HEAVY ALLOYS OBTAINED VIA MA SPS METHOD

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The structure and morphology of mechanocomposites in the system W-Ni, obtained as precursors for tungsten alloy, were investigated by X-ray diffraction, high resolution electron microscopy in direct and back scattering electrons (SE and BSE). It was shown that the highest density of sintered samples was achieved in interacting system W-10% Ni by a classical method of powder metallurgy (ρ = 14 – 15 g/cm^3). Materials based on tungsten alloys with such density can be used in solving the problem of replacement of lead (ρ = 11.34 g/cm^3) for a radiation protection.

The possibility of application of spark plasma sintering (SPS) of W-Ni mechanocomposites to obtain heavy alloys was demonstrated. SPS was carried out using a SPS Labox 1575 apparatus (Japan). The samples were heated at rate 50 °C/min. The maximal SPS temperature was 1250 °C. At the beginning of sintering a uniaxial pressure of 5 MPa was applied to ensure reasonable contact conditions. A pressure of 40 MPa was applied to the samples when the SPS temperature reached 300 °C. The materials obtained by this method have a density of 17.05 g/cm^3 (alloy W–10% Ni) and 18.01 g/cm^3 (alloy W–5% Ni).

Development of technology of obtaining high density materials, the study of the structure and properties of refractory metals, alloys and composite materials on their basis, as well as methods for their production are actual problems. Heavy alloys based on tungsten have found application as protection from radiation. This is due to their high X-ray density (60 % more density of lead), a high coefficient of absorption of X-ray and γ-radiation, high strength, good corrosion resistance. They are widely used in the nuclear industry (crucibles for storage of radioactive materials), such as high temperature and corrosion resistant – in rocket technology for devices operating at very high temperatures, for the manufacture of heat-resistant tool.

The most promising method of producing tungsten alloys is powder metallurgy, in which the basic operations are the compacting and sintering performed usually at a temperature of (0.6-0.8) × $T_{melting}$ of tungsten. To reduce the sintering temperature the minor additives of various metals with lower melting point are used.

A high density of tungsten alloys can be provided in the case of chemical reduction of double salts, when the mixing reaches molecular level [1-3]. However, chemical-metallurgical method is multistage (solid-phase sintering, liquid phase sintering, annealing in vacuum) and environmentally inexpendient.

Mechanochemical activation method is promising for obtaining composites with a homogeneous structure for the replacement of polluting chemical production, usually accompanied by a large number of sewage and other wastes, since the mechanochemical synthesis is a dry, waste-free, environmentally (ecologically) friendly method [4-7]. Previously we have shown that mechanochemical composites obtained in the system W–10% Me can provide the homogeneous distribution of metal additives in low concentration in the sintered alloy. The influence of the conditions of mechanical activation (MA) on morphological and structural characteristics of mechanocomposites is investigated. It is shown that classical methods of powder metallurgy allow achieving the highest density of sintered material in the interactive system W–10% Ni [8-10].

According to the equilibrium diagram of the system W–Ni, tungsten may chemically interact with Ni, and in the process MA one can expect the formation of intermetallic compounds [11]. However they are not detected by X-ray method. The diffraction reflections of Ni almost completely disappear on MA, while reflections of tungsten retain the intensity and position as evidence from the unchanging of parameters of its crystal lattice. The sizes of the crystallites are: for W ≈ 15 nm, and for Ni ≈ 4 nm. One can assume that at this stage of MA a composite structure W/Ni is formed. Electron microscopic analysis of particles of the composite in characteristic radiation of Ni reveales a continuous and a discrete location of the Ni-phase in a tungsten matrix (Fig. 1).

Microstructural analysis showed that composites W/Ni sintered by traditional powder metallurgy at temperatures of 1250 ºC and 1350 ºC had a very fine structure (Fig. 2). With increase of sintering temperature, the coagulation of Ni-inclusions located at the grain boundaries of the tungsten, and grain growth also occur. The increase of material density is not possible.

Reducing of metal additives up to 5% degrades a compressibility of the composites and limits a low concentration of the mechanochemical introduction of Ni. For interacting systems W–10% Ni, the research of technological properties showed that the traditional method of powder metallurgy allowed to reach a follow density values: 14.6 g/cm^3 at 1250 °C and 14.7 g/cm^3 at 1350 °C (Fig. 3).

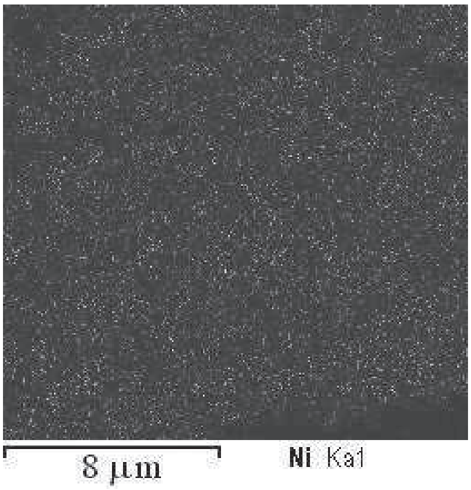

Fig. 1. The distribution of elements in mechanocomposite W/10% Ni (in characteristic radiation of Ni)

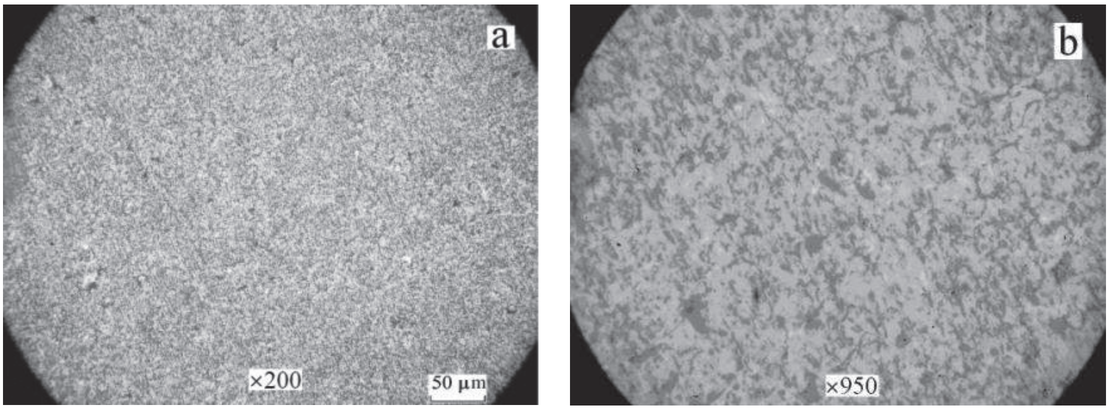

Fig. 2. The optical microscopic images of mechanocomposites W/10% Ni, sintered at 1250°

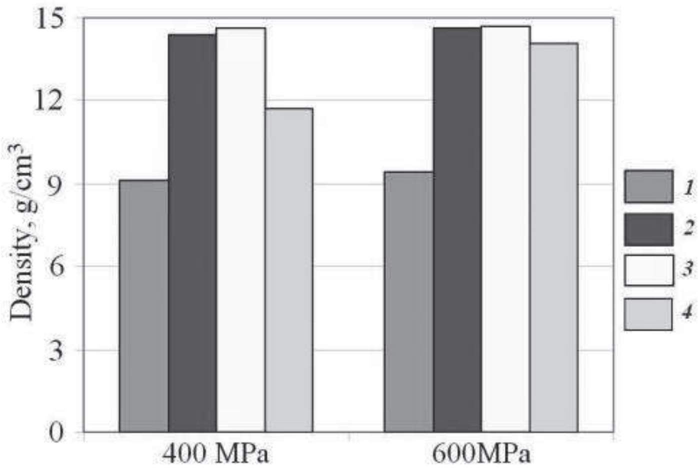

Fig. 3. The density of sintered mechanocomposites W/10% Ni:
after pressing (*1*); after pressing and sintering at 1250 °C (*2*), 1350 °C (*3*) and 1450 °C (*4*)

Materials based on alloys of tungsten with interacting metals, with a density of 14-15 g/cm^3, can be used as replacing a lead-containing materials for the manufacture of containers at the radioactive waste storage as protection from γ- and X-ray radiations.

For modern military equipment it is necessary to create new materials with significantly higher density (~18 g/cm^3). Therefore, we investigated the possibility of application of mechanocomposites W/Me as precursors to subsequent spark plasma sintering. Investigations showed that already at a temperature of 1200 ºC a high density of the materials was achieved. The density of the alloys W-10% Ni and W-5% Ni and is 17.05 and 18.01 g/cm^3, respectively, Brinell hardness ~ 380 HB. Electron microscopic studies showed that the obtained sintered materials were pseudoalloys based on tungsten (Fig. 4). At sintering of composite the intermetallic compound Ni_4W was formed with lattice parameters a = 0.5727 nm and c = 0.3553 nm. Coherence length of W is 152 nm, and of Ni_4W – 56 nm.

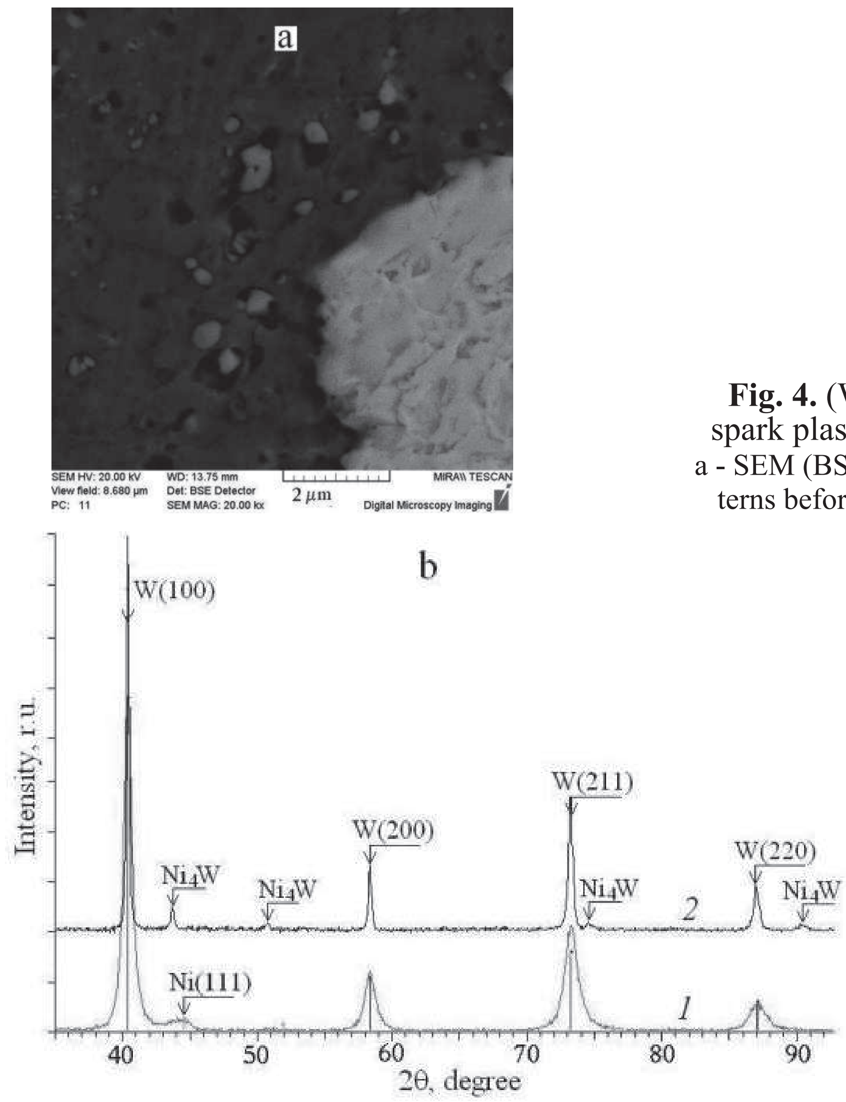

Fig. 4. (W-10% Ni) obtained by spark plasma sintering at 1200 °C: a - SEM (BSE) image, b - diffraction patterns before (*1*) and after sintering (*2*)

Spark plasma sintering (SPS) delivers significantly higher density and hardness of tungsten alloys in comparison with the samples obtained by the traditional powder metallurgy method. In addition, the SPS method allows obtaining sintered samples with lower content of metal additives (up to 5%) and higher density.

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