X-ray powder diffraction analysis of a tungsten carbide-based ceramic

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Abstract. The results of the qualitative and quantitative X-ray powder diffraction analysis of the W–C system samples are presented. Powder samples were nanopowders of α-WC/W₂C obtained by plasma chemical synthesis. High-density fine-grained structure of ceramics was formed using the method of electro pulse plasma sintering (spark plasma sintering) from the initial powder of the α-WC. The optimal experimental conditions for the X-ray diffraction proceeding of the tungsten carbide based ceramic samples were chosen according to the preliminary experiments. Reference intensity ratio method for quantitative phase analysis was used in this study.

1. Introduction
Tungsten carbide is of interest for various applications (cutting tools, dies, elements of ammunition, etc.) due to its favorable combination of physical and mechanical properties (high melting point, high hardness, low friction coefficient and chemical resistance against corrosion and oxidation). Development of heavy duty constructional ceramics based on pure tungsten carbide is an actual problem [1]. High-density fine-grained structure must be formed to ensure high physical and mechanical properties of tungsten carbide based ceramics.

The method of high-speed electropulse plasma sintering of powder materials (SPS – Spark Plasma Sintering) is one of the most effective ways to obtain high-density fine-grained ceramics based on tungsten carbide. The method represents high-speed heating of powder material by way of transmitting consecutive millisecond impulses of high power current through a conductive graphite compression mold [2–4].

Often initial powders represent the multiphase polycrystalline W–C system [4–6]. The presence in the initial powders of particles of the another crystal phase whose structure is other than monocarbide α-WC has an adverse effect on physical and mechanical properties of sintered ceramics, leading to decrease in crack resistance, bending strength, wear resistances and others [1, 4, 5, 7]. Note also that the area of tungsten monocarbide stability (homogeneity) on the W–C diagram is small [8], therefore, the phase composition of ceramics can change in the process of SPS [4, 5].

In this regard, the relevant task is to develop a method of controlling the phase composition of initial nanopowder compositions of W–C and fine-grained ceramic sample sintered from micron powders.

The study of the qualitative and quantitative phase composition of fine-grained ceramics based on tungsten carbide is usually carried out by the X-ray phase analysis (XRPA). Often researchers make use only of the semi-quantitative corundum number analysis involving well-known data from specialized databanks (for example, PDF–2, 4) [4, 9]. In this case, estimates of the errors and sensitivity of the method are given approximately based on published data.
At the same time, the sensitivity and accuracy of the XRPA depend on the qualitative composition of the sample and the quality of the observed data, which depends on the experimental conditions and the method of sample preparation. This task has particular difficulty and relevance for the XRPA of nanopowder compositions and fine-grained ceramics, the distinctive feature of which is the broadening and decrease in the intensity of X-ray peaks [4, 5, 9].

The purpose of this research was to define the sensitivity of the method of determining the qualitative and quantitative phase composition in fine-grained ceramics based on tungsten carbide.

2. Research objects
Tungsten carbide nanopowders obtained at the Baikov Institute of Metallurgy and Materials Science by plasma chemical synthesis from tungsten oxide and hydrocarbon in a stream of reducing gas and subsequent low-temperature furnace synthesis (reductive annealing in hydrogen) have been taken as objects of research [5, 6, 9].

Also the research deals with ceramic samples with a diameter of 20 mm and a thickness of 5 mm obtained by SPS in vacuum at the temperature of 1625°C (heating rate \( V = 50^\circ\text{C}/\text{min} \), applied pressure \( P = 60 \text{ MPa} \)) from micron powders. The results of the electron microscopic studies showed that the average grain size in ceramics was 1 \( \mu \text{m} \), just like the average particle size of tungsten carbide in the initial powder. The density of ceramics was 15.608 g/cm\(^3\) (98.97% of the theoretical density of tungsten monocarbide).

3. Description of the used equipment
SPS was conducted using the Dr. Sinter model SPS-625 (SPS Syntex, Japan). Polishing took place on the grinding and polishing machine “Buehler Eco Met 250”. X-ray phase analysis was performed with instrument for X-ray powder diffraction Shimadzu XRD-7000 (Japan) (CuK\( \alpha \), \( \lambda = 1.54 \) Å).

All the data of quantitative phase analysis in the present work were calculated by the Reference Intensity Ratio (RIR) method [10] based on the integral intensities of the diffraction peaks.

The powder diffraction patterns of the phases were calculated using the structural parameters of the crystalline phase (unit cell parameters, substance density, mass absorption coefficient, coefficients for approximation of the atomic factor, atomic coordinates, etc.) and the required theoretical values of the intensity ratios were obtained. Structural files were taken from a bank of inorganic structures ICSD: \( \alpha - WC \) (ICSD №5212), \( \alpha - W_2C \) (ICSD №619097), \( \alpha - \text{Al}_2\text{O}_3 \) (ICSD №31547). The Reference Intensity Ratio used for semi-quantitative phase analysis was \( I(W_2C)/I(WC) = 1.407 \).

Standard errors of quantitative phase analysis were calculated using the known formulas of mathematical statistics for indirect measurements which were carried out based on the determination error for the relative integrated intensities of X-ray peaks. The measurement errors of the relative integrated intensities of X-ray peaks were calculated using known methods based on data from several (at least three) experiments.

4. Choice of operating modes of the diffractometer
The choice of XRPA experimental conditions of the W – C system samples implies the optimal range of 20 angle, exposure time and slits system. The selected 20 angle range (30°–80°) contains peaks (001) and (100) of tungsten monocarbide \( \alpha - WC \) and peaks (100), (002) and (101) of tungsten semi-carbide \( \alpha - W_2C \). The following experimental conditions were chosen according to the preliminary experiments: wide-slit mode with a scanning step of 0.02° and exposure time of 3 s. The mass fraction of the \( W_2C \) crystal phase in the investigated powder sample under such experimental conditions is 26.0±1.2 wt %.
5. XRPA of the high density fine-grained ceramics based on tungsten carbide

The investigation of solid samples uniformity was carried out by the layerwise XRPA. First X-ray diffraction experiments was processed at both sides of ceramic sample without any preparation of the surface.

Quantitative calculation showed that the relative intensities of the diffraction peaks α-WC (00l) change with sample rotation. It proves the presence of the preferred orientation of crystallites at the surface. Also the tungsten semi-carbide W$_2$C peaks were not detected.

After that the surface layer of 50 μm was removed by mechanical grinding and XRPA carried out once again. Calculated depth of penetration of CuKα radiation for pure tungsten carbide is less than the selected depth of grinding (~7 μm).

Quantitative calculation showed that the considered ceramic sample was homogeneous in depth (starting at 50 μm). The presence of the preferred orientation of crystallites in the sample at such depth was not detect. It is interesting to note that there is a diffraction peak of the W$_2$C phase on powder diffraction pattern of the grinded sample surface. The mass fraction of the W$_2$C phase in the surface layer of sintered grinded ceramics is 5.7±0.6 wt %.

At the next stage, the level of surface roughness varied as a result of polishing with a diamond paste of various dispersion level (28/20 μm, 14/10 μm, 5/3 μm, 3/2 μm, 1/0 μm). The diffraction patterns of the ceramic sample mechanically grinded and polished with a diamond paste of 5/3 μm dispersion are shown in figure 1.

![Figure 1. X-ray powder diffraction patterns of ceramics based on tungsten carbide. Dashed line – diffraction pattern after grinding the sample at ~ 250 μm, solid line – after polishing the sample with diamond paste with a grain size 5/3 μm.](image-url)
Figure 2. X-ray powder diffraction patterns of mixtures of a powder sample of tungsten carbide with tungsten anhydride WO₃. Diffraction pattern: 1 80 wt % WO₃, 2 90 wt % WO₃.

The analysis of the results shows that intensity of the diffraction peaks increases with the decrease in surface roughness level. In our opinion, this is due to the fact that the roughness and strain hardening of a surface lead to “blurring” of the area of X-ray diffraction in the sample, which accounts for the broadening of the diffraction peaks. Ceramic sample surface polishing increases the sensitivity of the used XRPA method and allows specifying the mass fraction of the W₂C phase in the studied sample. The mass fraction of the semi-carbide W₂C in sintered ceramics was refined as 5.25 ± 0.11 wt %. Further polishing with diamond pastes of dispersion level 3/2 μm and 1/0 μm did not lead to any noticeable improvement of the experimental results.

Checking sensitivity on developed method to W₂C phase content in powders of tungsten carbide was conducted at the final stage of work. Tungsten anhydride was added to the studied powder of tungsten carbide to test the sensitivity of the method used. The content of WO₃ in the powder of tungsten carbide was 80 and 90 mass %. The analysis of XRPA results showed that the initial powder sample contains ~ 2 wt % W₂C phase.

Figure 2 shows that the peak of the W₂C phase, corresponding to the reflection (101), could be detected even at 90% WO₃ in the mixture, which corresponds to ~ 0.22 ± 0.04 wt % W₂C phase in the sample.

6. Conclusions
It was found that samples of ceramics based on tungsten carbide WC were characterized by the heterogeneity of the phase composition in depth and the preferred orientation of crystallites only near the surface layer (less than 50 μm). The surface roughness of such samples significantly affects the sensitivity of the used research method. Preliminary polishing of tungsten carbide ceramic samples with diamond paste of 5/3 μm dispersion level is proposed to increase the sensitivity of XRPA.

The developed research showed the sensitivity of the method to the presence of tungsten semi-carbide phase W₂C at the level of 0.2 wt %.

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References
[1] Panov V S and Chuvilin A M 2001 Technology and properties of \textit{cintered carbide alloys and products from them} (Moscow: MISIS)
[2] Somiya S 2013 \textit{Handbook of Advanced Ceramics} (Academic Press)
[3] Olevsky E and Dudina D 2018 \textit{Field-Assisted Sintering} (New York: Springer Int. Publ.)
[4] Chuvil'deev V N, et al 2017 J. Alloys Comp. \textbf{708} 547
[5] Blagoveshchenskiy Yu, et al 2015 \textit{Inorg. Mater.: Appl. Res.} \textbf{6} 415
[6] Blagoveshchenskiy Yu, et al 2018 \textit{Inorg. Mater.: Appl. Res.} \textbf{9} 924
[7] Zhao J, Holland T, Unuvar C and Munir Z 2009 \textit{Int. J. Refrac. Met. Hard Mater.} \textbf{27} 130
[8] Kurlov A and Gusev A 2014 \textit{Physics and chemistry of tungsten carbides} (Moscow: Fizmatlit)
[9] Isaeva N, et al 2013 \textit{Izvestia Vuzov. Powder metallurgy and functional coatings} \textbf{3} 7
[10] Andreev P, Trushin V and Faddeev M 2013 \textit{X-ray phase analysis of polycrystalline materials} (Nizhny Novgorod, Lobachevsky State University)
[11] Anselmi-Tambrini, et al 2005 \textit{Mat. Sci. Eng. A} \textbf{394} 139