REFRACTORY AND CERAMIC MATERIALS

THE STRUCTURE AND PROPERTIES OF THE MOLYBDENUM-DOPED WC–W$_2$C EUTECTIC ALLOY DEPENDING ON THE PRODUCTION METHOD

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Scanning and transmission electron microscopy and X-ray diffraction have revealed that the eutectic 5 wt.% Mo-doped WC–W$_2$C alloy changes its cooling rate in the melt crystallization process when produced in the Tammann furnace, by electron-beam evaporation, and by centrifugal sputtering. This increases the size of phase components by a factor of 2 to 2.5, decreases the number of phases, and reduces compressive stresses (in the W$_2$C matrix) and tensile stresses (in the WC, Mo$_2$C, and (W, Mo)$_2$C inclusions) to 50% and more. These changes result in one and a half times higher hardness and two times higher strength of doped relit, which is widely used for surfacing machine parts and mechanisms operating in conditions of abrasive wear and high dynamic loads.

Keywords: tungsten carbide, molybdenum, doping, cooling rate, stress–strain state, microhardness.

INTRODUCTION. LITERATURE REVIEW. PROBLEM STATEMENT

Ceramic materials, the eutectic WC–W$_2$C tungsten carbide alloy called relit being among them, have high hardness and are rather brittle [1]. Moreover, relit, consisting of W$_2$C (78–80 wt.%) and WC (20–22 wt.%), possesses the highest wear resistance and strength as it has an extremely high elastic modulus (E) of 710 GPa (for example, steel has E = 220 GPa) and a melting point of 2735°C. Plasma spraying with use of an electrically neutral relit additive produces a matrix consisting of a eutectic (solid solution of tungsten in iron) and complex iron–tungsten carbides [1–3]. The phases result from the dissolution of reinforcement relit grains combined with the saturation of the matrix melt with carbon and tungsten. Metallographic studies of both deoxidized and nondeoxidized matrices revealed a significant number of secondary iron–tungsten carbides 20–30 μm in size and a coarse eutectic making the matrix brittle [4]. This in turn proves that deoxidation alone is insufficient for depositing a composite alloy with required service properties.

Carbon formed in the dissolution of reinforcement relit grains is the main source of phases that exert a negative effect: secondary iron-tungsten carbides and a coarse eutectic. Hence, a promising way for the matrix to acquire the required structural arrangement is to dope the melt with elements that have greater affinity to carbon

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than iron and tungsten do and can take carbon from iron–tungsten carbides to form their own carbide but with a smaller specific volume. In terms of decreasing affinity, a number of elements (in particular, boron, titanium, niobium, vanadium, molybdenum, and chromium) that are favorable for forming the matrix and its structural components can be considered.

The choice of doping elements is also determined by the potential to prevent the formation of pores. Hence, boron carbide and titanium diboride that could be used to dope relit for their affinity to carbon form spherical pores, located mainly inside the particles. The pores emerge most likely because of oxygen present on the particles of these doping additions. Moreover, the use of boron carbide and titanium diboride results in numerous phase components and thus in several types of phase interactions with different strength at the boundaries between components, affecting the most important properties of relit. On the contrary, fewer phase components and homogeneous microstructure are peculiar to relit doped with niobium, vanadium, molybdenum, or chromium. The microstructure and morphology of these alloys correspond to the dendritic growth conditions and are characterized by lamellar phases, whose thickness depends on the type of doping element. The lamella thickness decreases and alloy microstructure becomes more homogeneous with increasing content of this element. In the alloys with molybdenum and chromium additions, the lamellas become so fine that microstructural phase inhomogeneity can hardly be revealed with an optical microscope [5].

The methods employed to produce tungsten carbides, which primarily differ by the cooling rate, also significantly influence the phase composition and microstructure of relit. Hence, relit structures were examined versus the cooling rates to find out [6] that centrifugal atomization at a cooling rate of $\sim 10^5$ °C/sec [7] produced a homogeneous fine crystalline structure without visible surface defects. In turn, higher cooling rates allowed the hardness of relit to be increased by a factor of 1.5 to 1.7, the hardness improvement effect being greater for the doped alloys than for the undoped ones [6]. The ceramic crystallization process changes when relit is doped with carbides that significantly decrease the melting point. Hence, when the crystallization range decreases, the process becomes shorter. This influences the microstructural state of ceramic phase components and the rate at which gaseous products resulting from interaction between the components and desorbed admixtures are removed and thus decreases the mechanical characteristics of doped relit.

Therefore, the choice of doping addition and crystallization conditions allows the phase composition, microstructure, porosity, and other properties of relit to be controlled. The use of molybdenum as a doping addition meets the conditions for both carbon affinity and oxygen cleanliness. In addition, molybdenum doping changes the crystallization range and temperature and hence permits the cooling rate to be controlled.

Our objective is accordingly to establish how the structure and properties of the eutectic molybdenum-doped WC–W_2C alloy depend on the method of its production.

EXPERIMENTAL PROCEDURE

To produce molybdenum-doped WC–W_2C tungsten carbides (relit), we ground ingots molten in the Tammann furnace at 3100°C and compacts molten by electron-beam evaporation and centrifugal sputtering. The cooling rate is about 10^2 °C/sec in the Tammann furnace, about $\sim 10^3$ °C/sec in electron-beam evaporation, and almost two orders of magnitude higher in centrifugal sputtering [7, 8].

A tungsten carbide alloy electrode connected to the holder was installed into the chamber filled with inert gas (argon). The rod end piece was melted with a plasma-arc discharge. Argon was the plasma gas. Under the action of centrifugal forces, the melt was ejected from the rod end piece as droplets and crystallized in air. The rod moved upwards as it melted. The chamber surface was cooled with water. The molybdenum-doped eutectic WC–W_2C alloy powder had spherical particles.

The microstructure of the alloys was examined employing a scanning electron microscope (REM-106I) and a transmission electron microscope (JEM-1200X). X-ray diffraction was used to study the phase composition and coherence scattering domain sizes with a RIGAKU ULTIMA IV diffractometer applying the RIR, Rietveld, and other methods in Cu-K_{α_1} radiation, where $\lambda_{\text{Cu-}K\alpha_1} = 0.1541$ nm. Stresses in the phase components of doped relit

were determined by the diffraction peak shift method [9]. The alloy microhardness was examined with the Vickers hardness test using a PMT-3 microhardness meter with an indenter load of 150 g.

EXPERIMENTAL RESULTS AND DISCUSSION

According to the phase diagram and our previous studies [10], the molybdenum-doped relit alloys consist of tungsten semicarbide, tungsten monocarbide, complex W–Mo carbide, and molybdenum carbide. The content and presence of phase components depend on the molybdenum amount in the alloy and its cooling rate. When the molybdenum content is ~20 wt.% and cooling rate is ~10^5 °C/sec, the alloy contains four phases: W_2C (to 77 wt.%), WC (to 3 wt.%), $(Mo, W)_2C$ (to 12 wt.%), and Mo_2C (to 8 wt.%). When the molybdenum content decreases to ~10 wt.% and cooling rate is ~10^5 °C/sec, the number of phases reduces (to three) and the content of each phase increases as follows: W_2C to 79 wt.%, WC to 4 wt.%, and $(Mo, W)_2C$ to 17 wt.%. When the molybdenum content is 5 wt.% and cooling rate is ~10^2 °C/sec, the alloy contains three phases, such as W_2C, WC, and Mo_2C, without complex $(Mo, W)_2C$ carbide. Instead, when the cooling rate increases to ~10^3 °C/sec, the phase composition changes and the amount of W_2C becomes higher, while the contents of WC and Mo_2C become lower. A cooling rate of ~10^5 °C/sec leads to a substantial change in the phase composition of doped relit, resulting in two phases: 89 wt.% W_2C and 11 wt.% $(Mo, W)_2C$. This leads to two types of phase interactions, making it possible to promote higher strength at the boundaries between components (Fig. 1).

Depending on the production conditions, even undoped relit can contain three phases (if there is no WC tungsten monocarbide phase, there may insufficient carbon in the chemical interaction area).

Metallographic analysis (Fig. 2) revealed that a cellular structure emerged in the melt crystallization process. In this structure, dendritic grains formed from columnar elements of regular shape: lateral branches crystallized at angles close to 90° and finer WC branches were located randomly. This structurization indicates that
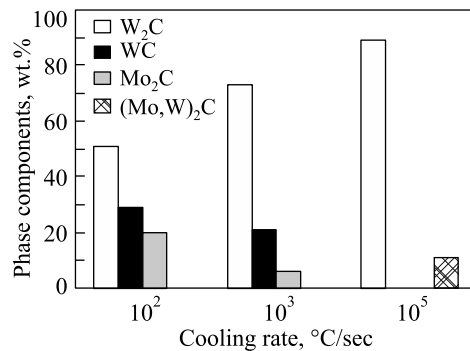

Fig. 1. Effect of the cooling rate on the content of phase components in the 5 wt.% Mo–WC–W_2C alloy
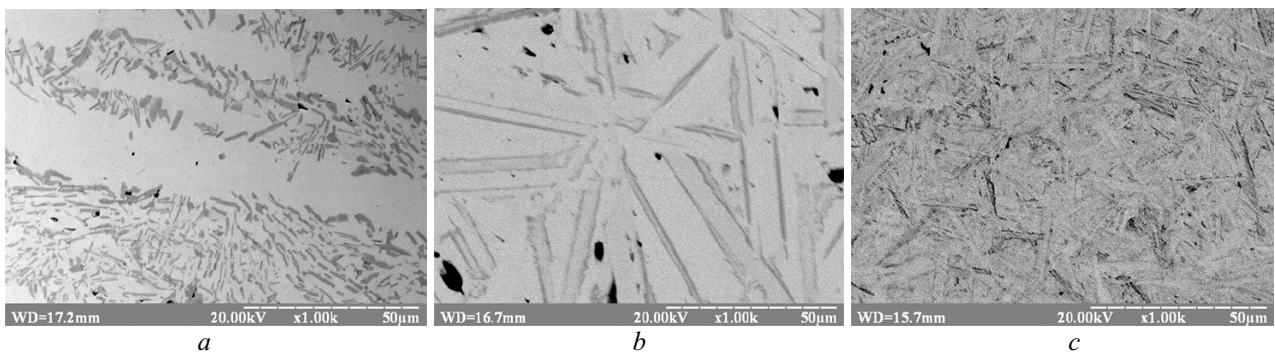

Fig. 2. Microstructure of the 5 wt.% Mo–WC–W_2C alloy produced at a cooling rate (°C/sec) of 10^2 (*a*), 10^3 (*b*), and 10^5 (*c*)
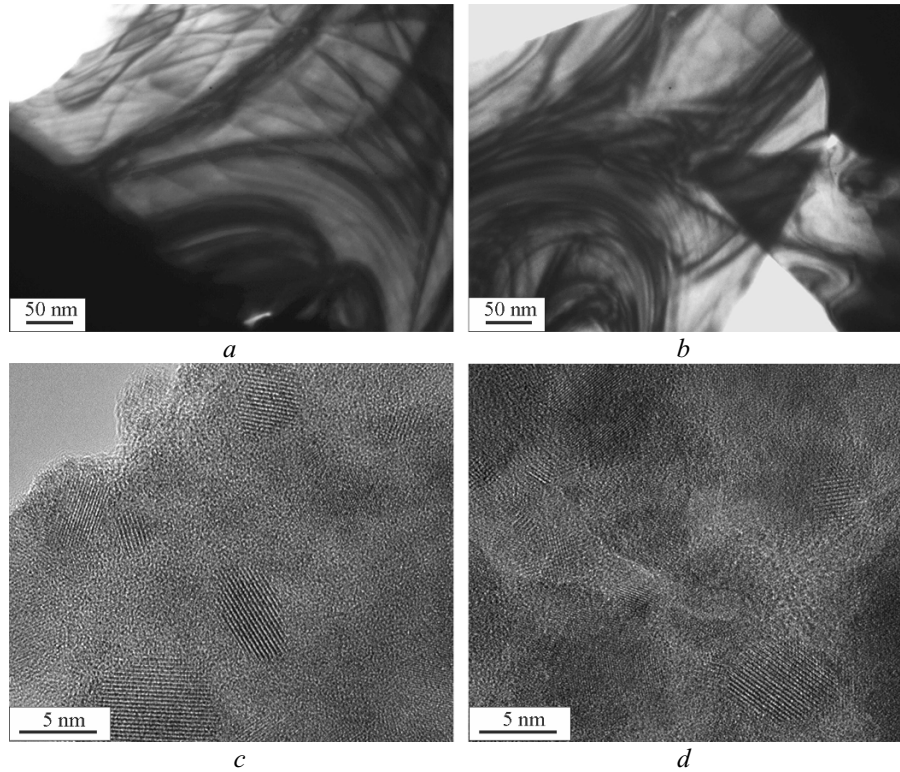
Fig. 3. Microstructure of the eutectic WC–W$_2$C (*a*, *c*) and 5 wt.% Mo–WC–W$_2$C (*b*, *d*) alloys produced at a cooling rate of ~10^2 (*a*, *b*) and ~10^5 (*c*, *d*) °C/sec

solutal undercooling changes in the melt causing its composition to deviate from the equilibrium one (in accordance with the phase diagram). Hence, excess carbon emerges when the eutectic alloy crystalizes and leads to dendritic WC growth, which changes to cellular growth with increasing melt temperature gradient.

A reinforcement network appears at a cooling rate of ~10^5 °C/sec. Inclusions of complex W–Mo carbide, such as (Mo, W)$_2$C, are located at grain boundaries of this network and promote the fine-grained alloy structure.

The service properties of ceramic materials can also be improved through the morphology of phase components. The reinforcement with evenly distributed fibers ensures the best possible increase in ductility and strength and decreases the brittleness of these materials [11].

The melt crystallization of eutectic alloys promotes the desirable fiber uniformity and results in coherent and semicoherent interfaces between the matrix phase and fibers, which is among the main conditions for improving the structure's thermal stability.

High-resolution transmission electron microscopy revealed that the matrix of both undoped (Fig. 3*a*, *c*) and molybdenum-doped relit (5 wt.% Mo; Fig. 3*b*, *d*) contained fine 5–10 nm inclusions of the other phase (Fig. 3). At the same time, there is a substantial difference between the doped and undoped relit. Hence, the undoped relit has a less defective matrix containing rather coarse areas with the same crystallographic orientation. The matrix of the molybdenum-doped alloy has greater defects (in particular, dislocations and low-angle boundaries). This difference is especially noticeable at a high cooling rate (~10^5 °C/sec) when the sizes of individual matrix fragments with the same crystallographic orientation match the sizes of reinforcement inclusions.

The dislocations move until they run into an obstacle (grain and subgrain boundaries, lattice distortions, other dislocations that cross the sliding plane, inclusions, etc.). More extensive boundaries (fine grains, admixtures, and lattice distortions caused by deformation) resist the motion of dislocations and increase the strength.

Besides the phase composition and the amounts and morphology of phase components, the mechanical properties of ceramic materials are largely determined by the potential to ensure continuous plastic deformation of the composition, zero porosity, and strong chemical bonds. The highest hardness and strength are known [11] to be
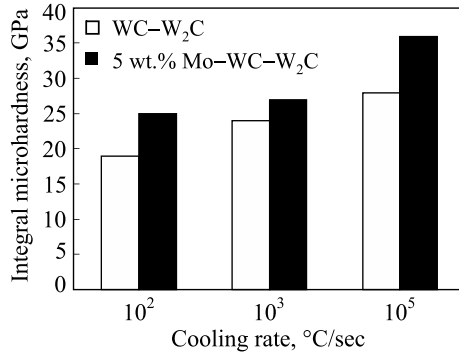
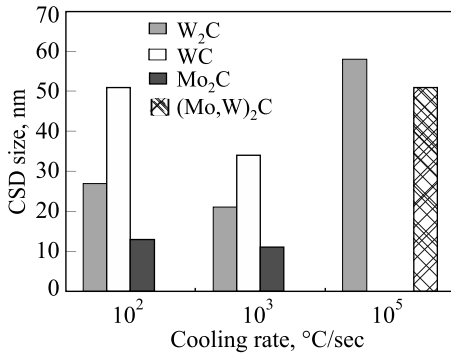*Fig. 4.* Integral microhardness of the undoped (WC–W$_2$C) and molybdenum-doped (5 wt.%) relit versus cooling rate
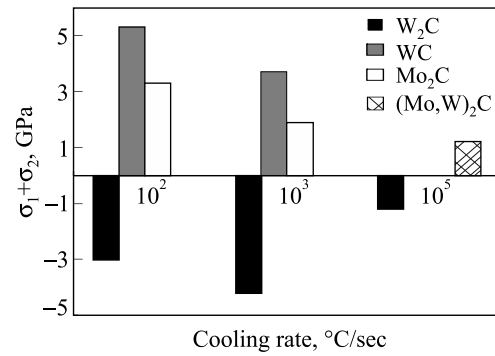

Fig. 5

Fig. 6

Fig. 5. Effect of the cooling rate on coherent scattering domain (CSD) sizes in the 5 wt.% Mo–WC–W$_2$C alloy

Fig. 6. Stresses in phase components determined by the diffraction peak shift method for the 5 wt.% Mo–WC–W$_2$C alloy

acquired by the materials including matrices of one refractory compound reinforced with single crystalline fibers of another refractory compound.

Hardness testing was used to establish the integral microhardness of both molybdenum-doped and undoped eutectic WC–W$_2$C alloys (Fig. 4). The highest microhardness of the 5 wt.% molybdenum-doped alloy produced at a cooling rate of ~10^5 °C/sec is ~36 GPa, which is 30% higher than that of the undoped relit. Many factors influence the hardness: shape and size of inclusions (Fig. 5), their location in the matrix, and mechanical stresses induced in phase components (Fig. 6).

Since stresses lead to a shift of the interference lines, which is most noticeable for reflections at large Bragg angles, stresses in phases were determined from the number of reflections in the range $2\theta = 65–125°$.

In turn, a higher cooling rate decreases compressive stresses in the W$_2$C matrix phase and tensile stresses in WC, Mo$_2$C, and (W, Mo)$_2$C inclusions. Compressive stresses in the W$_2$C phase come to 1.2 GPa at the maximum cooling rate, while stresses in the matrix phase of the undoped relit are 7 GPa [6].

With a greater cooling rate, the stress–strain state of the phase components does not change, but the stress intensity changes.

The alloys fail to a greater extent under tensile stresses, while compressive stresses decrease the material's sensitivity to stress concentrators and increase the material's fatigue strength.

The magnitudes of diffraction peak shifts lead to almost the same stresses at different lines despite potential deviations between the elastic moduli of reflections. This is attributed to the averaging of stresses within the fine crystalline structure.

CONCLUSIONS

The molybdenum-doped eutectic WC–W$_2$C alloy has a cellular structure containing randomly distributed hexagonal grains with complex (Mo, W)$_2$C carbide being formed at its boundaries. The undoped relit has a much less defective matrix consisting of rather coarse areas with the same crystallographic orientation, while the molybdenum-doped alloy has a matrix with greater defects.

With a higher cooling rate, the CSD sizes in the 5 wt.% Mo–WC–W$_2$C alloy increase in both the matrix phase and the inclusions (by about 2–2.5 times), but the number of phase components decreases to two (W$_2$C and (Mo,W)$_2$C)). Therefore, there are only two types of phase interactions, allowing high strength to be promoted at the boundaries between system components.

A greater cooling rate leads to decrease of compressive stresses in the W$_2$C matrix phase of the 5 wt.% molybdenum-doped WC–W$_2$C alloy (to about 50%) and tensile stresses in the WC, Mo$_2$C, and (W, Mo)$_2$C inclusions (to 50% and more).

An extreme composition dependence for the microhardness of molybdenum-doped relit has been established: the maximum hardness is shown by the 5 wt.% Mo–WC–W$_2$C alloy produced at a cooling rate of ~10^5 °C/sec. This agrees completely with changes in the phase composition and the stress–strain state and morphology of the composite's phase components.

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