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Investigation of self-validating thermocouples with integrated fixed-point units

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Abstract. Thermocouples are often exposed to harsh conditions when used for high-temperature measurements in industry. They suffer commonly from unavoidable drift effects which influence the required process efficiency and control. A self-validation concept for thermocouples to monitor their performance in the temperature range between 1000 °C and about 1800 °C in oxidizing atmospheres by using integrated miniature fixed-point units of different designs was tested. Two different models of fixed-point crucibles filled with high purity palladium (1553.4 °C) and platinum (1769 °C) have been constructed and assembled with type B thermocouples to be used as traceable references. Furthermore, two innovative self-validation methods by using thick wires of high purity gold (1064.18 °C), nickel (1455 °C), and palladium in multi-bore insulators as fixed-point materials were developed and investigated by assembling them with type B thermocouples. The measurement results obtained have demonstrated the suitability of the integrated fixed-point units to provide long-term confidence in industrial high-temperature measurements within about (2−3) K.

Keywords: Thermocouple, miniature fixed point, self-validation

1 Introduction

Self-validated measurements of temperatures above 1000 °C are difficult but are also essential for the technical feasibility of industrial processes e.g. for the manufacture of silicon, carbides, carbon/carbon composites, iron, steel, glass and ceramics. Many of these industrial sectors require improved process control to enhance efficiency in order to survive in competitive markets. Improvements in sensing methods, especially in-situ validation, may bring about a step change improvement in the practice of thermometry and hence in industrial process control by using lower uncertainties of the installed temperature sensors [1].

The self-validation concept presented in this paper is based on the use of miniature fixed-point cells and modules with defined and stable melting temperatures of pure metals which are combined directly with commonly used type B thermocouples to detect their drift effects. Similar self-validating concepts by using miniature fixed-point cells containing pure metals or metal-alloys with defined phase transition temperatures are described in references [2–4] for temperatures between 530 °C and 650 °C and at the melting point of gold (1064.18 °C). Applications of integrated miniature fixed-point cells for high temperatures in inert atmospheres by using a cobalt-carbon eutectic are described in references [5, 6]. In any case the small crucibles are permanently installed together with the thermocouple. By cycling the furnace temperature the fixed-point material undergoes a phase transition which results in a definite output-signal of the thermocouple. This signal is associated with a specific temperature value and can be used to check and adjust possible changes in the emf-temperature relationship of the thermocouple.

2 Designs of self-validating fixed-points cells and modules

Five miniature fixed-point cells have been constructed at Physikalisch-Technische Bundesanstalt (PTB) for the use with type B thermocouples up to temperatures of about 1800 °C in oxidizing atmospheres. Three of the cells were filled with pure palladium and the other two were filled with pure platinum. The miniature fixed-point crucibles were made of high purity (99.7%) alumina (Al_2O_3) and were annealed at about 1300 °C for several hours in air before filling. The two different designs A and B of the miniature fixed-point cells constructed at PTB are shown in the Figures 1 and 2.

The type B thermocouples used have also been constructed at PTB. The thermoelements with diameters of 0.5 mm and each with a length of 2000 mm were delivered by Alfa Aesar GmbH & Co KG – Karlsruhe, Germany. The dimensions of the ceramic insulation and protection tubes

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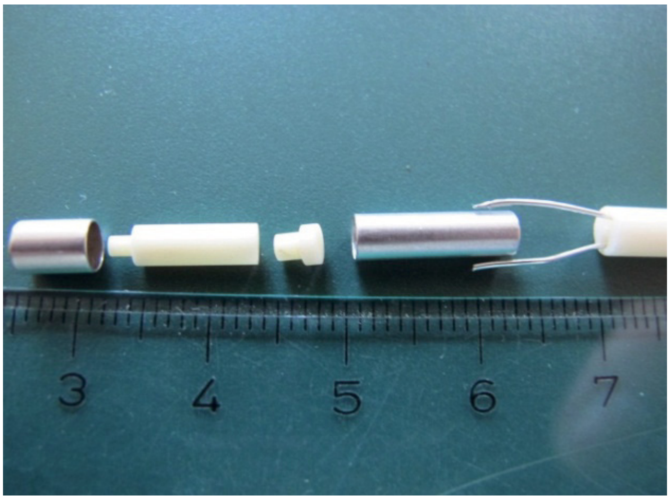

Fig. 1. Miniature fixed point of design A crucible.

Fig. 2. Miniature fixed points of design B crucible (left crucible for Pt, right crucible for Pd).

were adjusted to the dimensions of the miniature crucibles. The miniature fixed points of the design A are similar to the fixed-point cells described in reference [7]. The ceramic crucible containing the fixed-point metal was inserted into an auxiliary cartridge made of a platinum-rhodium alloy which was welded between the two thermoelements of the type B thermocouples. The miniature fixed point Pd-01-12 contains 0.23 g of high purity (99.99%) palladium and the miniature fixed point Pt-01-12 contains 0.53 g of high purity (99.997%) platinum. The outer diameter of the ceramic crucibles amounts to a value of 3 mm and their length is about 10 mm. These small dimensions allowed a simple integration of the fixed-point cells in a ceramic protection tube of 7 mm outer and 5 mm inner diameter typically used for standard thermocouples. An additional miniature fixed-point cell, Pd-03-12, with an outer diameter of 4 mm and a length of about 12 mm was constructed to replace the miniature fixed point Pd-02-12. This slightly larger crucible contains 0.58 g of high purity (99.99%) palladium.

The miniature fixed points of design B consist of a ceramic tube closed at one end with an outer diameter of 7.2 mm and a length of 22 mm. The central bore (3.2 mm in diameter) of the fixed-point cell is surrounded by outer bores (or slots) of 1.1 mm in diameter containing the fixed-point material in form of wires. The outer bores (or slots) were sealed with a ceramic adhesive after filling. The miniature fixed-point cell Pd-02-12 contains a total mass of 1.4 g of high purity (99.95%) palladium and the cell Pt-02-12 contains a total mass of about 2 g of high purity (99.99%) platinum. The insulation tube (3 mm in diameter) of the type B thermocouples used was inserted close fitting into the central bore of the miniature cell so that the measuring junction was partly surrounded by the fixed-point material in contrast to the design A miniature fixed-points.

Laboratoire commun de métrologie (LNE-Cnam) has developed two designs of miniature fixed-point devices as self-validating modules suitable to use at high temperatures in oxidising atmospheres. They were applied in practice to a home-made type B thermocouple [8]. The miniature fixed-point modules were made of high purity (99.7%) alumina (Al_2O_3) and were annealed at about 1300 °C for several hours in air before the filling. The devices require small amounts of pure metals; less than 0.2 g in the first device and less than 2 g in the second one. The phase transition plateaus of gold (1064.18 °C), nickel (1455 °C) [9] and palladium (1553.5 °C) [10] were assessed with these self-validation techniques.

The first design consists in the so-called "pulled-wire" (PW) technique. In the four-hole insulation tube of the thermocouple two holes are used for the thermoelements and the other two are filled with the fixed-point material over a length of about 25 mm symmetrically to the measuring junction of the thermocouple. A second design of a self-validating module, labelled "rolled-wire" (RW), consists of a pure metal mass encapsulated in a small-size alumina crucible in which the thermocouple measuring junction is embedded. Six self-validating modules of the two different designs have been constructed. They were filled with pure metals of gold, (2 × Au/PW and 2 × Au/RW), of nickel, (2 × Ni/PW and 2 × Ni/RW), and of palladium, (2 × Pd/PW and 2 × Pd/RW), respectively. The two different designs of the miniature fixed-point modules constructed at LNE-Cnam are shown in the Figures 3 and 4 [8]. The type B thermocouples used with the miniature fixed-point modules were constructed at LNE-Cnam.

3 Melting behaviour of the integrated miniature fixed points

A typical melting curve of palladium by using the type B thermocouple SV-B-Pd-01-12 with the integrated fixed-point crucible Pd-01-12 (design A) against the emf of the furnace control thermocouple is shown in Figure 5. The melting curve shows a constant increase of the emf before the melting process starts reflecting the applied constant heating rate. During the melting process the slope is

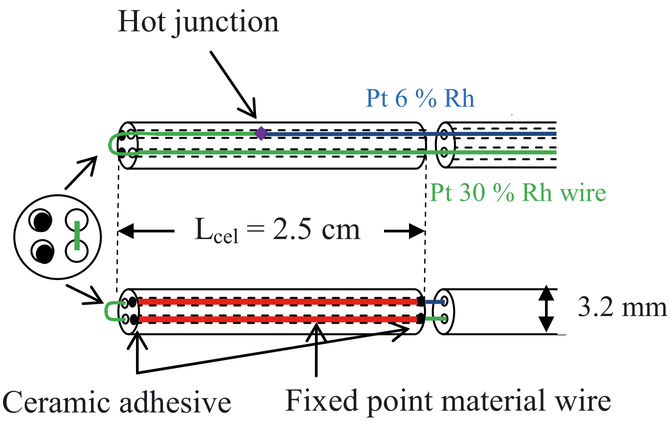

Fig. 3. Integrated self-validating pulled-wire module mounted on a type B thermocouple.

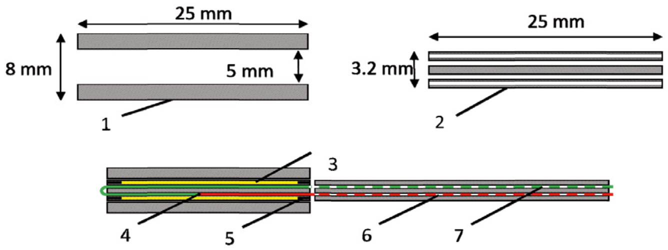

Fig. 4. Embedded self-validating rolled-wire module assembled with a type B thermocouple; 1: External alumina tube crucible. 2: Four bore alumina tube. 3: Pure metal. 4: Measuring junction. 5: Alumina based ceramic adhesive (to close the tube ends). 6 and 7: Type B thermocouple wires.

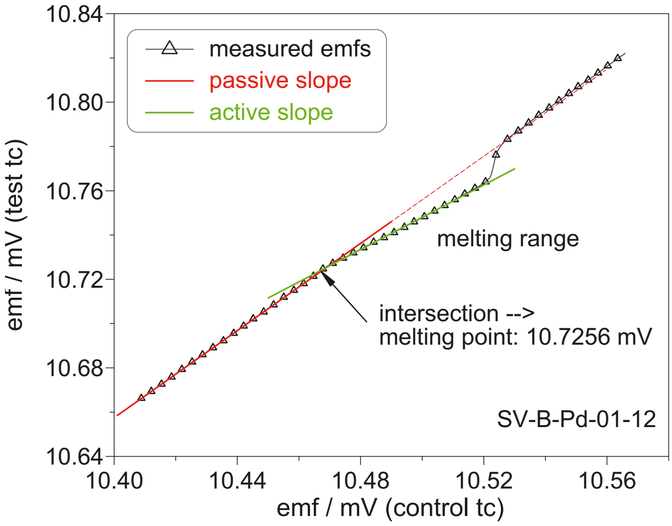

Fig. 5. Typical melting curve of palladium.

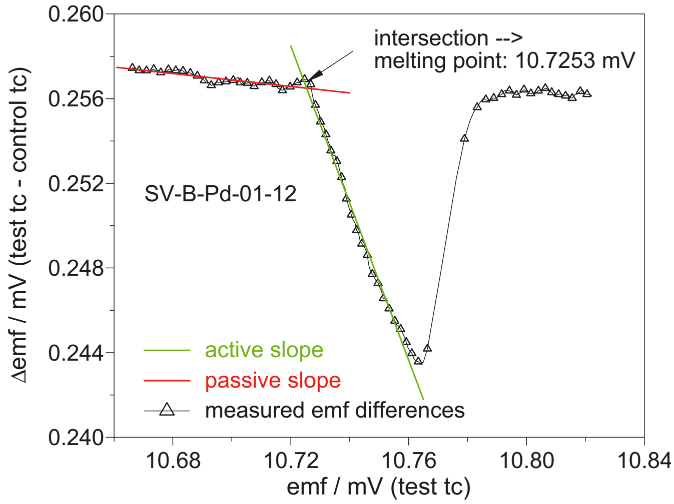

Fig. 6. Differential melting curve of palladium.

decreased. Both parts of the melting curve can be approximated by regression lines, respectively. The intersection point of the two straight regression lines corresponds to the emf of the melting point. The decreased slope indicates the beginning of the melt; the rapid increase of the slope marks the end of the melt.

An advanced detection of the start of the melt is obtained by calculating differential thermo-voltages (Δemf) for instance between the emfs of the test thermocouple and the control thermocouple (y-axis) against the emf of the test thermocouple (x-axis) as shown in Figure 6. In this case, the change of the slope is more significant abounded and the regression lines can be fitted unambiguously. A special feature of the melt by using the integrated fixed-point cells of design A was the dependency of the melting temperature on the heating rate, as visible in Figure 7. The melting curves of the integrated fixed-point crucibles of design B are very similar to the melting curves shown in Figure 5. Due to the higher amount of fixed-point metal in the crucible, the melting plateaus of the design B crucibles were slightly longer than these ones obtained by using design A crucibles.

The LNE-Cnam designs (RW and PW devices) were tested at the gold, nickel and palladium points. The characteristics of the self-validating thermocouples were evaluated by performing and exploiting melting and freezing point measurements of the self-validating modules, corresponding to the inflection point of the melting plateau and the maximum temperature on the freezing plateau, respectively [11]. The melting plateaus of gold, nickel and palladium were clearly observed with both the rolled-wire and the pulled-wire methods using the self-validated thermocouple. However, at the nickel and palladium fixed points, the freezing plateaus were not as repeatable as hoped; moreover the shape of the freezing plateau showed several small peaks indicating that different freeze processes were taking place of the independent pieces of metal.

Figure 8 shows the influence of the furnace heating rate on the melting temperature with the palladium of the rolled wire and pulled wire configurations. The palladium wire used had a nominal purity of 99.99%. The influence of the thermal environment was evaluated by adjusting the furnace temperature offset to ±12 K and changing the heating rate temperature of the furnace (1 K/min, 3 K/min and 6 K/min, successively). The duration of the melting was one minute and three minutes for heating

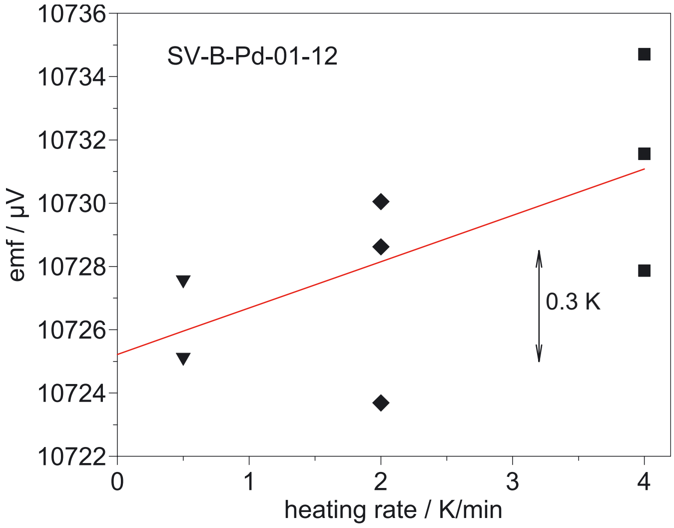

Fig. 7. Dependency of the melting temperatures on the heating rate by using the miniature fixed point Pd-01-12 of design A.

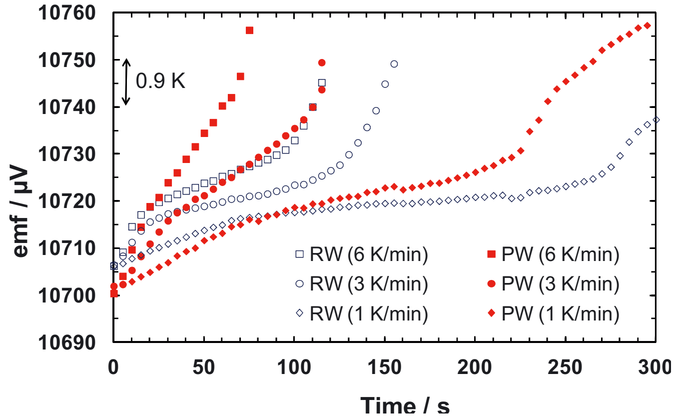

Fig. 8. Influence of the heating rate on the melting temperature plateaus within Pd /RW and Pd/PW.

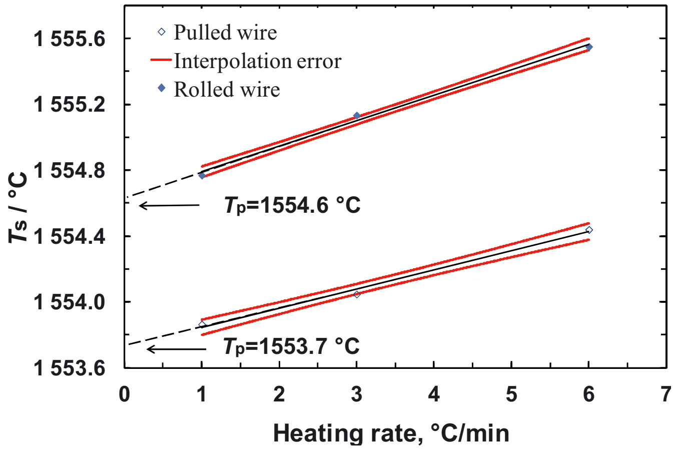

Fig. 9. Determination of the plateau temperature in stationary conditions with no heat flow within Pd /RW and Pd/PW.

rates of 6 K/min and 1 K/min, respectively. The melting plateau was clearly observable with a melting range of 3 K by using the pulled wire configuration and 1 K with the rolled wire devices. The repeatability was within 0.12 K which is satisfactory considering the very small masses of metal used (0.1 g and 0.9 g of palladium).

The emf of the plateau varies proportionally to the furnace heating rates. To determine and correct the influence of the heating rate on the melting temperature, the equilibrium temperature of the self-validating thermocouple corresponding to adiabatic conditions T_{p0} was determined by the back-extrapolation of the best fit T_{p} (plateau temperature during melting and freezing) as function of the heating rates of the furnace (Fig. 9).

4 Long-term investigation of the self-validating thermocouples

At PTB and LNE-Cnam the self-validating thermocouples with the integrated miniature fixed points were annealed in air by using horizontal furnaces. Several hundred hours and different temperatures were applied to investigate the long-term behaviour of the integrated fixed points and of the thermocouples. At PTB, the thermocouples were verified for their emfs by using the integrated fixed-point cells and by measurements at the freezing point of silver (961.78 °C) and at the melting temperature of the Co-C eutectic (1323.7 °C) before, in between, and after performing the heat treatment. Additional to this thermal aging, one thermocouple was systematic contaminated with iron powder to force an enhanced drift of its emf and to allow a verification of the stability of the integrated fixed-point crucibles. At LNE-Cnam a home-made type S thermocouple was used as a reference and was placed close to the self-validating thermocouples inside the furnace to control the stability of the furnace and to detect any drift.

The type B thermocouple SV-B-Pd-01-12 with the integrated fixed-point crucible Pd-01-12 (design A) was aged in 5 periods for a total time of about 2133 h at different temperatures. In the first period the thermocouple was annealed for 544 h at 1450 °C, in the second period for 928 h at 800 °C. The thermocouple was cycled over three days in the third period at temperatures of about 1600 °C, i.e. above the melting temperature of palladium for (4×6) h and at temperature of 1000 °C (3×18) h. In the fourth period the thermocouple was 3 times cycled within of about three weeks at temperatures of 1400 °C for 288 h and at 750 °C for 216 h. The last period was a rerun of the third period; the thermocouple was annealed for 24 h at 1600 °C and 54 h at 1000 °C.

The emfs measured at the external fixed points of silver and of the Co-C eutectic as well as the emfs measured by using the internal palladium fixed point in the course of the annealing procedure are presented in Figure 10. The investigated type B thermocouple showed an excellent thermoelectric stability in the order of 0.5 K at the freezing point of silver and at the melting point of the Co-C eutectic. In contrast the emf measured by using the internal palladium fixed point increased significantly by a value of about 50 μV (temperature equivalent of 4.5 K) over the total annealing time.

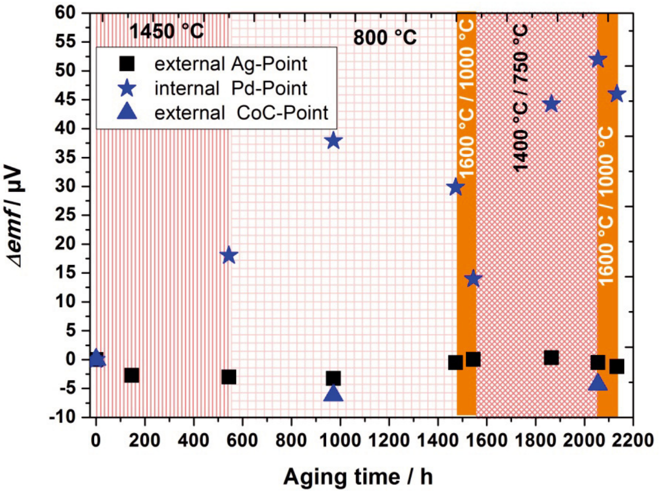

Fig. 10. Stability of the emfs at the external Ag and Co-C fixed points as well as at the internal palladium fixed point by using SV-B-Pd-01-12.

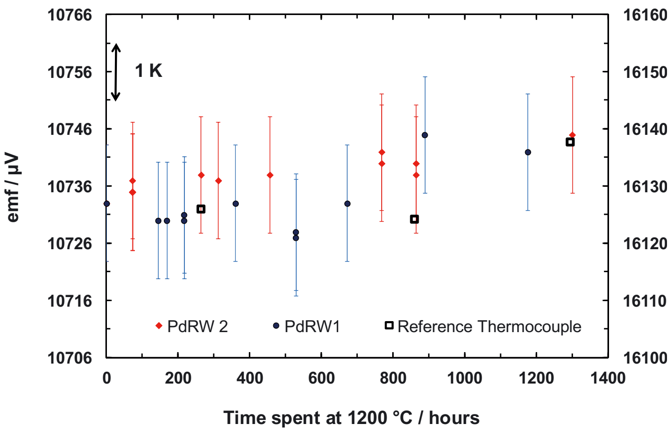

Fig. 11. Stability of PdRW1 and PdRW2 devices. The left axis is for type B thermocouple emf and the right axis indicates the emf of the type S drift-compensation thermocouple.

The type B thermocouple SV-B-Pd-02-12 with the integrated fixed-point crucible Pd-02-12 of design B was annealed together with thermocouple SV-B-Pd-01-12 for 544 h at 1450 °C. The emfs measured at the fixed points shows a similar behaviour as the emf measurements by using the thermocouple SV-B-Pd-01-12 with a slightly decrease of 0.5 μV (< 0.1 K temperature equivalent) at the silver fixed point and a moderate decrease of 5 μV (< 0.5 K temperature equivalent) at the melting point of palladium. During the measurement of the palladium fixed point after the annealing at 800 °C a leakage of liquid palladium from the miniature fixed point occurred due to a failure of the sealing of the bores with the ceramic adhesive. This caused an electrical short between the thermoelements which results in a failure of both; the thermocouple and the fixed point crucible Pd-02-12. A new type B thermocouple (SV-B-Pd-03-12) was constructed and a new miniature fixed point of design A (Pd-03-12) filled with pure palladium was used, which has proved to be more robust than design B fixed-point cells. The thermocouple SV-B-Pd-03-12 was annealed for 120 h at 750 °C. The following measurements by using the external fixed points show no change in the emf compared to the starting values of the calibration. To force a drift of the thermocouple a small amount of iron powder was filled into the holes of the insulation tube to affect the thermoelements. Then the thermocouple was exposed to a temperature of 1200 °C for 5 h. The resulting contamination of the platinum-rhodium thermoelements with iron led to a heavy drop of the emf measured at the external silver fixed point from 4494.6 μV to 4446.1 μV which corresponds to temperature equivalent of about −5.5 K. The measurement of the internal palladium fixed point showed an emf value which was lower by more than 900 μV (temperature equivalent of about 80 K) compared with the starting value. Therefore, the thermocouple was considered as unusable indicated by the strong emf drift. The used miniature fixed-point crucible Pd-03-12 was assembled to the thermocouple SV-B-Pd-01-12 (instead of crucible Pd-01-12) to recheck its melting temperature. The measured emf by using the crucible Pd-03-12 and thermocouple SV-B-01-12 agreed within ±4 μV to the emf measured with the same thermocouple and the miniature fixed point Pd-01-12. Therefore, the contamination of the thermoelements by iron had only changed the thermoelectric properties of the thermocouple, e.g. the Seebeck coefficient, but didn't affect the melting temperature of the palladium inside the crucible. This is a clear indication of the suitability of the self-validation concept by using integrated miniature fixed points to detect drift effects of thermocouples.

The two type B thermocouples SV-B-Pt-01-12 and SV-B-Pt-02-12 with the integrated platinum fixed points were annealed for 928 h at 800 °C in air. The reference emfs at the external silver freezing point increased linearly by about 7 μV for both thermocouples (temperature equivalent of 0.8 K) during the annealing procedure after 928 h. In contrast, the emfs measured by using the internal melting temperatures of platinum exhibited a decrease after the first 400 h of 92 μV (temperature equivalent of 8 K) for the crucible of design B, and 36 μV (temperature equivalent of 3 K) for the crucible of design A. A stabilizing of the emfs measured at the melting point of platinum (Pt-01-12, design A) was observable after a total of 928 h annealing at 800 °C. Both thermocouples failed during the following measurement at the melting point of platinum caused by an overheating. A further heat treatment of the miniature fixed point Pt-01-12 integrated into a new type B thermocouple over an additional period of about 690 h at temperatures between 750 °C and 1600 °C caused an only slight increase of the emf at the melting point of platinum by a temperature equivalent of about 1 K.

At LNE-Cnam the home-made type B thermocouple with the integrated fixed-point crucibles PdRW1 and PdRW2 was aged for a total time of about 1150 h at 1200 °C and cycles around the palladium melting temperature lasted about 100 h. Figure 11 shows the stability of the PdRW1 and PdRW2 modules versus the time spent in the furnace at 1200 °C. The melting points of palladium of the two cells are shown as a function of annealing time. The measured emfs of the type S reference thermocouple are also shown (second y-axis) as a function of annealing time.

The uncertainty associated with the measurements is in the order of 1.75 K ($k = 2$) and is given in detail in reference [8]. The uncertainty of the self-validating thermocouple measurements with rolled and pulled wire devices is composed of:

- repeatability of the measurements estimated from the maximum difference of three consecutive emf measurements in the same thermal conditions;
- reproducibility estimated by comparing the emf measurements of two miniature fixed-point devices in the same thermal conditions;
- uncertainty due to the determination of the inflection point of a single melting plateau;
- uncertainty due to the extrapolation to determine the temperature of the zero heat flow situation;
- uncertainty due to the temperature of the reference junction of the thermocouple (ice-water mixture at 0 °C);
- uncertainty of the voltmeter, which was considered as negligible.

The contribution of the reference thermocouple is composed of:

- the calibration uncertainty;
- the uncertainty of the interpolation of the calibration function;
- the stability of the calibration at the gold fixed-point cell of LNE-Cnam and propagated to nickel and palladium fixed point;
- the thermoelectric inhomogeneity measured by adjusting the immersion depth of the thermocouple during the freeze of the gold fixed-point cell available at LNE-Cnam.

We noticed a slight increase of the values measured at the melting point of palladium (PdRW1 and PdRW2) from 10 727 μV and 10 736 μV to 10 741 μV and 10 745 μV, respectively. The same behaviour was observed with the reference thermocouple, its value increased from 16 126 μV to 16 137 μV indicating a drift in the furnace temperature. However, the increase of the emf at the melting point of palladium is also within the uncertainty. The overall drift of the rolled-wire devices is therefore estimated to be well within 1 K over a period of about 1150 h at 1200 °C.

5 Conclusion

Different self-validating fixed-point designs to detect and correct drift effects of thermocouples at high temperatures were tested by using type B thermocouples. The miniature fixed-point cells of the design A and the pulled-wire and rolled-wire modules were found to be mechanical stable during repeated melting-freezing cycles whereas the miniature cells of the design B failed because of the mechanical weakness of the thin crucible walls and of a failure of the ceramic adhesive sealing. The miniature cells of design A filled with pure palladium showed a significant increase of the emf by about 50 μV (+4.5 K temperature equivalent) during the long-term thermal treatment (more than 2100 h) at different temperatures between 750 °C and 1600 °C. At the same time the emfs of the self-validating thermocouple measured at the external fixed points remained stable within about ±0.5 K. Therefore, the emf drift measured at the melting point of palladium was not caused by a change of the emf-temperature relationship of the thermocouple. The reason could be a diffusion of platinum from the auxiliary sheath which kept the ceramic crucible between the thermoelements into the palladium. Platinum and palladium form a solid solution of increasing melting temperatures with rising platinum fraction.

The melting temperature of platinum by using the miniature fixed-point cell Pt-01-12 showed an initial drop of its emf by a temperature equivalent of about −3.5 K after exposure to 800 °C for about 400 h but was stable within about ±1 K over the successive heat treatment of about 1200 h at temperatures between 750 °C and 1600 °C. This stability of the melting temperature of the integrated miniature fixed-point cell filled with pure platinum allows the detection and correction for drift effects at very high temperatures in the order of a few Kelvin.

The integrated pulled-wire and rolled-wire modules offer a simple and cost effective method to detect changes in the emf-temperature relationship of thermocouples within about (2−3) K up to the temperature of the melting point of palladium. Only short lengths of pure wires used as fixed-point materials are placed close to the measuring junction. The tested type B thermocouple with the integrated fixed-point crucibles PdRW1 and PdRW2 was aged for a total time of about 1250 h, but only a slight increase of the emf at the melting point of palladium was measured. This increase was within the measurement uncertainty of ±1.75 K ($k = 2$) at this temperature.

The melting temperatures of the miniature fixed points of design A and of the pulled-wire modules depended on the heating rates of the furnaces. The hot junction of the thermocouple is not or only partially surrounded by the fixed-point material and the measurements are sensitive to the heat flux from the furnace. Therefore, an extrapolation of the results to adiabatic conditions (heating rate of 0 K/min) is necessary to reach measurement uncertainties in the order of 1.75 K ($k = 2$). If not considered, this uncertainty contribution has to be added in calculating the uncertainty budget which would increase the combined uncertainty to about (2−3) K.

Due to the different heat treatment and annealing procedures for the thermocouples at PTB and LNE a direct comparisons of the results is difficult since different stress levels were applied to the thermocouples and crucibles. Even if the type B thermocouples showed excellent thermoelectric stabilities during the considerable heat treatment (within ±0.5 K at the external silver freezing point), the suitability of self-validating high miniature fixed points was proven.

The melting temperatures of pure metals (palladium and platinum) of integrated miniature fixed-point cells can be used as reference temperatures for self-validation of thermocouples. The measurement uncertainty of the melting temperatures was in the order of about ±1.75 K at the melting point of palladium (1553.4 °C) and increases to about ±3 K ($k = 2$) at the melting of platinum (1769 °C). These uncertainties are the detection limits of emf drift effects at the corresponding temperatures.

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