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Self-validating Contact Thermometry Sensors for Higher Temperatures

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Abstract:

This paper is focused on self-validation and in-situ validation methods of thermometry between 1000 ºC and about 1800 ºC. An operative approach of reliable self-validating contact thermometry sensors and the implementation of traceable measurement methods for the measurement of temperatures up to about 1800 °C in oxidizing atmospheres will be presented. Electrical noise thermometry, known as primary metrological method, has been applied for realization of the self-validation principle. Combined thermocouple-noise temperature sensors have been constructed to allow long-term determination of thermocouple drift. Electrical noise thermometry is a primary method to measure temperatures without drift effects even over long periods of time. An uncertainty of noise temperatures measured of 0.1% has been achieved which is sufficient to determine and correct for thermocouple drifts in industrial use. As alternative method miniature fixed points filled with high purity Au (1064.18 °C), Pd (1553.4 °C) and Pt (1769 °C) have been constructed and assembled with type B thermocouples to be used as traceable references in oxidizing atmospheres. Combined thermocouple-noise temperature sensors based on Type B thermocouples and on Type S thermocouples were measured against a radiation thermometer of Type, LP3. The agreement between the noise temperature and the radiation temperature (LP3) at about 1400 °C was found to be within ±1 K.

Key words: Thermocouple, Miniature fixed point, Noise thermometry, Self-validation

Kurzfassung:

Selbstvalidierende Verfahren für Hochtemperatur-Berührungsthermometer

In diesem Beitrag werden Selbst-Validierungsverfahren für Berührungsthermometer vorgestellt, die bei in-situ Validierungen von Prozesstemperaturmessungen im Bereich über 1000° C eingesetzt werden sollen. Rückführbare Messmethoden sind unter der Verwendung prozessgeeigneter Berührungsthermometer zu realisieren, wozu Sensorelemente benötigt werden, die bis ca. 1800°C in oxidierender Atmosphäre beständig sind. Die als primäre metrologische Methode bekannte Rauschthermometrie wurde gewählt und ein Messverfahren, das auf integrierten miniaturisierten Fixpunktzellen beruht. Zur Realisation der Rauschtemperaturmessungen wurden geeignete kombinierte Thermoelement-Rauschthermometer angefertigt, die simultan die Überprüfung der thermoelektrischen Stabilität von Thermoelementen des Typs B bzw. des Typs S gestatten. Die Rauschtemperatur-Messungen sind mit Messunsicherheiten kleiner ca. 0,1% behaftet, um den Anforderungen entsprechend, Prozesstemperaturmessungen hinreichend genau korrigieren zu können. Bei der anderen Validierungsmethode werden Thermoelemente vom Typ B zusammen mit miniaturisierten Fixpunktzellen verwendet, die mit hochreinen Au (1064.18 °C), Pd (1553.4 °C) oder Pt (1769 °C) befüllt sind. Die Messergebnisse kombinierter Thermoelement-Rauschthermometer mit Typ B- und mit Typ S-Thermoelementen wurden mit einem Strahlungspyrometer vom Typ LP3 verglichen. Bei 1400 °C ist zwischen der Rauschthermometriemessung und der Messung mit dem Strahlungspyrometer eine Übereinstimmung von ±1 K gefunden worden.

Stichworte: Thermoelement, Miniaturisierte Fixpunktzelle, Rauschthermometrie, Selbstvalidierung

Introduction

Self-validated measurements of temperatures above 1000 ºC are both difficult and vital for the feasibility and the success of industrial processes e.g. for the manufacture of silicon, carbides, carbon/Carbon composites, iron, steel, glass and ceramics. Many of these sectors of industry require improved process efficiency/control, also because of growing environmental concerns (emissions/”zero waste”) and ex-EU competition. One of the keys to making advances to these drivers is improving process control by improved high temperature measurement. [1]

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.

The self-validation concepts presented in this paper are based on the simultaneous use of a further (primary) method to measure temperatures without drift effects to validate for instance the thermoelectric stability of thermocouples as parts of a combined thermocouple-noise temperature sensor. Electrical noise thermometry was successful used for metrological applications [4], but had demonstrated its ability also for industrial applications [5]. Another approach has been given by the use of miniature fixed points with defined and stable melting temperatures of pure metals which are combined directly with commonly used thermocouples to detect their drift effects, similar as described in [2, 3] for lower temperatures.

Electrical noise thermometry

Noise thermometry uses the random thermal movement of the electrons in the conduction band of a metal to measure thermodynamic temperatures. It is based quantitatively on the Nyquist formula (1) and is independent of temperature depending material properties:

$$\overline{U^2} = 4kTR\Delta f \qquad (1),$$

where $\overline{U^2}$ is the mean square noise voltage, k the Boltzmann-constant, T the thermodynamic temperature, R the ohmic resistance and Δf the noise bandwidth over which the noise voltage is measured. Equation (1) is seldom used directly because parasitic noise sources (amplifiers, leads) are included, because of difficulties in measuring the equivalent noise bandwidth, and because of the necessity of the calibration of the gain of the measuring system [4]. Therefore, a comparison method by using reference resistors R_R and a correlation technique by using a consistent two-channel arrangement of parallel amplifiers are applied [7]. The noise temperature T_S is determined by comparing the mean square noise voltage of the reference resistor R_R at a known reference temperature T_R with the mean square noise voltage of the measuring resistor R_S within the same bandwidth Δf according to equation (2):

$$T_S = \overline{U_S^2}/\overline{U_R^2} \cdot R_R/R_S \cdot T_R \qquad (2).$$

Due to the stochastic nature of the thermal noise, the accuracy of the noise temperature measurement depends on the measuring time τ and the bandwidth Δf. The relative uncertainty of the noise temperature also takes into account the additional amplifier chain’s internal noises of the two channels and is given by equation (3) [7]:

$$\Delta T/T = [2\cdot(2+\mathrm{B/A}+\mathrm{C/A}+\mathrm{BC/A}^2)/(\Delta f\cdot\tau)]^{1/2} \qquad (3),$$

where A is the power spectral density of the measuring or the reference resistor ($R_S\cdot T_S$ or $R_R\cdot T_R$) and B and C are the power spectral densities of the amplifier chain’s internal noise of the two channels. The ratios B/A and C/A were in the order of 1 to 1.2 for all noise temperature measurements performed in this study.

Two combined thermocouple-noise temperature sensors consisting of two type B thermocouples (RT-B1) and of two type S thermocouples (RT-S1) have been constructed as described in [4] to investigate and to validate the thermal stability of the thermocouples used.

They can be used in air up to temperatures of 1800 °C / 1500 °C, respectively. Measurements were performed at the freezing points of copper (1084.62 °C) and silver (961.78 °C) by using two different, independent Noise-Thermometer-Electronics (NTE) [4, 5] to test the accuracy of the combined thermocouple-noise sensors. The mean noise temperatures measured agree to the well-known fixed-point temperatures (ITS-90) within about 0.4 K at the freezing point of copper and within 0.2 K at the freezing point of silver. These results demonstrate the principal suitability for the intended use of the combined thermocouple-noise temperature sensors based on type B and type S thermocouples as a suitable tool to detect and correct for drifts in the thermocouples within the relative target uncertainty of 0.1%. The noise temperatures measured at the two freezing points are presented in Figures 1 and 1. The error bars corresponds to the statistical uncertainty ($k = 2$), of the noise temperature calculated by using eq. (3).

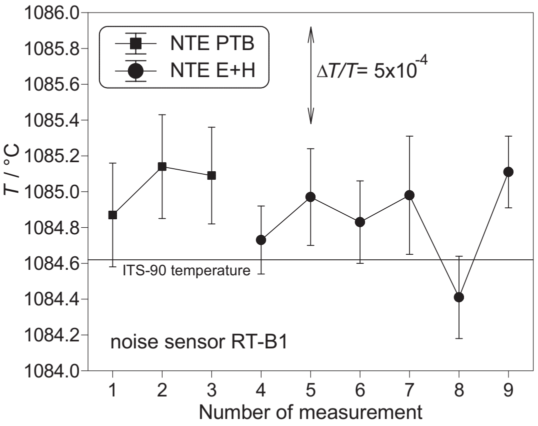

Fig. 1. Noise temperatures at the freezing point of copper by using sensor RT-B1

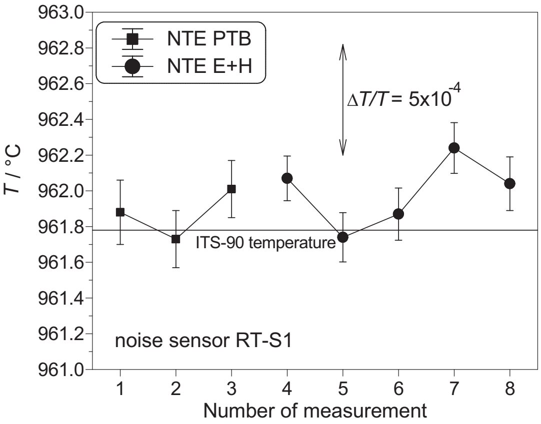

Fig. 2. Noise temperatures at the freezing point of silver by using sensor RT-S1

The two type B thermocouples of the combined thermocouple-noise temperature sensor RT-B1 were calibrated at the freezing point of copper; the type S thermocouples of the sensor RT-S1 were calibrated at the freezing point of silver. In this way additional reference values were established to confirm possible changes of the thermoelectric stability of the thermocouples which should be detected by the noise temperature sensor.

A first thermal treatment of the combined thermocouple-noise sensor RT-B1 at 1450 °C for about 80 hours under laboratory conditions caused an increase of the emfs at the freezing point of copper of the two type B thermocouples by about 3.3 µV (0.35 K) and 4.7 µV (0.5 K), respectively. This is less than 0.1 % and therefore in the order of the measurement uncertainty of the noise temperature, i.e. below the limit of detection. Beside the statistical uncertainty of noise temperature measurements other influences have to be considered. The noise temperature is calculated according to eq. (1). Therefore, the uncertainty of the electrical measurement of the parameters (R_S, R_R, and T_R) has to be taken into account. The values of the mean square noise voltages are influenced by electro-magnetic interference (EMI) which can be superimposed on the useful noise signal. Interferences in the frequency range are visible in the temperature spectra and could be removed subsequently by filtering (rejecting disturbed frequency ranges). Remaining interference was less than the limits of detection which are in the order of $1{\cdot}10^{-4}$. Transmission errors of the noise voltages caused by a possible mismatch of the impedance, Z_W, of the transmission lines (thermoelements) and the measuring resistance, R_S, also could be estimated from the recorded averaged temperature spectra within about $1{\cdot}10^{-4}$, because these errors depends on frequency. Non-linearity effects of electronic components (amplifiers) can be reduced significantly ($<5{\cdot}10^{-5}$) by choosing the value of the reference resistors in this way that its mean square noise voltage corresponds to about the same value like the mean square noise voltage of the measurement resistor, i.e. $\overline{U_S^2}/\overline{U_R^2} = 1$. A more detailed description and estimation of uncertainty contributions of noise temperature measurements can be found in [8].

The good performance of the combined thermocouple-noise temperature sensor RT-B1 is shown in Figure 3. The seven hour lasting measurement in the temperature range between 1438 °C and 1428 °C demonstrates the very good agreement between the two thermocouple temperatures and the noise temperature. This confirms again the suitability of this self-validating concept to detect possible drifts of thermocouples in the order of about 0.1 %. The statistic uncertainty (k = 1) of one measuring point corresponds to about ±0.6 K with an effective measuring time τ of 330 seconds within a frequency interval of about 270 kHz.

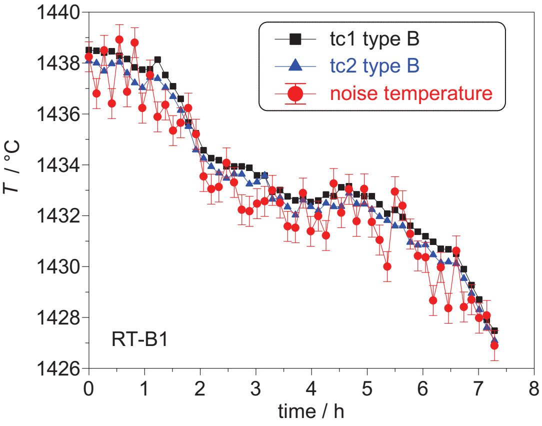

Fig. 3. Temperature course by using the combined thermocouple-noise temperature sensor RT-B1

Comparison to a radiation thermometer (LP3)

Another reliable performing by comparison of the combined thermocouple-noise temperature sensor RT-B1 to a radiation thermometer (LP3) will be presented in Figure 4.

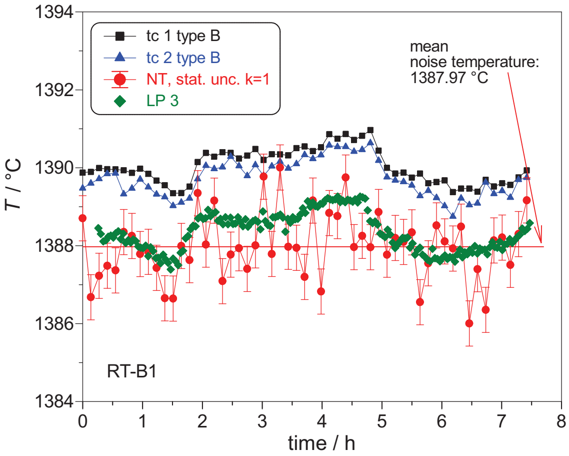

Fig. 4. Temperature comparison of sensor RT-B1 against a radiation thermometer, type LP3 Statistical uncertainty of one noise temperature (k=1): 0.6 K (τ = 330 sec, Δf = 259 kHz)

During an eight hours lasting measurement at 1388 °C a sound agreement between the noise temperature measurement and the radiation temperature (LP3) are observed.

Cell design of the miniature fixed points

The miniature fixed point, as shown in Figure 5, have been constructed similar to the fixed-point cells described in [6]. The ceramic crucible containing the fixed-point metal was inserted into an ancillary cartridge made of a PtRh 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, the miniature fixed point Pt-01-12 contains 0.53 g of high purity (99.997%) platinum.

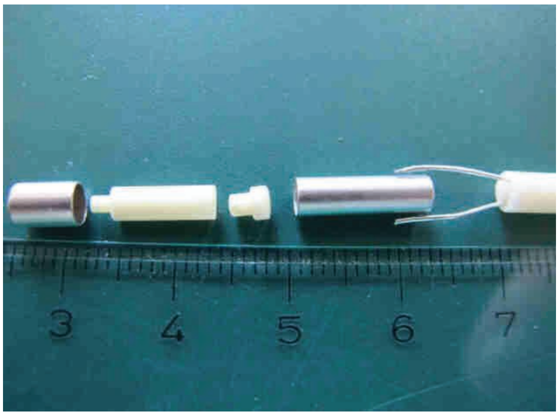

Fig. 5. Miniature fixed point

The outer diameter of the ceramic crucibles amounts to a value of 3 mm. Their length is about 10 mm. These small dimensions allowed a simple integration of the fixed-point cells in a ceramic protection tube of the size 7x5 mm typically used for standard thermocouples.

Melting behavior of the integrated miniature fixed points

A typical melting curve of palladium (T_S = 1553.4 °C) by using the type B thermocouple SV-B-Pd-01-12 with the integrated fixed-point crucible Pd-01-1 against the emf of the furnace control thermocouple is shown in Figure 6. The melting curve shows a constant increase of the emf before the melting process starts. During the melt the slope is 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 sudden reduced slope indicates the beginning of the melt; the rapid increase of the slope marks the end of the melt.

A more clear detection of the start of the melt is achieved by calculating the differential emfs (Δemf) between the emfs of the test thermocouple and the control thermocouple against the emf of the test thermocouple as shown in Figure 7. Here, the change of slope is more significantly and the regression lines can be fitted unambiguous.

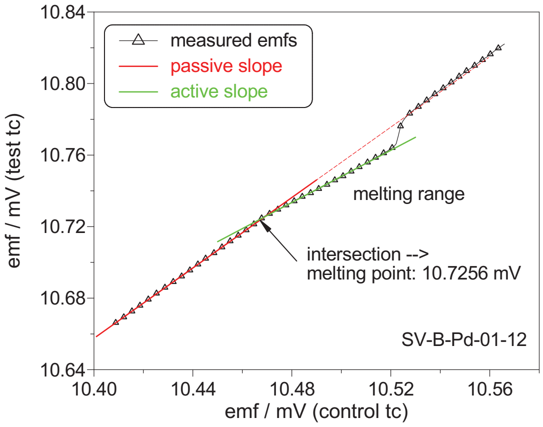

Fig. 6. Typical melting curve of palladium

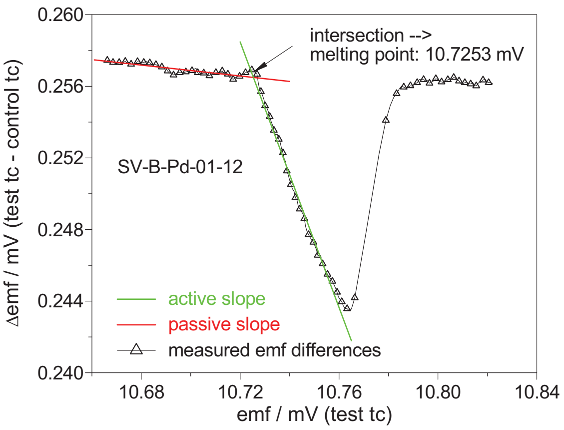

Fig. 7. Differential melting curve of palladium

A special feature of the melt by using the integrated fixed-point was the dependency of the melting temperature on the heating rate, as visible in Figure 8.

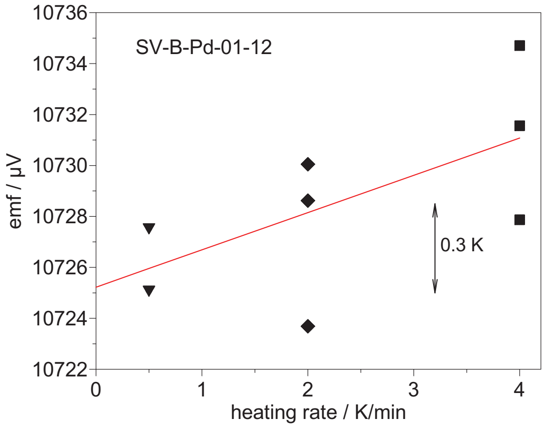

Fig. 8. Dependency of the melting temperatures on the heating rate by using the miniature fixed point Pd-01-12

This demonstrates a limit of this method. Since the hot junction it is not surrounded by the fixed-point material, the measurement is sensitive to the heat flux from the furnace. Therefore, an extrapolation of the results to adiabatic conditions (heating rate of 0 K/min) seems to be necessary. Otherwise, this effect could be integrated into the uncertainty budget which would increase the combined uncertainty slightly.

The melting temperatures of pure metals of integrated miniature fixed-point cells can be used as reference temperatures for self-validation of thermocouples. However, some specific features must be considered: the influence on the melting temperature of environmental conditions (heating rate, offset temperatures of furnaces) and the assignment of the melting temperature to the melting curve whose shapes are often no flat plateaus. Keeping this in mind, drift effects of thermocouples which exceed the uncertainty of the determination of melting temperatures by using the miniature fixed points can be validated in-situ and corrected for further use.

Conclusion

Regarding the influence quantities associated with noise temperature measurements, the selection of an undisturbed frequency-band has to be considered as a significant condition that shall be fulfilled during the measurement. If additionally a sufficient measurement time, τ is applicable, uncertainties of noise temperatures of 0.1% are practicable, which is sufficient to determine and correct for thermocouple drifts for industrial use.

The melting curves measured by using the thermocouples with integrated miniature fixed points allow a unambiguous assignment of the corresponding melting temperatures provided that agreed methods for analysis of the curves are used, for instance the application of regression lines. The measurement uncertainty of the melting temperatures increases with increasing temperatures and is in the order of (1-2) K at the melting points of palladium and platinum. Therefore, drift effects of thermocouples less than about (1-2)$\cdot 10^{-3}$ won't be detectable. In principle, both methods appear promising as self-validating concepts to detect drift effects in-situ, therefore their practical suitability should be confirmed by further investigation.

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Literaturhinweise

[1] G. Machin, K. Anhalt, F. Edler, J. Pearce, M. Sadli, R. Strnad, and E. Vuelban, 2012 HiTeMS: a project to solve high temperature measurement problems in industry, *9th Int.Temperature Symp. (ITS9) (Los Angeles, 19–23 March 2012)*

[2] S. Augustin and F. Bernhard et al, Industrially applicable miniature fixed point thermocouples, *Proceeding of TEMPMEKO 2001, 8th International Symposium on Temperature and Thermal Measurements in Industry and Science*, 2001, pp.3-8.

[3] H. Lehmann, Fixed-point thermocouples in power plants: long term operational experiences, *Int. J. Thermophys.,* **31,** 1599-1607 (2010)

[4] F. Edler, M. Kühne and E. Tegeler, Noise temperature measurements for the determination of the thermodynamic temperature of the melting point of palladium, *Metrologia* **41**, (2004) 47-55

[5] P. Seefeld, S. Damith, M. Konrad, M. Korn, A. Zotz, Prozessgeeignete Rauschtemperaturmessungen, *15th ITG/GMA conference, Proceedings of Sensoren und Messsysteme* 2010

[6] M. Tischler, W. Neubert, Miniature Thermometric Fixed Points, Calibration of a Pressure-controlled Heat-pipe furnace, and the Vapor Pressure of Na (660 °C to 1064 °C), Temperature: Its Measurement and Control in Science and Industry (Ed. Schooley), **6**, AIP, New York 1992

[7] H. Brixy, Noise Thermometry, *Sensors*, Vol.4, Thermal Sensors, ed. by T. Ricolfi and J. Scholz, VCH Verlagsgesellschaft, 1990, pp. 225-249

[8] F. Edler, E. Tegeler, E Zimmermann, Thermodynamic Temperature of the Freezing Point of Copper Measured by Noise Thermometry, Temperature: Its Measurement and Control in Science and Industry (Ed. D.C. Ripple), AIP conference proceedings 684, pp 13-18, (2003); doi: 10.1063/1.1627095