FORMATION OF TUNGSTEN MECHANOCOMPOSITES
WITH Ta, Hf, Zr

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Abstract

The structure and morphology of composites obtained through mechanical activation of tungsten with small fractions (not more than 10 %) of tantalum, hafnium and zirconium were investigated, as well as the formation of ternary mechanocomposites with the participation of organic substances.

Introduction

Because of the high density and melting point of tungsten (d (W) = 19.35g/cm³, tₘᵦ = 3395ºC), alloys based on it are widely used in industry: in rocket manufacturing, for protection from γ-radiation, for storing radioactive preparations, for manufacturing the rotors of gyroscopes, counterbalance, milling cutters, punches, stamps, electric heaters, welding electrodes etc. However, production of hardware from these materials requires high energy consumption. To decrease it, with the conservation of the high density of tungsten alloys, it is desirable to introduce metals with lower melting points and rather high density, as well as metals that chemically interact with W.

In this work, we carried out investigations in the systems for the chemically interacting couples of metals: W-Ta (ΔHₘᵕ = - 30kJ/mol), W-Hf (ΔHₘᵕ = - 27kJ/mol) and W-Zr (ΔHₘᵕ = - 39kJ/mol) [1]. According to the equilibrium state diagrams one intermetallic compound exists in each system W-Hf and W-Zr, as well as the regions of solid solutions, while there is only a continuous series of solid solutions in the system W-Ta [2, 3, 4]. The formation of either intermetallides or solid solutions is possible on the contact surface for these systems under mechanical activation.

Methods and materials

Tungsten powder of PV 1 grade, zirconium powder of M-41 grade, tantalum TaPA, and hafnium of GFN-1 grade were used as the initial materials.

Mechanical activation of the mixtures of initial powders was carried out in a high-energy ball planetary mill AGO-2 with water cooling and in the atmosphere of argon.

The structure of the resulting samples was studied with the high-resolution scanning electron microscope (SEM) MIRA²TESCAN with an attachment for micro-X-ray spectral analysis. The diameter of the electron probe was 5.2 nm.

X-ray structural analysis (XSA) and a semi-quantitative examination of the products were carried out using the D8 Advance Bruker diffractometer (Germany) by means of powder X-ray diffraction studies in the 0-2θ configuration in the stepwise mode with a step of 0.1º.

Phase identification was performed with the diffraction patterns recorded in Cu Kα₁ radiation (1.54051 Å).
The structure of the obtained phases was refined using Rietveld's method with the help of “Topas” software. The IR absorption spectra were recorded with a IFS – 66 spectrophotometer. The samples were prepared for recording using the standard procedure. The compressibility of samples was determined on the basis of density according to the State Standard (GOST) 25280 – 90 (ISO 3927-1985) using cylindric samples 10mm in diameter, 12mm high, pressed in a steel press tool under the pressure of 400 and 600MPa. The compacted samples were sintered in vacuum at 1350°C.

**Results and discussion**

Diffraction studies showed that after the joint mechanical treatment of the compositions W-10% Hf, W-10% Ta in the ball planetary mill for 4 minutes the diffraction peaks of Hf and Ta disappear completely (Figure 1(a) and (b)).

![Diffraction patterns of the W/10%Hf mechanocomposite (a); Diffraction patterns of the W/10%Ta mechanocomposite (b); after mechanical activation for 4 minutes.](image)

**Figure 1** Diffraction patterns of the W/10%Hf mechanocomposite (a); Diffraction patterns of the W/10%Ta mechanocomposite (b); after mechanical activation for 4 minutes.

Electron microscopy showed non-uniform distribution of hafnium in the tungsten matrix (Figure 2(a) and (b)).

![The SEM image of the W-Hf mechanocomposite in the characteristic radiation of Hf (a), W(b).](image)

**Figure 2** The SEM image of the W-Hf mechanocomposite in the characteristic radiation of Hf (a), W(b).
We failed to obtain compact samples from this composite for subsequent tests. In spite of the fact that the distribution of tantalum over W-Ta mechanocomposites (Figure 3) does not look like more uniform that hafnium distribution,

Figure 3 SEM image of W-Ta mechanocomposite in the characteristic radiation of tungsten (gree), tantalum (red) and iron (blue).

Figure 4 The density of W-Ta samples before (1) and after (2) sintering at 1350 °C. Compacting pressure, MPa: A – 400; B – 600.
In the system W-10%Zr after mechanical activation for 4 minutes the reflections of Zr disappear completely, similarly to the cases of the systems of W with Hf and Ta (Figure 5).

Figure 5 Diffraction patterns of the sample W/ 10% Zr, MA for 4 min.
Figure 6 SEM image and results of MXSA of mechanocomposite W/10%Zr (MA for 4 min), in the indicated points.
This phenomena is likely connected with the distribution of zirconium in a form of disordered thin layer (5-6 atoms) over the contact surface with tungsten and the formation of a core-shell structure, similarly to the behavior of Zr in the Fe-Zr system [5], for which it was demonstrated that Zr becomes invisible in the X-ray diffraction patterns rather rapidly under the conditions of mechanical activation.
In the system W-10% Zr, coherence lengths of tungsten decrease substantially (~60 nm) in comparison with the coherence lengths of initial W (~180 nm), that is, the crystal structure of tungsten gets destroyed but the destruction is not so substantial as in the interacting systems W-Ni, W-Fe [6]. The lattice parameter for tungsten remained close to the table value (a=0.3163nm).
The micro X-ray spectral analysis confirms the presence of zirconium in the mechanocomposite ~ 10% (Figure 6).
SEM in the characteristic radiation of zirconium and tungsten demonstrated the uniform distribution of Zr in the resulting mechanocomposite (Figure 7(a) and (b)).

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Fe</th>
<th>Zr</th>
<th>W</th>
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<tbody>
<tr>
<td>Spectrum1</td>
<td>0.41</td>
<td>8.5</td>
<td>91.09</td>
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<tr>
<td>Spectrum2</td>
<td>0.62</td>
<td>10.04</td>
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<tr>
<td>Spectrum3</td>
<td>0.53</td>
<td>9.33</td>
<td>90.14</td>
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</table>

Mass.% element in mechanocomposite W/10%Zr

Figure 7 SEM in the characteristic radiation: W (a), Zr (b), after MA for 4 min (c).
Electron microscopic studies of mechanocomposites showed that large agglomerates (d~7-8μm) start to form after MA for 4 minutes (Figure 7(c)).
It is known that the introduction of carboxylic acids into tungsten mechanocomposites enhances the mold ability of samples [6]. Investigations aimed at the preparation of ternary mechanocomposites in the systems W/Zr-organic compound showed that the introduction of carboxylic acids or polymers not only improves molding but also decreases aggregation. Carboxylic acids – stearic and lauric – and polymer – polyvinylpyrrolidone – were chosen as the organic components.
We suppose that a ternary mechanocomposite is formed during mechanochemical activation, and its structure is a "core - shell" type, with the W/Zr mechanocomposite as the core. Stearic and lauric acids have low melting points (80°C and 30°C, respectively) and melt during mechanical activation; due to the wetting they get spread over the surface of the metal cores as a thin layer, as a consequence of their low concentration (0.3 mass %). The X-ray studies (Figure 8(a) and (b)) showed that the joint mechanical activation with either stearic or lauric acid does not bring any substantial changes into the diffraction patterns. The lattice parameter of tungsten is conserved, and the coherence length remains at the initial level 50-60 nm.

![Figure 8](image_url) Diffraction patterns of sample W/10%Zr/0.3%HSt (a); Diffraction patterns of sample (W/10%Zr/0.3%HLaur) (b); mechanical activation for 2 min. Lattice parameter for W is $a = 3.1637(3)$ Å.

![Figure 8](image_url) SEM image of ternary mechanocomposites after MA for 2 min: W/10%Zr/0.3% stearic acid (a); W/10%Zr/0.3% lauric acid (b). At the same time, electron microscopic studies revealed substantially lower agglomeration ($d \sim 0.5-3 \mu m$) in the presence of carboxylic acids (Figure 5(c) and (d)). Another class of organic compounds that are interesting as components for the formation of ternary mechanocomposites is the polymers for which mechano-
destruction during mechanical activation is characteristic, with the formation of short-lived radicals, which allows the formation of a shell on the surface of metal composite. For example, with polyvinylpyrrolidone as a plasticizer, X-ray diffraction studies showed (Figure 6(a)) that the coherence length of W decreases by a factor of 2 (26 nm).

According to the scanning electron microscopic data, polyvinylpyrrolidone also depresses agglomeration of mechanocomposites W/10%Zr (Figure 9(b)).

![Figure 9](image.png)

Figure 9 Diffraction patterns of the ternary mechanocomposite (W/10%Zr/0.3%PVPr) (a), SEM image of ternary mechanocomposite (W/10%Zr/0.3%PVPr) (b).

The IR spectroscopic investigation of the samples with stearic, lauric acids and polyvinylpyrrolidone allow us to assume that the disappearance of diffraction reflections during mechanical activation is connected with melting and spreading over the surface of W/Zr mechanocomposite without the formation of chemical bonds between them.

**Conclusion**

Thus, mechanocomposites of tungsten with hafnium, tantalum and zirconium were obtained. It was demonstrated that rather uniform distribution of Zr in the case of its content up to 10 mass % was achieved in the system W/Zr.

Investigation results allow us to assume that zirconium, hafnium and tantalum, similarly to previously studied plastic metals (Ni, Fe) [7], are located at the interfaces with tungsten. It was shown that a decrease in the level of agglomeration of metal mechanocomposites is achieved through the mechanochemical preparation of ternary composites, for example W/Zr/organic substance.

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Referenses