REFRACTORY AND CERAMIC MATERIALS

EFFECT OF MOLYBDENUM ADDITIONS ON THE MICROSTRUCTURE AND PROPERTIES OF WC–W$_2$C ALLOYS

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The paper examines how additions of 5, 10, and 20 wt.% molybdenum influence the structure, stress–strain state, phase composition, and size of phase components in WC–W$_2$C alloys. It is found that 5 wt.% molybdenum leads to 30% increase in the microhardness and twofold to threefold increase in the wear resistance of cast tungsten carbide compared to the alloy without additions. Higher molybdenum content of the WC–W$_2$C alloys changes the phase composition and increases compressive stresses in the W$_2$C matrix phase and tensile stresses in WC, (Mo, W)$_2$C, and Mo$_2$C inclusions.

***Keywords**: tungsten carbide, molybdenum, stress, microstructure, microhardness, wear resistance.*

INTRODUCTION

An important task of mechanical engineering is to increase the longevity and reliability of machines [1]. Cast tungsten carbide exhibits a unique combination of mechanical properties: high strength, hardness, and elastic modulus. Cast tungsten carbide is a eutectic alloy of WC and W$_2$C (78–80 wt.% W$_2$C, 20–22 wt.% WC, and 3.8–4.2 wt.% C) with a melting point of 2735°C. Its structure represents a matrix of tungsten semicarbide W$_2$C pierced with elongated tungsten monocarbide WC grains. The WC grains are 2–5 μm in size, ensuring high hardness, strength, and wear resistance of the alloy.

Tungsten monocarbide combines adequate hardness (92−94 HRA), plasticity, and elastic modulus (710 GPa) and is capable of resolidifying in molten metals. In this connection, it is widely used as the main component of cermet alloys. Tungsten monocarbide has two crystallographic modifications: hexagonal α-WC (lattice parameters $a = 0.2906$ nm and $c = 0.2839$ nm) and face-centered cubic β-WC ($a = 0.4220$ nm), remaining stable at temperatures above 2525°C [2]. Both phases exist in the range 2525–2755°C. The α-WC phase has no homogeneity range, so deviation from stoichiometric composition leads to W$_2$C or graphite. When heated above 2755°C, α-WC decomposes to form carbon or β-WC. This phase is described as β-WC$_{1−x}$, where $0 \leq x \leq 0.41$, and has a wide homogeneity range, narrowing with temperature decrease.

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Tungsten semicarbide W_2C is also of technical significance. It is a high-temperature compound forming fine-grained eutectic alloys with tungsten monocarbide. Tungsten semicarbide has hexagonal syngony (lattice parameters a = 0.29948 nm and c = 0.47262 nm, Z = 1). At temperatures above 1427°C, it transforms to a cubic phase (a = 0.4220 nm, Z = 4). Tungsten semicarbide is a brittle material (hardness ~90 HRA and elastic modulus 428 GPa), which possesses high wear resistance and is used in surfacing coatings for high-wear machine parts.

Spherical eutectic $WC–W_2C$ powders show record-high abrasive wear resistance at moderate and shock loads [3]. They are components of wear-resistant materials used to fabricate and repair drilling, oil, mining, metallurgical, and chemical equipment.

Tungsten carbide alloy powders produced by centrifugal atomization are known [3] to have regular spherical particles and high mechanical characteristics, resulting from the formation of a uniform fine structure with grains being evenly distributed over the $WC–W_2C$ alloy matrix.

It is established [4] that higher cooling rates lead to higher stresses in composite components: compressive stresses in the W_2C matrix phase and tensile stresses in the WC reinforcing phase. With increasing cooling rate, the coherent scattering domains decrease from 50.8 to 14.6 nm for W_2C, from 26 to 12.3 nm for WC, and from 15.5 to 9 nm for WC_{1-x}, i.e., the microstructure is refined.

Since doping is one of the factors that may influence the phase composition, stresses, structural refinement, and properties of cast tungsten carbide, our objective is to examine the effect of molybdenum additions on the structure, phase composition, sizes of phase components, and stress–strain state of the $WC–W_2C$ alloy.

EXPERIMENTAL PROCEDURE

Spherical $WC–W_2C$ alloy powders were produced by centrifugal atomization of cylindrical rods at a cooling rate of 10^5 deg/sec. Argon was a plasma-supporting gas. The melt was atomized by centrifugal forces from the rod end as 50–400 μm droplets that solidified in air. The chamber was cooled with water. The $WC–W_2C–Mo$ alloy powders had spherical particles.

We employed a 106I scanning electron microscope for metallographic analysis of the alloys. X-ray diffraction studies of the phase composition, stress–strain state, and size of coherent scattering domains were conducted using a RIGAKU ULTIMA IV diffractometer with Rietveld and Reference Intensity Ratio (RIR) techniques in Cu-$K_{\alpha_{1,2}}$ radiation, $\lambda_{Cu-K_{\alpha1}}$ = 0.1541 nm. The X-ray θ–2θ diffraction patterns were used to determine the phase composition and stresses of the alloys involving shifts of diffraction peaks [5]. Stresses in the W_2C phase were evaluated from reflections in the range 2θ = 65–145°. Despite possible deviations in elastic modulus for reflections, the magnitude of their shift leads to almost the same stresses at different lines, probably because of averaging to 3–5%. Besides stresses in the alloys, the shift of reflections may also result from point defects. Hence, we defined the shift of reflection as stress contribution.

The alloy microhardness was determined with a PMT-3 microhardness meter at a load of 150 g on the diamond pyramid.

The abrasive resistance of spherical particles of molten tungsten carbides was tested using an NK-M machine and abrasive quartz sand with 0.05–0.5 mm particles. The test samples were cylinders 10 mm in diameter with a copper–nickel–manganese matrix alloy (60 Cu, 20 Ni, and 20 vol.% Mg). Wear of the samples was evaluated from their weight loss. The samples were tested at a specific load of 0.5 Pa, friction speed of 0.58 m/sec, and sliding distance of 3500 m.

EXPERIMENTAL RESULTS

The $WC–W_2C$ microstructure is represented by a matrix of tungsten semicarbide W_2C pierced by elongated WC grains (Fig. 1a). Melt solidification results in a cellular structure whose dendritic grains emerge from columnar elements of regular shape with side branches that solidify at about 90° angle and with finer, randomly oriented branches of tungsten monocarbide. This structurization process suggests that increase in the solidification rate primarily changes the concentration overcooling, causing the melt to deviate from equilibrium composition according
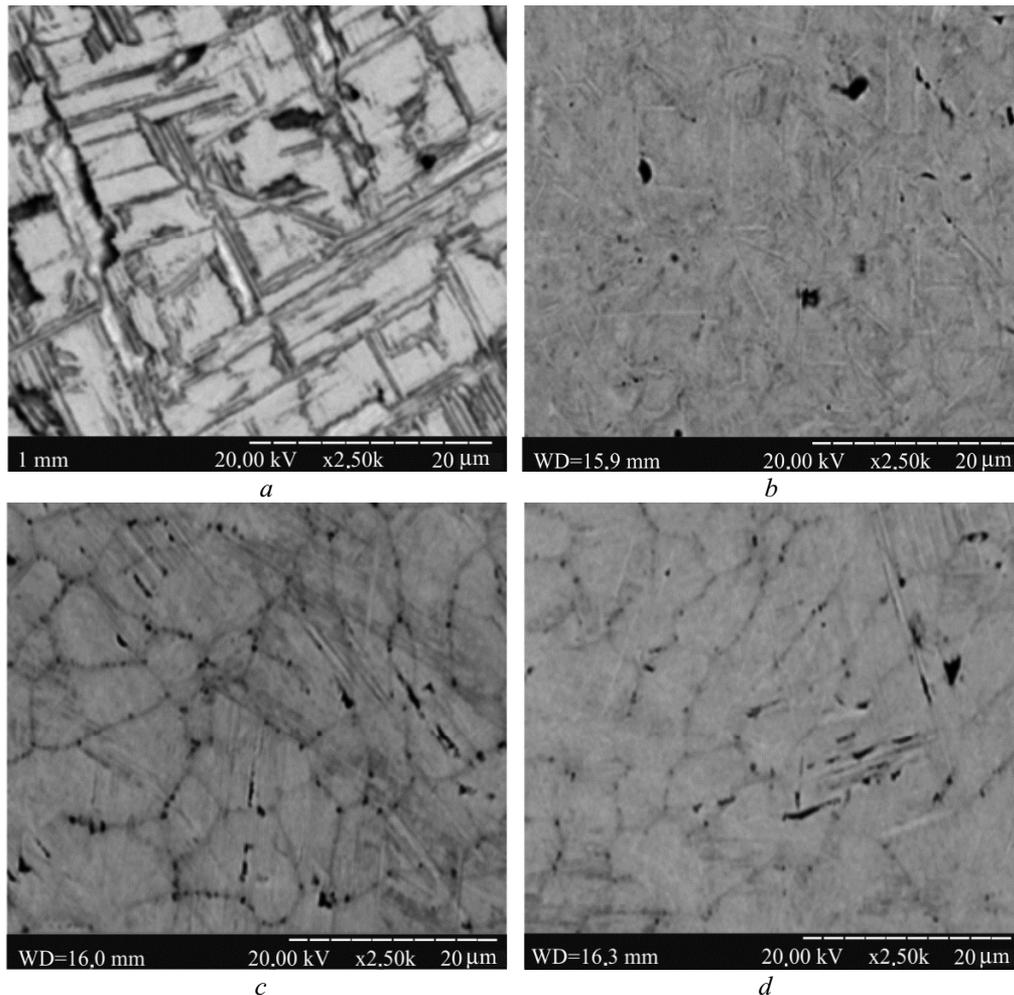
Fig. 1. Microstructure of the WC–W$_2$C alloys (*a*) with additions of 5 (*b*), 10 (*c*), and 20 (*d*) wt.% Mo

to the phase diagram. Excess carbon forms before the solidification front and leads to dendritic growth of tungsten monocarbide, which changes to cellular growth with increasing temperature gradient in the melt.

Figure 1*b–d* shows the microstructures of WC–W$_2$C with molybdenum additions. Their analysis revealed a strengthening mesh with inclusions of complex carbide (Mo, W)$_2$C being located at its boundaries. With 5 wt.% Mo, the alloy has a greater amount of the complex Mo–W carbide phase evenly distributed over the material. The complex (Mo, W)$_2$C phase is located at grain boundaries, thus forming a grained structure. Therefore, the lower the content of addition, the higher the amount of the complex carbide in the alloy and, as a result, the finer the structure.

With higher molybdenum content, temperature of the melt decreases, so it takes less time to melt the material to be poured into a mold and to form the alloy, and the amount of tungsten monocarbide that has not reacted with molybdenum increases. That the tungsten monocarbide phase is absent in the 5 wt.% Mo–WC–W$_2$C alloy may be due to inadequate carbon content in the chemical interaction zone. Increase in the molybdenum content to 10 wt.% leads to the formation of a cellular structure with hexagonal domains of irregular shape and a clear mesh of complex Mo–W carbide. With 20 wt.% Mo, the alloy shows a cellular structure as well, but with lower content of complex Mo–W carbide and more ordered domains separated by this carbide.

Analysis of the X-ray θ–2θ diffraction patterns (Fig. 2) for the WC–W$_2$C alloy with molybdenum additions shows the formation of two basic phase components: W$_2$C and (Mo, W)$_2$C. The number and presence of phases depend on the molybdenum content of the WC–W$_2$C alloy. With 5 wt.% Mo, the alloy has two phases: 89 wt.% W$_2$C and 11 wt.%. (Mo, W)$_2$C. When molybdenum content increases to 10 wt.%, 4 wt.% WC emerges in the alloy
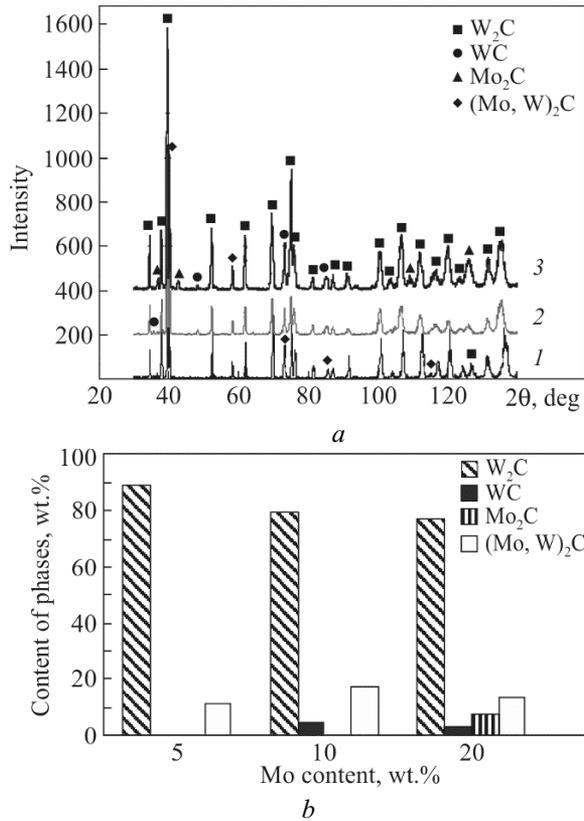
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Fig. 2. X-ray θ–2θ diffraction patterns showing distribution of phases in the WC–W$_2$C alloy (*a*) with additions of 5 (*1*), 10 (*2*), and 20 (*3*) wt.% Mo, and content of phases (*b*)

and the amount of W$_2$C decreases to 79 wt.% and that of complex W–Mo carbide increases to 17 wt.%. With up to 20 wt.% Mo, the alloy contains 8 wt.% Mo$_2$C besides the above phases, and the W$_2$C matrix phase decreases to 77 wt.%, WC to 3 wt.%, and complex W–Mo carbide to 12 wt.% (Fig. 2*b*). With higher molybdenum content, the latter phase seems to fail to mix and fully interact with the melt, which leads to higher WC content. It should be noted that addition of 5 wt.% Mo results in the formation of two phase components; i.e., there are only two types of phase interaction, allowing greater strength at boundaries between the components. Even cast tungsten carbide without additions has three phase components [4], and their number increases with higher molybdenum content.

We established the average integral microhardness of the WC–W$_2$C alloys with and without molybdenum additions (Fig. 3) by hardness measurement. The highest hardness and strength are known [6] to be exhibited by materials representing a matrix of one refractory compound reinforced by single-crystalline fibers of another refractory compound. The highest microhardness of WC–W$_2$C (with 5 wt.% Mo) is 36 GPa, which is 30% higher
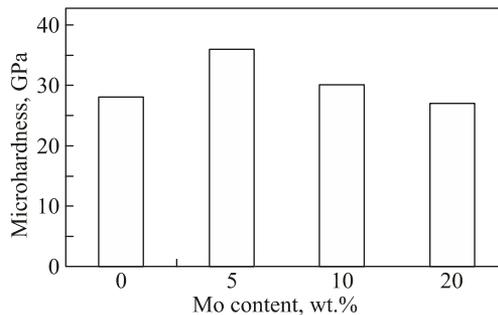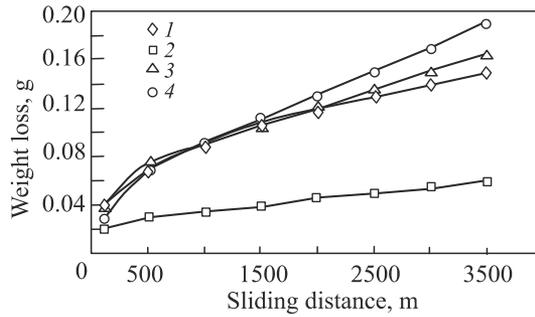

Fig. 3. Microhardness of the WC–W$_2$C alloys

Fig. 4. Wear resistance of the WC–W$_2$C alloy without additions (*1*) and with 5 (*2*), 10 (*3*), and 20 (*4*) wt.% Mo

than that of cast tungsten carbide without additions. In turn, addition of 10 wt.% Mo increases the microhardness by 8% and up to 20 wt.% Mo decreases it by 4% compared to cast tungsten carbide without additions.

Figure 4 shows the wear resistance of cast tungsten carbide and associated alloys. Addition of 5 wt.% Mo increases the wear resistance of spherical particles. The weight loss of this alloy during friction decreases at the beginning of test but increases for the alloys with 10 and 20 wt.% Mo. The weight loss becomes constant after a sliding distance of 1000 m and is the lowest for the alloys with 5 wt.% Mo. Moreover, additions of 10 and 20% Mo decrease long-term wear resistance of spherical particles.

Many factors may influence the microhardness and strength of materials: shape and size of inclusions and their location in the matrix, phase composition, number and mechanical characteristics of the phases, as well as mechanical stresses induced in phase components (Fig. 5).

Low-temperature strength is determined by elastic characteristics, grain size, presence of grain boundaries, micropores, and other defects, representing stress concentrators and accumulations of dislocations whose combination leads to cracks. Fracture occurs by cleavage, mainly at grain boundaries.

The stresses also result in a shift of interference lines, which is the most evident in reflections at large Bragg angles. The θ–2θ diffraction patterns for the WC–W$_2$C alloy with molybdenum additions show a shift of reflections. Stresses in surface layers of the sample in the direction perpendicular to its surface ($\sigma_1 + \sigma_2$) are determined as:

$$(\sigma_1 + \sigma_2) = -\frac{E}{\mu} \cdot \frac{\Delta d}{d_{us}},$$

where E is elastic modulus (Young's modulus), μ is Poisson's ratio, and Δd is change in spacing ($\Delta d = d_{us} - d_s$) between atomic planes parallel to the sample surface in unstressed (d_{us}) and stressed (d_s) states.
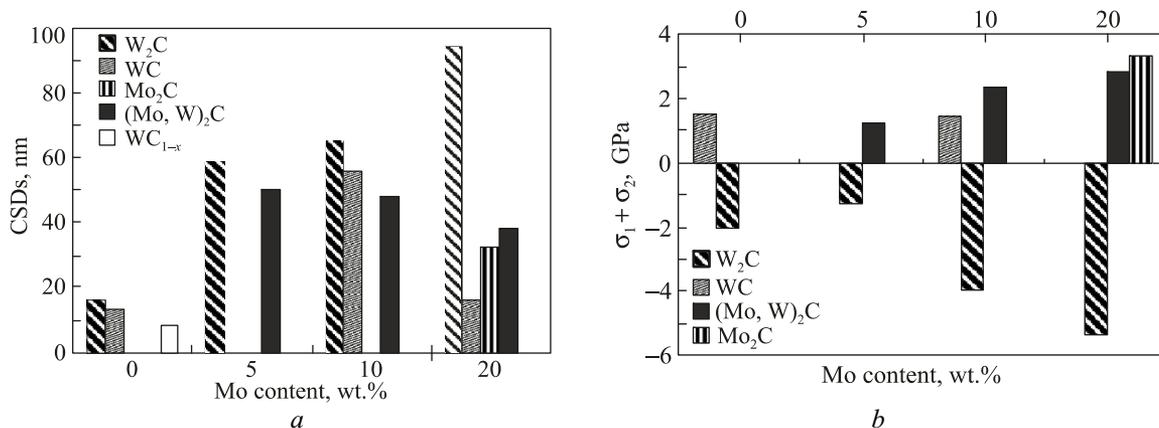

Fig. 5. Effect of molybdenum on the size of coherent scattering domains (CSDs) (*a*) and stresses in phase components (*b*) of cast tungsten carbide with and without additions

Stresses in the W_2C phase are compressive and constitute 1.2, 4, and 5.5 GPa for 5, 10, and 20 wt.% Mo, respectively. Stresses in WC, Mo_2C, and $(W, Mo)_2C$ inclusions are tensile. With 5 and 10 wt.% Mo, stresses are 1.2 and 2.3 GPa in the $(Mo, W)_2C$ phase, respectively, and 1.5 GPa (with 10 wt.% Mo) in the WC phase. When molybdenum content of the alloy increases to 20 wt.%, stresses in the $(Mo, W)_2C$ phase are 2.9 GPa and those in Mo_2C are 3.3 GPa. Hence, higher molybdenum content of the $WC–W_2C$ alloys increases compressive stresses in the W_2C matrix phase and tensile stresses in WC, Mo_2C, and $(W, Mo)_2C$ inclusions.

The alloys mainly fail under tensile stresses. Compressive stresses in turn reduce the sensitivity of materials to stress concentrators and increase their fatigue strength. Despite possible deviations in elastic modulus for reflections, the magnitude of their shift leads to almost the same stresses at different lines. Besides stresses, the shift of reflections may also result from lattice defects of the first kind according to [5], where stresses are rapidly relieved with a distance from defects. These may be point defects (pores, interstitial atoms, etc.).

CONCLUSIONS

It has been established that $WC–W_2C$ alloys with molybdenum additions have a cellular structure with hexagonal grains that are randomly distributed over the material. Complex $(Mo, W)_2C$ carbide forms at grain boundaries.

Molybdenum additions of 5 to 20 wt.% to the $WC–W_2C$ alloys increase compressive stresses in the W_2C matrix phase and tensile stresses in WC, Mo_2C, and $(W, Mo)_2C$ inclusions, decrease the coherent scattering domains for WC and $(W, Mo)_2C$ inclusions and increase those for the W_2C matrix phase, as well as decrease the content of W_2C and increase that of WC and $(W, Mo)_2C$. With 20 wt.% Mo, Mo_2C forms besides the above phases.

The microhardness of cast tungsten carbide with molybdenum additions shows an extreme composition dependence. The 5 wt.% $Mo–WC–W_2C$ alloy has the maximum hardness and twofold to threefold higher wear-resistance. This agrees well with change in the phase composition, stress–strain state, and morphology of the composite phase components.

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