Optimization of the phase composition of hard alloys obtained by spark plasma sintering of powders WC + 10% Co

Ksenia E. Smetanina, Pavel V. Andreev, Natalia V. Malekhonova, Evgeny A. Lantsev
Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, Russia
E-mail: smetanina-ksenia@mail.ru

Abstract. Parameters of powder WC + 10% Co sintering modes that exclude the possibility of η-phase (Co3W3C) formation were determined. The phase composition was controlled by introducing colloidal graphite into the original powder.

Keywords: tungsten carbide; nanopowder; fine-grained ceramic; spark plasma sintering; X-ray powder diffraction analysis.

1. Introduction
Pure tungsten carbide and hard alloys based on it can be considered as materials suitable for a wide range of applications due to the winning combination of their properties such as high resilience, high melting point, and significant chemical resistance to corrosion and oxidation. It is also worth noticing that pure tungsten carbide alloys are characterized by high brittleness [1].

Hard alloys are produced by sintering tungsten carbide powders with various additives [2]. Original tungsten carbide powders can be obtained by various methods [3] (e.g. plasma chemical synthesis [4]). This method allows to obtain powders with a dispersion level of 30 ÷ 80 nm.

The most promising method of hard alloys’ manufacturing is spark plasma sintering (SPS) of powders. This method consists of heating the powder up to the sintering temperature in a controlled medium under pressure [5–7].

Adding a metal bond (e.g. cobalt) reduces brittleness of tungsten carbide. However, during the process of sintering cobalt interacts with tungsten and carbon. This interaction results in the emergence of triple compounds called η-phases: Co3W3C (space symmetry group – \( \overline{Fm\overline{3}}m \)) is the most frequent one. Numerous studies have shown that the presence of η-phase in carbide alloys leads to a decrease in their wear resistance and crack resistance.

An approach aimed at eliminating the η-phase formation in the sintering process is proposed in [1]. It consists of adding optimal amounts of carbon to the original powders. Thus, the carbon deficit would have been filled. The deficit arises due to the fact that adsorbed oxygen on the surface at heating begins to react with tungsten carbide, forming gases CO and CO2.

However, there is a non-trivial question concerning the amount of additional carbon. It has been observed that excess carbon included into the original powder composition causes formation of graphite particles in the ceramic workpiece and the consequential increase in its fragility. Moreover, there is a disadvantage concerning formation of η-phase that should be taken into account.
The amount of carbon needed to suppress the \( \eta \)-phase also depends on the amount of cobalt and tungsten semi-carbide included into the original powder, the dispersion level, and the properties of the carbon material used as a carbon source.

The process of \( \eta \)-phase formation depends not only on the structural parameters of the original powders but also on the sintering temperature, heating rate, isothermal holding time, the value of the applied pressure etc. In addition, one can measure temperature at which \( \eta \)-phase formation will be prevented in each of the carbon concentration.

The purpose of the work is to define the so-called “concentration – temperature” window of conditions at which \( \eta \)-phase emergence can be excluded.

2. Materials and techniques

The object of this study was a tungsten carbide powder with an average particle dispersion of 50 nm.

The original tungsten carbide powder was obtained at Baikov Institute of Metallurgy and Materials Science with the help of plasma chemical synthesis: the tungsten oxide \( \text{WO}_3 \) was reduced during the gas phase in the hydrocarbon medium [4].

Cobalt (10% wt.) was applied to the surface of tungsten carbide particles by precipitation from solution its salts followed by hydrogen recovery [8].

The carbon source was colloidal graphite [9] which was introduced into the mixture of \( \text{WC} + 10\% \text{Co} \) by mixing them in a planetary mill. The amount of input graphite ranged from 0% wt. to 0.5% wt. in increments of 0.1% wt.

SPS of WC – Co ceramic samples was performed on the “Dr. Sinter model SPS-625” (SPS Syntex, Japan). Sintering was carried out in a vacuum in a graphite mold with an internal diameter of 12 mm. Heating speed was 50°C/min and pressure was 70 MPa. Degassing exposure at 800°C was conducted during the sintering process to remove adsorbed oxygen powder particles from the surface, then – cure at the specified sintering temperature of 1100°C or 1400°C.

“Solid-phase” sintering was performed at 1100°C and “liquid-phase” – at 1400°C.

Mechanical polishing of the sintered samples surface was carried out using diamond paste to a particle dispersion of 1/0 μm for X-ray phase analysis (XRPA).

X-ray diffraction experiments were performed on a powder diffractometer “Shimadzu XRD-7000” (CuK\( \alpha \), \( \lambda = 1.54 \) Å). Optimal shooting conditions were selected on the basis of previous studies [10]: “wide slit mode” in the range of angles of 30 – 80° with a scanning step of 0.04° and an exposure time of 3 s.

Qualitative phase analysis of sintered samples was performed in the program “Diffrac. EVA”. Original PDF-cards were taken from the powder diffraction bank PDF-2: WC (PDF №00-051-0939, \( \text{P6m2} \), Co (PDF №00-015-0806, \( \text{P6} \), /mmc), \( \text{Co}_3\text{W}_3\text{C} \) (PDF №01-078-4940, \( \text{Fd} \text{3m} \)).

Quantitative phase analysis was carried out according to the method based on the reference intensity ratio method thereunder of integral intensities of diffraction maximaums, worked out in [10].

The refinement of the unit cell parameters of investigated phases was spent by a method of Rietveld in a program complex “Topas” with use of structural cif-files: WC (ICSD №5212), Co (ICSD №53805), \( \text{Co}_3\text{W}_3\text{C} \) (ICSD №166747).

3. Description of experimental results

Figure 1 shows the results of X-ray diffraction studies of ceramic samples sintered under different conditions.

The content of \( \eta \)-phase is \( 6 \pm 0.3\% \) wt. in a sample sintered without carbon under “solid-phase” sintering conditions, under “liquid-phase” conditions – \( 4 \pm 0.2\% \) wt.
Figure 1. Diffraction patterns of ceramic samples based on WC – Co sintered under conditions of “solid-phase” (a) and “liquid-phase” (b) sintering with different contents of introduced carbon.

η-phase is not observed in a sample sintered under “solid-phase” sintering conditions with carbon addition of 0.2% wt. This means that its quantity does not exceed 0.2% wt. – limit of detection by XRPA method. Figure 2 shows that the addition of 0.3% wt. of carbon to the original mixture WC + 10% Co was required for a similar result under “liquid-phase” sintering conditions.
Figure 2. Dependence of the content of $\eta$-phase in samples sintered under “solid-phase” and “liquid-phase” sintering conditions on the amount of introduced carbon into the original powder WC + 10\% Co

4. Discussion

It is known that carbon not only prevents $\eta$-phase (Co$_3$W$_3$C) formation during sintering but also dissolves in cobalt. The difference in the amount of carbon required for suppression of $\eta$-phase in case of “solid-phase” and “liquid-phase” sintering is obviously connected with the fact that at “liquid-phase” sintering more carbon dissolves in cobalt (see the phase diagram of the system W – C – Co [1]).

Displacement of cobalt peaks is observed on the experimental diffractograms (fig. 3). By changing the angular positions of diffraction peaks, in accordance with the Wulf-Bragg equation (1), one can speak of a change in the unit cell parameter (2).

$$2d \sin \theta = n\lambda$$  \hspace{1cm} (1)

$$a = \frac{n\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \theta}$$  \hspace{1cm} (2)

Shift of cobalt peaks towards large angles corresponds to reduction of its unit cell (figure 4).

Figure 3. Dependence of the Co cell parameter on the amount of introduced carbon

It is known that a solid substitution solution is formed at dissolution of tungsten in cobalt, increasing the average parameter of the cobalt unit cell [1]. It can be seen from figure 4 that the reduction of the cell parameter occurs with the increase of carbon content in the original powders. This can be explained as follows: with increasing carbon content rising the intensity of the introduction of carbon atoms into the octahedral cavities of the cobalt structure it can prevent dissolution of the tungsten atoms into the cobalt.
Decrease in the intensity of diffraction peaks Co is also observed with the increase in carbon content (figure 4). This can be explained by the fact that the carbon atoms introduced into the cobalt reduce its average atomic factor [11] which leads to a decrease in the intensity.

Figure 4. Dependence of Co peak intensity (111) on carbon content

5. Conclusion
This study was undertaken to determine conditions in the “concentration – temperature” coordinates at which the weight fraction of η-phase (Co₃W₃C) is at the limit of detection by the XRPA method (0.2% wt.): 0.2% wt. carbon introduction is required under "solid-phase" sintering conditions (T = 1100°C), when at “liquid-phase” (T = 1400°C) – 0.3% wt.

Acknowledgments
The work was financial supported by Russian Science Foundation (RSF) and conducted under the grant №18-73-10177.

References
[1] Kurlov A and Gusev A 2014 Physics and chemistry of tungsten carbides (Moscow: FIZMATLIT) p 272
[2] Panov V S and Chuvilin A M 2001 Technology and properties of cintered carbide alloys and products from them (Moscow: MISIS) p 428
[3] Tokita M 2013 Spark Plasma Sintering (SPS) Method, Systems, and Applications (Chapter 11.2.3) Handbook of Advanced Ceramics (Second Ed.) Ed. Shigeyuki Somiya (Academic Press) p 1149-77
[4] Olevsky E and Dudina D 2018 Field-Assisted Sintering (Springer Int. Publ.) p 425
[5] Chuvildev V et al 2017 Journal of Alloys and Compounds 708 547-61
[6] Blagoveshchenskii Yu et al 2018 Inorganic materials: applied research 9(5) 924-29
[7] Blagoveshchenskii Yu et al 2015 Inorganic materials: applied research 6(5) 415-26
[8] Isaeva N, Blagoveshchenskiy Yu, Blagoveshchenskaya N, Melnic Yu, Samohin A, Alekseev N and Astashov A 2013 Izvestia Vuzov, Powder metallurgy and functional coatings 3 7-14
[9] Starostin A, Kuzina E 2016 Vestnik PNIPU Chemical Technology and Biotechnology 2 20-128
[10] Andreev P, Smetanina K, Lantsev E 2019 IOP Conference Series: Materials Science and Engineering 558 (1) 012003
[11] Porai-Koshits M 1989 Fundamentals of Structural Analysis of Chemical Compounds (Moscow Vyssh. Shkola) p 192