EFFECT OF THE COOLING RATE DURING MELT SOLIDIFICATION ON THE STRUCTURE AND PROPERTIES OF WC–W₂C

I. Yu. Trosnikova,^{1,4} P. I. Loboda,¹ O. P. Karasevska,²
and O. I. Bilyi³

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The paper examines the effect of cooling rate on the structure, phase composition, size of coherent scattering domains, and stress–strain state of relit commercially used to strengthen machine parts and mechanisms that perform under abrasive wear and high contact loads. Optical and scanning electron microscopy, quantitative X-ray diffraction, and electron microprobe analysis have been employed to reveal that higher cooling rates during melt solidification decrease the sizes of phase components in the 20 wt.% WC–80 wt.% W₂C alloy and increase compressive stresses in the W₂C matrix phase and tensile stresses in WC inclusions, improving the hardness of relit (by 1.5 times).

Keywords: tungsten carbide, cooling rate, stresses, hardness, grain-boundary strengthening mechanism.

INTRODUCTION

Melt-solidified eutectic alloys, representing a matrix from one refractory compound reinforced with inclusions of another refractory compound, are among the most promising materials that can efficiently be used to protect metal and alloy parts and structures against abrasive wear [1]. Relit is a eutectic alloy of tungsten carbides WC–W₂C (78–80 wt.% W₂C, 20–22 wt.% WC), whose production process has been adequately studied [2]. The melting point of relit is 2735°C.

The tungsten carbide WC–W₂C alloy is used as wear-resistant coating material for parts that perform under intensive abrasive wear and moderate impact loads, specifically for coating of drill bits, parts of blast furnace feeders, and metalworking tools [2].

High strength at boundaries between components (the hardest inclusions and the matrix) is a necessary condition for wear-resistant material to perform in a reliable manner. Note that hard inclusions in the material are crumbled out if the components have low adhesion strength; i.e., there is abrasive wear. The wear rate of two-phase materials is determined by the chemical composition or nature and grain size of their components, as well as by loading and temperature in the contact area. Hardness and strength are the main criteria for assessing the wear resistance. The greatest wear resistance is exhibited by the WC–W₂C alloy, but its main drawback is high brittleness [3]. One of the ways to improve the wear resistance of ceramic composites may be to increase the rate at which the

¹National Technical University of Ukraine ‘Kiev Polytechnic Institute’, Kiev, Ukraine. ²Kurdyumov Institute for Metal Physics, National Academy of Sciences of Ukraine, Kiev, Ukraine. ³Paton Electric Welding Institute, National Academy of Sciences of Ukraine, Kiev, Ukraine.

⁴To whom correspondence should be addressed; e-mail: irina2510@ukr.net.

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eutectic alloy solidifies from melt through grain refinement and fiber reinforcement. The papers [4, 5] show that higher cooling rates significantly improve the hardness of relit, but the nature of this phenomenon is still to be understood.

Our objective is to examine how the cooling rate influences the structure, phase composition, size of coherent scattering domains, and stress-strain state of relit.

EXPERIMENTAL PROCEDURE

Tungsten carbides WC–W₂C were produced by grinding the ingots smelted in a Tammann-type furnace at 3100°C. The grains are primarily fragmental. Mechanical grinding leads to numerous cracks in grains, decreasing their strength.

The alloy formation process was also studied by melting of relit compacts by an electron beam and centrifugal atomization of cylindrical billets smelted in a Tammann furnace. The cooling rate was 10² °C/sec during smelting in a Tammann furnace and 10³ °C/sec during electron-beam melting. In the centrifugal atomization process, the cooling rate increased by two orders of magnitude and reached 10⁵ °C/sec, which is due to fusion of the rod end with arc discharge. Argon was a plasma-supporting gas. The melt is removed by centrifugal forces from the rod end as 50–400 µm droplets that solidify in air. The chamber is cooled down with water. The WC–W₂C alloy powder particles are spherical.

Metallographic analysis employed optical (NEOPHOT 21) and scanning electron (REM 106I) microscopes.

X-ray diffraction studies of the phase composition, stress-strain state, size of coherent scattering domains, etc., were conducted using a RIGAKU ULTIMA IV diffractometer with different techniques, such as Rietveld and Reference Intensity Ratio (RIR) methods in Cu-K_{α1,2} radiation, $\lambda_{\text{Cu-K}\alpha_1} = 0.1541$ nm.

The stresses were determined with the $\sin^2\psi$ and diffraction peak shift methods [6]. The phase composition of the alloys and the reflections on the θ –2 θ diffraction patterns allowed us to use the $\sin^2\psi$ method to locate the peaks of the same X-ray line for alloys produced by different methods.

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

EXPERIMENTAL RESULTS

X-ray diffraction has shown that the alloys solidified at all cooling rates in question mainly consist of tungsten monocarbide and semicarbide. The phase content is not dependent on the solidification rate. The main phase components, WC and W₂C, have been revealed by X-ray diffraction of the WC–W₂C alloy on θ –2 θ patterns (Fig. 1). Regardless of the cooling rate, the WC phase content is almost the same, 18–19 wt.%, and that of the W₂C

Fig. 1. X-ray diffraction patterns showing distribution of phase components (a) and phase contents (b) in the WC–W₂C alloy: cooling rate is 10² (1), 10³ (2), and 10⁵ °C/sec (3)

phase is 74–82 wt.%. Besides the said phases, we revealed insignificant amounts of WC_{1-x} both in a Tammann furnace (6 wt.%) and during centrifugal atomization (9 wt.%).

Electron-beam melting promoted solidification of the $WC-W_2C$ alloy with the phase ratio being the closest to the stoichiometry of relit. This is associated with more complete homogenization of the melt and hence of the solidified alloy. The presence of WC_{1-x} in the alloys produced by centrifugal atomization and in a Tammann furnace testifies that carbon is partially lost in the solidification process.

Figure 2*a–c* shows microstructures of the alloys produced at different cooling rates in a Tammann furnace, during electron-beam melting, and by centrifugal atomization.

The microstructures formed in a Tammann furnace are the most inhomogeneous. The microstructure is more uniform, fine-crystalline, and with elongated grains following centrifugal atomization. According to scanning electron microscopy, the alloy microstructure represents a matrix from tungsten semicarbide W_2C pierced with elongated WC grains (Fig. 2).

Electron microprobe analysis has confirmed that the darker phase contains less tungsten than the light matrix phase of tungsten semicarbide. With increasing solidification rate, the tungsten carbide grains are refined in cross-section and become more elongated. At the lowest cooling rates, the WC grains are elongated, interconnected plates and rods.

When the cooling rate increases, the plates become dendritic branches, which are several times thinner than the plates and rods of tungsten monocarbide solidified at the minimal cooling rate. Solidification at the maximal cooling rate leads to a cellular structure whose dendritic grains emerge from columnar elements of regular shape with side branches that solidified at about 90° and with finer, randomly placed 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 to the phase diagram. Excess

Fig. 2. Microstructure (*a–c*) and microhardness (*d*) of the $WC-W_2C$ alloy: cooling rate is 10^2 (*a*), 10^3 (*b*), and 10^5 °C/sec (*c*)

Fig. 3. Size of coherent scattering domains of WC–W₂C alloy phase components versus cooling rate

TABLE 1. Stresses in the WC–W₂C Alloy Determined with the sin²ψ Method

Cooling rate during solidification, °C/sec	σ ₁ + σ ₂ , GPa	
	W ₂ C	WC
10 ²	–0.781	–0.820
10 ³	0.72	–1.124
10 ⁵	2.033	–1.479

Note. 2θ and *hkl* for W₂C are 84° and 202 and for WC are 98° and 112.

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.

Hardness measurement has established the average integral microhardness of the alloys produced at different cooling rates (Fig. 2*d*). The highest microhardness (28 GPa) is observed at a cooling rate of 10⁵ °C/sec. The greatest hardness and strength are known [7] to be reached by materials that represent a matrix from one refractory compound reinforced with single-crystalline fibers of another refractory compound. This mechanism takes place in the WC–W₂C alloy, where W₂C is a matrix reinforced with fine WC grains.

As already noted, hardness of the WC–W₂C alloy depends on the cooling rate. The phase amounts remaining practically the same, the structure, size, and shape of the components change substantially. Higher cooling rates accelerate structural transformations, stimulate the formation of finer grains (Fig. 3), and influence their crystallographic orientation with respect to the direction of indentation during hardness measurement.

The hardness may also increase under mechanical stresses in phase components. Table 1 shows stresses (σ₁ + σ₂) in the WC–W₂C alloy determined by the sin²ψ method (Fig. 4*a*).

The W₂C and WC phases in the alloy produced in a Tammann furnace show tensile stresses between 0.78 and 0.82 GPa, respectively. The stresses increase during electron-beam melting and centrifugal atomization. The WC phase is elongated and the W₂C phase is compressed in the alloys. The highest stresses in the two phases are observed after centrifugal atomization at the greatest cooling rate. 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–W₂C alloy produced at different cooling rates show a shift of reflections. Stresses in surface layers of the sample in the direction perpendicular to its surface (σ₁ + σ₂) are determined as [6]:

$$\varepsilon = -\frac{\mu}{E}(\sigma_1 + \sigma_2),$$

where *E* is elastic modulus (Young's modulus) and μ is Poisson's ratio.

Fig. 4. Stresses in the WC– W_2C alloy phases determined with the $\sin^2\psi$ method (a) and diffraction peak shift method for W_2C (b) and WC (c)

The calculation of $\varepsilon = \Delta d/d_{us}$ is based on determining the 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:

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

The positions of peaks on the WC– W_2C diffraction patterns were used to determine d_{us} , d_s , and Δd and calculate $(\sigma_1 + \sigma_2)$ for the alloys under study (Fig. 4b and c). Stresses in the W_2C phase determined from reflections in the range $2\theta = 65\text{--}145^\circ$ are negative (compressive) at all cooling rates. They are 5.7, 5.6, and 7 GPa at cooling rates of 10^2 , 10^3 , and 10^5 °C/sec, respectively.

Stresses in the WC phase were also determined from a series of reflections in the range $2\theta = 65\text{--}125^\circ$. They have the opposite sign at all cooling rates (10^2 , 10^3 , and 10^5 °C/sec) and are 1, 3, and 1 GPa, respectively.

Note that alloys fail to a greater extent under tensile stresses. Compressive stresses reduce the sensitivity of materials to stress concentrators and increase their fatigue strength. Despite possible deviations in elastic modulus for reflections, the absolute values of their shift influence the stresses, which are almost the same at different lines.

Besides stresses, the shift of reflections may also result from lattice defects of the first kind [6]. This can explain the difference in stresses determined with the diffraction peak shift and $\sin^2\psi$ methods.

Stresses are induced in the following conditions:

- plastic deformation of a polycrystalline sample through elastic and plastic anisotropy of crystals;
- nonuniform heating or cooling of the sample that leads to tensile and compressive stresses that are likely to induce plastic shear, causing residual stresses (they will be higher in a multiphase material if the phases have different thermal expansion coefficients);*

* The thermal expansion coefficient is $(5.2\text{--}7.3) \cdot 10^{-6}$ °C⁻¹ for WC and $(1.2\text{--}11.4) \cdot 10^{-6}$ °C for W_2C .

- decomposition of a supersaturated solid solution (aging) when stresses emerge in the matrix and at the boundary of the precipitating phase;
- local structural or chemical transformations involving change in the specific volume of the phases relative to the alloy.

Stresses in crystallites cause the interference lines to increase by $\Delta\beta/\beta$, where $\Delta\beta$ is deviation of broadening for a given line from β in equilibrium solidification conditions.

CONCLUSIONS

It has been established that centrifugal atomization leads to a more homogenous fine structure with grains being uniformly distributed in the matrix of the WC–W₂C alloy. The alloy microstructure represents a matrix from tungsten semicarbide W₂C reinforced with fine grains of tungsten monocarbide WC.

It has been revealed that higher cooling rates increase stresses in the composite, compressive stresses being observed in the matrix phase and tensile stresses in the reinforcing phase.

It has been determined by electron microprobe analysis that microstructure is refined: coherent scattering domains decrease from 508 to 146 μm for W₂C, from 260 to 123 μm for WC, and from 155 to 90 μm for WC_{1-x} with increasing cooling rate.

It has been shown that microhardness of the alloys increases by a factor of 1.5 with higher cooling rates. This fact agrees with the grain refinement and change in stress–strain state of phases in the composite, which can be attributed to grain-boundary strengthening.

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