Int J Thermophys (2017) 38:174
DOI 10.1007/s10765-017-2315-6

TEMPMEKO 2016

Stability Evaluation and Calibration of Type C Thermocouples at the Pt–C Eutectic Fixed Point

Jianping Sun[1] · Xiaofeng Lu[1] · Meng Ye[2] · Wei Dong[1] · Yalu Niu[3]

Received: 27 June 2016 / Accepted: 7 October 2017 / Published online: 14 October 2017
© Springer Science+Business Media, LLC 2017

Abstract Tungsten–rhenium thermocouples (type C thermocouples) are used to measure temperatures higher than 1500 °C under protective, inert, or vacuum conditions in a wide range of industries, such as metallurgy, power generation, and aerospace. Generally, the measurement uncertainty of a new tungsten–rhenium thermocouple is about 1 % (20 °C at 2000 °C), and a significant drift is always observed above 1200 °C. Recently, the National Institute of Metrology, China, has spent great efforts to calibrate tungsten–rhenium thermocouples with high-temperature fixed points of up to 2000 °C. In the present work, three tungsten–rhenium thermocouples made by two manufacturers were calibrated at the Pt–C eutectic fixed point (1738 °C) and their stability was investigated. A linear fitting and extrapolation method was developed to determine the melting and freezing temperatures of the Pt–C eutectic fixed point for avoiding the effect of thermal resistance caused by the sheath and protection tube. The results show that the repeatability of the calibration is better than 0.9 °C from the melting curve of the Pt–C fixed point and better than 1.2 °C from the freezing curve of the Pt–C fixed point, and a good agreement was obtained for the calibration with the melting and freezing temperature plateau through the linear fitting and extrapolation method. The calibration uncertainty of the thermocouples at the Pt–C eutectic fixed point was 3.1 °C (k = 2).

Selected Papers of the 13th International Symposium on Temperature, Humidity, Moisture and Thermal Measurements in Industry and Science.

✉ Jianping Sun
sunjp@nim.ac.cn

1 National Institute of Metrology, Beijing, China

2 Xi'an Polytechnic University, Xi'an, China

3 Taiyuan University of Technology, Taiyuan, China

Keywords Calibration · Pt–C eutectic fixed point · Stability · Tungsten–rhenium thermocouple

1 Introduction

Reliable high-temperature measurement ($> 1100\,^{\circ}$C) under special environments is a difficult problem in the process control of many industrial fields. The tungsten–rhenium thermocouple (type C thermocouple) is typically used to measure a temperature higher than $1500\,^{\circ}$C under protective, inert, or vacuum conditions in a wide range of industries, such as metallurgy, power generation, and aerospace [1]. Generally, the thermocouples can be calibrated at pure metal fixed points at a temperature up to the copper freezing point ($1084.62\,^{\circ}$C). Due to the lack of reliable high-temperature fixed points, a larger uncertainty at higher temperatures is obtained with the calibration performed at $1554\,^{\circ}$C using the "wire bridge method" and a blackbody comparator [2]. Research on high-temperature fixed points above the freezing point of silver ($961.78\,^{\circ}$C) has gained significant progress since they were firstly reported in 1999 [3], and the calibration uncertainty of high-temperature thermocouples could be reduced through the application of high-temperature fixed points of up to $1953\,^{\circ}$C in the contact thermometry field [4–7]. Due to the variety of sources of tungsten and rhenium and different structure designs of tungsten–rhenium thermocouples, the uncertainty in calibration of a tungsten–rhenium thermocouple is about 1 % ($20\,^{\circ}$C at $2000\,^{\circ}$C) and a significant drift is always observed above $1200\,^{\circ}$C. Recently, the National Institute of Metrology (NIM), China, has spent great efforts to calibrate tungsten–rhenium thermocouples with high-temperature eutectic fixed points, including Co–C ($1324\,^{\circ}$C), Pd–C ($1492\,^{\circ}$C), Pt–C ($1738\,^{\circ}$C), and Ru–C ($1953\,^{\circ}$C), for satisfying the increasing requirements of contact high-temperature measurements in special fields. In the present work, three tungsten–rhenium thermocouples made by two manufacturers were calibrated at the Pt–C eutectic fixed point and their stability was investigated. The results of calibration and uncertainty are reported.

2 Apparatus and Measurement System

2.1 Tungsten–Rhenium Thermocouples

The chemical and physical properties of tungsten and rhenium, such as embrittlement of tungsten at high temperature, high vapor pressure of rhenium, and easy oxidation of tungsten–rhenium alloy, limit their use in certain applications [8]. Stability evaluation and calibration were performed on three type C thermocouples from two manufacturers (C1 and C2 from a US company, C3 from a Japanese company). The thermocouples are similar with a thermoelement wire of 2–3 m length and 0.2 mm diameter and a molybdenum sheath of 3.2 mm diameter and 0.6 mm wall thickness. The length of the molybdenum sheath is 400 mm for C1 and C2 and 450 mm for C3. Hafnium oxide insulation with two holes and 400 mm length is used in C1 and C2. Alumina insulation with two holes and 450 mm length is used in C3. An inert gas (argon) is sealed in the

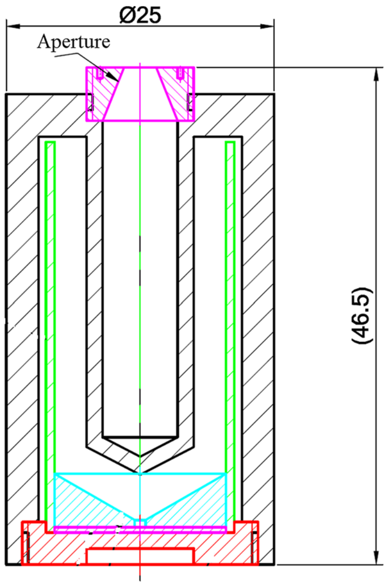

Fig. 1 Pt–C eutectic fixed-point cell

sheath of the thermocouples so that they can work in any gas environment. According to the information from manufacturers, the thermocouple wires are annealed during their production.

2.2 Pt–C Eutectic Fixed Point

In contrast to the high-temperature fixed point for a radiation thermometer, the fixed-point cells used for calibrating thermocouples generally have a longer immersion depth (more than 100 mm) to reduce the effect of thermal conduction and to evaluate the thermoelectric inhomogeneity, but it is difficult to create a long uniform temperature region in a furnace at high temperatures and the cell is expensive due to the use of more noble metals. As an initial study, a small Pt–C eutectic fixed-point cell with a large cavity for being conveniently calibrated using the primary radiation thermometer in NIM and an immersion depth of 40 mm was designed (see Fig. 1). The diameter of the cavity is 7 mm, which matches the outer diameter of a protective tube. In the front of the cavity, a 3 mm aperture was installed for radiation thermometer measurements. The Pt powder, graphite powder, and graphite crucible used in the cell had purities of 99.999 %, 99.9999 %, and 99.9995 %, respectively.

2.3 Furnace and Measurement System

A Chino IR-R80 high-temperature furnace with a Pt–C fixed point was used to calibrate the thermocouples (see Fig. 2). The temperature profile of the furnace at about 1300 °C has variations of < 8 °C within 100 mm. The protective argon gas entered the

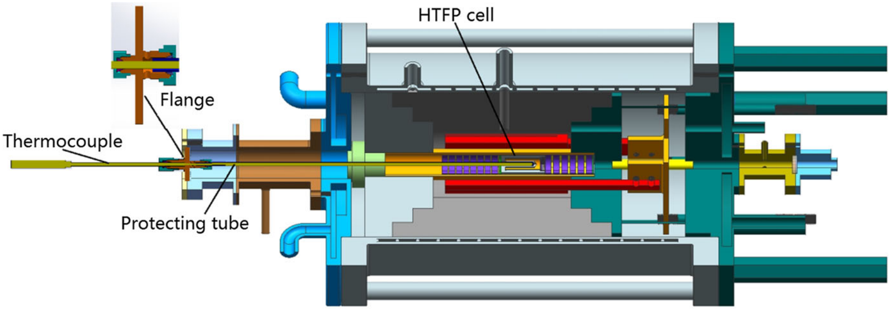

Fig. 2 High-temperature furnace with the Pt–C fixed point for calibration of type C thermocouples

center cavity from the rear of the furnace during the experiment. The furnace window was removed, and a steel plate was installed to insert the thermocouple. The high-temperature eutectic point cell was not strictly sealed in the graphite crucible. It is necessary to avoid contamination between the fixed-point cell and the thermocouple and from the environment. Previous studies have attempted to identify a material suitable for such protection [1,9,10]. As reported in [1], a Mo sheath deteriorated quickly at 2000 °C in the graphite environment. Considering the thin-wall graphite thermometer well, a protective tungsten tube of 300 mm length, 4.3 mm inner diameter, and 6 mm outer diameter was used between the Mo sheath and graphite thermometer well. The sheath and protection tube immersed in argon were fixed on a flange. The tip of the tungsten tube contacts the bottom of the cavity during measurements at the Pt–C point. The distance between the junction of the thermocouple in the sheath and the bottom of the cavity is <5 mm. The cold end of the thermocouple was inserted into the ice point. The electromotive force (emf) of the thermocouple was measured with a Keithley2010 multimeter. The multimeter was connected to a computer through a GPIB port, and the data were recorded automatically through LABVIEW software.

3 Experiments and Results

3.1 Temperature Determination of Pt–C Cell

The Pt–C cell was first calibrated using a standard radiation thermometer. It was also compared with another Pt–C cell as an artifact during the comparison of ITS-90 among NPL, CEM, and NIM in 2009 [11]. The temperature was about 0.1° higher with the 3 mm diameter aperture. The radiation temperature of the cell was also compared with and without the aperture. The calculated emissivity was about 0.9997 with the aperture and 0.9986 without the aperture. The temperature discrepancy was <70 mK after correcting the emissivity. The typical melting and freezing curve is shown in Fig. 3. The international temperature scale of 1990 (ITS-90) temperature of the Pt–C cell was 1738.1 °C with an uncertainty of 0.5 °C ($k = 2$).

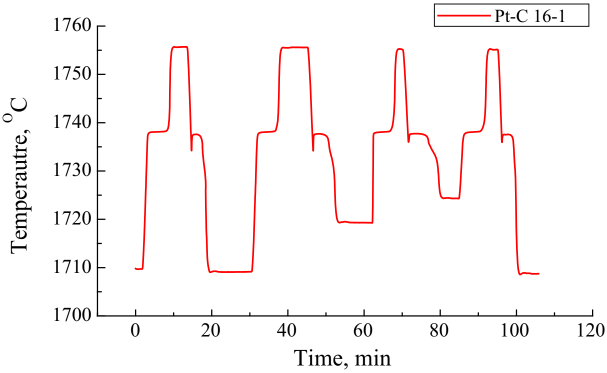

Fig. 3 Typical melting and freezing curve of Pt–C eutectic fixed point

3.2 Stability and Calibration

C1, C2, and C3 were annealed three times at the freezing point of Cu for about 1 h and kept at about 1738 °C for 1.5 h twice before the measurements at about 1738 °C. The stability of C1, C2, and C3 at the freezing point of Cu was better than 0.72 °C. Because of the thermal resistance of the sheath and protection tube, the melting temperature of the Pt–C eutectic point measured by the thermocouples depends on the setting temperature of the furnace. To determine and correct this deviation, the realization of the Pt–C eutectic point was carried out at different furnace temperatures so that the melting and freezing temperature for the thermocouple measurement was obtained at 0 °C above the melting temperature of the Pt–C eutectic point through linear fitting and extrapolation. The furnace was set at about 15 °C, 20 °C, and 30 °C above and below the melting temperature of the Pt–C eutectic point, and three melting and freezing processes were performed for one thermocouple during each experiment. An example of the melting and freezing curve for calibration of a tungsten–rhenium thermocouple with different furnace temperature offsets is shown in Fig. 4. The point-of-inflection of the Pt–C eutectic melting curve is determined based on the method reported in the literature [12]. The freezing temperature is the maximum temperature of the Pt–C eutectic melting curve. An example of linear extrapolation to zero offset in the furnace temperature is shown in Fig. 5. ΔT is the difference between the setting temperature of the furnace and the melting temperature of the Pt–C eutectic point, and the intercept is the melting and freezing temperature at 0 °C above the melting temperature of the Pt–C eutectic point.

For each thermocouple, calibration experiments were repeated three times with a different furnace temperature offset each time. Table 1 shows the calibration results. The results show that the repeatability of the calibration is better than 0.9 °C from the melting curve of the Pt–C fixed point and better than 1.2 °C from the freezing curve of the Pt–C fixed point. In [13], the emf of thermocouples with twin-bore beryllia tubes and a tantalum protective tube increased rapidly around 1500 °C within the first 30 h and then decreased gradually. In this work, the thermocouples show good stability through three calibrations at the Pt–C eutectic point and more experiments are

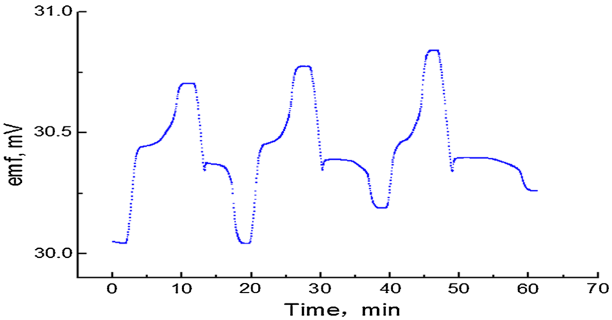

Fig. 4 Example of melting and freezing curve for the calibration of a tungsten–rhenium thermocouple with different furnace temperature offsets

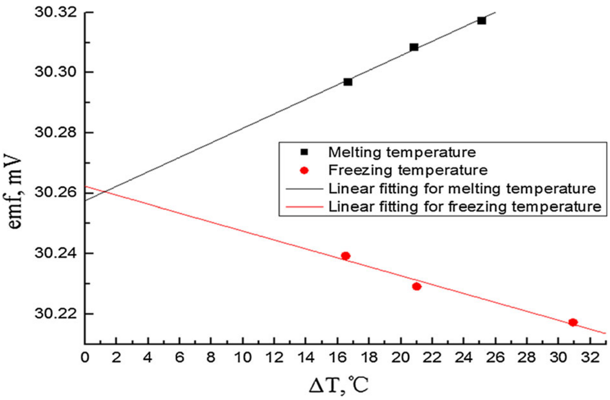

Fig. 5 Example of linear extrapolation to zero offset in the furnace temperature

needed to confirm the results. For C1 and C2, the difference between the mean melting temperature and freezing temperature of the Pt–C fixed point for the calibration of the thermocouples through the linear fitting and extrapolation method is $< 0.3\,°\mathrm{C}$, and for C3, it is up to $1.3\,°\mathrm{C}$. Considering the thermal history effect, the melting temperature plateau is generally higher than the freezing temperature plateau and is selected for the determination of the thermodynamic temperature and realization of a high-temperature eutectic fixed point [12]. For determination of the melting and freezing temperature at $0\,°\mathrm{C}$ above the melting temperature of the Pt–C eutectic point through the linear fitting and extrapolation method, the uniformity of the furnace and the uncertainty of ΔT are the key factors. The melting temperature plateau is lower than the freezing temperature plateau in this work, but the difference is within the uncertainty and the melting and freezing temperature plateau may be used for calibration.

After all thermocouples were tested, the stability of the Pt–C cell was better than 30 mK as examined by a standard radiation thermometer, which proved that the protective tube and sheath did not pollute the Pt–C eutectic fixed point. The uncertainty sources in the calibration of type C thermocouples include the repeatability of realization of the Pt–C eutectic fixed point, thermal conduction, emf measurement system,

Table 1 Calibration results of tungsten–rhenium thermocouples with different furnace temperature offsets and extrapolation to zero offset

Thermocouple	$Emf_{melting}$ (mV)				$Emf_{freezing}$ (mV)			
	0 °C	15 °C	20 °C	30 °C	0 °C	15 °C	20 °C	30 °C
C1	30.2598	30.3062	30.3139	30.3366	30.2699	30.2489	30.2401	30.2223
	30.2575	30.2970	30.3086	30.3175	30.2623	30.2393	30.2291	30.2172
	30.2693	30.2976	30.3039	30.3132	30.2598	30.2385	30.2263	30.2172
C2	30.2969	30.3208	30.3287	–	30.2974	30.2757	30.2667	30.2512
	30.2954	30.3237	30.3327	30.3376	30.3024	30.2819	30.2742	30.2602
	30.2948	30.3319	30.3406	30.3455	30.2962	30.2847	30.2772	30.2612
C3	30.3900	30.4353	30.4452	30.4557	30.4053	30.3855	30.3762	30.3622
	30.3998	30.4476	30.4588	30.4688	30.4211	30.3984	30.3910	30.3765
	30.3961	30.4499	30.4678	–	30.4132	30.4014	30.3933	30.3753

Table 2 Uncertainty budget for the calibration of type C thermocouples with the melting plateau of the Pt–C eutectic fixed point

Sources	Uncertainty (°C)
Repeatability of Pt–C eutectic fixed-point realization	0.90
Temperature determination of Pt–C cell	0.51
Measurement system of emf	0.10
Thermocouple stability	0.72
Thermocouple inhomogeneity	0.70
Thermal conduction	0.30
Linear fitting and extrapolation	0.30
Combined standard uncertainty	1.51
Expanded uncertainty ($k = 2$)	3.1

stability and inhomogeneity of the thermocouple, and linear fitting and extrapolation. The uncertainty of the inhomogeneity of the thermocouple is reported in [13], and the effect on the inhomogeneity of the thermocouple is measured at 160 °C by the oil bath with the stability and uniformity of < 10 mK in the working area, where the thermocouples were moved upward at a rate of about 10 mm to 20 mm per min from full immersion to approximately 300 mm. The maximum difference is < 1.2 °C, and the uncertainty of the inhomogeneity of the thermocouple is 0.7 °C (uniform distribution). The uncertainty budget for the calibration of a type C thermocouple with the melting plateau of the Pt–C eutectic fixed point is shown in Table 2.

4 Conclusion

Three tungsten–rhenium thermocouples (C1, C2 and C3) from two manufacturers were calibrated at the Pt–C eutectic fixed point. The stability of the C1, C2 and C3 is

$< 0.9\,°C$ from the melting curve of the Pt–C fixed point and $< 1.2\,°C$ from the freezing curve of the Pt–C fixed point. A linear fitting and extrapolation method is used to determine the melting and freezing temperature of the Pt–C eutectic fixed point for avoiding the effect of thermal resistance caused by the sheath and protection tube, and the difference between the mean melting temperature and freezing temperature of the Pt–C fixed point is not more than 1.3 °C. The results prove the melting and freezing temperature plateau of the Pt–C eutectic fixed point may be used for the calibration of the thermocouple within the certain uncertainty. The calibration uncertainty of the tungsten–rhenium thermocouples at the Pt–C eutectic fixed point is 3.1 °C (k = 2). During experiment process, the Pt–C eutectic fixed point is not polluted due to the existence of the protective tube and sheath. More experiments are needed to prove the stability of the tungsten–rhenium thermocouples at Pt–C eutectic fixed-point temperature.

Acknowledgements This work was supported by the National Natural Science Foundation of China (No. 51576181).

References

1. J.V. Pearce, C.J. Elliott, G. Machin, O. Ongrai, in *Proceedings of Ninth International Temperature Symposium (Los Angeles), Temperature: Its Measurement and Control, in Science and Industry*, vol. 8, ed. by D.C. Ripple, AIP Conference Proceedings, 1552, (AIP, Melville, 2013), pp. 595–600
2. R. Morice, F. Edler, J. Pearce, G. Machin, J. Fischer, J.R. Filtz, Int. J. Thermophys. **29**, 231 (2008)
3. Y. Yamada, H. Sakate, F. Sakuma, A. Ono, Metrologia **36**, 207 (1999)
4. F. Edler, R. Morice, J. Pearce, Int. J. Thermophys. **29**, 199 (2008)
5. F. Edler, A.C. Baratto, Metrologia **42**, 201 (2005)
6. Y.G. Kim, I. Yang, S.Y. Kwon, K.S. Gam, Metrologia **43**, 67 (2006)
7. D.T. Yokoyama, SICE JCMSI **3**, 81 (2010)
8. J.L. Rempe, D.L. Knudson, J.E. Daw, S.C. Wilkins, Type C thermocouple performance at 1500°C. Meas. Sci. Technol. **19**, 9 (2008)
9. R. Morice, J.O. Favreau, T. Deuze, J.R. Fultz, in *Proceedings of SICE 2005* (Okayama, 2005), pp. 678–682
10. G. Machin, G. Beynon, F. Edler, S. Fourrez, J. Hartmann, D. Lowe, R. Morice, M. Sadli, M. Villamanan, in *Proceedings of Eighth International Temperature Symposium (Chicago), Temperature: Its Measurement and Control, in Science and Industry*, vol. 684, ed. by D.C. Ripple, AIP Conference Proceedings 1551 (AIP, Melville, 2003), pp. 285–289
11. G. Machin, W. Dong, M.J. Martín, D. Lowe, Z. Yuan, T. Wang, X. Lu, Int. J. Thermophys. **31**, 1466 (2010)
12. E.R. Woolliams et al., Thermodynamic temperature assignment to the point of inflection of the melting curve of high-temperature fixed points. Phil. Tans. R. Soc. A **374**, 20150044 (2015)
13. H. Ogura, M. Izuchi, J. Tamba, Int. J. Thermophys. **32**, 2420 (2011)