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NANOPOWDERS ON BASIS OF TUNGSTEN: METALLURGICAL METHOD OF RECEIPT, PHYSICAL AND CHEMICAL PROPERTIES

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The combined chemico-metallurgical method of obtaining of alloyed nanopowders on the basis of tungsten is elaborated. Synthesis regimes were worked out allowing to obtain nanopowders on the basis of tungsten with the given complex of properties. There were studied chemical and phase composition and also sizes of nanoparticles and agglomerates of obtained alloyed nanopowders on the basis of tungsten.

Keywords: nanopowders, tungsten, synthesis, chemico-metallurgical method, alloying

Introduction. The use of sintering nanomaterials in a technique is one of perspective directions of modern material-technology. During the last years intensive researches are carried out in relation to creation of heavy tungsten alloys with enhanceable content of tungsten and with matrices which provide a high capacity for localization of the adiabatic moving, that allows to improve the special properties of alloys [1-4]. One of methods of receipt of such alloys there is a high temperature electrochemical synthesis [5-7]. However, the high temperatures of process (1173-1223 K) limit possibilities of its practical application.

For today, for the receipt of nanopowders on the basis of tungsten apply such methods: method of arc discharge in thermal plasma [8], plasmochemical synthesis [9], method of chemical condensation [10-11], method of thermolysis of cabbonylates [12], and synthesis in aqueous solutions [13]. These and other methods are classified in work [14]. There are perspective works in relation to the receipt of nanodimensional powders on the basis of tungsten from tungsten containing wastes [15-17]. Lately, large attention is spared to the receipt of nanodimensional powders of tungsten by hydrogen reduction practical realization of which is thoroughly described in works [18-23]. For application of nanopowders a conclusive value is had their lifetime to oxidation [24-25] and grain-size distribution [26].

The purpose of this work is development of low temperature methods which allow during making of nanopowders to regulate a structure and properties of the got eventual materials.

Materials and methods of experiment. In work for the synthesis of nanopowders of given composition on the basis of tungsten there is used the combined chemical and metallurgical method which combines besieging of hydroxides of metals from

solutions of corresponding salts with next hydrogen reduction of the got intermediate product. An intermediate product for powders was got two methods: mechanical mixing of hydroxides of nickel, iron and cobalt with tungstating acid; by treatment of tungstating acid by aqueous solutions of salts of nickel, iron, cobalt with evaporation of mixture at continuous interfusion to the dry residuum and washing by an acetone or alcohol for moving away of anions of chlorine. As a result got semiproduct - powder on the basis of tungsten, which on data of x-ray phase analysis is mixture of oxides.

At the first method it is difficult to control chemical composition of nanopowders, as in the process of their receipt there is contamination of product by impurities. Except for that, a process is many-stage that can result in instability of descriptions of the eventual alloyed nanopowders of tungsten.

The second method differs in technological simplicity and flexibility, does not need the use of the special technological equipment. There is a high producibility of results that is why further researches of powders carried out on such methods.

Initial materials for the receipt of intermediate product were: tungstating acid, chlorides of iron, cobalt and nickel.

For the analysis of materials used corresponding methods:

- content of nickel, iron and cobalt was determined by the methods of atomic-adsorption spectroscopy (AAS) and atomic-emission spectroscopy with induction plasma (AES and INP); used the plasma spectrometer «*Yl'tima*-2» (firms «*Zhben Ivon*», France) and atomic-adsorption spectrometer of firm «*AAS*-3» (Germany);
- content of chlorine was determined by titrimetric;
- phase composition of powders was determined by the method of x-ray phasic analysis on the x-ray photography diffractometer «*DRON*-3» with mathematical treatment of the got results and use of information of ASTM data catalogue;
- the specific surface of powders was determined at the method of low temperature adsorption-desorption of nitrogen on apparatus GKh-1.

The basic stages of metallization of the got intermediate product on the basis of tungsten carried out on apparatus «*Setaram Tag* 24» in the interval of temperatures 20-900 °C. Electronic-microscopic researches of size and morphology of parts of powders executed on the sweepable electronic microscope of «*Leo*-430*i*».

Results and their discussions. There are certain conditions of co-operation of hard tugatating acid with solutions of salts for iron, nickel and cobalt. It is set that the most exact results in relation to chemical composition of nanocompositions on the basis of tungsten it is possible to get, if concentrations of solutions are in an interval 5-75 g/l. If to take solutions of greater concentration, then authenticity of error in relation to chemical composition considerably increase through the errors of devices at determination of concentration of solutions. If, opposite, the concentrations of solutions to decrease, then it will be to produce their large volumes, that considerably will prolong duration of synthesis and will affect on quality of the finished product. In a table. 1 and on fig. 1, and The results of x-ray phasic analysis and fragments of sciagram of the got product on the basis of tungsten accordingly are given.

Table 1 - Phase composition of intermediate product on the basis of tungsten

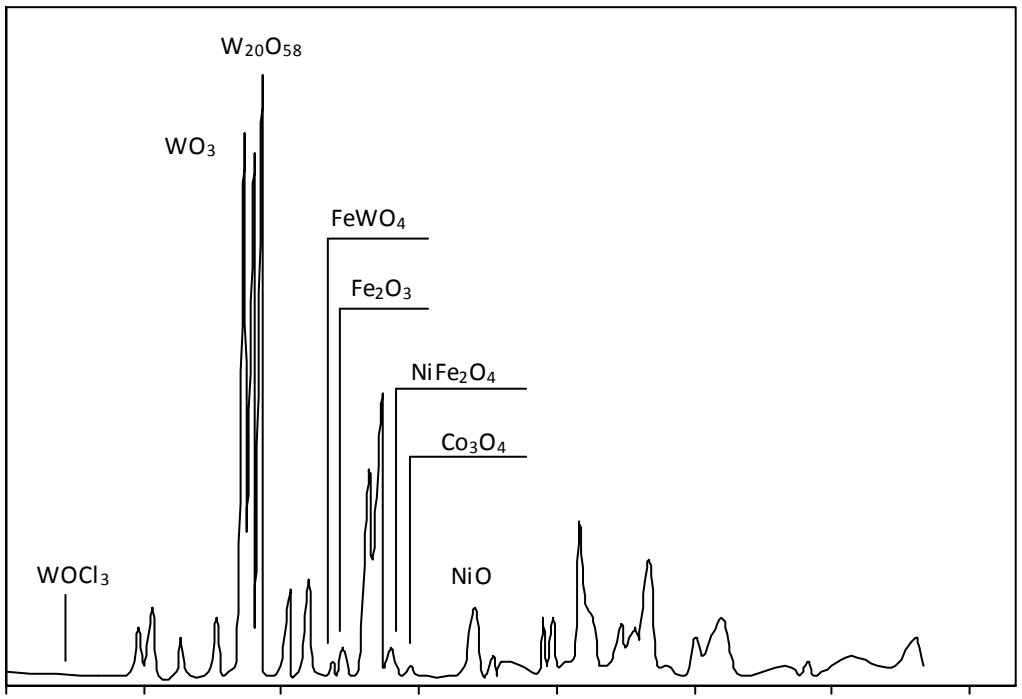
Phase	WO_3	$W_{20}O_{58}$	Fe_2O_3	$NiFe_2O_4$	Co_3O_4	NiO	$FeWO_4$	$WOCl_3$
Content, vol. %	64,12	21,98	3,72	3,36	2,54	2,02	1,92	0,34

On fig. 2 it is resulted thermogravimetry of intermediate product, which are got in two environments: in hydrogens and in helium. As evidently from the given data, metallization of chemical mixture takes place in a few stages and in different temperature intervals. However temperature intervals and temperature maximums, which characterize reduction both ferrifrous, nickeliferous, cobalt and tungsten constituents in mixtures, displaced in more low temperature area. The analysis of the got experimental data for phase analysis allows to assume that a mechanism of cross-effect of one component on other is different. The decline of temperature of metallization of oxides of iron, nickel, cobalt is constrained, presumably, with diminishing of area of mutual contacts of separate particles of these phases, and also with the decline of partial pressure of water in the volume of reduction charge in this temperature range (200-500 °C) as a result of presence of oxide of tungsten. Except for that, tungsten oxigencontaining constituent presumably is an restriction for enlargement of particles of iron, nickel and cobalt which also can result in the decline of temperature of proceeding in ferrifrous, nickeliferous and cobalt constituents. Last, in turn, at data of work [27] can influence on the electronic structure of the virgin oxide system of tungsten, reducing the induction period of creation of nucleuses and accelerate the process of metallization of oxide of tungsten. Thus the not oxides of iron, nickel and cobalt have influence on proceeding in the oxide of tungsten, but them reduction phases. The increase of quantity of centres of criation of nusleoses on the surface of crystallines for oxide tungsten, which reduction particles of iron, nickel and cobalt serve as, accelerate the process of metallization of oxide of tungsten.

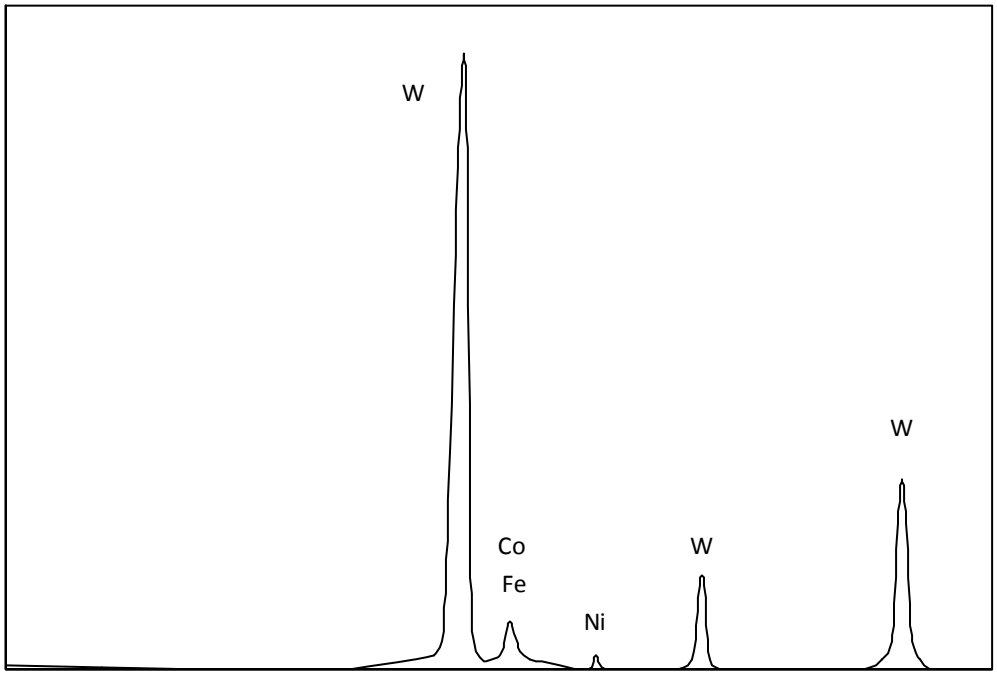
In an experiment a few temperature regimes of hydrogen reduction for the synthesis of powders of composition of 7.2 % tungsten; to a 1.9 % cobalt; 1.8 % nickel and 1.0 % iron are tested. Such parameters of reduction, as a temperature and duration of the noted process, varied in a range 923-1173 K during 1-2 hours. A structure, phase composition and dispersion of the synthesized powders which influence on the mechanism of consolidation and property of massive samples, was investigated. A sciagram reduction over of the reduction on the basis of tungsten is brought on fig 1.

An x-ray photography analysis is set next phase composition of reduction nanopowders of alloy on the basis of tungsten, at. %: W - 87,72; Ni - 6,14; γ-Fe - 2,63; Fe-Ni - 0,88; Co - 0,88. Chemical composition of the reduction nanopowder of alloy on the basis of tungsten was characterized by the presence of 89,9 % tungsten, 7,2 % nickel, 1,8 % iron and 1,1 % cobalt.

From the results of phase and chemical analyses of the reduction powder is follows that oxide and intermetalide phases in samples are expensed, and chemical composition of powder answers set.



a

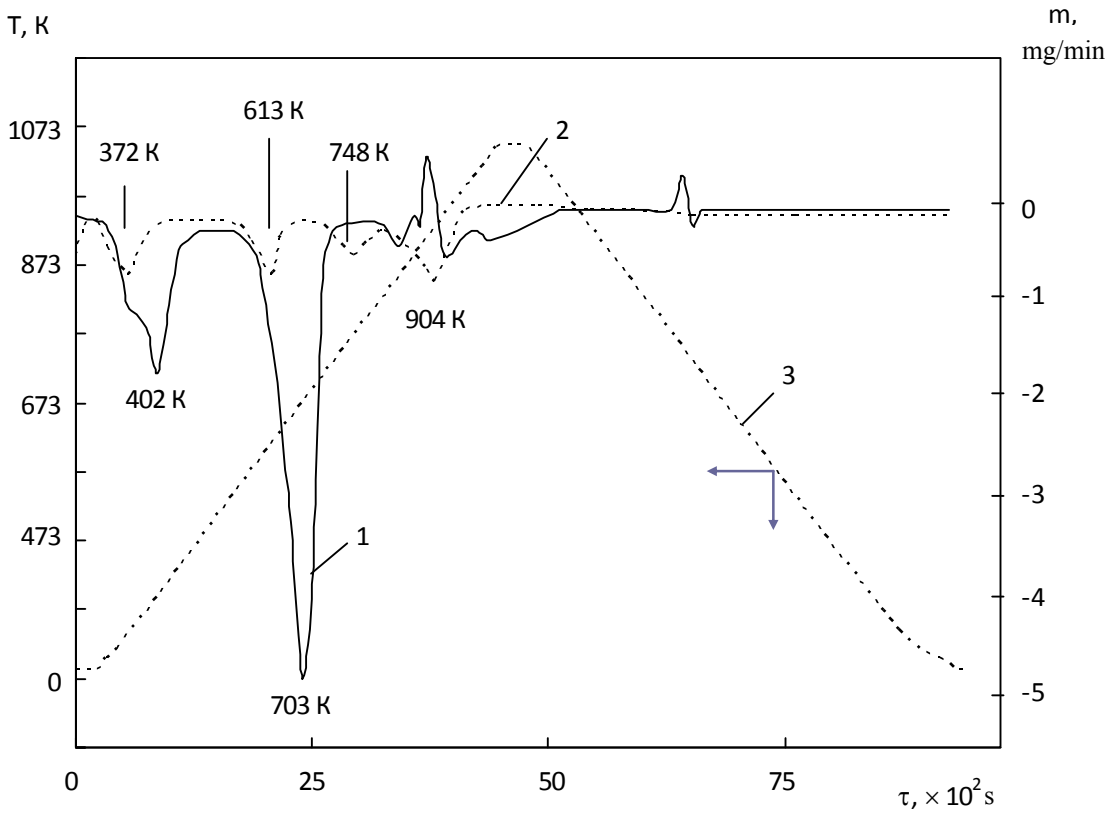


b

a is an intermediate product; b is reduction powder of alloy

Figure 1 - Sciagrams of products on the basis of tungsten

The microphotograph of nanopowders of the alloyed alloy on the basis of tungsten is given on fig. 3. Electronic-microscopic researches showed that material appeared dense agglomerates the middle size of which presents 300-400 nm with the size of separate particles of 100 nm.



1 is dependence of speed of mass treason m sample of intermediate product on the basis of tungsten at heating in the environment of helium from duration of process; 2 is dependence of speed of mass treason in m sample of intermediate product on the basis of tungsten at heating in the environment of hydrogen from duration of process; 3 is a curve of treason of temperature

Figure 2 - Thermogravimetry curves

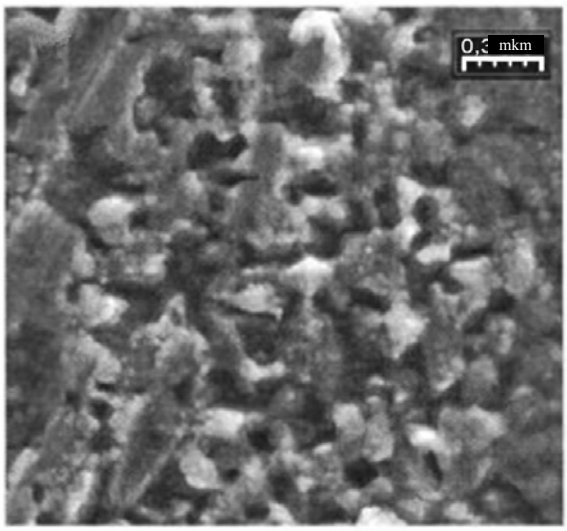


Figure 3 - Electronic-microscopic photography of alloy powder on the basis of tungsten

Conclusions. The regimes of synthesis of powders which allow with the use of metallugical method to get nanopowder alloys on the basis of tungsten with set chemical composition and physical and chemical properties are offered. On the basis of the set conformities choose near the management of nanopowders properties on the basis of tungsten on the stage of their forming are worked out.

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