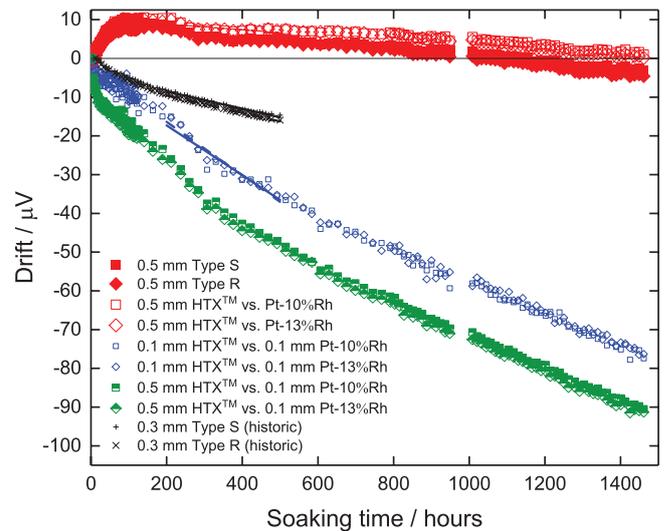
**Figure 3.** Drift of the thermocouple emf as a function of time at high temperature for each of the thermocouples measured.

then connected to an isothermal junction to enable branching so that multiple combinations of wires could be attached to a switchbox. The high-performance switching unit (Keithley Model 7001) could only accommodate eight thermocouple inputs, so the pairs of wires to be measured were prioritised accordingly. These were (dimensions indicate wire diameter): 0.5 mm Type R, 0.5 mm Type S, 0.5 mm HTX™ Type S, 0.5 mm HTX™ Type R, 0.1 mm HTX™/0.5 mm Type R, 0.1 mm HTX™/0.5 mm Type S, 0.5 mm HTX™/0.1 mm Type R, and 0.5 mm HTX™/0.1 mm Type S. The thermocouple emfs were measured with a Keithley Model 2182A nanovoltmeter. The reference junctions were maintained at a temperature of 0 °C with stability of about  $\pm 0.01$  °C in a Fluke 7312 stirred water bath.

The thermocouple, protected by a recrystallized alumina sheath (inner diameter 5 mm, outer diameter 7 mm, length 700 mm), also baked in the same way as the insulator, was placed in a Co–C high temperature fixed point (HTFP, apparatus described in [37]) and held just below 1324 °C (i.e. the melting point of the Co–C HTFP) for about 1500 h. Periodically (about every 8 h) the cell underwent a melting/freezing cycle. This yielded an *in situ* calibration of each thermocouple.

## 5. Results

For each thermocouple, the difference in the measured emf at the melting point (point of inflection) from the value at the start, i.e. the thermoelectric drift, is shown as a function of time in figure 3, and also figure 4 which contains additional historical data for further analysis, as described below. The results are characterised by an initial transient drift behaviour for a duration of about 100 h, followed by a settling into a steady, slower drift rate which is approximately linear as a function of time. The initial transient drift up to 100 h has been observed elsewhere by Bentley [38], and was originally thought to arise from contamination of the wires by residual



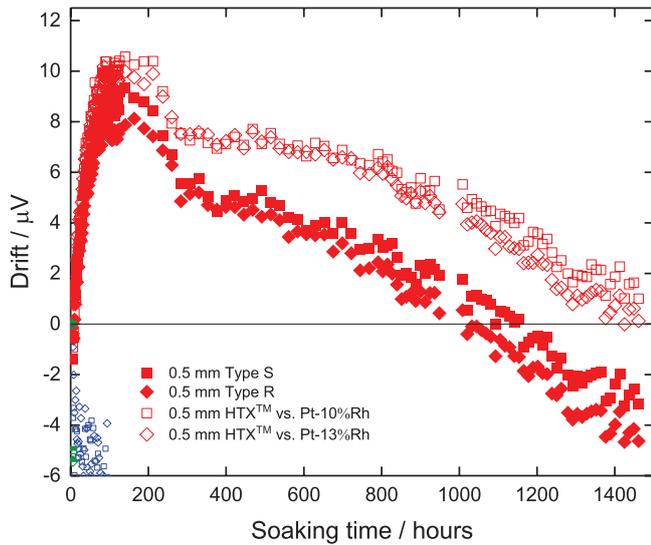
**Figure 4.** As for figure 3, with the addition of drift data of 0.3 mm diameter wire from [5] measured under identical conditions (black crosses). Lines show fits to selected data between 200 h and 500 h to yield the drift rate.

impurities in the insulator; as the impurities in the insulator are depleted, the drift from this cause diminishes. However, Bentley's work was on measurements up to 1700 °C, far higher than those measured in this study. Bentley suggested an upper limit of 1300 °C for accurate thermometry using Type R and S thermocouples, as above this temperature irreversible contamination processes begin. A more plausible cause for the initial rise of emf followed by a slow decay is the early development of ordering in the Pt–Rh leg (region less than 600 °C), followed by a slow coating of the Pt–Rh leg by rhodium oxide (region between 600 °C and 950 °C) and lastly the long 'soak' behaviour observed in this study (region above 1100 °C), most likely due to rhodium migration. All these effects are also mentioned in [38]. The first effect causes a rise in the combined Seebeck coefficient, the second a decrease, and the last, also a decrease. Large drifts of up to 0.5 °C are caused by the first two effects in parts of the thermocouple exposed to temperatures between about 200 °C and 1000 °C. These effects have been individually observed by Bentley [39], Jahan and Ballico [40, 41] and Webster [36].

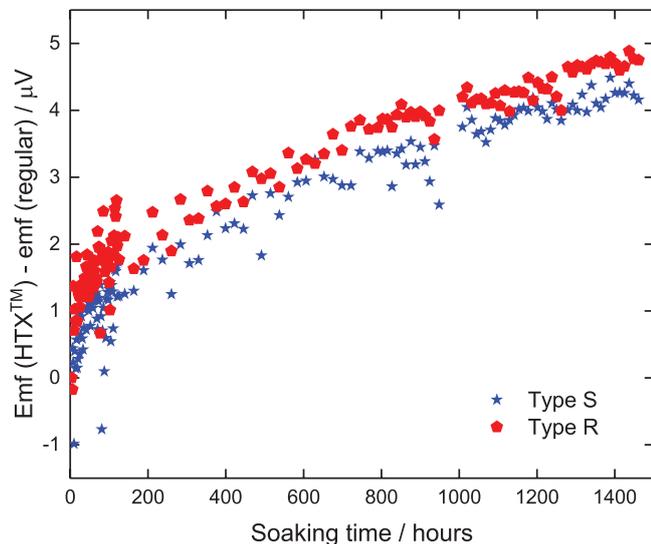
A key parameter of interest is the difference between Type R and S thermocouples made with HTX™ platinum wire and those made with regular platinum wire. This difference is shown in detail in figure 5, and the difference is plotted in figure 6 to show the constant rate of divergence with time.

Also of interest in this study is the dependence of the drift rate on wire diameter for a given thermocouple. To aid in this, drift data for Type R and S thermocouples constructed from wire with 0.3 mm diameter from a previous study performed under identical conditions [5] was added to the current data; the new drift data set is shown in figure 4.

A straight line was fitted to the emf drift between 200 h and 500 h to yield the drift rate, in the same manner as that of the previous study [5] (see figure 4), and the drift rate was plotted against the surface area to volume ratio for each of the Type R and S thermocouples constructed with 0.1 mm and 0.5 mm

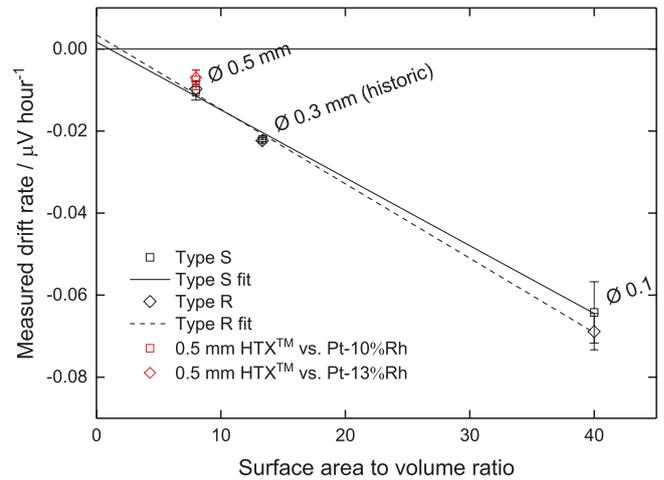


**Figure 5.** Close-up of emf drift of the HTX™ wire and regular wire (0.5 mm diameter).



**Figure 6.** Difference between the emf drift of the HTX™ wire and the regular wire (0.5 mm diameter), showing constant rate of divergence.

diameter wires. The result is shown in figure 7. The standard uncertainty of the drift rate is given by the standard deviation of the gradient yielded by the linear fit. Note that the trend seen in figure 7 may be affected by the fact that the amount of free volume surrounding the wires is different in each case, so in addition to the wire diameter dependence, there is also disproportionately more platinum and rhodium evaporation from the thinner wires: the wire of diameter 0.1 mm has almost twice as much empty space around it than the 0.5 mm wire, so as it stands any quantitative conclusions to be drawn from figure 7 are approximate. Although the drift rate appears to have a linear dependence on the surface area to volume ratio, there are only three points so it is difficult to make a definitive statement on the nature of the relationship. It could be that a linear relationship is consistent with the hypothesis that the thermoelectric drift arises from a surface effect, being



**Figure 7.** Measured drift rate as a function of the surface area to volume ratio for the Type R and S thermocouples shown in figure 4. Error bars correspond to a coverage factor  $k = 1$  (about 67% coverage probability). Thermocouples using HTX™ are not considered in the fit but data points are shown for comparison.

associated with the evaporation, condensation and transport in the vapour phase of Pt and Rh and their oxides. The finding of a strong dependence of the drift on wire diameter contradicts some of the results of [42], although that study was concerned with thermocouples in a range of different environments, including the effect of impurities. On the other hand, the study of Glawe and Szaniszlo [43] did observe a dependence of the drift rate on wire diameter for measurements at a similar temperature (1327 °C).

## 6. Discussion

It is now widely acknowledged that localised change of the Pt and Rh content of wires, and the resulting change in Seebeck coefficient, is a significant contributor to the long-term drift of Pt–Rh thermocouples above 1200 °C. This localised change can arise from migration of Pt and Rh and their oxides by vapour transport, as well as by diffusion in the bulk wire. Ordering effects and the formation of oxide layers on the wire surface can also significantly affect the emf [39–36], although this is probably only at temperatures below about 1100 °C [44]. Surface oxide effects have been observed directly between 600 °C and 950 °C [36]. As a significant part of the emf will be generated in a region affected by depleting effects of rhodium oxidation, and will contribute to the slowly increasing drift error.

The drift shown in figures 3 and 4 exhibits two separate regimes (initial relatively fast drift up to 100h followed by slower, long-term linear drift). The initial upward transient regime has been explained in terms of the different ordering and oxidation effects [39–36]. The second drift regime, a steady, almost linear drift of the emf downwards which emerges beyond about 100h duration, is thought to be due to migration of platinum and rhodium, in the vapour phase and by diffusion.

Figure 5 shows that the Type R and S thermocouples made with HTX™ platinum wire are more stable than the

corresponding regular thermocouples, which is consistent with the hypothesis that the dissolved zirconium is gradually being converted to zirconium oxide with time, causing a corresponding change in the Seebeck coefficient and hence a change in the emf. It has been shown that Zr increases the emf of a Pt/Pt–Zr thermocouple by  $0.632 \mu\text{V ppm}^{-1}$  atomic or  $1.36 \mu\text{V ppmw}^{-1}$  [45]. The current wires are doped with between  $10 \text{ mg kg}^{-1}$  and  $100 \text{ mg kg}^{-1}$  of zirconium, implying an emf increase of a Pt/Pt–Rh thermocouple of  $6.32 \mu\text{V}$  to  $632 \mu\text{V}$ . As this drift is introduced progressively due to the *in situ* conversion of zirconium to zirconium oxide over hundreds of hours, the rate of drift would be of the order of a few  $\mu\text{V}$  to a few hundred  $\mu\text{V}$ , in the opposite direction to the inherent downward drift of the Pt/Pt–Rh thermocouple. The difference between the drift of the HTX thermocouple and the regular one shown in figure 6 indicates a difference in drift over 1500h of about  $5 \mu\text{V}$ , which is consistent with the lower end of the zirconium dopant concentration (i.e.  $10 \text{ mg kg}^{-1}$ ), at least over this duration.

An important caveat concerns the irreversible nature of the conversion of zirconium to zirconium oxide. This generates a permanent change in the Seebeck coefficient in the regions of the thermocouple exposed to temperatures sufficient to cause this transformation. In consequence, any movement of the thermocouple away from the hot region will cause significant errors as regions of the thermocouple having undergone significant chemical changes will then be moved into the temperature gradient region where the bulk of the thermocouple emf is generated. Hence, stability can only be maintained at a constant immersion with a static temperature profile.

The current study has been performed with only a very limited selection of wires; it is entirely possible that there is some batch-to-batch variability which could affect the conclusions presented here. Wires from different manufacturers may also perform differently. There is clearly a need for further measurements in this area. Nonetheless, overall, this enhanced stability is a key finding, since it demonstrates conclusively that the Type R and S thermocouples made with HTX™ wire are at least as stable as those made with regular wire, and, at least up to 1000h, are actually more stable. This has been established thanks to the extremely high precision *in situ* thermoelectric stability measurements afforded by the Co–C HTFP. While the main benefit of using HTX™ wire is the enhanced mechanical strength at high temperature over long durations, the additional thermoelectric stability is an important aspect of its overall performance.

## 7. Conclusion

A new format of Pt wire doped with zirconium oxide, developed by Johnson Matthey and denoted ‘HTX™’ wire, has been presented. The doping is to prevent the growth of grain boundaries, which leads to embrittlement in regular Pt wire during prolonged exposure to high temperatures. The inhibition of grain growth by pinning of the grain boundaries has been demonstrated with electron microscopy. The thermoelectric

stability of a selection of Type R and Type S thermocouples of different wire diameters with HTX™ Pt wire and regular Pt wire has been objectively measured at NPL by exposure to temperatures of around  $1324 \text{ }^\circ\text{C}$ , with periodic *in situ* calibrations using a Co–C HTFP (melting temperature  $1324 \text{ }^\circ\text{C}$ ), for a duration of about 1500h. The thermocouples made with HTX™ wire exhibit comparable or slightly better thermoelectric stability than the corresponding regular thermocouples, which shows that the zirconium oxide doping does not adversely affect the thermoelectric stability, at least for high temperature exposure durations up to 1500h. This does not constitute or imply an endorsement of the product by NPL.

An intriguing finding is that the drift rate is broadly inversely proportional to the surface area to volume ratio, which supports the hypothesis that the thermoelectric drift rate is dominated by surface effects, most likely by evaporation, condensation, and transport of Pt and Rh in the vapour phase.

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