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Mechanocomposites on the Basis of Tungsten for Obtaining Pseudo Alloys

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Abstract

The structure and morphology of tungsten mechanocomposites with the addition of copper, nickel of iron were studied by means of X-ray diffraction, electron microscopy and micro X-ray spectral analysis. The possibilities of pressing dense samples from the mechanocomposites were demonstrated.

Key words: mechanical activation, mechanocomposites, tungsten, pseudoalloys

INTRODUCTION

Materials based on tungsten are used to manufacture the hardware for electrotechnical purposes (contacts), electrodes for spot weld, cathodes for sputtering *etc*. Tungsten powder possesses poor moldability and sintering ability, so the additives of iron, nickel, niobium, copper, tin and so on are introduced into tungsten to improve these characteristics.

By present, the best-studied composition is tungsten–copper. According to the equilibrium state diagram [1, 2], tungsten does not interact with copper. However, the authors of [3] stated on the basis of the X-ray investigation of W–Cu pseudo alloys that at room temperature tungsten may dissolve up to 0.019 mass % copper. In the majority of cases, such a low solubility has no noticeable effect on the structure of pseudo-alloys. Tungsten–nickel composition is distinguished by the high solubility of tungsten in nickel (up to 30 mass % even at room temperature), lower solubility of nickel in tungsten (~0.3 mass %) and the presence of one intermetallic compound Ni_4W with the homogeneity region 2 mass % [4].

There are several intermetallic compounds in the composition tungsten–iron: WFe_2, W_2Fe_3 (or W_6Fe_7), WFe, as well as the solid solutions based on tungsten (up to 2.6 at. % at 1677 °C), α-iron (up to 14.3 at. % at 1548 °C) and γ-iron (up to 1.46 at. % at 1140 °C) [2].

Investigation of the processes of agglomeration of W–Cu composition showed [5] that the density of the product depends on the particle size of the initial powder and on the composition of the mixture. For instance, for tungsten particles having the size 10–15 μm, the maximal compaction is observed for the mass fraction of copper 50 %. With a decrease in copper content (below 35–40 mass %) the density of the composition decreases sharply. At the same time, compositions with copper content not more than 10 % are in demand; to prepare these compositions, one should use special operations.

It is known [6] that active compaction (from 44 to 12 %) during the agglomeration of composition W–20 vol. % Cu with tungsten particle size less than 1 μm occurs at 1100–1200 °C. Even higher rate of compaction is observed in the composition obtained by the reduction of copper tungstates when components mixing achieves almost the molecular level [7].

In this direction, a very promising process is mechanical activation of initial compositions [8–10].

The goal of the present work was to study the structure and morphology of composites formed during the mechanical activation of the mixtures of tungsten with copper, nickel, and iron.

EXPERIMENTAL

Tungsten of PV1 grade, copper PMS-1, carbonyl iron PZhK and carbonyl nickel of PNK grade were used in the work. The mechanochemical experiment was carried out in a high-energy ball planetary mill AGO-2 with water cooling in the atmosphere of argon (cylinder volume: 250 cm^3, ball diameter: 5 mm, total mas of balls: 200 g, weighted portion of the material under treatment: 10 g, the frequency of cylinder rotation around a common axis: 1000 rpm).

X-ray examination was performed with a D500 Siemens diffractometer (Germany) using Polikristall software.

Examination of powders was carried out with a focused beam microscope with high resolution Mira (Czechia) with a micro X-ray spectral attachment.

RESULTS AND DISCUSSION

To obtain mechanocomposites of tungsten with a metal (Cu, Ni, Fe), mechanical activation was carried out in two stages. At the first stage only tungsten was ground for 4 min. The initial tungsten powder has a prismatic shape with the average particle size 2.5 μm (Fig. 1, *a*). Mechanical activation for 4 min leads to particle flattening to the size of 15–50 μm and to the formation of smaller particles having splintered shape (see Fig. 1, *b*). An increase in the time of mechanical activation to 5 min results in cold-hardening of particles and corresponds to the change of size up to 20–90 μm (see Fig. 1, *c*).

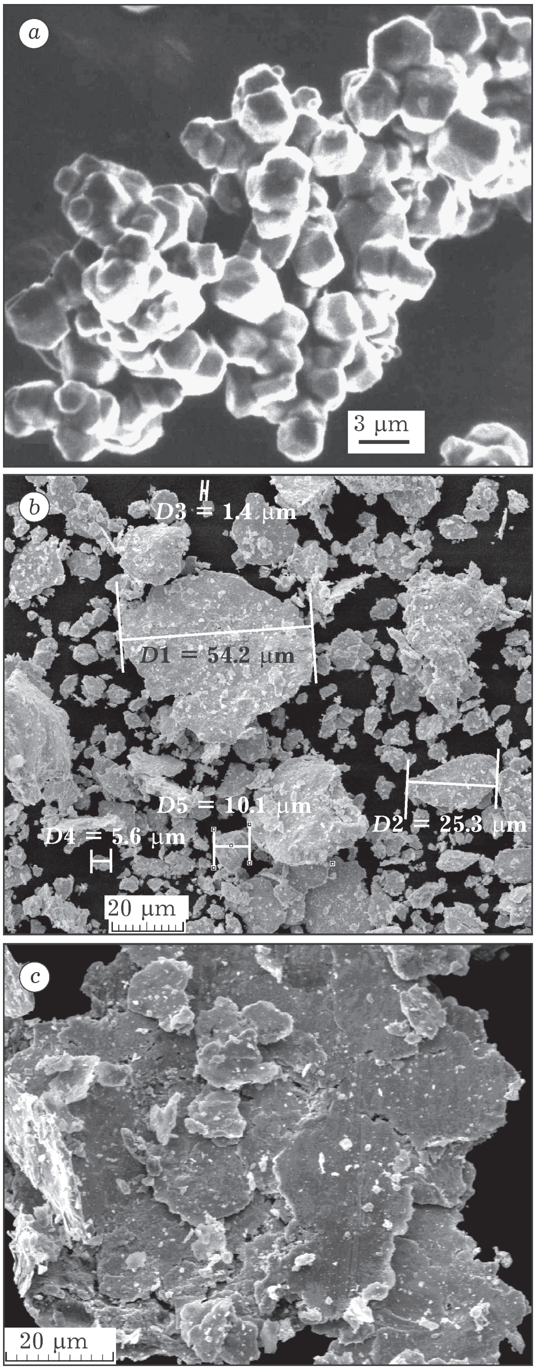

Fig. 1. Shape of the particles of tungsten powder: *a* – initial; *b*, *c* – mechanically activated for 4 and 5 min, respectively.

According to the X-ray data, the initial tungsten sample is a well crystallized power with the coherence length more than 150 nm (peaks have only instrumental broadening) (Fig. 2, *a*). Redistribution of the intensities of diffraction peaks is likely to provide evidence of the presence of texture (preferential orientation) along direction 110.

The X-ray diffraction patterns of tungsten samples activated for 4 min (see Fig. 2, *b*) are characterized by somewhat broadened peaks. The analysis of broadening shows that it is

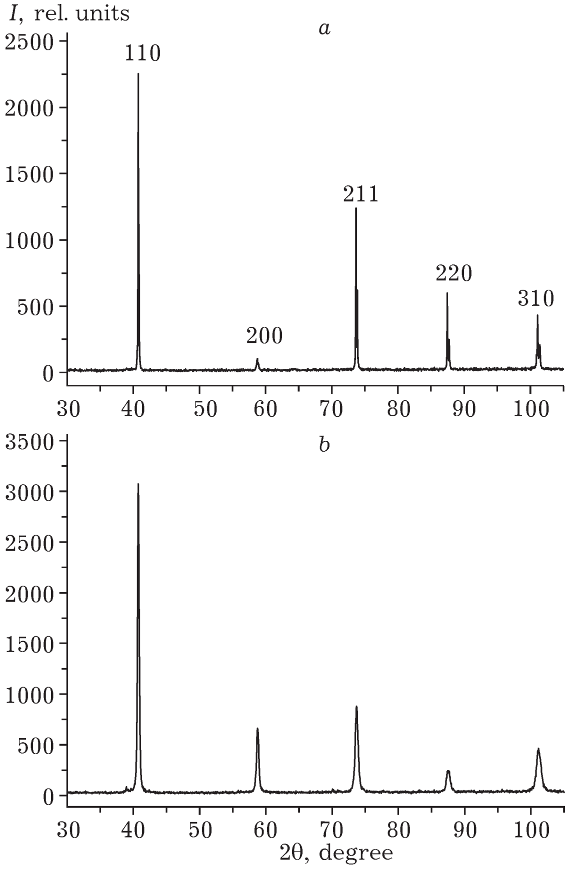

Fig. 2. X-ray diffraction patterns of the initial tungsten sample (*a*) and the sample activated for 4 min (*b*).

mainly due to the presence of micro-distortions in tungsten structure (with the conservation of large particle size). It should also be noted that the ratio of peak intensities provides evidence of the absence of texture (equiprobable distribution of particles in the powder from the viewpoint of their crystallographic orientation).

Pliant metals are characterized by the ability to adhere to the balls and cylinder walls even during short-time mechanical activation in high-energy ball planetary mils. In this connection, they were introduced into the composition after tungsten had been activated for 4 min, then the mixture was treated 2 min more.

X-ray studies showed that the samples with the addition of Cu, Ni, Fe behave in different manners (Fig. 3). One can see that in all the cases along with W phase the phase of a second metal is present in well crystallized form (the coherent length is not less than 40 nm), however, the relative intensity of copper peaks is much higher than the intensity of the peaks of nickel, and the latter, in turn, exceed the intensity of iron peaks. This is the evidence of different concentrations of crystal phases Cu, Ni, Fe in the samples, that is, more ductile metals can partially be present in composites in the form of very thin amorphous layers [11] Increased intensity of copper peaks with respect to the peaks of nickel and iron is likely to be connected with lower recrystallization temperature of copper.

Further change of the relations between the intensities of tungsten peaks should also be noted. With an increase in the total time of

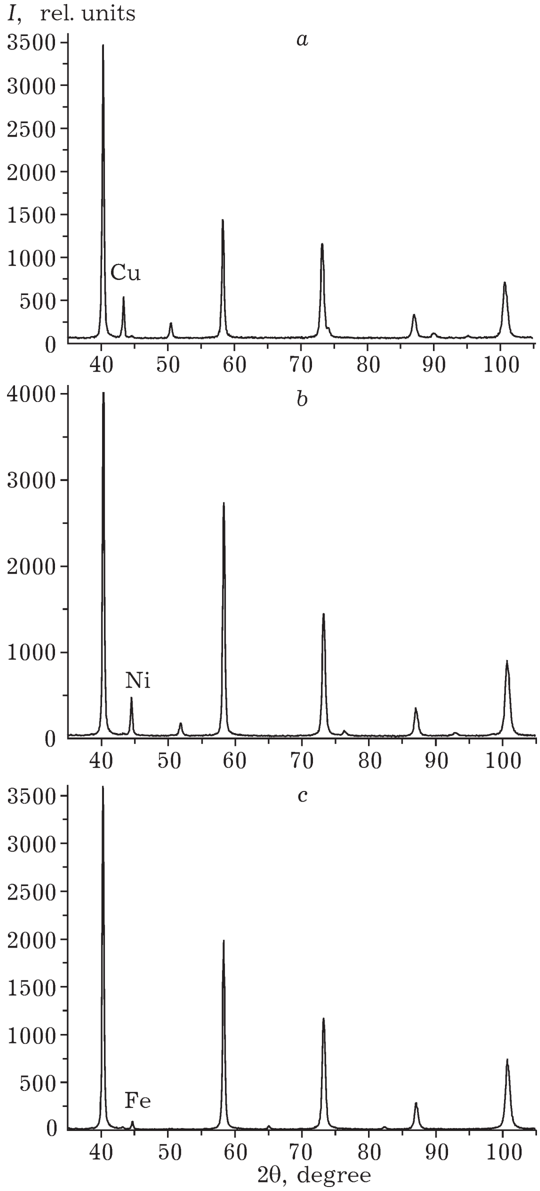

Fig. 3. Diffraction patterns of tungsten samples with the addition of copper (*a*), nickel (*b*) and iron (*c*) activated for 2 min.

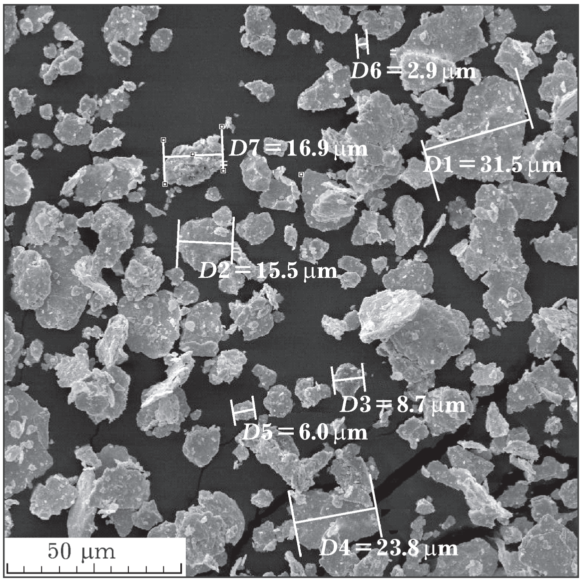

Fig. 4. Shape of the particles of mechanically activated composition W–Cu.

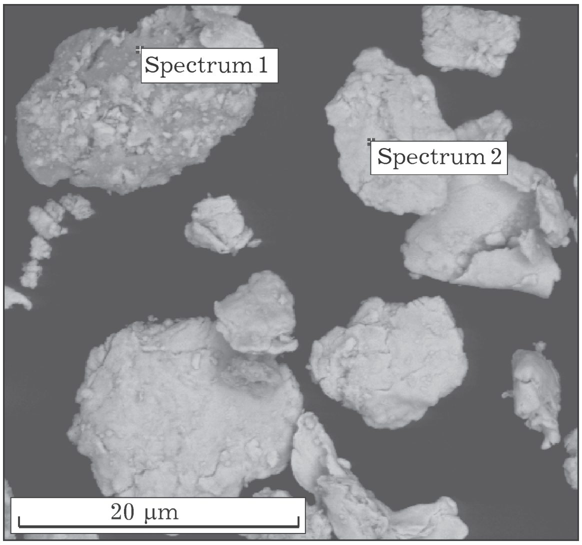

Fig. 6. Micro-X-ray structural analysis of the composition of W–Cu composite particles, %:

Spectra	Fe	Cu	W
Spectrum 1	0.74	81.87	17.39
Spectrum 2	1.20	0.22	98.58

activation, the intensity of the diffraction peak 200 increases, which is likely to be the evidence of the formation of a texture of the new type (in comparison with the initial sample) with the preferential direction 100.

A significant fact is that the mechanical activation of tungsten with nickel and iron does not lead to the mechanochemical formation of intermetallic compounds in these systems.

Electron microscopic studies showed that the mechanical activation of the powder of W–10 mass % Cu powder does not lead to any changes of the shape of particles in mechanically activated tungsten (Fig. 4): particle size has the same order of magnitude and is equal to 6–17 μm.

The results of metallographic and micro X-ray spectral analysis provide evidence that the particles of the composition are built according to the sandwich principle so that the copper phase is situated in the tungsten basis (Fig. 5). In addition, micro-X-ray spectral analysis points to the presence of 0.7–1.2 % iron in the composite (Fig. 6). Iron appears in the powdered composition during activation as a result of rubbing in steel cylinders.

The size of powder particles in W–Ni composition after mechanical activation is substantially smaller (1–5 μm) (Fig. 7, *a*) in comparison with that for the composition W–Cu. In addition, the formation of conglomerates is observed (see Fig. 7, *b*).

Micro-X-ray spectral analysis of the powders of the composition revealed the uniform distribution of nickel over the tungsten particle.

The behaviour of the composition tungsten–iron during mechanical activation is similar to that of the composition tungsten–nickel.

Preliminary investigation of the technological properties showed that mechanocomposites

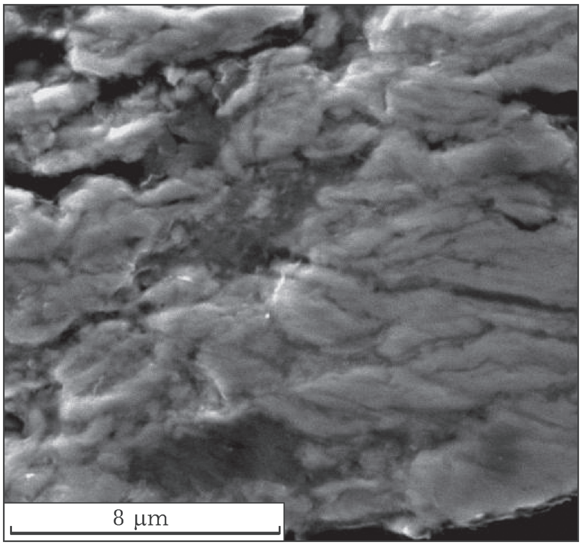

Fig. 5. Structure of the particle of W–Cu powder.

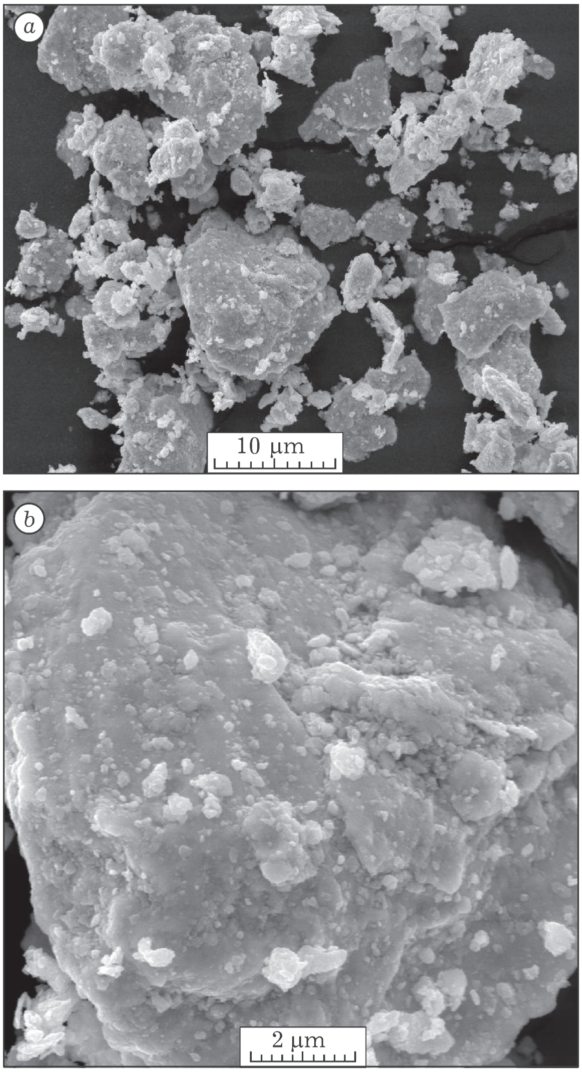

Fig. 7. Shape of the particles of mechanically activated W–Ni composition. Scale: 10 (*a*) and 2 μm (*b*).

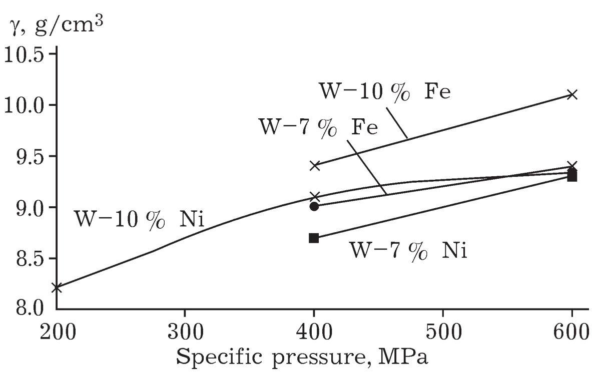

Fig. 8. Effect of specific compacting pressure on sample density.

with the mass fraction of copper 7 or 10 % are not pressed under normal conditions. The data on the density of samples pressed from mechanocomposites with the addition of iron and nickel are shown in Fig. 8. One can see that the formation of rather dense samples is possible at a pressure above 400 MPa in the compositions of tungsten with the metals interacting with it.

CONCLUSION

It was shown in the investigation that the composites of tungsten with copper obtained mechanochemically are characterized by the inhomogeneous distribution of the second component even if it possesses high plasticity. These composites are distinguished by very low moldability.

Mechanical activation of the metals interacting with tungsten (nickel, iron) provides rather homogeneous distribution of the second component, and these composites form dense samples after pressing.

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