Thermoelectric Properties Of W-Re Composite Strengthened By Nanoparticles Of Yttrium Oxide

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Abstract. Characteristics of the thermocouples with W5%Re against W20%Re thermoelements were studied when the positive thermoelement was made of a composite with addition of 0.1% yttrium oxide nanoparticles having an average size of 50nm. Physical, mechanical and thermoelectric properties of the composite as well as its structural features were determined. The conditions of thermal EMF stabilization for the modified thermocouple were established under high temperatures annealing.

Keywords: tungsten-rhenium thermocouples, EMF stability, standard specimen of thermoelectric material, disperse hardening by nanoparticles.

INTRODUCTION

Calibration characteristics of the thermocouples made of tungsten-rhenium alloys with 5 and 20 % of rhenium content were included for the first time into the USSR standard (GOST 3044-77) in 1977. The reference table contained three close calibrations: A-1, A-2, and A-3. The two last calibration curves were above and below the basic calibration A-1. Their upper temperatures were limited by 1,800ºC and the basic calibration had the highest temperature 2,500ºC.

The temperatures below 1800 ºC are typical for the gauges widely applied in metallurgy for short-term measurements of liquid metals temperature. W-Re thermocouples allowed to refuse from application of expensive platinum thermocouples for these purposes.

The temperatures closed to the upper limits were often realized in nuclear and space industries, and also while carrying out of high-temperature scientific researches. At the last Temperature symposium in Chicago (2002) there were discussed, for example, the specific features of temperature control for a nuclear jet propulsion unit on the base of nuclear rocket engine with a working temperature of a gas coolant to 2,700ºC. The results obtained were published in [1].

Such developments dramatically expanded a nomenclature of the investigated high-temperature materials and increased quantity of the high-temperature technological processes to be controlled. Simultaneously, demands to their temperature control became more severe and they required a new quality level of certification for high-temperature and test equipment.

By the time manufacturers had succeeded in development of the methods of essential increase in life-time and EMF (electro-motive force) stability of high-temperature thermocouples. Measuring device efficiency was provided at the temperatures up to 1800°C both in air and in neutral ambient during a few thousand hours by placing their sensitive elements in gas-tight protective tubes filled with an inert gas. Similar designs with sapphire and molybdenum protective tubes are described in [2, 3].

Because of remarkable increase in the volume of high-temperature measurements working group 5 of IEC's (International Electrotechnical Commission) subcommittee TC65B initiated the standardization of tungsten-rhenium thermocouples reference tables in the IEC standards (60584-1 and 2). The thermocouples suggested to be standardized were thermocouples of type A (W5%Re / W20%Re) and C (W5%Re / W26%Re).

The validating calibrations for the type A thermocouple were carried out by specialists of Russian and foreign metrological organizations. The results of this activity were considered at the meetings of the IEC working group in Tokyo, Saint-Petersburg, Seattle, and were summarized in [4]. The limit of admissible EMF deviations from reference table for a W-Re thermocouple was established in the 60584 IEC Standard at the level of ±1% in all temperature range.

One of the new measurement tasks in Russia is connected now with the project of creating power and propulsion module based on a nuclear reactor of a megawatt power for a manned space complex to Mars. The project development was begun in 2010 within the scope of the President program of industry modernization. Direct consequence was the increased requirements in accuracy and stability, first of all, for standard devices of high-temperature measurements made of platinum-rhodium and tungsten-rhenium alloys [5].

EXPERIMENTAL PROCEDURES

Certain progress for platinum-rhodium thermoelements (type B thermocouple) has already appeared due to development of the technology of disperse hardening platinum materials by oxide nanoparticles. Thermoelements strength and technological effectiveness were essentially improved by including the nanoparticles into a metal matrix [6] (Fig.1).

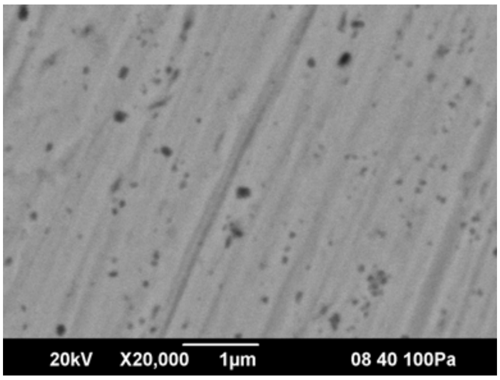


Figure 1. Platinum disperse hardened by barium oxide nanoparticles of 20-80 nm dimension.

As for the tungsten-rhenium alloys including standard specimens of thermoelement materials SOTM [7], it was established long ago that alkaline-silicon additive mixed with fine-dispersed particles of aluminum oxide have positive effect on their physical and mechanical properties.

Such approach was realized in this study while manufacturing a new generation of SOTM. Since it was known that EMF instability of tungsten thermocouples at high temperatures was caused, mainly, by a positive thermoelement [8], an experimental batch of wire 0.35 mm in diameter was fabricated of W5%Re alloy with addition of 0.1% mass of yttrium oxide nanoparticles having average size of 50nm.

The composite material was obtained using a powder metallurgy method. Powders of tungsten, ammonium perrhenate (NH_4Re0_4) and nanoparticles were preliminary mixed then the mixture was pressed into cylindrical columns and melted. The wire bars were forged and drawn into the wire which was subjected to stabilizing annealing in hydrogen by passing through a furnace.

The structural material features were specified on microsections of the wire (optical microscopy) and fractures occurred while the wire "bending-unbending" (electronic microscopy) (Fig.2).

Thermoelectric characteristics of the composite material were determined under heating in a vacuum furnace by comparing with standard SOTM wires or it was investigated in the reference to W20%Re thermoelement in argon. The equipment and techniques used are described in [4]. Uncertainty of measurement results was close to ±10 degrees at 2000 ºC.

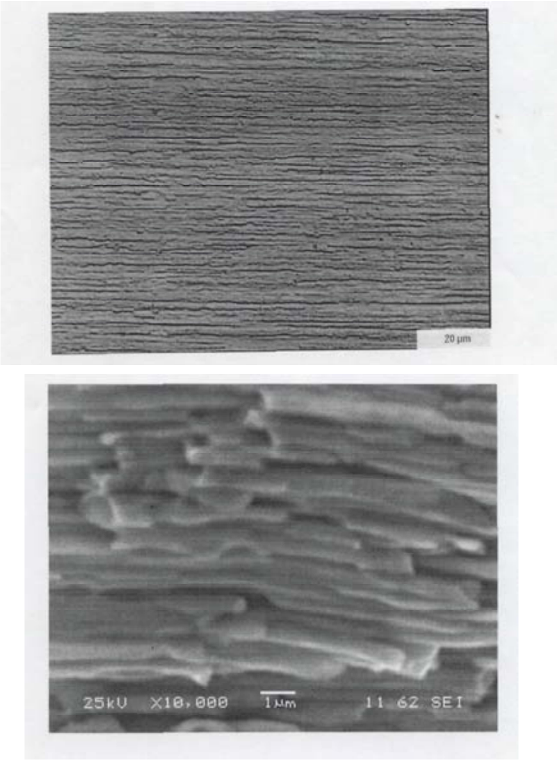


Figure 2. Microstructure of experimental W5%Re thermoelement containing 0.1% of yttrium oxide nanoparticles

RESULTS AND DISCUSSION

Such factors as thermoelectric uniformity, durability, microhardness (530-540 kg/mm^2) of the composite material investigated, practically, did not differ from the values determined for the alloy WAR5 (W5%Re alloy with Al oxide additives) described in [8]. Its microstructure is homogeneous along the whole wire cross-section and consists of long grains drawn along the wire drawing direction, having ~ (1÷5) µm in transverse dimension (Fig.2). The results of electronic microscopy testify that under plastic deformation intensive stratification of the material occurs on the grains borders and separate grains destruction having place by spall along the cleavage planes.

As for the thermoelectric characteristics of the alloy hardened by yttrium oxide nanoparticles, the first comparison of the initial alloy with corresponding SOTM wire performed before and after 30-minute annealing in vacuum at 1650°C, have revealed a small difference in thermal EMF calibration curves received under direct (heating) and reverse (cooling) actions in each cycle, but there was essential difference in calibration curves between two consequent heating-cooling cycles.

The results obtained under subsequent cyclic annealings in argon at 1700°C confirmed that conclusion. Fig. 3 shows how the thermocouples EMF changed during three consecutive heating-cooling cycles after annealing at 1700°C for 4, 5, and 2 hours.

It is obvious that the EMF of the thermoelement investigated stabilized only after almost 10-hour annealing when forward and reverse trends in the last cycle practically coincided.

It is interesting to observe the thermocouple EMF change during isothermal annealing at the temperature 1700°C. As it is shown in Fig. 4, during the first hours a working signal of the thermocouple decreased with the rate almost coinciding with the phenomena earlier observed for the alloy WAR5 in [8]. After the second cycle the calibration curve was restored practically to the initial level.

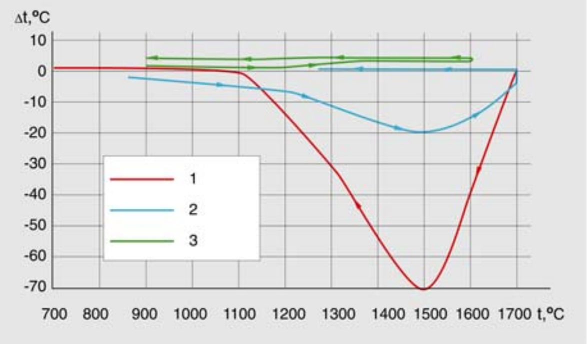


Figure 3. Changes in EMF value for the thermocouple consisted of W5%Re (0.1% of yttrium oxide nanoparticles) against W20%Re (wire coil 311, type A) during three consequent heating-cooling cycles in the temperature range of 700-1700°C. The curves represent EMF differences from nominal values for given temperatures (reference table).

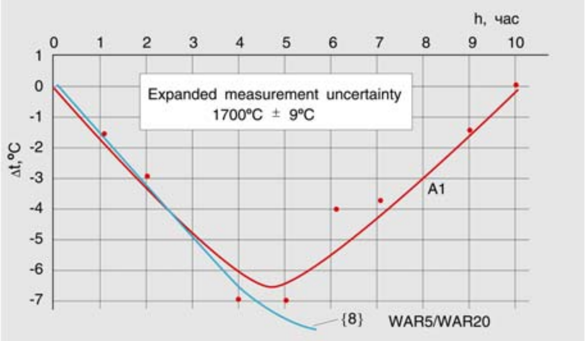
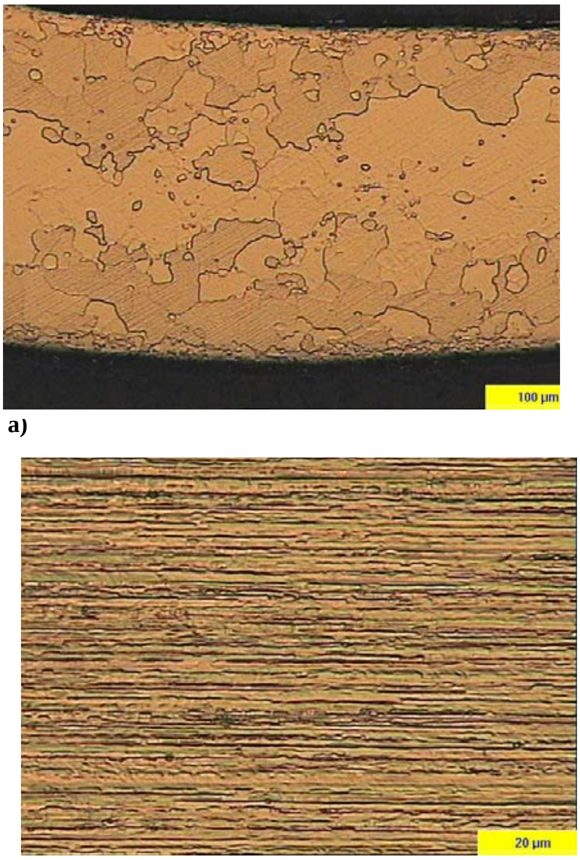


Figure 4. Changes in EMF value for the thermocouple having modified W5%Re thermoelement (0.1% of yttrium oxide nanoparticles) compare to the initial value in the first cycle during isothermal annealing at 1700°C.

A control check of such behavior was repeated for a few thermocouples fabricated during 2011. In all cases, after 8-10 h annealing at the temperature 1700°C deviations of calibration curves from the initial curve did not exceed the evaluated measurements uncertainty. The structural changes fixed (Fig. 5a) confirmed the development of recrystallization process within the composite material accompanied by double –triple grains growth.

As for the composite material behavior at 2000°C, annealing of the thermocouples for only 1 h eliminated non-monotonic changes in thermal EMF of the composite material while cooling. For 1 h annealing at that temperature EMF drift slightly exceeded 6 degrees similar to WAR5 thermoelement [8]. In this case the material microstructure changed a little (Fig. 5b). With increasing of annealing longitude to 3-5 h, a working signal of the thermocouple consisted of the composite and W20%Re wires changed more essentially than it is shown in Fig.4, but the changes did not exceed the evaluated uncertainty.



a)

b)

Figure 5. Microstructure of nano-hardened composite material after 11 h annealing at 1700°C (a) and one-hour annealing at 2000°C (b).

CONCLUSION

The results obtained allow to assume that the key influence on the composite behavior at the initial stage have excessive internal stresses induced by oxide nanoparticles embedded into the metal matrix. It seems that stresses were caused an irregular nature of the thermal EMF changes which were observed during the first heating-cooling cycles to 1700° C.

It is obvious, that the typical stabilizing annealing of a thermoelement wire in hydrogen at 1500°C stated in [10] is not sufficient for the material investigated, and its annealing temperature has to be increased, as minimum, by 400-500°C. It would be correspond to the temperature of the beginning of collecting recrystallization process.

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