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

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Abstract

In the temperature range (900-2800) K there has been confirmed a 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 and 0,5 mm. Stability indicators were thermal EMF changes after two-hours annealing at 1773 K.

It was found, that inhomogeneity of thermoelements did not exceed (4-5) K for paired wire coils with a thermoelectric stability within a temperature equivalent of (1.0-1.5) K. EMF deviations from the reference table values for the thermocouples investigated did not exceed 1% in the temperature range (900-2773) 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 done under vacuum, argon 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, the 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 present time.

Rhenium contents of 5% and 20% in tungsten for thermoelements of industrial thermocouples had been chosen based on the results of complex researches of electric, thermal and mechanical properties of solid solutions for the system "tungsten-rhenium" [1-3]. Thermoelement materials were produced according to specifications in [4]. Calibration curves, published in 1968 [5], have been included into the national standard GOST 3044-77 for the first time. The top 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, Ta wires wounded on measuring junction of a thermocouple. The expanded uncertainty of calibration at fixed points up to platinum melting point was evaluated to be ±1 K, in 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 generalised 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. There have been developed thermoelectric thermometers 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. Manufacturing of W5%Re/W20%Re thermocouples is normalised 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 the present article the results obtained by Russian researchers are generalised.

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 preliminary mixed, then the mixture is pressed into cylindrical columns and melted. The columns are forged and drawn into a wire of diameters varied from 0,5 to 0,1 mm. Finished wire is subjected to stabilizing annealing in hydrogen. The paired coils of wires before calibration passed through surface cleaning in a bath with mixture of nitric and hydrofluoric acids during (3-5) h. The thermocouples under test were made from thermoelements of (2-3) 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 (5-9) 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 (90-120) mm from the measuring junction. The remaining parts of the thermoelements were insulated by using sapphire tubes. Outer protective tubes were not used in vacuum or hydrogen.

2.2 Procedures

2.2.1 Temperatures

In the temperature range (900-1950) K W/Re thermocouples in sealed tubes were calibrated by a comparison method against a standard thermocouple Pt30%Rh/Pt6%Rh (type B) in the high-temperature tubular furnace in air (Fig.1). Measurements were done according to the technique developed by OTC’s 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 black body. The temperature of the black body was measured by using a standard pyrometer as 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. Actual furnace temperature was determined by EMF value of standard thermoelement. This method allows calibrations up to temperatures of 2300 K. The procedure

of the wires assembling 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 (totally 6 wires) were insulated against each other at a distance of 90 mm 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 or 0.5 mm wires were rigid enough to evoid electrical contact in the "bare wires" region (90 mm). The maximum temperature of the insulating tubes in all experiments did not exceed 1900 K. Using of bare wires in the highest temperature region enabled to minimize the influence of a signal shunting through electroinsulation for measurement results. An exterior view of the measuring system used is shown in Fig.3. Measurements were performed in vacuum at pressures of 10^{-3} Pa with the temperature rising stepwise by 100 K per step. Thermal EMF differences between the same wires of SOTM and the tested thermoelements were registered under increasing/decreasing temperatures.
The calibration technique for W-Re thermocouples in the temperature range (2300-2800) K was described in [3], but the actual measurements were performed in a modified measurement arrangement developed in co-operation between SIA"LUCH" 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 limit temperature 2773 K. The measuring junctions of the thermocouples were attached to a black body model made from tungsten. The model was suspended along the axis of annular vertical heater. It's wall had 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 by using the comparison method against a type B thermocouple in air was evaluated to a value of ±3.9 K at a temperature of 1773 K. The uncertainty budget is discussed in detail in [13]. The main uncertainty contribution was the uncertainty of the temperature of the furnace used (±3.2 K for k = 2).

The expanded uncertainty of the type A thermocouples calibrated in a black body 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 main uncertainty contribution was the uncertainty due to inhomogeneity which was estimated to a 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 at the level ±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 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 value for the furnace temperature additional experiments were performed to measure the melting temperatures of pure molybdenum and tantalum. In these experiments the black body models were prepared from a foil of refractory metals of 0.05-0.1mm 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 were known. Taking into account all uncertainty contributions, the expanded uncertainty (k = 2) was estimated to a value of ±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 front and rear sections of the paired coils 55/74. Two calibration curves differ from each other on (2-4) K. This fact approves that the homogeneity of investigated materials corresponds to the specifications requirements [4]. The specifications fixed up that the difference in thermal EMF values for two thermocouples (front and rear of paired coils) should not exceed 100 μV (7.7 K) at the temperature 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 Figure 5 also confirmed the wires' compliance of the stability requirements. It is considered satisfactory, if thermal EMF change after two-hour annealing at the temperature 1773 K does not exceed 50 μV (for the 2-nd class thermocouple) and 70 μV (for the 3-rd class). Actual changes in thermal EMF value at control temperature had been limited by (14-20) μV equivalent to (1.0-1.5 K).

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

"ROSTEST-MOSKVA" carried out the calibrations with the specimens made of the most inhomogeneous wires (according to OTC's 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 873-1923 K results correlate satisfactory for quite different calibration methods. For higher temperatures EMF deviation from nominal values increased. More important, however, is the fact that even in the most unfavourable case of inhomogeneous materials a total EMF deviation did not exceeded 1%. It is quite admissible in frame 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 EMF deviations are in the range of (0.1-0.8)% 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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References

1. S.K.Danishevskiy Research and development of high-temperature thermocouples made of refractory metals and their alloys. *Thesis for a Doctor's degree*, Moscow Power Engineering Institute, Moscow, 1964. (In Russian)
2. B.I. Stadnyk Research and development of high-temperature tungsten-rhenium thermocouples and graphite resistance thermometers. *Thesis for a Doctor's degree*, Polytechnical institute, Kiev, 1967. (In Russian)
3. Oleynikova L.D. Research of new types of thermocouples for high-temperature measurements. *Thesis for a Doctor's degree* , D.I.Mendeleev Institite for Metrology, Leningrad, 1969. (In Russian)
4. SUO.021.142 Specifications. A wire made of tungsten and rhenium alloy, annealed, calibrated for thermoelements of thermocouples. *Specifications,* 1976, Moscow. (In Russian)
5. S.K.Danishevskiy, L.D.Oleynikova, P.P. Oleynikov, et al. Calibration curves for tungsten-rhenium thermocouples W-Re 5/20. *Measurement Technics*, 1968, No7, pp.20-21. (In Russian)
6. MI 1745-87 Methodical instructions. Russian State Measurements System. Standard specimens of thermoelement materials made of W-Re5 and W-Re20 alloys (SOTM W-Re 5/20). Certification technique. (In Russian)
7. O. A. Gerashchenko, A.N. Gordov, V. I. Lakh et al. Temperature measurements. The guide, 1984, Kiev, Naukova dumka, p.494. (In Russian)
8. I.I. Fedik, V.P. Deniskin, V.I. Nalivaev, et al. The problem of high-temperature measurements in a fuel assembly of nuclear rocket engine. *Pribory+Avtomatizatsija*, 2002, No 3 (21), pp. 20-27. (In Russian)
9. V.B. Pampura, V.A. Povalajev, P.P. Olejnikov, A.G. Khotkin. High-temperature thermoelectric thermometers for the furnaces for fuel tablets sintering. *Novye Promyshlenniye Technologii*, 2007, No 6, 2007, pp.61-63. (In Russian)
10. A.A. Ulanovskiy, B.L. Shmyrev, Ju.N. Altukhov Multi-purpose tunsten-rhenium thermoelectric thermometers in high-temperature thermometry. *Pribory + Avtomatizatsija*, 2006, No 5 (71), 2006, pp. 4-13. (In Russian)
11. The interstate standard GOST 6616-94. Thermoelectric converters. General specifications. Euro-Asian Council for standardization, metrology and certification (EASC), 2000, Minsk, Standards Publishing House, 2000. (In Russian)

12. Russian State Standard GOSTR 8.585-2001. Thermocouples. Reference tables. 2002, Gosstandard of Russia, Moscow, Standards Publishing House. (In Russian)
13. A.A.Ulanovskiy Report on the calibration results for W-Re 5/20 type A thermocouple obtained at Obninsk Thermoelectric Company (OTC, Ltd.). Meeting of the working group 5 of IEC TC65, May 2009, D.I.Mendeleyev Institute for Metrology, St-Petersburg.
14. V.A. Nikonenko, A.I. Pokhodun, M.S. Matveyev, et al. Metrological maintenance in radiation thermometry: problems and solutions. *Pribory+Avtomatizatsija*, 2008, No 10, pp.3-7. (In Russian)
15. Application guide for standard specimens of thermoelement materials made of W-Re5 and W-Re20 alloys (SOTM-1 and SOTM-2, W-Re 5/20), 1987, Institute for Metrology (VNIIMSO), Sverdlovsk. (In Russian)

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

Temperature, (K)	Deviations, (K)
1473	-3.0
1673	-0.6
1873	4.7
2123	5.5

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)	Deviations, (K), for wires 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

Figure captions

Fig. 1 High-temperature furnace for calibration of thermocouples in air.

1 – $LaCrO_3$ annular heater;

2 – alumina tube for insertion of thermocouples

Fig. 2 Black body 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, the power supply and the control unit)

Fig. 4 Measurement setup for the calibration of thermocouples at high temperatures in hydrogen

1. insulated thermoelements;
2. black body model;
3. frame of a high frequency generator(inner diameter 0.4 m);
4. optical quartz glass;
5. standard optical micropyrometer;
6. sighting axis;
7. inductor;
8. heater

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

Fig. 6 Initial calibration curve (deviations from nominal values) for W5%Re/W20%Re thermocouple made from the paired wire coils 89/95, wires diameter 0.5 mm. Comparing with the calibration curve for the same thermocouple received after 24 thermal cycles (calibrations and annealings), ~100 h at the temperatures higher 1273 K up to 1973 K

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

1, 2 – OTC’s data (comparison with standard type B thermocouple);

3, 4 – ”ROSTEST-MOSKVA” data (“wire-by-wire” comparison with standard SOTM specimens)

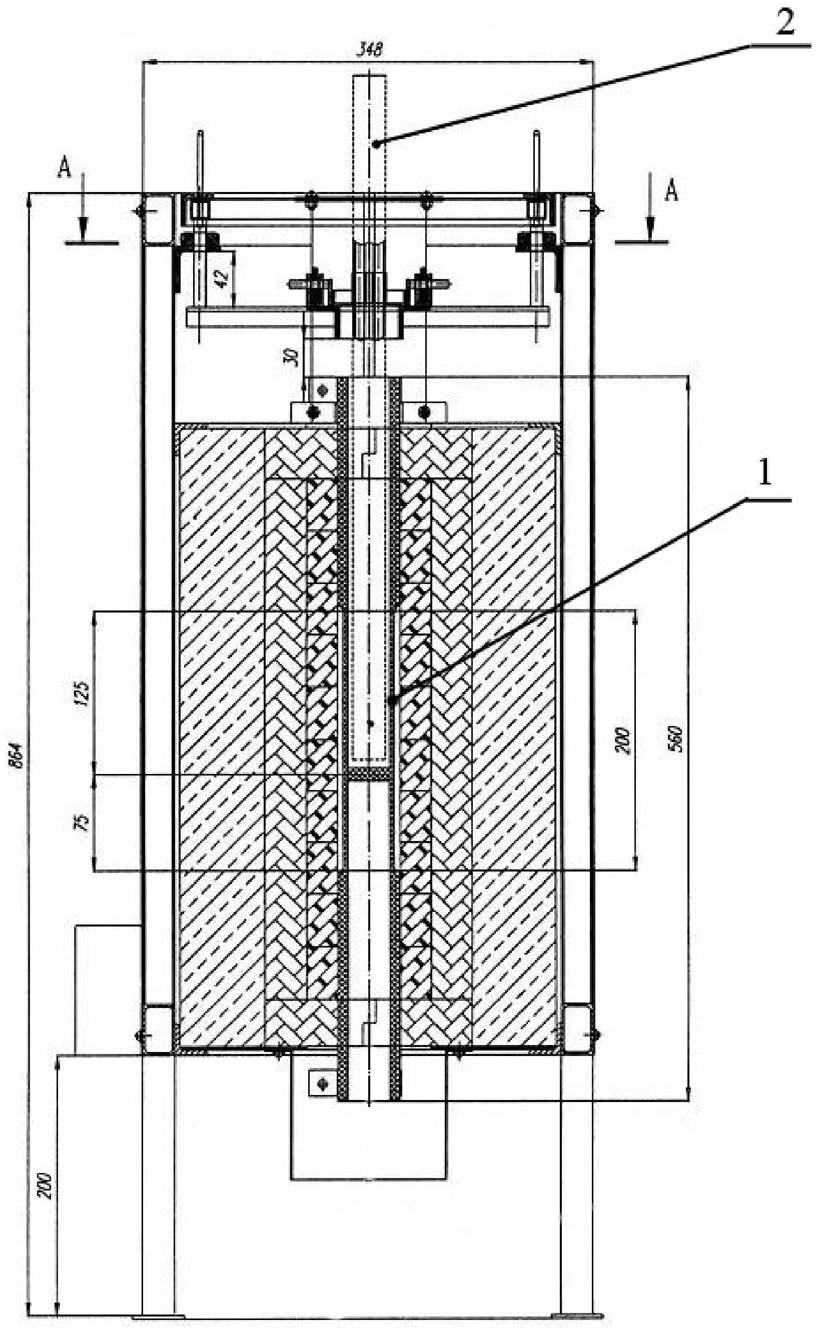


Fig. 1

Graphite heater of the furnace

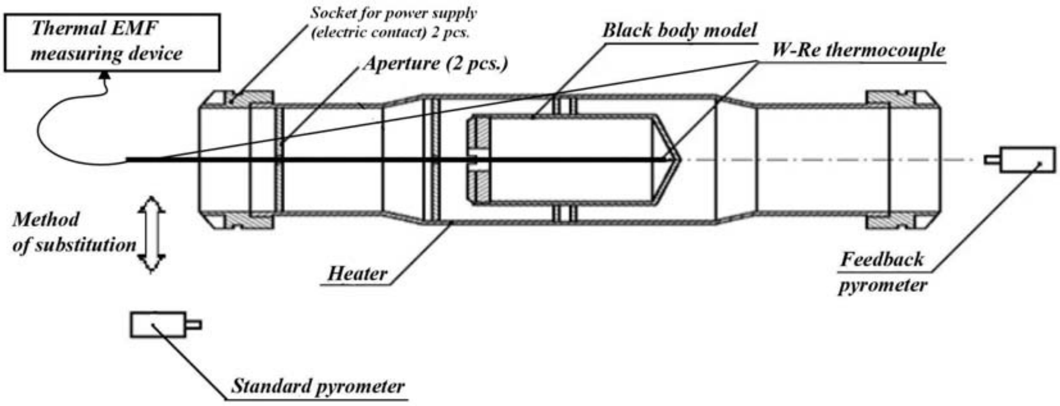


Fig. 2

Fig. 3

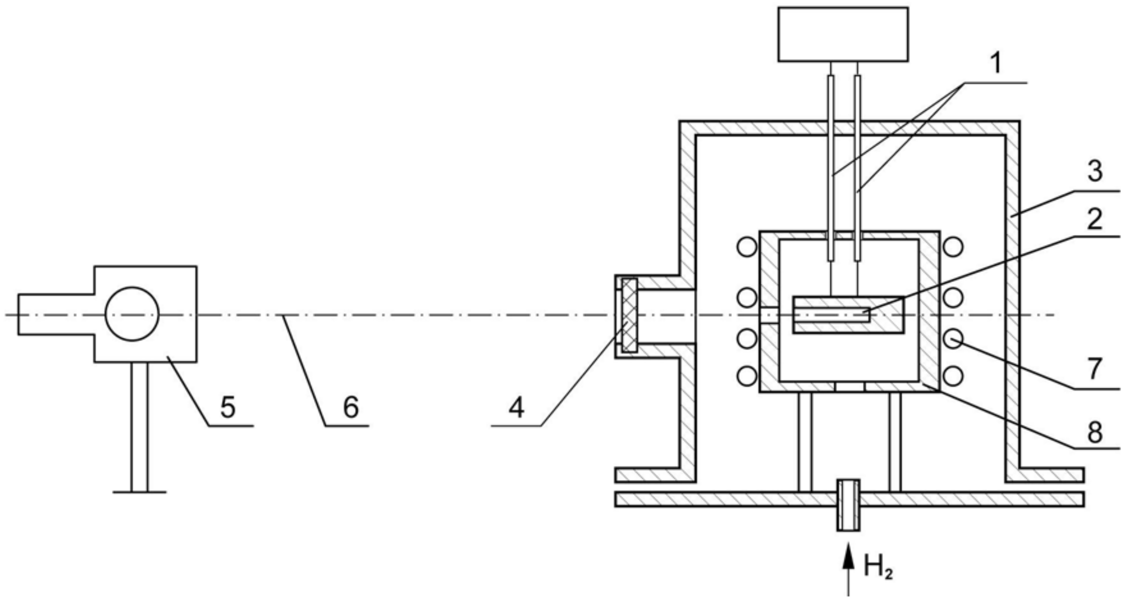
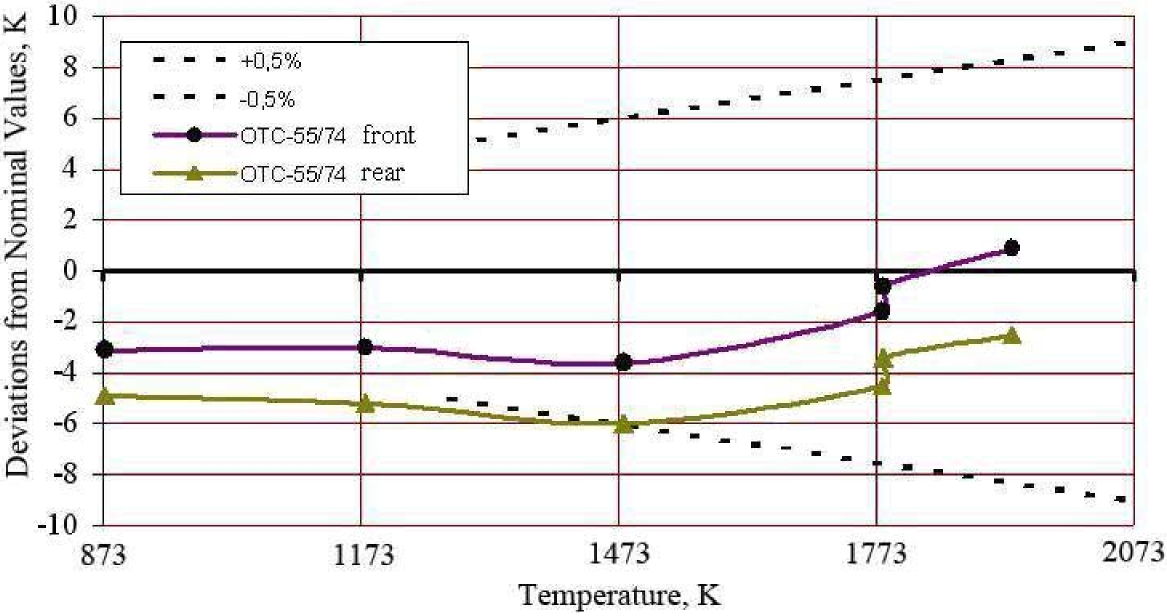


Fig. 4



+0,5%
-0,5%
OTC-55/74 front
OTC-55/74 rear
Deviations from Nominal Values, K
10
8
6
4
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0
-2
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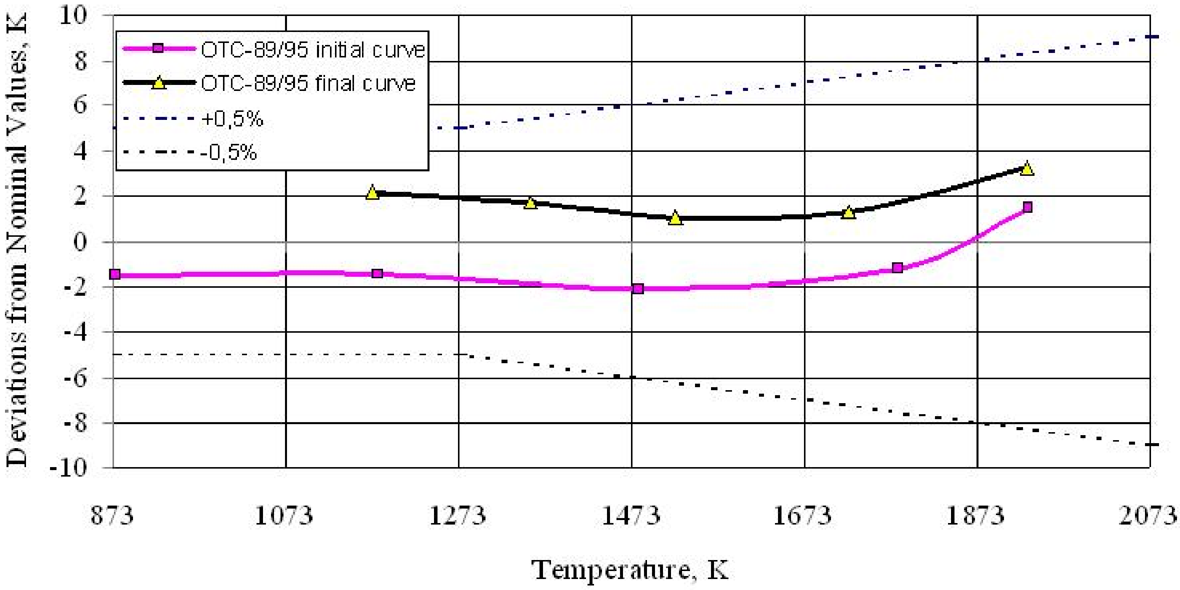
-8
-10
873
1173
1473
1773
2073
Temperature, K

Fig. 5


Deviations from Nominal Values, K
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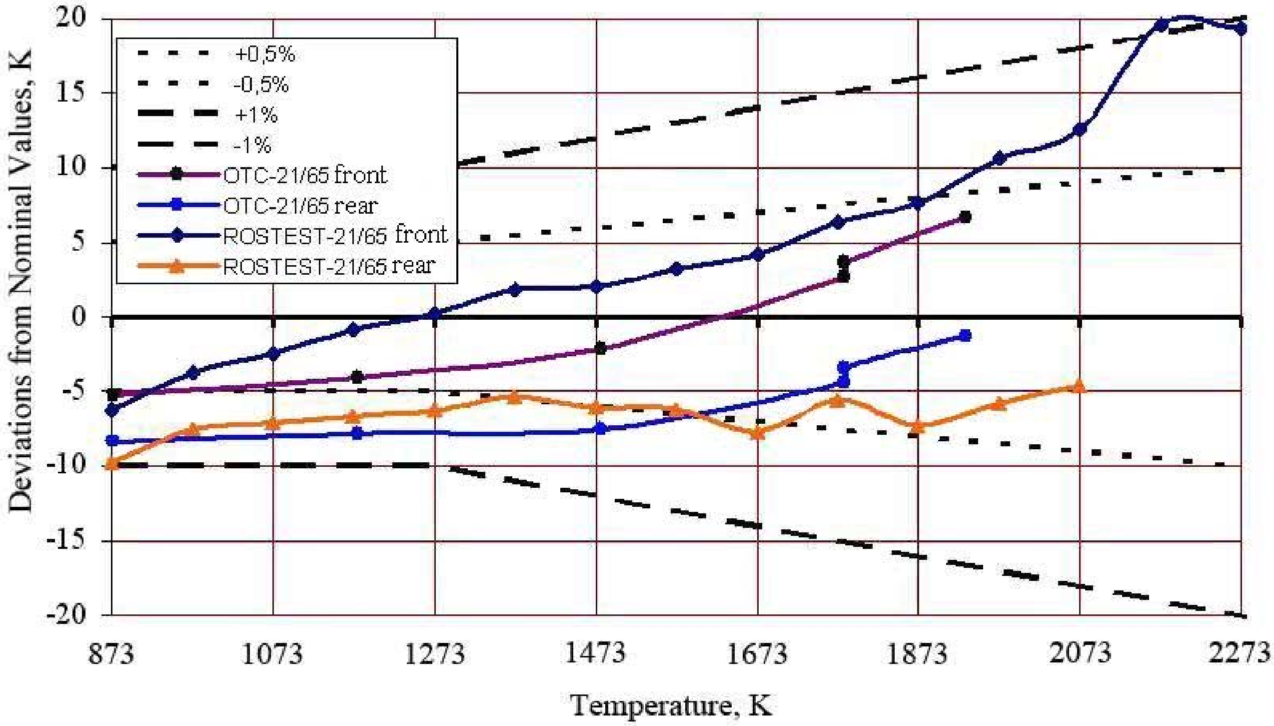
8
6
4
2
0
-2
-4
-6
-8
-10
OTC-89/95 initial curve
OTC-89/95 final curve
+0,5%
-0,5%
873
1073
1273
1473
1673
1873
2073
Temperature, K

Fig. 6



+0,5%
-0,5%
+1%
-1%
OTC-21/65 front
OTC-21/65 rear
ROSTEST-21/65 front
ROSTEST-21/65 rear
Deviations from Nominal Values, K
Temperature, K
20
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5
0
-5
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Fig. 7