

Thermoelectric Characteristic of High-Temperature Thermocouples W5%RE/W20%RE

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Abstract In the temperature range (900 to 2800) K, there has been confirmed compliance with the existing national standards for thermocouple wires W5% Re/W20%Re (type A) produced in Russia. The homogeneity within a lot of wires was evaluated by measuring the emf deviations from the corresponding reference function of thermocouples constructed from the front and the rear sections of paired coils of wires. The diameter of the wires amounted to 0.35 mm and 0.5 mm. Stability indicators were thermal emf changes after annealing for 2 hours at 1773 K. It was found that the inhomogeneity of thermoelements did not exceed (4 to 5) K for paired wire coils with a thermoelectric stability within a temperature equivalent of (1.0 to 1.5) K. EMF deviations from the reference table values for the thermocouples investigated did not exceed 1% in the temperature range of (900 to 2773) K. Such deviations meet the requirements of the new draft of IEC standards 60584-1 and 2. Thermocouples were calibrated in four laboratories by comparison with various standard temperature gauges (type B thermocouple, radiation pyrometer, standard specimens of thermoelements). Measurements were carried out under vacuum, argon,

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and hydrogen. Depending on the calibration method, the expanded uncertainty of the measurements at 1773 K varied from (2.8 to 8) K.

Keywords Calibration curve · High temperature · Reference table · Thermal EMF · Tungsten–Rhenium thermocouple · Type A thermocouple · W5%Re/W20%Re thermocouple

1 Introduction

Taking into account the preparation of a new draft of IEC standards 60584-1 and 2 which will also include tungsten–rhenium (W/Re) thermocouples, working group 5 of IEC TC65 recommended to execute control calibrations of W5%Re/W20%Re thermocouples (type A) made of thermoelement wires produced in Russia at the present time. Rhenium contents of 5 % and 20 % in tungsten for thermoelements of industrial thermocouples had been chosen based on the results of complex research of electrical, thermal, and mechanical properties of solid solutions for the “tungsten–rhenium” system [1–3]. Thermoelement materials were produced according to specifications in [4]. Calibration curves, published in 1968 [5], have been included in the GOST 3044-77 national standard for the first time. The maximum value of the reference table had been limited to 2773 K. Standard specimens of thermoelement materials (SOTM, W5%Re/W20%Re standard wires) had been developed for calibration of industrial thermocouples [6]. SOTM calibration was done in a vacuum furnace by a “wire-bridge” method with Ag, Cu, Ni, Pt, Rh, Ir, and Ta wires wound on the measuring junction of a thermocouple. The expanded uncertainty of calibration at fixed points up to the platinum melting point was evaluated to be 1 K; at the rhodium point, 3 K; and at the level of 2773 K, 6.5 K.

Operating experience of W5%Re/W20%Re thermocouples at temperatures below 2100 K was generalized in [7], and features of their application in the temperature range between 2200 K and 2800 K were discussed in [8].

Requirements for a long shelf life of W5%Re/W20%Re thermocouples have sharply increased at this time. Thermoelectric thermometers have been developed with tight gas-filled protective tubes made from molybdenum [9] or sapphire [10]. They could be used for several thousand hours at temperatures up to 2000 K. Manufacture of W5%Re/W20%Re thermocouples is normalized by the CIS standard [11], and the corresponding reference table [12] is based on the International Temperature Scale of 1990 (ITS-90).

To perform calibration studies with W5%Re/W20%Re thermocouples, a number of experts were invited from Russia (“ROSTEST-MOSKVA”, VNIIM, OTC, SIA “LUCH”) and several other research laboratories from Germany, USA, Japan, and Canada. Test specimens of the thermocouples were made of the same paired coils of thermoelement wires. They had been sent to all participants. In this article, the results obtained by Russian researchers are generalized.

2 Measurements

2.1 Specimens

Thermoelement materials are produced by a method of powder metallurgy. Powders of tungsten and ammonium perrhenate (NH_4ReO_4) are preliminarily mixed, and then the mixture is pressed into cylindrical columns and melted. The columns are forged and drawn into a wire of diameters ranging from 0.5 mm to 0.1 mm. The finished wire is subjected to stabilizing annealing in hydrogen. The paired coils of wires before calibration passed through surface cleaning in a bath with a mixture of nitric and hydrofluoric acid for (3 to 5) h. The thermocouples under test were made from thermoelements of (2 to 3) m length cut from various sites of paired coils. For investigations at temperatures below 2100 K, thermoelements were insulated along their length by sapphire or alumina tubes. Then the thermocouples were inserted in sapphire protective tubes of 700 mm length and (5 to 9) mm outer diameter, closed at one end. The tubes were filled with pure argon and sealed at the other side of thermocouple free ends. Thermocouples of such a design could be calibrated in air. For experiments in vacuum or hydrogen in the temperature range between 2100 K and 2800 K, the thermoelements were used as bare wires without electrical insulation over a length of (90 to 120) mm from the measuring junction. The remaining parts of the thermoelements were insulated using sapphire tubes. Outer protective tubes were not used in vacuum or hydrogen.

2.2 Procedures

2.2.1 Temperatures

In the temperature range of (900 to 1950) K, W/Re thermocouples in sealed tubes were calibrated by a comparison method against a standard thermocouple Pt30%Rh/Pt6%Rh (type B) in a high-temperature tubular furnace in air (Fig. 1). Measurements were done according to the technique developed by OTC experts [13].

At VNIIM the thermocouples were calibrated in a high-temperature furnace described in [14] (Fig. 2) in the temperature range between 1450 K and 2150 K. The thermocouple under test equipped with a protection tube made of sapphire was immersed into a cavity of a blackbody. The temperature of the blackbody was measured using a standard pyrometer as a reference. The measurements were performed under a constant flow of argon.

In the laboratory of “ROSTEST-MOSKVA,” the “wire-by-wire” calibration method was used. Thermoelement wires W5%Re and W20%Re were calibrated against corresponding standard SOTM wires. The actual furnace temperature was determined by the emf value of a standard thermoelement. This method allows calibrations up to temperatures of 2300 K. The procedure of the wire assembly is described in [15]. In fact, the bare thermoelements of two thermocouples under test were bound together with the standard SOTM wires at their hot junctions. The thermoelements and standard wires (total of six wires) were insulated against each other at a distance of 90 mm

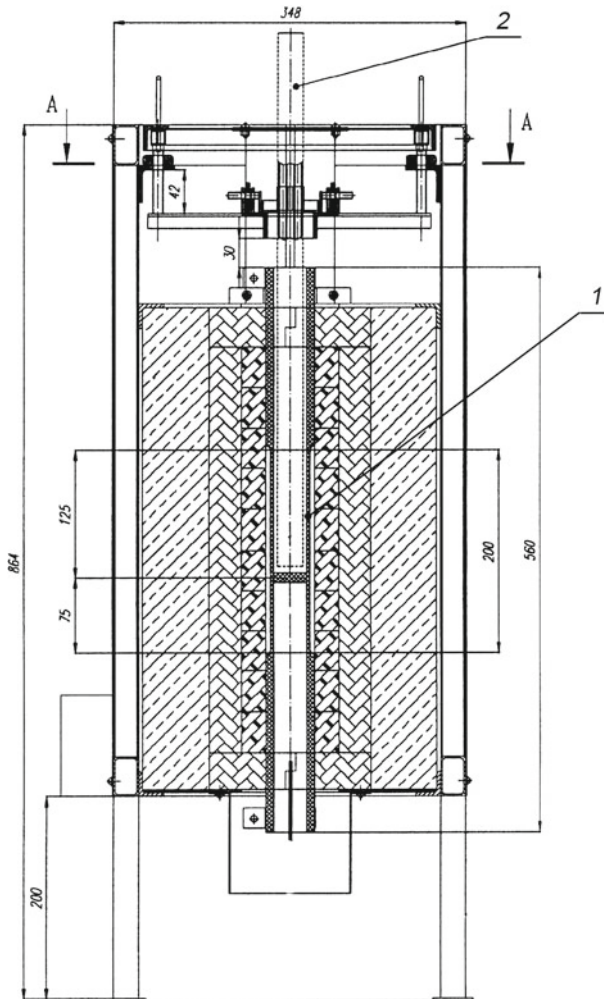


Fig. 1 High-temperature furnace for calibration of thermocouples in air: (1) LaCrO_3 annular heater, (2) alumina tube for insertion of thermocouples

from the measuring junction by using bored sapphire tubes. The tubes were spaced on the mounting element inside the furnace. The assembly was located vertically, and 0.35 mm or 0.5 mm wires were rigid enough to avoid electrical contact in the “bare wires” region (90 mm). The maximum temperature of the insulating tubes in all experiments did not exceed 1900 K. The use of bare wires in the highest temperature region enabled minimization of the influence of a signal shunting through electroinsulation for measurement results. An exterior view of the measuring system is shown in Fig. 3. Measurements were performed in vacuum at pressures of 10^{-3} Pa with the temperature rising stepwise by 100 K. Thermal emf differences between the same wires of

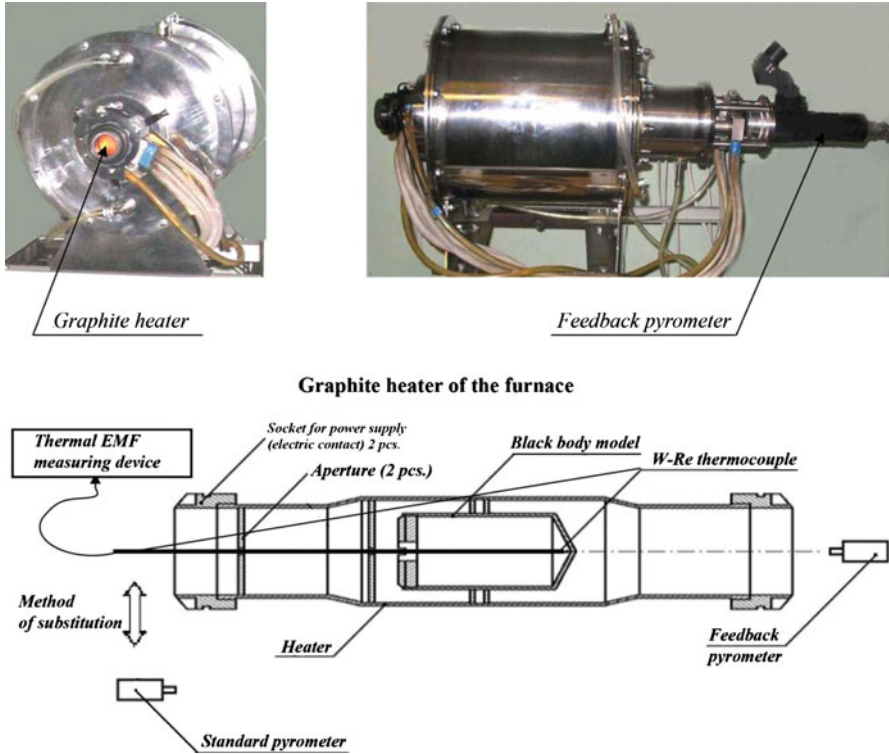


Fig. 2 Blackbody furnace with a W–Re thermocouple to be calibrated



Fig. 3 Exterior view of the measuring system used for the “wire-by wire” calibration (components of the measuring system are the vertical vacuum furnace, power supply, and control unit)

SOTM and the tested thermoelements were registered under increasing/decreasing temperatures.

The calibration technique for W–Re thermocouples in the temperature range of (2300 to 2800) K was described in [3], but the actual measurements were performed in a modified measurement arrangement developed in co-operation between SIA “LUCH”

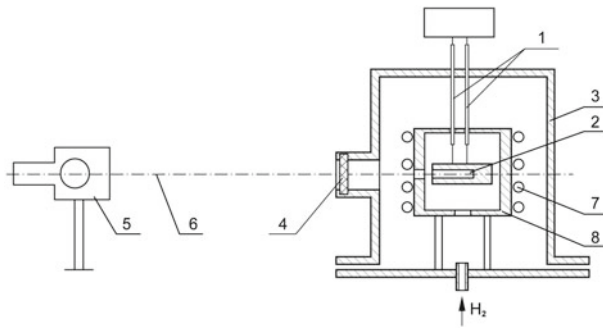


Fig. 4 Measurement setup for the calibration of thermocouples at high temperatures in hydrogen: (1) insulated thermoelements, (2) blackbody model, (3) frame of a high frequency generator (inner diameter of 0.4 m), (4) optical quartz glass, (5) standard optical micropyrometer, (6) sighting axis, (7) inductor, (8) heater

and “AEROJET” company (USA) for high-temperature tests of materials. Earlier measurements [3] were done in a furnace with a graphite heater, but in this case the heating element of the installation was placed into the internal space formed by inductor coils of the high-frequency generator (Fig. 4). The working space of installation was flushed with pure hydrogen or helium, and the gas content was controlled at the exit. The temperature gradient within the working part of the heater did not exceed 20 K per 80 mm at the minimum temperature of 2773 K. The measuring junctions of the thermocouples were attached to a blackbody model made from tungsten. The model was suspended along the axis of an annular vertical heater. Its wall had a window for sighting a standard micropyrometer at the model to measure the reference temperature.

2.2.2 Uncertainties

The expanded uncertainty of the OTC-measurements of the W/Re thermocouples was evaluated to be 3.9 K at a temperature of 1773 K using the comparison method against a type B thermocouple in air. The uncertainty budget is discussed in detail in [13]. The main uncertainty contribution was the uncertainty of the temperature of the furnace (± 3.2 K for $k = 2$).

The expanded uncertainty of the type A thermocouples calibrated in a blackbody cavity (VNIIM) was 1.9 K at a temperature of 1473 K and increased to 3.4 K at 2123 K. Here, the uncertainty of the temperature of the furnace could be significantly reduced as shown in [14].

One of the main uncertainty contributions of the “wire-by-wire” method (“ROSTEST-MOSKVA”) near the maximum calibration temperature was the uncertainty of the calibration of the standard SOTM wires. It was estimated to 0.1 % for $k = 2$ in the temperature range between 773 K and 2773 K. A further major uncertainty contribution was that due to inhomogeneity which was estimated to be about 0.3 %. Taking into account the data of the standard deviation of the measurement results mentioned in [15], the expanded uncertainty of measurements with this installation at 2273 K was estimated to be at the level of 11 K. The uncertainty contribution due to

heat flux along the bare thermoelements was negligible since the temperature gradient within the central part of the vacuum furnace (± 30 mm) did not exceed 20 K at the highest temperature.

With regard to an uncertainty estimation of the measurements at 2773 K (installation of SIA “LUCH”), it is necessary to note that similar to [3], it was necessary to determine the correction caused by the absorption of the window of the working chamber. The correction factor was determined experimentally by a change of the radiation intensity of a standard tungsten strip lamp without and with glass of the window. This component was considered as an uncertainty of type B. To decrease the uncertainty for the furnace temperature, additional experiments were performed to measure the melting temperatures of pure molybdenum and tantalum. In these experiments the blackbody models were prepared from a foil of refractory metals of 0.05 mm to 0.1 mm thickness. The melting point of the models was determined visually. These experiments gave the possibility to verify reproducibility of temperature measurements with the installation since the melting-temperature values for pure metals (secondary fixed points) were known. Taking into account all uncertainty contributions, the expanded uncertainty ($k = 2$) was estimated to be 20 K at 2773 K.

3 Results

Deviations of calibration curves from nominal values for W5%Re/W20%Re thermocouples (according to GOSTR 8.585-2001 standard [12]) are shown in Fig. 5. Thermocouples were made of thermoelements cut off from the front and the rear sections of the paired coils 55/74. The two calibration curves differ from each other by (2 to 4) K. This result demonstrates that the homogeneity of the investigated materials corresponds to the specification requirements [4]. The specifications determined that the difference in thermal emf values for two thermocouples (front and rear of paired coils) should not exceed $100 \mu\text{V}$ (7.7 K) at 1773 K. This requirement had been formulated as a result of the “wire-by-wire” measurements, performed and described in [1].

The results of the calibration presented in Fig. 5 also confirmed the wires’ compliance of the stability requirements. It is considered satisfactory if the thermal emf change after 2-h annealing at 1773 K does not exceed $50 \mu\text{V}$ (for the 2nd class thermocouple) and $70 \mu\text{V}$ (for the 3rd class). Actual changes in the thermal emf value at a control temperature had been limited to (14 to 20) μV equivalent to (1.0 to 1.5) K.

In Fig. 6, the initial calibration curve for the paired wire coils 89/95 (0.5 mm) is shown compared with the calibration curve determined after 24 thermal cycles (calibration and annealing over 100 h in the temperature range between 873 K and 1973 K). The difference between the curves is not great, which demonstrates indirectly the sufficiently high stability of the thermocouple. Both curves are close to nominal values of the reference table. They have good correlation with calibration results obtained with the thermocouple made of the same paired wire coils 89/95, which were calibrated at VNIIM (see Table 1).

“ROSTEST-MOSKVA” carried out the calibrations with the specimens made of the most inhomogeneous wires (according to OTC data) from the paired coils 21/65 (front and rear). The calibration results from both laboratories are compared in Fig. 7. In the temperature range from 873K to 1923 K, the results correlate satisfactorily for quite different calibration methods. For higher temperatures, the emf deviation from nominal values increased. More important, however, is the fact that even in the most unfavorable case of inhomogeneous materials, the total emf deviation did not exceed

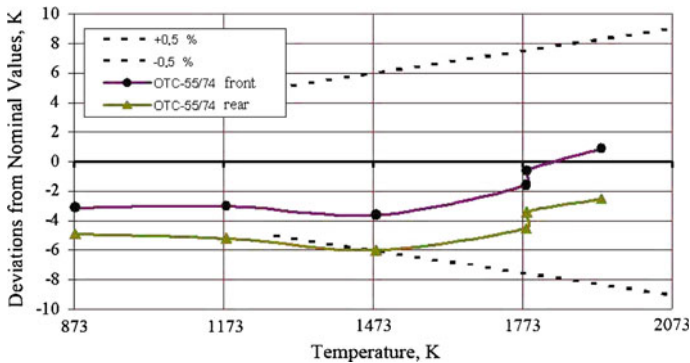


Fig. 5 Deviations from nominal values for W5%Re/W20%Re thermocouples with 2 h annealing at 1773 K. Thermocouples were made from the paired wire coils 55/74 (front and rear of the coils), wire diameter of 0.35 mm

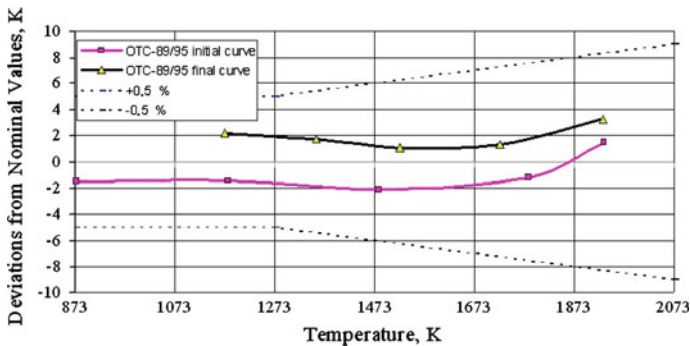


Fig. 6 Initial and final calibration curves (deviations from nominal values) for W5%Re/W20%Re thermocouple made from the paired wire coils 89/95, wire diameter of 0.5 mm

Table 1 Deviations from nominal values for W–Re 5/20 thermocouples made of paired wire coils 89/95, wire diameter of 0.5 mm, based on the results of VNIIM’s calibration in a blackbody furnace

Temperature (K)	Deviation (K)
1473	−3.0
1673	−0.6
1873	4.7
2123	5.5

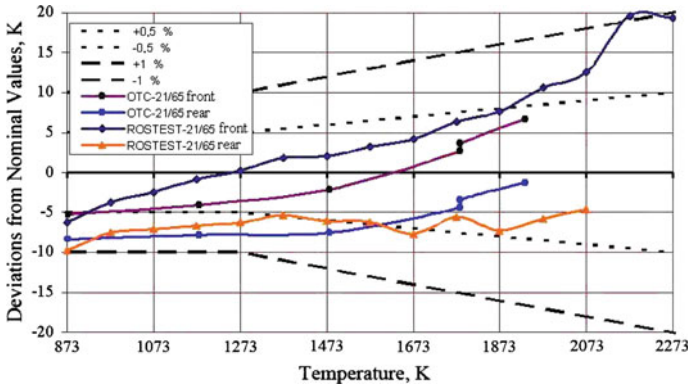


Fig. 7 Comparison of the EMF deviations from the nominal values for W5%Re/W20%Re thermocouples made from the paired wire coils 21/65, wire diameter of 0.5 mm (front and rear of the coils)

Table 2 Deviations from nominal values for W-Re 5/20 thermocouples made of paired wire coils 55/74 (diameter: 0.35 mm) and 89/95(diameter: 0.5 mm) based on the results of SIA “LUCH” calibration in hydrogen

Temperature (K)	Deviation (in K) for wire diameter	
	0.35 mm	0.5 mm
2173	8.0	2.0
2373	10.0	4.0
2573	15.0	8.0
2773	20.0	12.5

1 %. It is quite satisfactory in the framework of the new draft of IEC standards 60584-1 and 2. The results found for the highest temperatures up to 2773 K (see Table 2) support this conclusion. In this case, the emf deviations are in the range of (0.1 to 0.8) % from nominal values.

Thus, the presented results confirm that thermoelements of W5%Re/W20%Re thermocouples currently produced in Russia correspond to the national standard GOSTR 8.585-2001 type A thermocouple and the new draft of IEC standards 60584-1 and 2.

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