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Mechanocomposites for the Interacting System W–Zr*

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Abstract

Mechanocomposites composed of tungsten and zirconiums interacting with the former according to the equilibrium diagram of states were studied. The composition, structure and morphology of the samples obtained at the stages of mechanical activation are considered. The effect of the introduction of organic compounds into W/Zr mechanocomposites is studied.

Key words: tungsten, zirconium, mechanochemical interaction, mechanocomposites, carboxylic acids, poly(N-vinylpyrrolidone)

INTRODUCTION

Materials based on tungsten find a functional application due to a high density (19.35 g/cm^3) and high melting point of tungsten (3990 °C). As heavy alloys, they are used as radiation protection from X-rays and γ-radiation. This is due to their high roentgenographic density (higher by 60 % than that of lead), high radiation absorbing ability, high strength and good corrosion stability. They are widely used as weights and counterweights, for crankshaft balancing, as ammunition components, in atomic industry (crucibles to store radioactive materials). In addition, as high-temperature and corrosion-proof materials they are used in rocket technology to manufacture details operating at very high temperatures, and high-temperature work tools. Tungsten pseudo-alloys with copper and silver have the electrotechnical application for circuit breaker and switchers of high-voltage electric current.

It is impossible to obtain tungsten alloys using traditional methods because these alloys have very high melting points. A promising method to obtain these alloys is powder metallurgy: the agglomeration temperature is substantially lower and is equal to (0.6–0.8)T_m of the major metal.

To decrease the temperature of agglomeration of tungsten-based materials, minor additives of different metals with lower melting points are used, such as iron, nickel, copper etc. It is practically impossible for traditional solid-phase methods to achieve the homogeneous distribution of a lower-melting additive introduced in small amount into powder alloy. To obtain the uniform structure of the systems with a heterostructural density, it is desirable to use mechanochemistry, at that; the level of the chemical interaction of components also has a great importance. For example, it was shown in [1–5] that mechanochemically obtained tungsten composites with interacting metals (Fe, Ni)

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are characterized by rather uniform distribution of these metals. Quite contrary, it is practically impossible to achieve the uniform distribution in mechanochemically obtained tungsten composites with non-interacting metals (Cu, Ag, Sn *etc*.). It is necessary to stress that the homogeneity of component distribution in mechanocomposites is determined not only by thermodynamic parameters but also by the physical and mechanical properties of the system.

Nickel and iron are more plastic than zirconium, which also interacts with tungsten. In this connection, zirconium distribution in the mechanocomposite should differ from the distribution of iron and nickel.

It is known that the interaction of tungsten with zirconium leads to the formation of intermetallic compound W_2Zr and tungsten-based solid solutions (about 3.5 at. % at 2160 °C) and β-zirconium (about 4 at. % at 1739 °C) [6].

The authors of [7] studied the mechanochemical interaction between Fe and Zr in the system Fe/20 % Zr and showed that zirconium is distributed over the boundaries of host metal (Fe) grains with the formation of a core–shell structure in which a layer of 7–8 atoms is formed and becomes X-ray invisible. The authors suppose that this is connected with the destruction of the crystalline phase of Zr (over atoms or small clusters) and the accumulation of these atoms on the intergrain boundaries of iron in the form of thin grain-boundary interlayers.

The goal of the present work was to study the structure and morphology of composites formed during the mechanical activation of tungsten with a small amount (10 %) of zirconium, and develop mechanocomposites with the participation of organic substances (W/Zr/organic substance).

EXPERIMENTAL

Tungsten powder of PV-1 grade (TU 48-19-101–84) and zirconium of M41 grade (TU 48-4-234–84) were used to make mechanocomposites.

The mechanical activation of a mixture of initial tungsten powder with 10 mass % of zirconium was carried out in a high-energy ball planetary mill with water cooling in the atmosphere of argon. Cylinder volume was 250 cm^3, ball diameter 5 mm, powder/balls = 1 : 20, the frequency of cylinder rotation around the common axis was ~1000 min^{-1}, treatment time 10 s–8 min.

We studied the effect of the mechanochemical introduction of organic compounds on the morphology of metal mechanocomposites W/10 % Zr with 0.3 % of organic compounds: stearic acid (HSt), lauric acid (HLaur), poly(N-vinylpyrrolidone) after mechanical activation for 2 min.

To study the structure of the obtained samples, we used a MIRA/TESCAN high-resolution SEM with an attachment for micro X-ray

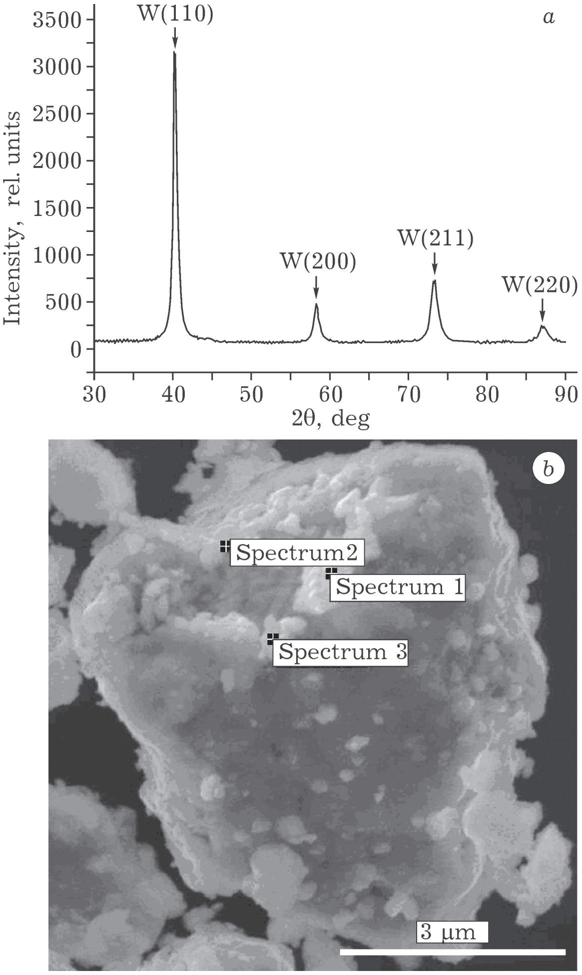

Fig. 1. Diffraction patterns of the sample W + 10 % Zr, 4 min MA (*a*), SEM image and results of MXSA of mechanocomposite W/10 % Zr (4 min MA) in the indicated points (*b*):

Spectra	Content, mass %		
	Fe	Zr	W
1	0.4	9.76	89.24
2	0.7	9.91	89.09
3	0.5	9.67	89.33

spectral analysis. The diameter of the electron probe was 5.2 nm.

X-ray structural analysis (XSA) and semi-quantitative evaluation of the products were carried out with the help of a Bruker D8 Advance diffractometer (Germany) by means of powder X-ray diffractometry in $\theta-2\theta$ configuration in the step-by-step mode with a step of 0.1°. Phase identification was carried out on the basis of diffraction pattern recorded in Cu$K_{\alpha 1}$ radiation (1.54051 Å). The structure of the resulting phases was refined according to Rietveld method using Topas software. Approximation of peak profiles was carried out using pseudo-Voigt function. Chebyshev polynomial of the 7th order was used to calculate the background.

The IR absorption spectra were recorded with an IFS-66 spectrophotometer. The samples were prepared for recording using the standard procedure.

RESULTS AND DISCUSSION

X-ray studies showed (Fig. 1, *a*) that zirconium reflections disappear almost completely from W/Zr mechanocomposite even after mechanical activation for 4 min. This may be due to the distribution of zirconium as a thin layer (several atoms thick) at the interfaces with tungsten and the formation of the core–shell structure similarly to the behaviour of Zr in the system Fe–Zr [7] where it becomes also X-ray invisible. At the same time, micro X-ray spectral analysis confirms the presence of zirconium in the mechanocomposite (see Fig. 1, *b*).

It was established by means of SEM in the characteristic radiation of zirconium and tungsten that Zr is fairly even distributed in the resulting mechanocomposite.

The lattice parameter of tungsten does not change (a = 0.3163 nm), which means that the formation of solid solutions of zirconium in tungsten are not formed under the conditions of mechanical activation. The regions of coherent scattering (r. c. s.) of mechanically activated tungsten decrease substantially (~60 nm) with respect to the initial value (~180 nm). So, the crystal structure of tungsten undergoes substantial distortions; however, they are not so strong as those observed in the interacting systems WE–Ni, W–Fe [4].

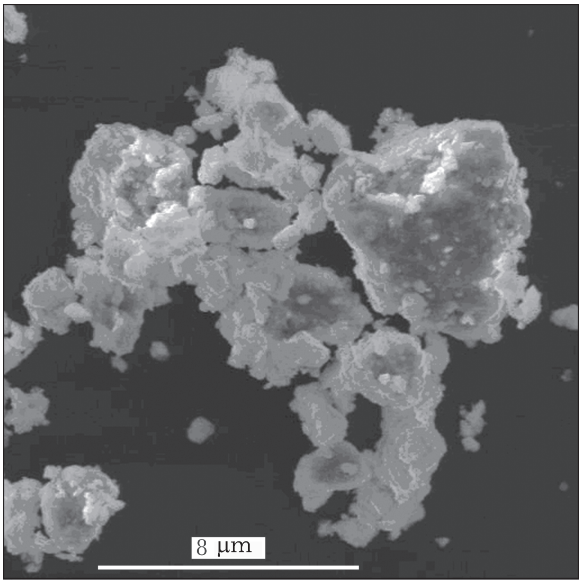

Fig. 2. SEM image of mechanocomposite W + 10 % Zr, 4 min MA.

Electron microscopic studies of mechanocomposites showed that even after mechanical activation for 4 min coarse agglomerates (d ~ 7–8 μm) start to appear (Fig. 2).

The mechanochemical introduction of carboxylic acids or polymers promotes a decrease in the aggregation of metal mechanocomposites. Carboxylic acids (stearic and lauric), and a polymer poly(N-vinylpyrrolidone) were chosen as organic substances. Stearic and lauric acids have low melting points (70 and 44.3 °C, respectively) and melt during the mechanical activation covering the surface of the metal core with a thin layer in view of their low concentration (0.3 mass %) thus preventing the formation of aggregates. It may be assumed that mechanocomposite with the structure metal core–shell with W–Zr mechanocomposite as a core is formed during the mechanochemical activation.

In order to understand whether carboxylic acids enter chemical interaction with metal composites during the mechanochemical introduction, we used IR spectroscopy. The analysis of vibrational spectra allows us to reveal how the support and the organic substance are bound with each other in the mechanocomposite, including the states that cannot be determined using the X-ray method.

It follows from the data of IR spectroscopy of W/Zr mechanocomposites with carboxylic acids that after mechanical activation for dif-

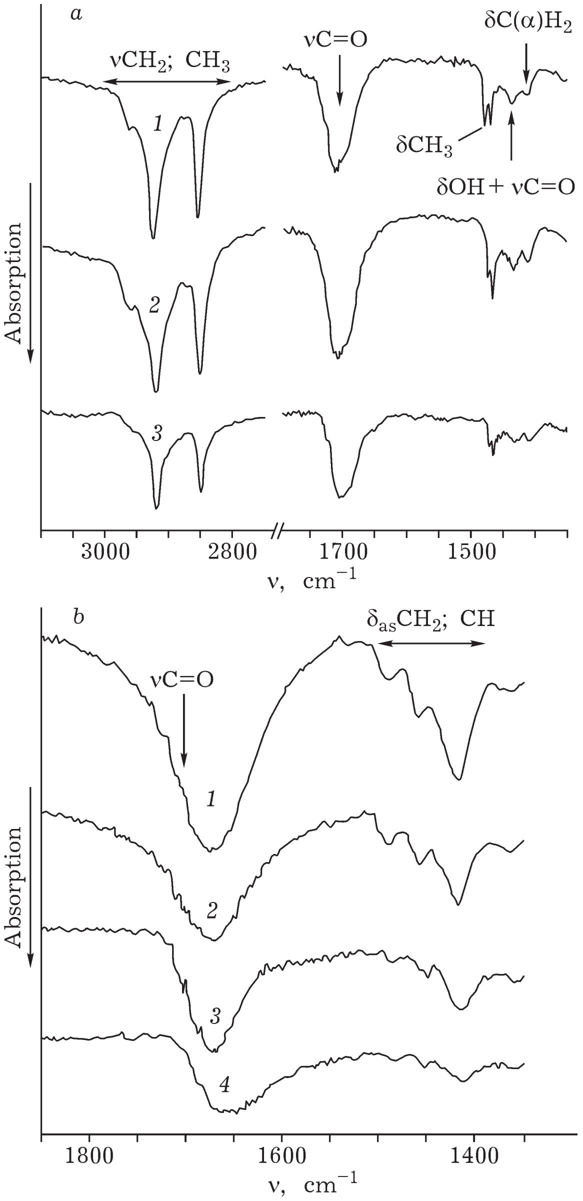

Fig. 3. IRS of mixtures: *a* – W/Zr + HSt: before *(1)* and after MA (*2*, *3*) fore 10 s (*2*) and 2 min (3); *b* – PVP + W/Zr before *(1)* and after MA (*2*–*4*) for 10 s (*2*), 1 (*3*) and 2 min (*4*).

ferent time intervals the intensity of absorption bands decreases and splitting disappears. Stearic and lauric acids do not form chemical bond (Fig. 3, *a*); the disappearance of their diffraction reflections from diffraction patterns is connected with the fact that they get spread over the surface of W/Zr composite.

One can see (see Fig. 3, *a*, curve *2*) that within the mechanical activation for 10 s the splitting of the band of asymmetric bending vibrations related to CH$_3$ groups of stearic acid (related to inversion doubling) almost completely disappears. This kind of band splitting is typical for pyramidal molecules (groups of atoms) XY$_3$ for which two mirror structures are equally probable. Mechanical activation likely causes structural distortions excluding inversion. Nevertheless, bands related to acids remain rather clear after mechanical activation for τ_a = 3 min (see Fig. 3, *a*, curve *3*).

X-ray studies (Fig. 4) showed that the joint mechanical activation with both lauric or stearic acid did not bring substantial changes to the diffraction patterns. The lattice parameter of tungsten (*a*) is conserved, and the size of coherent scattering region remains at the same level (50–60 nm). The lattice parameter refined by means of the least squares is 3.1637(3) Å for W. Microdistortion values are also similar (0.005). At the same time, according to the data of electron microscopy, the agglomeration is sub-

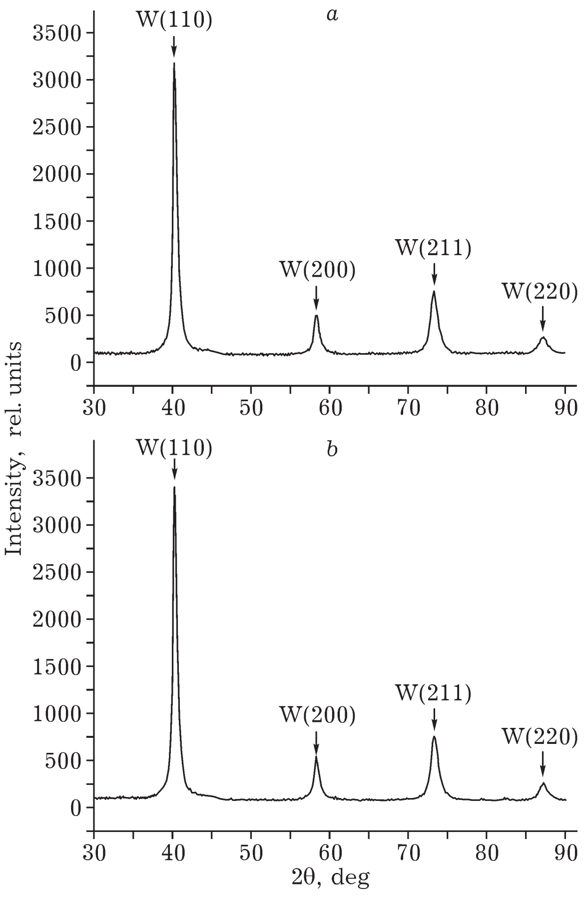

Fig. 4. Diffraction patterns of the samples with the composition W + 10 % Zr + 0.3 % HSt (*a*) and W + 10 % Zr + 0.3 % HLaur (*b*) mechanically activated for 2 min.

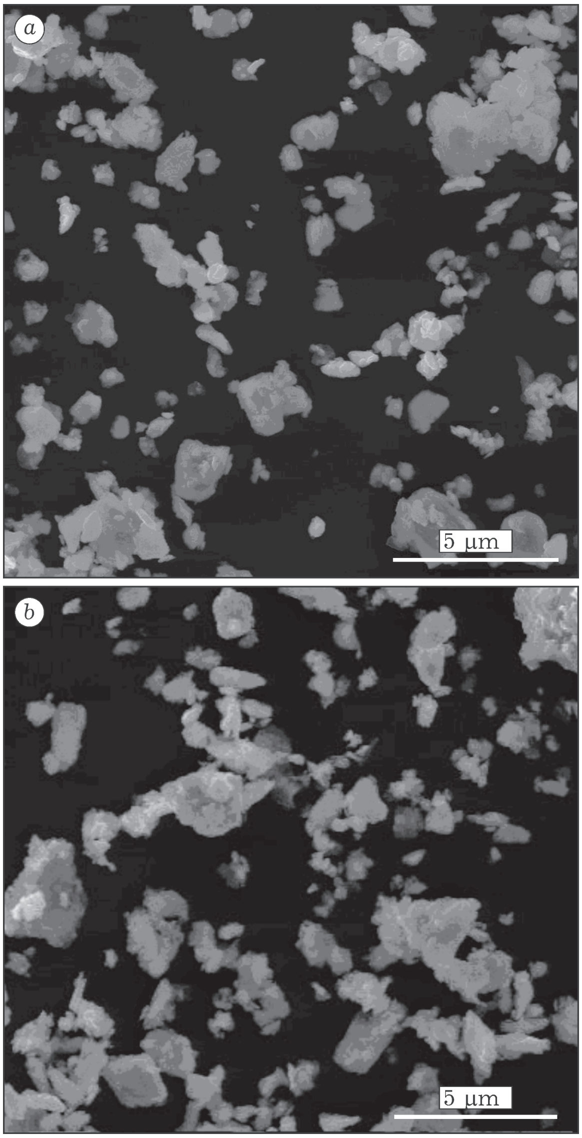

Fig. 5. SEM image of mechanocomposites after mechanical activation for 2 min: *a* – W/10 % Zr + 0.3 % stearic acid; *b* – W/10 % Zr + 0.3 % lauric acid.

stantially lower (d ~ 0.5–3 μm) in the presence of carboxylic acids (Fig. 5).

From the viewpoint of mechanocomposite formation, polymers are also interesting. In the course of the mechanical activation, they undergo mechanical destruction with the formation of short-lived free radicals [8, 9] that form a shell on the surface of metal composite. According to the IRS data, for the mechanochemical introduction of poly(N-vinylpyrrolidone), mechanical activation of a mixture of W/Zr + PVP for 40 s causes a decrease in the intensities of all the bands in the spectrum, the bands broaden but the positions of their maxima does not change (see Fig. 3, *b*). Therefore, the polymer (PVP) does not interact with the W/Zr composite.

X-ray studies showed (Fig. 6, *a*) that the size of the regions of coherent scattering for tungsten decreases by a factor of 2 (26 nm), microdistortion value decreases (0.004). According to SEM data, PVP also promotes a decrease in the agglomeration of mechanocomposites W/10 % Zr (see Fig. 6, *b*).

Results of IR spectroscopic studies of the samples with stearic, lauric acids and PVP allow assuming that the disappearance of diffraction reflections during the mechanical activation is due to melting and spreading of acids over the surface of W/Zr mechanocomposite, and chemical bonds between them are not formed.

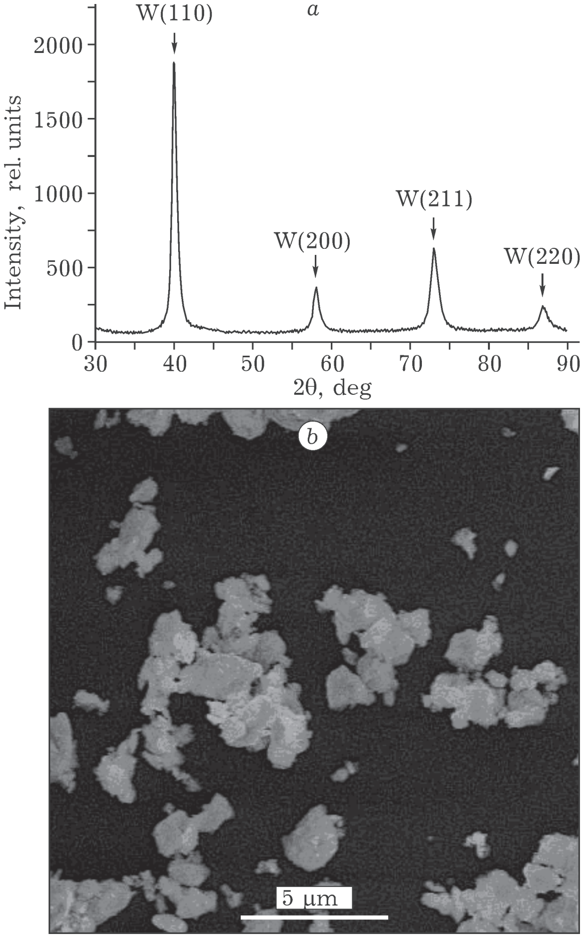

Fig. 6. Diffraction patterns of mechanocomposite W/10 % Zr + PVP (*a*) and SEM image of mechanocomposite W/10 % Zr + 0.3 % PVP (*b*).

CONCLUSION

Thus, mechanocomposites of tungsten with zirconium were obtained, and it was demonstrated that rather the uniform distribution of Zr in tungsten matrix is achieved in this interacting system in case of low Zr content (up to 10 mass %). Results of studies allow us to assume that zirconium is present on the boundaries of tungsten grains. It as been established that a decrease in the agglomeration of metal mechanocomposites is achieved with the mechanochemical introduction of acids and polymers.

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