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Stability Studies of a New Design Au/Pt Thermocouple Without a Strain Relieving Coil

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Abstract The performance of a simple, new design Au/Pt thermocouple developed by NMIA is assessed. This thermocouple is proposed as a more accurate replacement, over the temperature range from 0 to 1,000°C, for the commonly used Type R and S industrial transfer standards, in a robust form familiar to industrial calibration laboratories. Due to the significantly different thermal expansions of the Au and Pt thermoelements, reported designs of the Au/Pt thermocouple incorporate a strain-relieving coil or bridge at the thermocouple junction. As the strain relieving coil is mechanically delicate, these thermocouples are usually mounted in a protective quartz tube assembly, like a standard platinum resistance thermometer (SPRT). Although providing uncertainties at the mK level, they are more delicate than the commonly used Type R and S thermocouples. A new and simple design of the Au/Pt thermocouple was developed in which the differential thermal expansion between Au and Pt is accommodated in the thermocouple leads, facilitated by a special head design. The resulting thermocouple has the appearance and robustness of the traditional Type R and S thermocouples, while retaining stability better than 10 mK up to 961°C. Three thermocouples of this design were calibrated at fixed points and by comparison to SPRTs in a stirred salt bath. In order to assess possible impurity migration, strain effects, and mechanical robustness, sequences of heat treatment up to a total of 500 h together with over 50 thermal cycles from 900°C to ambient were performed. The effect of these treatments on the calibration was assessed, demonstrating the sensors to be robust and stable to better than 10 mK. The effects on the measured inhomogeneity of the thermocouple were assessed using the NMIA thermocouple scanning bath.

Keywords Au/Pt thermocouple · Annealing · High stability · Pt–Rh thermocouple

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1 Introduction

Thermocouples constructed from platinum (Pt) and platinum–rhodium (Pt–Rh) alloys are currently used as secondary reference standards in the temperature measurement range of 0–1,600°C. Although the best achievable calibration uncertainty obtained from these thermocouples is 0.1°C at 1,100°C [1,2], the in-use uncertainty increases to 0.3°C, mainly because of reversible hysteresis due to preferential oxidation of rhodium at a temperature range from 500 to 900°C [3]. Thermocouples constructed from pure elements do not suffer from this preferential oxidation problem. Being pure elements, these thermocouples are inherently more thermoelectrically homogeneous and their stability is not limited by shifts in alloy composition caused by preferential oxidation. The performance of Au/Pd, Pt/Pd, and Au/Pt elemental thermocouples has been investigated by a number of laboratories [4–6]. In most of these studies of Au/Pt thermocouples, a stress relieving coil or bridge was used at the tip to minimize the deformation stress due to the different thermal expansion of the Au and Pt wires [6,7]. As a result, these thermocouples need a special and complicated manufacturing technique. They are also not as robust as conventional Type R or S thermocouples.

In this study, instead of an expansion coil to accommodate the differential thermal expansion, we used a special head assembly and choice of insulators resulting in a simple design of Au/Pt thermocouple, similar to that of Type R or S thermocouples. The calibration stability and the mechanical stability of thermocouples of this design were previously tested, up to a temperature of 600°C [8]. In the work presented here, we assess the calibration and mechanical stability of three such thermocouples when exposed for 500 h at 900°C and 50 thermal cycles between ambient and 900°C.

2 Construction of Thermocouples

Three gold–platinum(Au/Pt) thermocouples were constructed from 0.5 mm-diameter gold and platinum wires of 99.999% purity purchased from Sigmund-Cohn Corp., USA. The insulator used was high-purity (99.8%) recrystallized alumina of length 750 mm and diameter 4.75 mm with two 1.57 mm diameter bores, from Vesuvius McDanel, USA. High-temperature annealing of the thermoelements is thought to be essential to the stability of the Au/Pt thermocouple, and different labs have adopted different annealing processes [5–7]. In this work, the platinum wires (1,500 mm long) were firstly electrically annealed at 1,400°C by passing electric current (approximately 12 A) through the wire for 6 h and then quenched by switching off the current. As the gold wire does not have sufficient mechanical strength for electrical annealing, it was annealed only in a furnace. In order to ensure that the full length of the Au wire was annealed uniformly, two 750 mm long pieces of Au wire were cut from the reel. They were fed into the two bores of a long alumina insulator. The alumina insulator had been pre-baked at 1,100°C for 6 h and dedicated to Au wire annealing. The alumina insulator holding the Au wires was then placed inside a protective quartz tube, in a long horizontal furnace such that the full length of the Au wires were in the uniform temperature zone of the furnace. A horizontal Kanthal-on-alumina tube furnace with a quartz tube liner was used for this purpose. The temperature of the furnace was

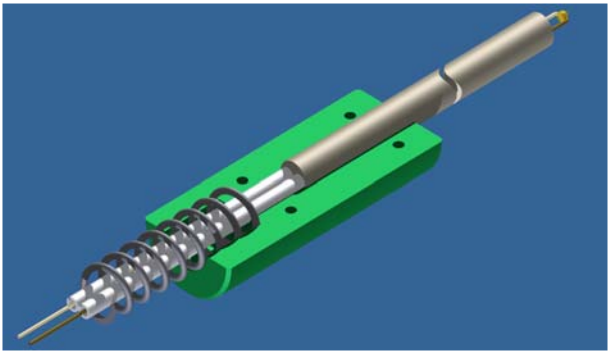

Fig. 1 Schematic diagram of simple design Au/Pt thermocouple

uniform to ±8°C at 1,000°C over the central 750 mm region. The Au wires were annealed at 1,000°C for 6 h and then for 16 h at 450°C. The two Au wires were then welded together to form the gold wire for the thermocouple. After the annealing of the individual wires, they were threaded into the 1.6 mm bores of a pre-baked twin bore insulator by using a ‘pull-wire technique’ [8] (as the annealed gold wire is very soft). The tip was made by welding the Au and Pt wires using an oxygen–hydrogen flame. The assembled thermocouples were then given a final 4-h anneal at 1,000°C followed by an overnight anneal at 450°C.

The wires emerging from the alumina insulator were insulated with relatively stiff Teflon tube with a bore diameter of 1.37 mm. This avoided cold-working the soft, annealed thermocouple wire and thus introducing inhomogeneity. The large bore size of the Teflon and the alumina insulators ensured that the wire could move freely within the insulators, as they expanded with heating. A special head assembly (Fig. 1) was designed to secure the thermocouple insulator and the Teflon insulation tubes without restricting the ability of the thermocouple wires to move freely. A pair of insulated Cu wires was soldered to the open ends of the thermoelements to form reference junctions. The reference junctions of the thermocouples were mounted in a single stainless steel tube of 220 mm length, closed at one end. Two out of the three thermocouples, PtAu-0103 and PtAu-0203, were constructed in 2003 and had been tested for stability for up to 500 h at 600°C [8]. The third thermocouple was constructed for this study in 2006, using the same reels of Pt and Au wire.

3 Experimental Procedures

3.1 Calibration of the Thermocouples

Prior to each calibration, the thermocouples were annealed in a furnace for 16 h at 450°C and thermoelectrically scanned [9,10] in an oil bath at 200°C to determine their thermoelectric signature up to a length of 550 mm from the tip. The thermocouples were calibrated using two methods: (i) by comparison with a standard platinum resistance thermometer (SPRT) up to 550°C in a salt bath followed by a silver fixed point [2] and (ii) calibration using the ITS-90 fixed points: ice point, Ga, Sn, Zn, Al, and Ag [11]. In both methods, the calibrations were performed from lower to higher temperatures. During calibration, the thermocouples were contained in closed-end, sandblasted quartz tubes to protect them from contamination. The thermocouple *EMF* was measured using an Agilent 34420A nanovoltmeter calibrated by NMIA's electrical standards group. During both the calibration and inhomogeneity measurements, the reference junctions were immersed 180 mm into a crushed ice slurry in a 30 cm deep dewar.

3.2 Thermal and Mechanical Stability

After the initial scanning and calibration, the thermocouples were given five heat treatments (in a horizontal annealing furnace) at a temperature of 900°C for a cumulative period of 500 h. After each heat treatment, they were annealed at 450°C, scanned, and calibrated. In order to assess the mechanical stability of these Au/Pt thermocouples, they were also subjected to 50 thermal cycles between ambient and 900°C. For each cycle, the thermocouples were put into a horizontal tube furnace at 900°C for 30 min, removed quickly from the furnace to ambient to cool for 20 min, and then returned to the 900°C furnace. During the measurements, the thermocouples also experienced thermal cycling in a vertical orientation, as they were inserted and removed more than 20 times into the Ag point furnace during the course of this study.

4 Results and Discussion

4.1 Thermoelectric Inhomogeneity

A typical thermoelectric scan of the Au/Pt thermocouples is shown in Fig. 2. The inhomogeneity of the thermocouple is the relative difference in thermocouple *EMF* at different immersions. Note that the curves have been shifted for clarity; it is only the shape that is important. The initial inhomogeneity of the thermocouples from 200 to 550 mm is 0.1 μV, which is equivalent to ±0.003% of *EMF* (± 5 mK at 200°C). Due to thermal conduction along the thermocouple, inhomogeneity cannot be measured at an immersion less than 200 mm (although this can be reduced using an appropriate convolution [12]).

Figure 2 shows a selection of the 15 scan results of a typical Au/Pt thermocouple 'as prepared' and after annealing at 900°C for different periods of time. It can be seen that the inhomogeneity of the thermocouples does not change significantly after heat treatment at 900°C. The inhomogeneity of all three thermocouples in all scans remained within ±0.05 to ±0.08 μV at 200°C. No oxidation or hysteresis was observed in the scan graphs of these thermocouples after 600 h of heat treatment at 900°C. In [13], the author studied the thermoelectric changes in Pt and Au wires in detail. In that study, no reversible or irreversible changes in Seebeck coefficient were detected in Pt wire, unless they were contaminated. The change found was 0.1 μV for Pt wire at 900°C, which is insignificant. However, the author reported a reversible change of the Seebeck coefficient of Au wire above about 550°C. The maximum change was about

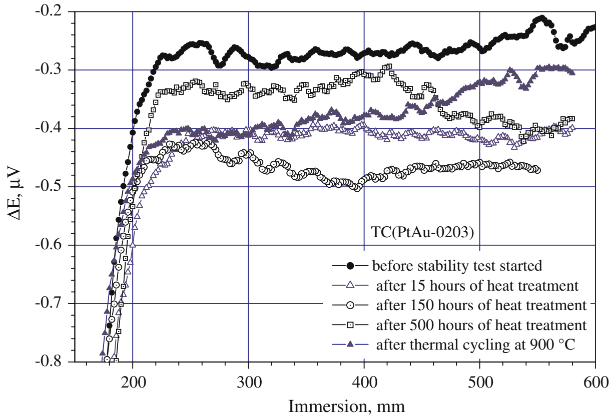

Fig. 2 Thermoelectric scans of a typical Au/Pt thermocouple after different cumulative periods of heat treatment at 900°C

0.2 μV at 650°C for Au wire, which was suggested as due to the oxidation of metallic impurities. Au wire is very vulnerable to contamination and the insulator was changed a couple of times during the course of the measurements; the wires may have been contaminated during the process. In the present study, no such changes are evident.

Due to the different thermal expansion coefficients of Au and Pt, some research groups [5,7] have used a stress-relieving coil of thin Pt wire at the hot junction to reduce the strain on the wires. Kim et al. [7] used a 0.1 mm diameter Au wire as a bridge across the Au and Pt wires at the tip. In the present design, there was no expansion coil or bridge at the tip, and the tip was formed by simple welding as in a conventional Type R or S thermocouple. In this design, the thermal expansion of the gold wire pushes wire out of the insulator into the head and cold junction, rather than out of the "hot" end into an expansion coil. It may be expected that this design would generate more stress and inhomogeneity in the wire near the head. However, the scan results after thermal cycling (vertically and horizontally) show no change in the thermoelectric signature, indicating that no additional strain or stress was introduced into the thermoelements. In an isothermal heat treatment at 900°C over a length of 400 mm, the difference in expansion between the Pt and Au wires is expected to be about 4 mm [10]. The large bore size of the insulator and the special head design allow the wire to easily move longitudinally to accommodate the expansion.

4.2 Calibration Stability

The Au/Pt thermocouples were calibrated in the 450°C annealed state, from lower to higher temperatures, using both comparison and fixed-point methods.

4.2.1 Fixed-Point Calibration

The average values of the measured *EMF* at the fixed points of Ga, Sn, Zn, Al, and Ag are given in Table 1 for three thermocouples. The standard deviation of the data from

Table 1 Summary of measured average *EMF* and standard deviation at different fixed points for three Au/Pt thermocouples

Fixed point	ITS-90 temperature (°C)	Measured *EMF* (μV)		
		PtAu-0103	PtAu-0203	PtAu-0106
Silver	961.78	16120.27 ± 0.08	16120.31 ± 0.04	16119.72 ± 0.10
Aluminum	660.323	9320.10 ± 0.03	9320.17 ± 0.04	9319.77 ± 0.05
Zinc	419.527	4945.44 ± 0.07	4945.42 ± 0.07	4945.24 ± 0.06
Tin	231.928	2235.99 ± 0.05	2235.94 ± 0.02	2235.89 ± 0.03
Ga	29.7646	196.170 ± 0.001	196.123 ± 0.004	196.135 ± 0.003
Ice Point	0.0	–	−0.13 ± 0.02	−40.11 ± 0.02

the six sets is less than 0.1 μV at the Ag point, which is equivalent to 3–4 mK, and about 0.05 μV at the Al point, equivalent to 2–3 mK. At the lower-temperature fixed points, the standard deviation at the Ga point is less than 1 mK, and at the Sn point, it is only 2 mK. The *EMF* values measured by the nanovoltmeter were corrected by applying the calibration correction and the zero offset. Figure 3 shows calibration results for two Au/Pt thermocouples using fixed points after different periods of heat treatment at 900°C. The agreement of all the measurement sets is remarkable. No systematic shifts in calibration were observed over a cumulative 500 h of heat treatment at 900°C for any of the thermocouples used in this work. As these Au/Pt thermocouples are constructed from high-purity metal elements, the deviation of the measured *EMF*s from the reference function [5] is small—usually less than 10 mK. Figure 3 shows that the deviation from the reference function for thermocouples PtAu-0103 and PtAu-0203 are both within 0.25 μV at 961°C, but for thermocouple PtAu-0106, the deviation is somewhat larger (up to 0.8 μV at 961°C, Fig. 5). Although this thermocouple was constructed in 2006 from the same reel, some white spotted marks were noted over most of the length of its Au wires, suggesting some contamination might have been present. Cleaning with acetone and alcohol did not remove these marks. However, the measured inhomogeneity and stability of this thermocouple were as good as the other two thermocouples, suggesting that whatever contaminant was present was uniformly distributed, and was unaffected by the extensive heat treatment.

The measurements reported here span a period of 2–3 years during which different fixed-point cells, furnaces, and nanovoltmeters were used. Altogether, we have six sets of fixed-point data from the three thermocouples. The change in calibration (difference of the third and sixth sets of calibrations from the initial calibration) due to the heat treatments and thermal cycling is plotted in Fig. 4 for the three thermocouples. The figure clearly shows that any changes in calibration are less than 10 mK.

4.2.2 Comparison Calibration

Two of the three thermocouples were also calibrated by comparison using a salt bath up to 550°C against an SPRT and the result for one thermocouple is shown in Fig. 5. The scatter of data from the comparison calibration is slightly larger, especially at higher temperatures. This was attributed to the melting of the ice in the dewar for

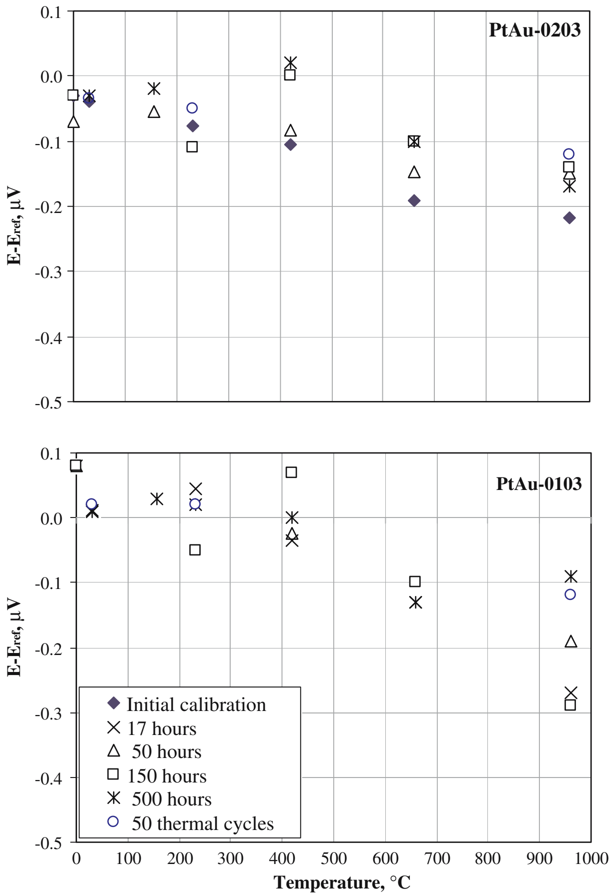

Fig. 3 Calibration results of two Au/Pt thermocouples using ITS-90 defined metal fixed points: initially and after different hours of heat treatment and thermal cycles at 900°C

the reference junction during the 8-h automated salt-bath calibration sequence, thus affecting the immersion of the ice-point section of the thermocouple. This would result in additional scatter, as the ice-point section may have some inhomogeneity given that this section did not experience further furnace annealing after construction, as the main thermocouple section did, and may have suffered slight mechanical strain during assembly. The calibration data using the fixed points are also included in the same figure, which shows that the fixed-point calibration gives the same results as the comparison calibration; however, the fixed-point calibration has a lower uncertainty and so is more useful for assessing this high precision Au/Pt thermocouple and its stability.

4.2.3 Mechanical Stability

In the present design of the thermocouples, there is no stress-relieving coil, so the thermoelements must slide in the insulator as they expand. Otherwise, strain in the

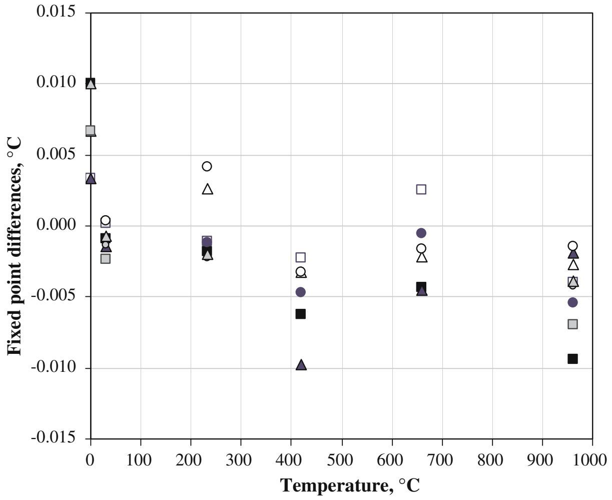

Fig. 4 Differences of the third and sixth sets of fixed-point measurements from the first set, for the three Au/Pt- thermocouples: PtAu-0103 (●, ○, ●), PtAu-0203 (▲, △, ▲), and PtAu-0106 (■, □, ■)

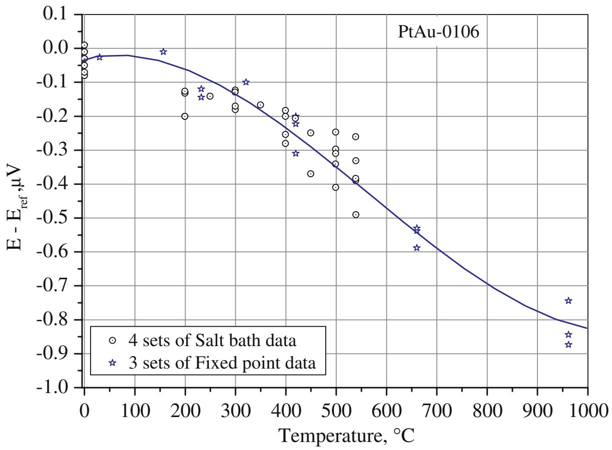

Fig. 5 Comparison calibration data of thermocouple PtAu-0106, after different durations of heat treatment at 900°C, includes also the fixed-point data

wires and thermocouple junction will lead to its failure. We tested the design by repeatedly thermally cycling the thermocouples between 900°C and ambient.

The thermal cycling test was carried out with the same thermocouples that had been heat treated at 900°C for 500 h. During these measurements, all thermocouples were heat-treated in a horizontal furnace at 900°C for a cumulative period of 500 h, calibrated in the salt bath up to 550°C, and used in fixed-point furnaces in a vertical position. During each calibration, they experienced several hours in the salt bath and at each of the fixed points. The scan also involved 5–6 h in an oil bath at 200°C. Thus, each thermocouple experienced significant handling and movements, both horizontally and vertically. As mentioned before, two of these thermocouples were constructed in 2003 and tested previously for stability up to 600°C [8]. There was no sign of mechanical failure or broken tips in any of these thermocouples during the tests. The inhomogeneity scan after 50 thermal cycles is included in Fig. 2, which shows no change in the thermoelectric signatures, indicating good thermal and mechanical stability. The sixth set of calibrations was performed after the thermal cycling test and, as evident from Figs. 3 and 4, the change in calibration is less than 10 mK.

Another important advantage of this present design is that they can be used in both the horizontal and vertical positions. They can also survive thermal shock, unlike an SPRT. They can be put directly into the Ag-point furnace at 961°C from ambient and also can be removed directly from the Ag point, as in the case of Type R or S thermocouples, unlike SPRTs that require vacancy annealing.

5 Uncertainty of the Thermocouple Calibration

The process of thermocouple calibration requires measurement of the thermocouple *EMF*, while maintaining the reference and measuring junctions at known temperatures. The uncertainty of thermocouple *EMF* measured at different fixed points includes the following terms:

(i) Uncertainty due to fixed point impurities and freezing plateau realization: from 1 to 3 mK for the range of 0–660°C, and 7 mK at Ag (961.78°C) [11].
(ii) Voltage measurements: calibration uncertainty of 0.1 μV over the range and a measured gain stability of 10 ppm per year (∼7 mK at Ag-point)
(iii) Reproducibility of fixed-point voltage measurements: less that 5 mK (see Table 1).
(iv) Thermocouple inhomogeneity (∼0.003%): one of the dominant components, it is measured at 200°C and propagated proportionally to temperature (e.g., 10 mK at Ag point). Note: There is presently little information on the temperature dependence of the inhomogeneity of Au/Pt thermocouples.
(v) Uncertainty in the ice-point reference junction temperature is about 2 mK.
(vi) Conduction or immersion error which is negligible at the lower-temperature fixed points and of the order of 5 mK at the Ag point.

The total combined uncertainty at the Ag point at present is ±15 mK, of which the components of thermocouple inhomogeneity and voltage measurement contribute the most. The uncertainty in the NMIA Ag fixed point is also one of the dominant components, at present of the order of 7 mK. The expanded uncertainty U_{95} is ±32 mK with a coverage factor $k = 2.0$. Kim et al. [7] reported a similar uncertainty for their design of Au/Pt thermocouple with a Au wire bridge at the tip.

Other research groups [5, 14] reported lower uncertainty for their Au/Pt thermocouples because they used a value of 2–3 mK for inhomogeneity, measured by changing the immersion in the fixed point cell up to 10 cm. In the present study, the inhomogeneity was determined in an oil bath over a length of 50 cm from the thermocouple tip, and propagated proportionally to temperature. NMIA's calibration uncertainty applies to use in any enclosure up to 50 cm in depth.

The uncertainty in corrections away from the fixed point values will be somewhat larger due to the uncertainty of the curve fitted to the data. For Au/Pt thermocouples, this is usually small because, unlike Pt-alloy thermocouples, they have very small deviations from the reference function.

6 Conclusion

A simple Au/Pt thermocouple design was developed that is similar to the conventional Type R or S thermocouple, but far better in performance. The present work showed that this simple design Au/Pt thermocouple has good thermal and mechanical stability up to 960°C. It is reproducible to better than ±10 mK up to the Ag point. This thermocouple could be calibrated with an expanded uncertainty of 32 mK at 960°C, which is more than an order of magnitude better in high-precision temperature measurements than the conventional Type R or S thermocouples. SPRTs can offer still lower uncertainties; however, they are also significantly more expensive and fragile, and require special annealing procedures. This simple design Au/Pt thermocouple is a useful transfer standard thermocouple for high-precision temperature measurements at a level of 0.03°C up to 1,000°C.

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