

Mechanochemical Activation and Agglomeration of Tungsten and Its Mixtures with Copper and Nickel

ANDREY N. STRELETSKII¹, VALERY K. PORTNOY², ALEXANDER V. LEONOV², ANNA B. BORUNOVA¹, PAVEL F. PSHECHENKOV³, IL'YA O. LEYPUNSKY³, NADEZHDA G. BERIOZKINA³ and PAVEL YU. BUTYAGIN¹

¹*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Ul. Kosygina 4, Moscow 117977 (Russia)*

E-mail: str@centere.chph.ras.ru

²*M. V. Lomonosov State University, Vorobyevy gory, Moscow 117899 (Russia)*

³*Institute of Energetic Problems of Chemical Physics, Russian Academy of Sciences, Leninsky Pr., Moscow 117829 (Russia)*

Abstract

Defect formation and activation of agglomeration during mechanochemical treatment of tungsten powder and its mixtures with copper and nickel are considered. Mechanochemical activation in high-energy strain mills is accompanied by the decrease of coherent lengths (to 10 nm), accumulation of microdeformations (up to 0.2–0.3 %) and increase of tungsten lattice parameter, as well as by profound mixing of the components. Besides, the system gets contaminated with iron impurities. Chemical transformations during the annealing of samples with different doses of mechanical treatment are analyzed. The application of mechanochemical activation allowed us to obtain well agglomerated W/Ni/Cu alloys at annealing in the absence of hydrogen (density: up to 16 g/cm³; Wickers' hardness: up to 550 kg/mm²). Optimal dose of mechanochemical activation is determined (10–115 kJ/g); optimal regime of powder pressing is revealed. The effect of iron impurities on the hardness of agglomerated tablets is investigated.

INTRODUCTION

Mechanical treatment of powders in mechanochemical reactors is accompanied by the formation of various defects, which activated the mobility of structural elements during annealing and allows one in some cases to decrease substantially agglomeration temperature or improve the properties of cakes [1, 2].

The present investigation deals with the possibilities to activate agglomeration in the W/Ni/Cu system by mechanical treatment in energy-strain mills.

The first data on mechanical activation of the W/Ni system (for example, [3, 4]), W/Cu [5] were reported; agglomeration processes in W/Cu mixture [6–8] after its mechanical treatment were investigated. We carried out a systematic investigation of all the three stages of the formation of three-component material

(mechanical activation, pressing, and agglomeration), and determined optimal conditions of obtaining it. Besides, we tested the possibility to agglomerate activated materials in the absence of hydrogen (agglomeration of tungsten-based alloys is usually carried out in hydrogen atmosphere).

Experiments were carried out both with pure W, and with its mixtures with Cu and Ni. The idea of adding copper into the system is due to the fact the presence of sublayers composed of easily melting substance (melting point of copper is 1057 °C) insoluble in tungsten promotes the mobility of tungsten at a temperature within the range 1100–1200 °C. Addition of nickel is due to the fact that, on the one hand, this metal helps activating tungsten agglomeration [9]; on the other hand, it is soluble in tungsten and forms unlimited solid solutions with copper. One may expect that nickel

will provide a «connection» between the phases of tungsten and copper.

Addition of relatively light-weighted copper and nickel to heavy tungsten decreases absolute density of the composite. Because of this, we selected an optimal concentration of these additives to achieve maximal possible density and to simplify agglomeration.

EXPERIMENTAL

Mechanical activation of powders was carried out in argon atmosphere in planetary or vibrational mills with energy input (I) 2.5 to 6.5 W/g. The dose (D) of mechanical treatment was determined as $D = It$ (kJ/g), where t is time of mechanical treatment. After mechanical treatment, powders were pressed into tablets in air and agglomerated at 1200 °C in vacuum.

In order to investigate mechanically activated powders and agglomerated tablets, we used X-ray diffraction and electron microscopy. X-ray diffraction patterns were recorded with DRON-3 diffractometer (copper anode) with step-by-step scanning. Broadening of the 110 and 220 diffraction lines of tungsten was analyzed. The size of coherent lengths and deformations was calculated using the OUTSET and PROFILE programmes [10]. Electron microscopic studies of agglomerated and polished tablets were carried out with CAMEBAX MBX-1M instrument in the modes recording absorbed (AE) and back-scattered electrons (BSE), as well as the characteristic radiation of W, Cu, Ni, and Fe. Contrast of image in the AE and BSE modes is formed both by the relief and by the chemical composition of the surface. The larger is atomic number of an element, the lighter is image. In the mode recording the characteristic radiation of an element, the density of white points at images is proportional to the concentration of this element. Concentrations of different elements in the sample, in particular iron, were calculated using the integral intensity of the characteristic radiation of this element divided by the intensity of the reference (pure element).

Besides, we measured density, porosity and Wickers' hardness of the agglomerated tablets based on tungsten. Density was determined according to Archimedes' procedure by weigh-

ing in air and in liquid (diethyl phthalate). The through and surface densities were investigated by means of ammonia response (DAR) [11]. Aqueous-alcoholic solution of ammonia was poured onto one of the faces of the sample. Ammonia was accumulated in surface pores; in the case if through pores were present, it diffused to the opposite face of the tablet. After evaporating ammonia from defect-free surface, both sides of the sample were brought in contact with the indicator paper to visualize the presence of ammonia. The change of paper colour at the face on which ammonia was applied was the evidence of surface pores, while at the opposite face is the was the evidence of the through pores. Hardness was measured by the IT-5010 device at loading with a four-side pyramid. The load was 5 kg, exposure was 30 s. Dimensions of prints were analyzed by optical method. Results were averaged over ten measurements. Hardness was calculated according to [12].

RESULTS AND DISCUSSION

Mechanochemical activation

Various tungsten-based systems (W, W/Cu, W/Cu/Ni, see Table 1) were subjected to mechanical treatment. Figure 1 shows diffraction patterns of the $W_{80}Cu_{20}$ system after different doses of mechanical treatment. One can see that lines related to tungsten and copper broaden; at doses above 36 kJ/g, lines of the iron phase appear in spectra. At very high doses of mechanical treatment, a definite amount of X-ray amorphous phase appears in the system. On the basis of the analysis of line broadening, the size of coherent lengths and microdeformations of tungsten were calculated. One can see that the tungsten coherent length (Fig. 2, a) decrease to 10–15 nm, the limiting value being achieved at a dose about 15 kJ/g; microdeformations (see Fig. 2, b) achieve 0.2 % at doses of about 40 kJ/g and remain unchanged further on. Lattice parameter of tungsten (see Fig. 2, c) at first decreases; at doses above 50 kJ/g it remains constant.

Lines of the second component (copper) get broadened, too. However, because of low intensity, the analysis of line shapes is impossible.

TABLE 1

Properties of tablets agglomerated at 1200 °C from mechanically activated powders of different composition

Tablet No.	Initial composition	D , kJ/g	r , g/cm ³	r/r_0 , %	Fe content, mass %	Phase composition	H_V , kg/mm ²
1	W ₈₀ Cu ₂₀	15	12.69	75	4.12	W, Cu, FeWO ₄ , Fe ₇ W ₆	384±35
2		53	10.25	70	15.58	W, Cu, FeWO ₄ , Fe ₇ W ₆	346±13
3		90	9.18	66	21.83	W, Cu, FeWO ₄ , Fe ₇ W ₆	260±19
4	W	0	14.77	77	0	W	151±15
5		7	15.25	79	0.57	W	97±32
6		18.6	11.36	68	10.71	W, FeWO ₄	364±20
7	W ₈₀ Cu ₁₀ Ni ₁₀	7.9	14.92	85	1.47	W, Ni/Cu, FeWO ₄	228±28
8	W ₈₀ Cu ₁₆ Ni ₄	11.9	15.96	92	1.1	W, Ni/Cu	219±21
9	W ₉₃ Cu ₄ Ni ₃	7.9	14.85	92-82	2.03	W, Ni/Cu, FeWO ₄	547±17
10	W ₈₀ Cu ₁₆ Ni ₄	7.9	15.65	92	0.49	W, Ni/Cu	224±17
11	W ₆₀ Cu ₂₇ Ni ₁₃	7.9	15.68	99	0.59	W, Ni/Cu	287±7

Note. D is the dose of mechanical treatment; r and r/r_0 are absolute and relative densities of tablets, respectively; H_V is Wickers' hardness.

Because of balls' wearing, iron appears in the system during mechanical treatment of hard tungsten and mixtures based on it. Concentration of the iron admixture (see Fig. 2, d)

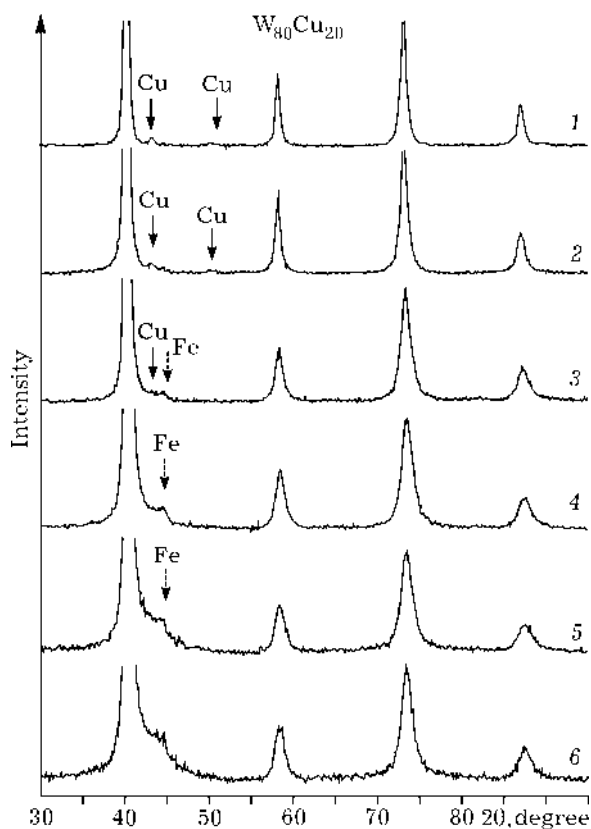


Fig 1. Diffraction patterns of W₈₀Cu₂₀ after mechanical treatment in argon at different doses. D , kJ/g: 7.5 (1), 15 (2), 36 (3), 53 (4), 90 (5), 98 (6).

increases proportionally to the time of mechanical action; at a dose of about 100 kJ/g its amount becomes equal to the amount of initial tungsten (the stoichiometry being W₄₅Cu₁₀Fe₄₅). Iron appearing in the system at the initial stage of mechanical treatment gets dissolved in tungsten causing the decrease of tungsten lattice parameter. After the saturated solid solution W(Fe) with the mass fraction of Fe ~10 % is formed, iron gets accumulated as a separate phase; because of this, at doses above 50 kJ/g the lattice parameter of tungsten remains unchanged, while the intensity of lines related to iron increases.

Mechanical treatment of W and a three-component mixture W/Cu/Ni is also accompanied by the broadening of tungsten lines and by the decrease of its lattice parameter. The character of changes of the coherent length (see Fig. 2, a) and tungsten lattice parameter (see Fig. 2, c) is similar for different activated systems (W, W/Cu, W/Cu/Ni). The rate of iron accumulation is maximal at mechanical treatment of pure tungsten and decreases while copper and nickel content of the mixture increases (see Fig. 2, d). A mutual solid solution is formed by copper and nickel during mechanical treatment of the three-component system W/Cu/Ni.

According to the data of electron microscopy, mechanically activated powder consists of grains with a mean size of 2–3 μm; however,

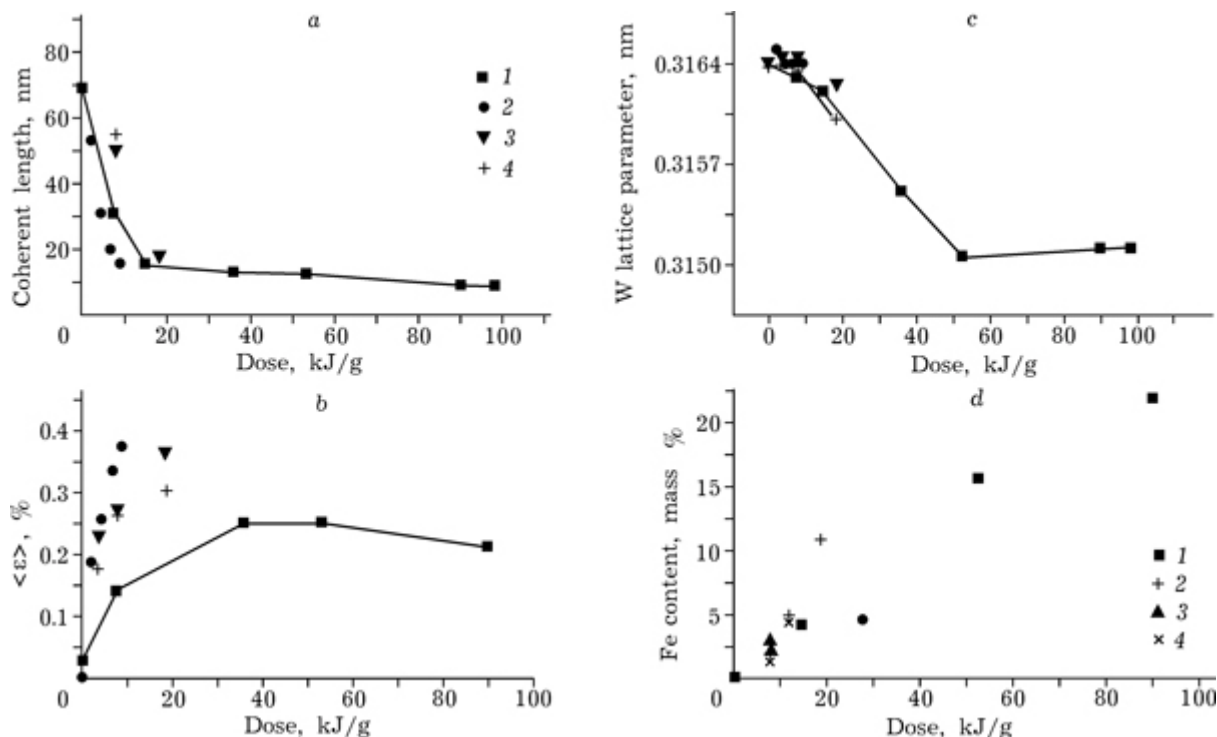


Fig. 2. The effect of mechanical treatment on coherent lengths (a), microdeformations (b), tungsten lattice parameter (c) and iron content of mixtures (d): a–c – $W_{80}Cu_{20}$ (1), W, balls of WC (2), iron balls (3), $W_{80}Cu_{10}Ni_{10}$ (4); d – $W_{80}Cu_{20}$ (1), W_{100} (2), $W_{80}Cu_{10}Ni_{10}$ (3), $W_{80}Cu_{16}Ni_4$ (4).

grains with minimal size of 0.2 μm are present. larger aggregates with the size up to 20 μm also occur. Microanalysis showed uniform distribution of elements. Since tungsten is much harder than other components, one can assume that all the tungsten grains are covered with copper and nickel layer.

So, mechanical treatment of tungsten-based mixtures is accompanied by the accumulation of defects in tungsten and copper (copper/nickel), mixing of the components, at least at the submicron level, and contamination of the system by iron.

Thermal relaxation

A series of phase transitions occur during the heating of mechanically activated tungsten-based mixtures. Diffraction patterns of the sample activated at maximal dose and containing maximal amount of iron ($W_{80}Cu_{20}$, $D = 90$ kJ/g, $[Fe] = 21.8$ mass %) after heating to different temperatures are shown in Fig. 3, a. Changes of phase composition are summed up in Table 2. The analysis of the data suggests

that the most easily formed (below 700 $^{\circ}C$) phase is the oxide $FeWO_4$. Within temperature range 700–1000 $^{\circ}C$, we observed the decomposition of the amorphous phase and the tungsten-based solid solution, and the formation of a metastable intermediate phase which was supposed to be $E9_3$ phase. Within the same temperature range, the width of tungsten lines decreases noticeably, which means that the microdeformations get annealed and coherent length increases. Finally, at temperatures 1000–1200 $^{\circ}C$, the $E9_3$ phase decomposes with the release of copper and with the formation of the Fe_7W_6 phase. Thus, in samples with high iron content, after annealing at 1200 $^{\circ}C$, along with tungsten and copper, there are two iron-containing phases ($FeWO_4$ and Fe_7W_6).

At the mass fraction of iron below 4–5 %, the annealed samples contain one iron-containing phase $FeWO_4$, as well as W and Cu (or Cu/W solid solution) (see Fig. 3, b, and Tables 1, 2). Finally, in the samples with the iron mass fraction less than 1.5 %, no iron-containing phases are formed; the samples contain two phases: tungsten and copper (solid solution copper/nickel) (see Fig. 3, c, and Table 2). In both cases,

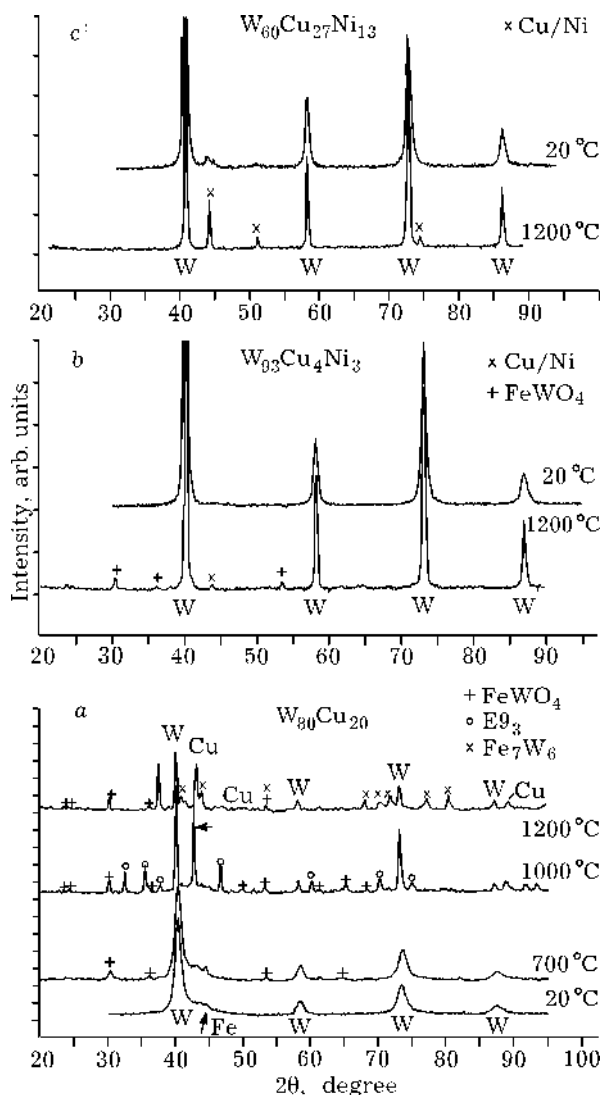


Fig. 3. Diffraction patterns of W/Cu and W/Cu/Ni after mechanical treatment and annealing. D , kJ/g: 7.9 (a, b), and 90 (c); Fe content, %: 21.8 (a), 2.03 (b) and 0.59 (c).

TABLE 2

Phase composition and tungsten lattice parameter $a(W)$ of the samples W/Cu and W/Cu/Ni after mechanical treatment and annealing

T , °C	$W_{80}Cu_{20}$ ($D = 90$ kJ/g, [Fe] = 21.83 %)		$W_{93}Cu_4Ni_3$ ($D = 7.9$ kJ/g, [Fe] = 2.03 %)		$W_{60}Cu_{27}Ni_{13}$ ($D = 7.9$ kJ/g, [Fe] = 0.59 %)	
	Phase composition	$a(W)$, nm	Phase composition	$a(W)$, nm	Phase composition	$a(W)$, nm
20	W, Fe, amorphous phase	0.3151	W, Cu/Ni	0.3163	W, Cu/Ni	0.3163
700	W, Fe, amorphous phase, $FeWO_4$					
1000	W, $FeWO_4$, $E9_3$					
1200	W, $FeWO_4$, Cu, Fe_7W_6		W, Cu/Ni, $FeWO_4$	0.3167	W, Cu/Ni	0.3167

Note. [Fe] is atomic fraction of iron impurity after mechanical treatment..

tungsten lattice parameter returns to the initial value during annealing. One may assume that this is connected with the decomposition of the solid solution of iron in tungsten.

Thus, a two-component system tungsten + copper (or copper-nickel solid solution) is formed during annealing only at low content of iron impurity. If the mass fraction of iron exceeds 1.5 %, an oxide phase $FeWO_4$ additionally appears in the system. The presence of this phase can be expected to affect agglomeration and mechanical properties of the samples. At high iron content, profound phase transformations occur in the system; they get finished at temperatures about 1200 °C. At low iron content, heating is accompanied by the decomposition of tungsten-based solid solution and annealing of the defects (coherent lengths, microdeformations) in tungsten.

Selection of conditions for mechanical activation and pressing of powders

It may be assumed that the creation of defect-bearing nano-crystal structure of metals and profound mixing of components occurring during mechanical activation will simplify agglomeration. At the same time, contamination with iron should lead to the decrease of the density. Because of this, one can assume that optimal doses of mechanical treatment are 10–15 kJ/g, when at minimal iron content defect concentration reaches nearly a limiting level (see Fig. 2, a).

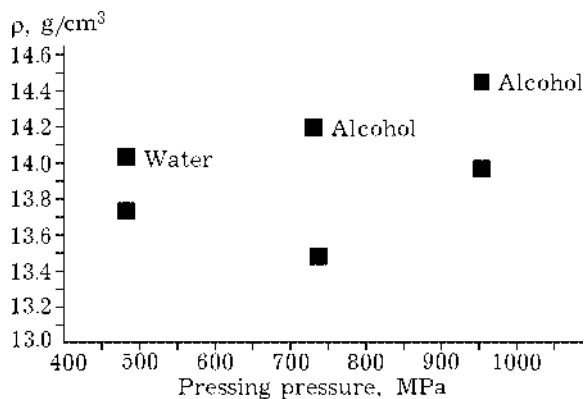


Fig. 4. Effect of pressing pressure and addition of surfactants on the density of $W_{80}Cu_{10}Ni_{10}$ tablets agglomerated at 1200 °C. $D = 7.9$ kJ/g.

In the first series of experiments, we checked the density of agglomerated tablets at high doses of mechanical treatment (the $W_{80}Cu_{20}$ system, tablets No. 1–3, see Table 1). One can see that at doses above 15 kJ/g, while dose increases the density of samples decreases. Because of this, in the further experiments, samples were mechanically treated with doses 8–12 kJ/g.

In order to choose optimal conditions for pressing, a series of experiments with the samples of one and the same mixture lot with identical composition and mechanical treatment dose was performed.

Figure 4 shows results of two series of measurements corresponding to pressing in air and pressing the mixture wetted with water or alcohol. In each group, the density of material after agglomeration is observed to increase with pressure increase from 485 to 970 MPa; density after pressing in active medium is systematically higher than after pressing in air. An increase of pressure to 1450 MPa leads to cracking of the pressed material after agglomeration. Because of this, optimal pressure for press-

ing mixture under our experimental conditions is within the range 900–1100 MPa.

So, optimal conditions for preparing tablets are mechanical treatment with a dose of about 10 kJ/g and pressing at a pressure of about 900 MPa in the presence of a surface-active medium.

Properties of agglomerated tablets

Density, porosity, structure. Results of tests of different samples are shown in Tables 1 and 3.






Table 1 shows major characteristics of the agglomerated tablets. It lists the composition of mixture, the dose of mechanical treatment, amount of iron brought during treatment, phase composition of the agglomerated tablets, experimental, theoretical and relative densities, and hardness. Table 3 shows selected data on the porosity of tablets, obtained by measuring ammonia penetration. Dark regions correspond to high permeability for ammonia, *i. e.* to high porosity.

Reference experiments show that it is impossible to obtain rather well-agglomerated tungsten samples at temperature about 1200 °C without using mechanical activation. Tablet 4 was prepared using the initial tungsten powder. One can see that it is characterized by low density and hardness (see Table 1), and high porosity (see Table 3). An attempt to obtain a dense sample at this temperature, even with ultrafine tungsten with particle size of about 500 Å as the initial material, was unsuccessful.

Mechanical treatment of tungsten and its mixtures with different additives allows to substantially activate agglomeration processes and to obtain rather well agglomerated samples at 1200 °C. For the mechanical treatment of pure

TABLE 3

Through porosity of different tablets

Tablet 4		Tablet 10	Tablet 11	Tablet 9
				

Note. Tablet numbers correspond to those indicated in Table 1.

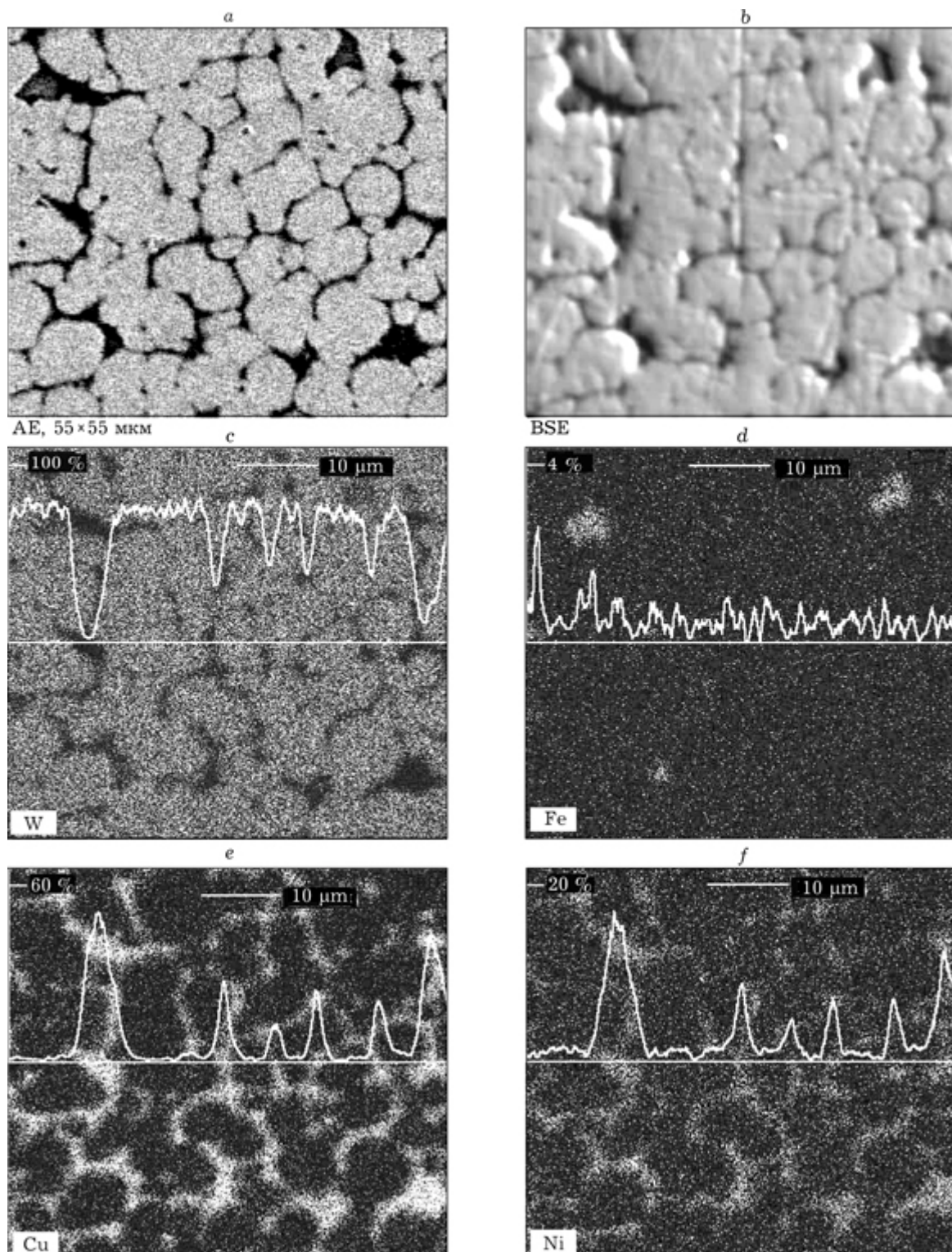


Fig. 5. Structure of agglomerated tablet W/Cu/Ni (No. 10, see Table 1) in absorbed (a) and scattered (b) electrons and characteristic radiation: W (c), Fe (d), Cu (e), and Ni (f). Observation field is the same. The distribution of the intensity of radiation of a given element when scanning along the line passing through the image centre is shown in c-f. Intensity is normalized as shown in the left upper corner (content, mass %).

tungsten, the contamination of the system with iron is maximal (tablet No. 6, see Table 1); the sample is characterized by very low density. The best results were obtained for three-component mixtures W/Cu/Ni (tablets No. 7–11, see Tables 1 and 3). In this case, we succeeded in obtaining well agglomerated samples with absolute density of 15–16 g/cm³ and relative density up to 95–97 % of the theoretical density of corresponding compositions.

Figure 5 shows an image of well-agglomerated tablet in absorbed and back-scattered electrons, as well as in characteristic W, Fe, Cu and Ni radiation. All the images were obtained from one and the same observation field. Bright points at the images of element distribution (see Fig. 5, c–f) correspond to the presence of a given element in these points. Figure 5, c–f also shows quantitative data on the distribution of elements along the line that passes through the centre of observation field. One can see that the distributions of nickel and copper repeat each other; these metals are located in sites where amount of tungsten is small.

So, a typical structure of rather well agglomerated samples is composed of tungsten grains 5–10 mm in size, surrounded by copper/nickel sublayers. The thickness of these sublayers depends on the amount of copper and nickel in the system. Results of the determination of the composition of grains and sublayers showed that copper/nickel sublayers contained a definite amount of tungsten while tungsten grains contain also copper and nickel. The presence of copper in tungsten grains can point to the existence of smaller tungsten grains coated with a thin layer of copper and nickel.

Iron content of well-agglomerated tablets is low; iron is distributed more or less uniformly, though coarse iron particles sometimes occur (see Fig. 5, d). Phase composition of this tablet is W and copper/nickel solid solution (see Fig. 3, c).

Hardness. Results of Wickers' measurements of hardness are shown in Table 1 and in Fig. 6. The hardness of the initial tungsten (not subjected to mechanical treatment) agglomerated at 1200 °C (tablet No. 4 in Table 1) is 150 kg/mm², which corresponds to literature data [12].

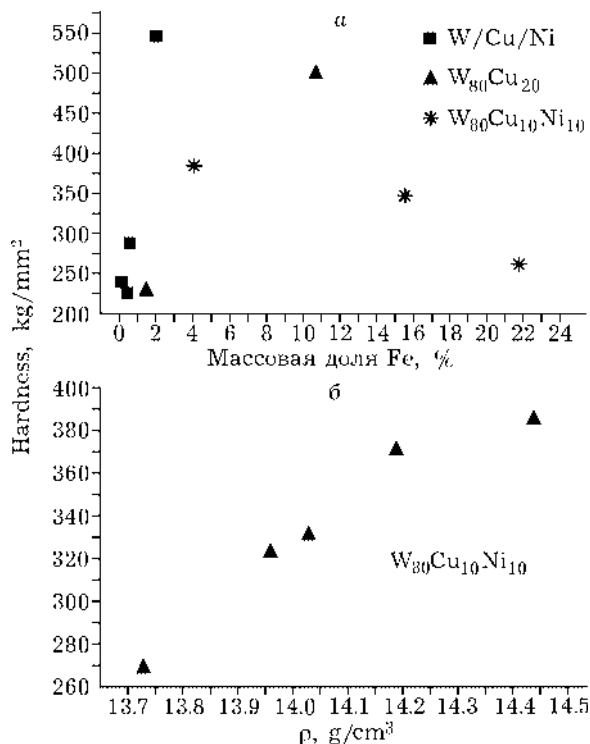


Fig. 6. Wickers' hardness of agglomerated tablets depending on iron concentration (a) and density of tablets (b). $D = 7.9$ kJ/g.

Figure 6 shows the effect of iron content and density of pressing on the hardness of tablets in three-component system W/Cu/Ni. Figure 6, a shows the dependence of hardness on iron concentration in the sample. One can see that at small iron concentrations, hardness increases with increasing [Fe], while at large ones it decreases. Maximal hardness is observed in samples with iron mass fraction within the range 3–10 %. It should be noted that maximal hardness is 500–550 kg/mm², which exceeds literature data on the hardness of agglomerated tungsten more than three times, and is much better than the hardness of cast tungsten.

The results of measurements of the hardness of tablets with similar iron content and phase composition but different density due to different pressing conditions are shown in Fig. 6, b. One can see that at identical composition the higher is density of material, the higher is its hardness.

An example of the structure of a sample with high hardness and rather high iron content is shown in Fig. 7. In this case, three phases (W, Cu/Ni and FeWO₄) were detected in the sample by means of X-ray diffraction stud-

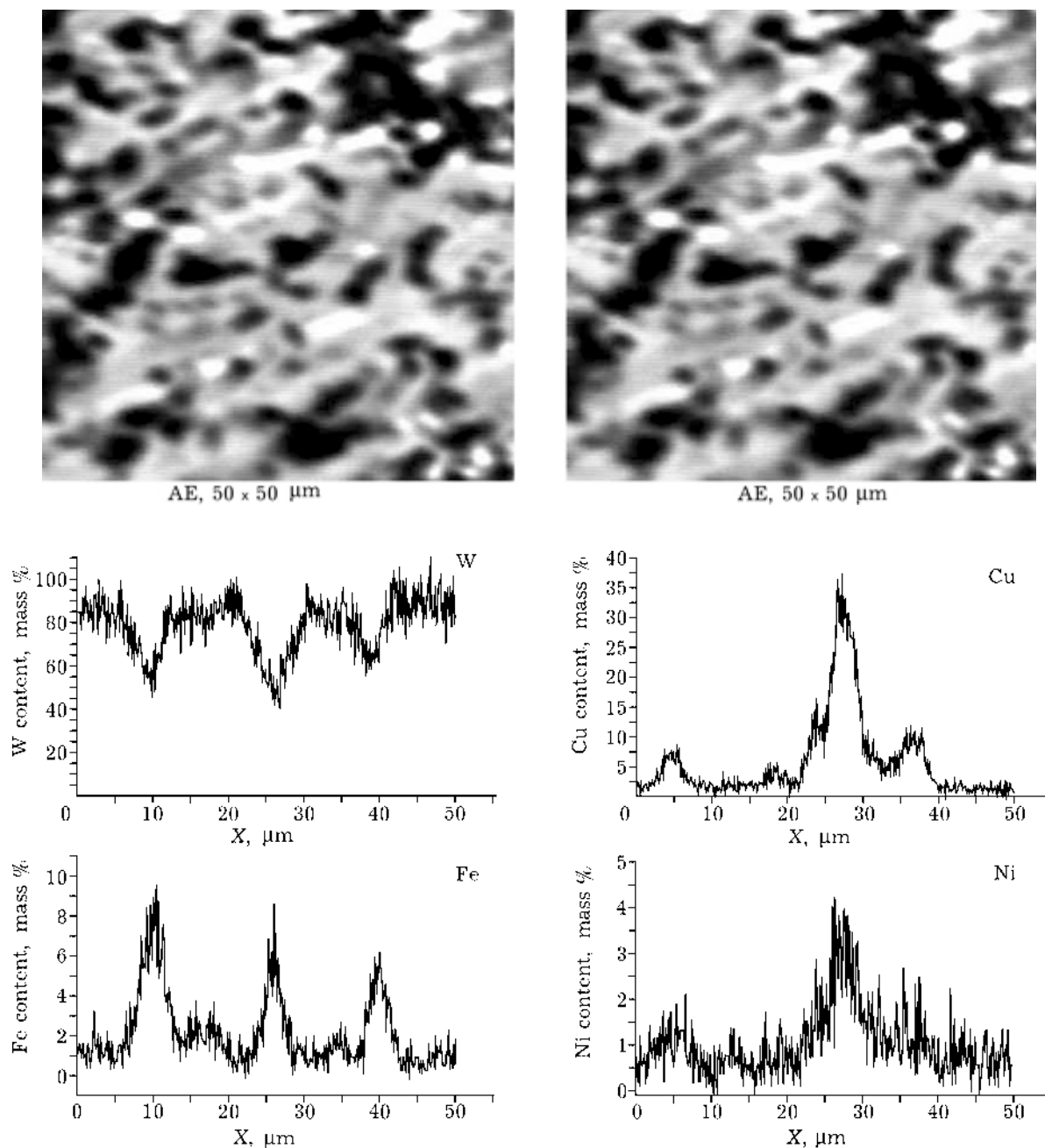


Fig. 7. The structure of the surface of W/Cu/Ni tablet with high hardness (No. 9, see Table 1): electron microscopic image and profiles of element concentrations over cross section through the middle of the image.

ies (see Fig. 3, b). Iron is distributed not uniformly but mainly in regions with a size of 5 mm. The regions of maximal iron content correspond to the regions of decreased tungsten concentrations. It may be assumed that these regions are composed mainly of the FeWO_4 phase. A detailed quantitative analysis of the local composition in the regions with increased iron content showed that the FeWO_4 phase in some cases was mixed with tungsten phase,

while in other cases with the copper/nickel phase.

So, according to the data obtained, two factors affect the hardness of the material. Introduction of iron (at its mass fraction below ~5 %) and the formation of the oxide phase FeWO_4 help to increase hardness. Another factor increasing the hardness is the increase of the density of agglomerated pressed tablets. Competition between these two factors at the in-

crease of iron mass fraction above 10 % is exhibited in the decrease of the sample hardness at very high doses of mechanical treatment.

CONCLUSIONS

The use of mechanical activation allowed us to obtain, at 1200 °C without the presence of hydrogen, well-agglomerated materials of two types: 1) with high density ($\rho = 15.5\text{--}16\text{ g/cm}^3$) and hardness $H_V = 220\text{--}280\text{ kg/mm}^2$; 2) with high hardness (H_V up to 550 kg/mm^2) and density $14.4\text{--}14.9\text{ g/cm}^3$.

The physical essence of mechanical activation from the agglomeration of this system is likely to be the formation of a homogeneous mixture of fine crystal defect-bearing tungsten (with grain size of hundreds angstroms) and sublayers of easier melting metal (copper). Heating of the system above the melting point of copper leads to the possibility of tight packing of small tungsten crystallites in the liquid sublayers of melted copper. Nickel provides a «connection» between the copper sublayers and the tungsten matrix. Copper does not interact with tungsten; nickel, on the one hand, is infinitely soluble in copper; on the other hand, it is well soluble in tungsten thus providing higher uniformity of the system.

Acknowledgements

The work has been supported by the Russian Foundation for Basic Research (Grant 01-03-32803) and Federal Program «Integration». The authors also thank A. N. Solonin for assistance in measuring hardness.

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