PROSPECTS FOR DEVELOPMENT OF HIGH-TEMPERATURE THERMOELECTRIC THERMOMETRY

I. I. Fedik[1], P. P. Oleinikov [1], A. A. Ulanovsky [2]
([1]Research and Production Association "LUCH", Podolsk, Moscow region; [2] "Obninsk Thermoelectric Company" Ltd, Obninsk, Kaluga region, Russia)

- *Brief historical reference is given on the development of high-temperature thermoelectric thermometry. It is shown that the largest spread in industrial practice has been gained by primary converters with sensing elements made of tungsten-rhenium alloys [1]. In Russia and CIS countries thermoelectrodes comprise 5 and 20% of rhenium. In the USA most popular converters include 5 and 26% of rhenium addition in thermoelectrodes. Certain spread has been gained by converters with 3% of rhenium in one of the electrodes [2]. Some idea on the nomenclature of tungsten-rhenium converters in China is given by the Internet site of Chinese company Wuxi Guotao Tungsten Rhenium Alloy Factory. The volume of consumption of thermo electrode alloys in Russia in recent years has been preserved at the level of 100 kg/year. The basic technological processes and structural peculiarities of measuring means manufactured in Russia are discussed [3-5]. The state of measurement assurance is characterized. Due to drastically increased interest in developed countries in high-temperature measurements, the working group №5 TK65 of IEC started activities for international recognition of nominal static characteristics of tungsten-rhenium thermocouples. Presentation of thermocouple BP5/20 was made by director of Obninsk thermoelectric company at the meeting of IEC working group №5 TK65 in Tokyo in May, 2008. As a result, the Russian side was proposed to prepare samples and conduct control calibration of samples of thermocouple BP5/20 in metrological centres of Germany, USA and Japan. The results of this work will be discussed at the meeting of IEC working group №5 TK65, planned for May, 2009 in D. Mendeleyev Research Institute for Metrology (Saint-Petersburg). It would be advisable for specialists from Ukraine to join in this work. The samples of thermocouples for similar works are ready. Based on the studies of superdispersed hardening of tungsten-rhenium alloys [6], the pilot part of the project "Modernization on the basis of nanotechnologies for production of primary temperature converters of increased precision and stability for the needs of nuclear industry" [7] has been prepared and launched.*

The history of development and application in various fields of science and technology of the most high-temperature to date thermoelectric primary temperature converters based on tungsten-rhenium alloys numbers half a century already. As far back as 1957 the USSR certificate of authorship given to Danishevsky S.K. Gurevich A. M., Smirnova N.I. et al. [1], fixed the priority in creation of thermocouples on molybdenum and tungsten basis.

Later on, in their dissertation papers, Danishevsky S.K., Stadnyk B.I., Oleinikova L.D., Stolyarchuk P.H. et al. recommended BP5 and BP20 alloys as the best combination of thermoelectrodes of tungsten-rhenium thermocouple, studied reproducibility of its calibration characteristic, estimated the effect on its nominal static characteristic of thermoelectrodes inhomogeneity and their shunting at high temperatures, stability under different application conditions, including the influence of radiation fields of different intensity.

Somewhat later in the USA there were patented thermocouples BP0/BP26, BP5/BP26, and then BP3/BP25 [2].

Calibration of home thermocouples BP5/20 was made independently in Central Automation Laboratory of Ferrous Metals (Moscow), the Urals Institute for Metrology (Sverdlovsk), Design Bureau "Termopribor" (Lviv), Scientific-Production Association "Luch" (Podolsk). Nominal static characteristic of thermocouple was determined in vacuum furnace by melting *Ag*, *Cu*, *Ni*, *Pt*, *Rh*, *Ir*, *Ta* wires wound on the operating junction of thermocouple or in argon by comparison to readings of thermocouple ПР30/6 (up to 1800°C) and optical pyrometer ЭОП-66. In the former case the mean-square calibration error to platinum melting point was estimated ±1°C, at rhodium point ±3°C.

Analysis of all studies has shown that 80% of thermocouples BP5/20 had close calibrations with a spread in values not more than ±1%, the distribution in pilot lots was close to normal [3].

Technical specifications for thermoelectrode wire manufacturing at Moscow Electric Bulb Factory were elaborated in 1974 [4]. The alloys were manufactured using powder metallurgy method by premixing powders of tungsten and perrhenate ammonium salt (NH_4ReO_4), compacting the mixture into rods, melting and subsequent peening.

According to technical specifications for thermoelectrode wire, rhenium content in the alloys was controlled to an accuracy of ±0.5 mas.%, and the content of impurities and additives – at the level of 0.1 mas.%. This resulted in appreciable spread of thermoEMF in different wire lots. Within each coil the inhomogeneity of thermoelectrodes was normalized at the level ±50 µV at 1500°C.

Standardized nominal static characteristic of thermocouple BP5/20 was first included into State Standard 3044-77. The table comprised three close calibrations: A-1, A-2 and A-3. The latter two were above and below the basic calibration A-1. Their upper limits were restricted by 1800ºC, and the basic – 2500ºC (Fig. 1). The same figure shows for comparison characteristics of thermocouples BP3/25 and BP5/26, as well as platinum-rhodium thermocouple ПР30/6. The differential sensitivity of tungsten-rhenium thermocouples is compared in Fig. 2. In the range 900-2100°C for thermocouple BP5/20 it is reduced almost linearly, which is very convenient for nominal static characteristic approximation in the secondary instruments.

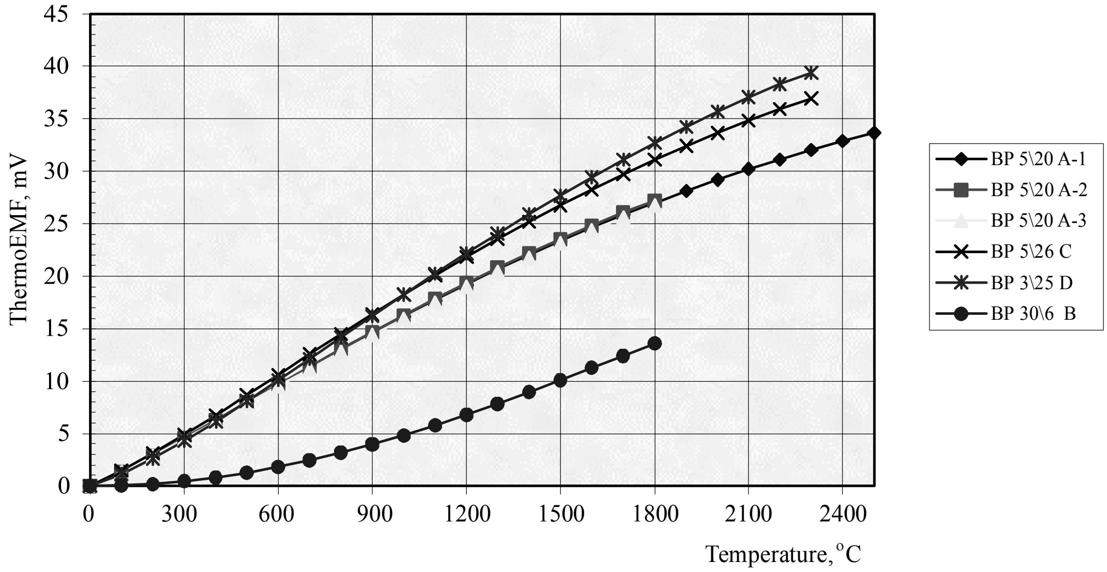
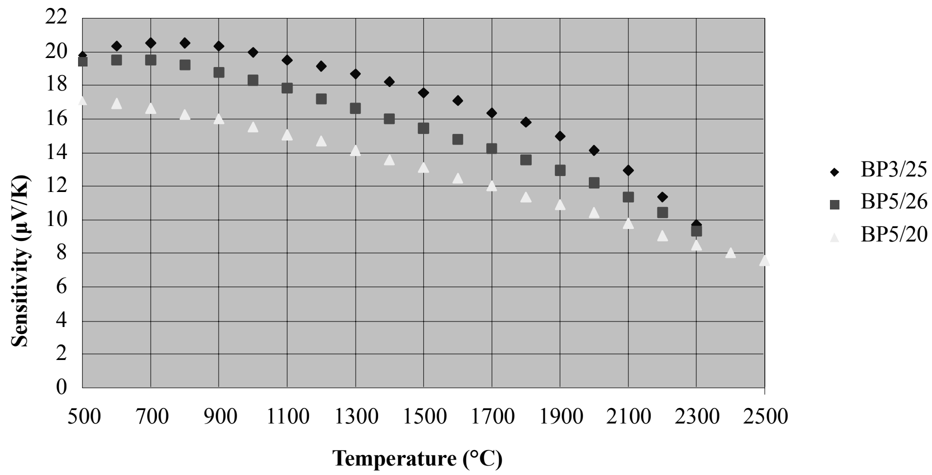


Fig. 1. Nominal static characteristics of thermocouples.

Minimum tolerance on the deviations of thermoEMF from nominal static characteristic for thermocouple BP5/20 of 2-nd class was established at the level ±0.5%, and 3-d class – ±0.7%. Procedure for certification of standard samples of thermoelectrode alloy materials for BP5 and BP20 electrode-to-electrode comparison is described in [5].

In the 80-s of the last century the volume of production of thermoelectrode wire was nearly 150 kg per year. For thermocouple BP5/20 there were developed compensating conductors "copper-alloy MH2, 15" that reproduced nominal static characteristic to temperature 100°C.

The largest volume of consumption of thermoelectrodes was in metallurgy for performing short-term temperature measurements in metal melts. Tungsten-rhenium thermocouples have advantageously replaced thermocouples of platinum-rhodium alloys, having cut consumption of precious metals. Thermocouples were also widely used in scientific studies, production of composite materials, in aeronautical and rocket engineering.



Sensitivity of BP5/20 in the range 900-2100°C uniformly drops by 1 µV/K per each 200 degrees of temperature rise.

Fig. 2. Comparison of sensitivity of tungsten-rhenium thermocouples.

One of examples of their successful use was a system of developments of zone, cantilever and antenna thermocouples for nuclear rocket engine. The results of these activities were stated in detail in report to “8-th Temperature Symposium” in October, 2002 in Chicago, USA [6].

A distinguishing feature of the initial stage of using tungsten-rhenium thermocouples was relatively restricted time of their operation not exceeding tens of hours.

In the early 90-s, a drastic recession of industrial production caused certain decrease in thermoelectrode wire consumption. Because of financial difficulties, production at Moscow Electric Bulb Factory became irregular and, finally, was stopped.

It was not until a decade later that a demand for high-temperature measurements in Russia started growing. Apart from traditional interest for metallurgy, the demand drastically increased due to development in a variety of fields of technology of such branches as high-temperature sintering of refractory metals, oxides, carbides, nitrides, etc, gasostatic pressing of various structural elements, their metallization, soldering with various high-temperature solders. High-temperature vacuum annealing is one of the basic preparatory operations in manufacturing broad nomenclature of ceramic metal units with which present-day industrial installations are filled. They are exemplified by different high-voltage penetrations at nuclear power stations.

All this has forced to recommence production of tungsten-rhenium thermoelectrodes at “Riniy” Ltd. Besides, for more reliable deliveries of thermoelectric materials it is planned to organize their duplicate production at closed joint-stock society “Promelektronika”. Wire production volume achieved by now is about 90 kg per year (up to 20000 m of thermoelectrodes of diameters 0.35 and 0.5 mm).

At the present time production of temperature converters based on thermocouples BP5/20 is normalized by standard of CIS countries State Standard 6616-94 [7], and its nominal static characteristics – by Russian State Standard 8.585-2001 [8], already developed in conformity with the International temperature scale МТШ-90.

Essential difference of present-day period of using high-temperature thermocouples lies in drastically increased requirements to their service life. Thus, for examples, scientific and production association “Luch” has developed hermetically sealed thermal converter (Fig. 3) in molybdenum cover for control of sintering

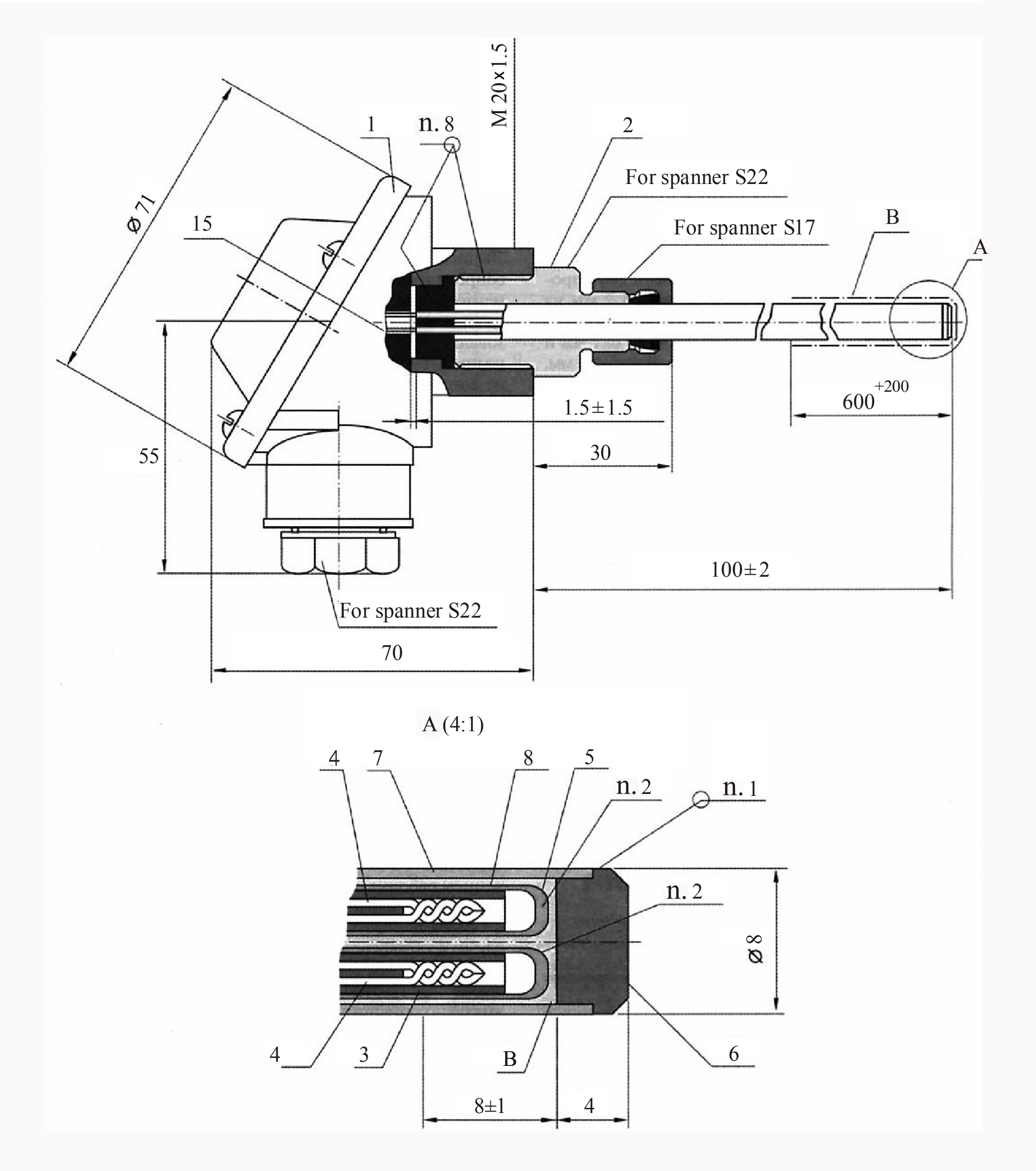


Fig. 3. Design of high-temperature thermoelectric converter of tungsten-rhenium thermocouple type:
1 – junction box; 2 – threaded connection; 3 – electric insulation; 4 – tungsten-rhenium sensing elements; 5 – protective cover bottom; 6 – end cap for thermoelectric converter case; 7 – common thermoelectric converter case; 8 – protective cover; n.1 – electron-beam welding; n.8 – filling with glue K-400; Б – $MoSi_2$ *coating 50-70 μm thick; B – argon-filled cavity.*

temperature of fuel element pellets at open join-stock society "MSZ" (Electrostal'), its service life exceeding 1000 hours at 1750°C [9]. "OTK" Ltd offers for delivery hermetically sealed tungsten-rhenium thermal converters (Fig. 4) in leucosapphire covers, the service life of which reaches 2000-3000 hours at temperatures up to 1600°C in oxidizing media [10]. Besides, they are widely used in thermoprobes for short-term temperature measurement of molten metal, salts or glass (Fig. 5). The application of such converters is justified in particularly corrosive media, when service life is primarily determined by working cover durability.

"OTK" Ltd has also developed procedure for verification of thermocouples and certification of coils of thermoelectrode materials BP5/20 in a conventional high-temperature resistance furnace in the air. Thermocouples BP completed from portions of thermoelectrode wire cut off from the beginning and end of coils, are placed in leucosapphire cover for sealing. Calibration of thermocouples is made by reference thermocouple ПР30/6 in the range 600÷1700 °C. Such procedure is much simpler and cheaper than calibration in vacuum furnace, covering up to 90% of applications for certification of thermoelectrode materials.

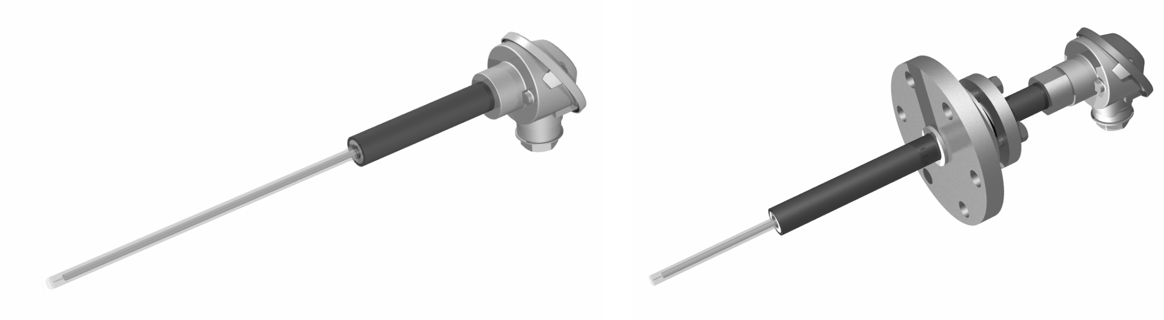


Fig. 4. Sealed tungsten-rhenium thermal converters in leucosapphire covers.

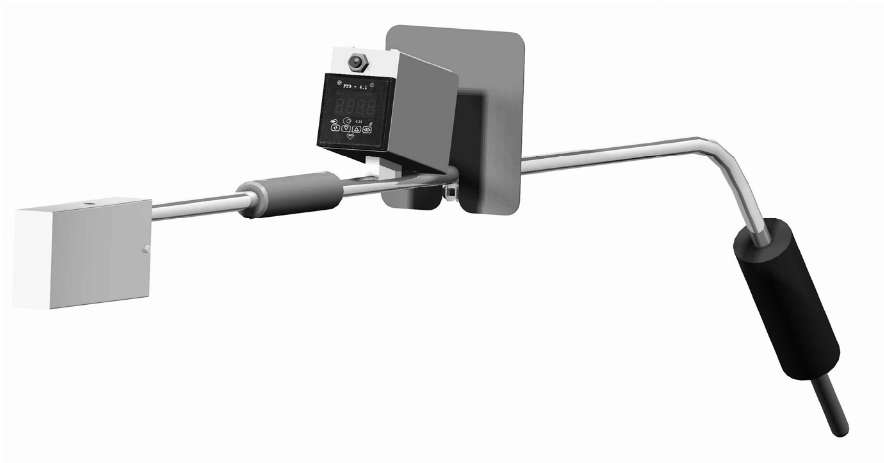


Fig. 5. Thermoprobe with tungsten-rhenium thermocouple for short-term temperature measurement in metal melt.

According to recommendations of the International Bureau of Weights and Measures (BIPM, Paris) at calibration of tungsten-rhenium thermocouples at standard melting points of the International temperature scale МТШ-90 from 1000 to 2000°C (*Au*, *Ni*, *Pd*, *Pt*, *Rh*) the uncertainty of calibration varies from 0.5 to 5.0 degrees, respectively [11]. General uncertainty of interpolation dependence of thermoEMF on temperature should vary from 2.7 to 7.0 degrees, respectively.

Due to drastically increased requirements to service life, works on stability increase of thermal converters due to superdispersed hardening of thermoelectrode BP5, have been planned, as proposed earlier [12]. Note that positive effect was achieved by adding silicon-alkali additives to alloy BP5 (0.1÷0.5% KCl; 0.1÷0.5 SiO_2, 0.1÷0.5 Al_2O_3), which allowed increasing the temperature of collective recrystallization of thermoelectrode BP5 and increased thermocouple stability in the range 1500÷2000°C by a factor of 2-3, without altering its thermoelectric characteristic.

Naturally, in the work of that time one could not precisely fix and scale highly dispersed inclusions in the bulk of thermoelectrodes, however, it can be supposed that the use of nanoparticles will only improve the situation. Considering tentatively these results as model ones, the course of subsequent investigations was predicted, beginning with the choice of electrically neutral additions and ending with economic efficiency of work.

Pilot part of the project “Modernization on the basis of nanotechnologies for production of primary temperature converters of increased precision and stability for the needs of atomic power stations and nuclear industry” [13] included:

- predicted results of performing R&D work: technology, degree of its completeness after performing R&D work;
- prospects of creating the objects of intellectual property;
- planned production of pilot production lots;
- potential volumes of home and foreign markets of products created in performing R&D work with indication of possible basic consumers and competitors;
- assessment of products competitiveness, its advantages over the analogues (import replacing and export-oriented materials);
- assessment of organization provision with scientific and technical potential (production, experimental bases, qualified personnel);
- analysis of opportunities for commercialization.

The relevance of such work became much more urgent due to the fact that according to proposal of Erich Tegeler, coordinator of IEC working group №5 TK 65, in 2008 efforts were started on the international recognition of nominal static characteristic of high-temperature thermocouples and their inclusion into IEC standard.

Presentation of thermocouple BP5/20 was made by director of Obninsk thermoelectric company at the meeting of IEC working group №5 TK65 in Tokyo in May, 2008.

According to the results of discussion, the USA representatives did not find it advisable to raise the problem of including into the standard the nominal static characteristic of the two thermocouples BP 5/26 and BP 3/25 with similar characteristics and measured temperature ranges (Fig. 1). It was recognized more promising to include into new project of the international IEC standard 6584 the nominal static characteristic of thermocouple BP5/20, but the Russian side was proposed to prepare samples and perform control calibrations of thermocouple samples in metrological centres of Germany, USA and Japan.

At the present time a schedule of joint efforts for realization of these proposals has been prepared, approved at the meeting of TK on metrology “Temperature, thermophysical and dilatometric measurements” at Directorate for Metrology of the Russian Federation Federal Agency for Technical Control and Metrology. Control target dates for delivery of samples of thermal converters BP 5/20 with diameters of thermoelectrodes 0.35 and 0.5 mm were met in December, 2008.

The results of this work will be discussed at the meeting of IEC working group №5 TK 65, planned for May 2009 in D.Mendeleyev Research Institute of Metrology (S.-Petersburg). It would be advisable for specialists from Ukraine to join in this work. The samples of thermocouples for these investigations can be transferred to Ukrainian side during this Forum.

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