



# Article Nonuniform Distribution of Crystalline Phases and Grain Sizes in the Surface Layers of WC Ceramics Produced by Spark Plasma Sintering

Ksenia E. Smetanina <sup>1,\*</sup>, Pavel V. Andreev <sup>1,\*</sup>, Evgeny A. Lantsev <sup>1</sup>, Aleksey V. Nokhrin <sup>1</sup>, Artem A. Murashov <sup>1</sup>, Natalia V. Isaeva <sup>1,2</sup>, Yury V. Blagoveshchensky <sup>2</sup>, Maksim S. Boldin <sup>1</sup>, and Vladimir N. Chuvil'deev <sup>1</sup>

- <sup>1</sup> Materials Science Department, Research Institute of Physics and Technology, Lobachevsky State University of Nizhny Novgorod, 603022 Nizhny Novgorod, Russia; elancev@nifti.unn.ru (E.A.L.); nokhrin@nifti.unn.ru (A.V.N.); aamurashov@nifti.unn.ru (A.A.M.); felix-2001@mail.ru (N.V.I.); boldin@nifti.unn.ru (M.S.B.); chuvildeev@nifti.unn.ru (V.N.C.)
- <sup>2</sup> Laboratory of Plasma Processes in Metallurgy and Metal Processing, A.A. Baykov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, 119334 Moscow, Russia; yuriblag@imet.ac.ru
- \* Correspondence: smetanina@nifti.unn.ru (K.E.S.); andreev@phys.unn.ru (P.V.A.)

Abstract: The research results conducted on binderless tungsten carbide (WC) ceramics obtained by spark plasma sintering (SPS) of WC powders with different average particle sizes (95, 800, 3000 nm) are presented. Nonuniform distribution of crystalline phases and microstructure of the WC ceramics was studied using layer-by-layer X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM). Surface layers of the WC-based ceramics are characterized by nonuniform distribution of W<sub>2</sub>C crystalline phase and grain sizes, including the appearance of abnormally large grains. Thickness of the nonuniform layer was at least 50  $\mu$ m. The effect under study is associated with an intense carbon diffusion from graphite foil. On the one hand, this contributed to a decrease in the intensity of W<sub>2</sub>C phase particle formation, which is transformed into  $\alpha$ -WC phase due to the carbon. On the other hand, it caused abnormal grain growth in the layer where the carbon diffused. The obtained value of the carbon diffusion even at temperature of 2370 °C and exposure time of ~60 h). The use of boron nitride (BN) as a protective coating on graphite mold parts did not prevent the formation of nonuniform layer on the ceramic surface.

Keywords: tungsten carbide; spark plasma sintering; carbon diffusion; grain size distribution

# 1. Introduction

Hard alloys based on tungsten carbide (WC) with the addition of cobalt (Co), iron (Fe), nickel (Ni) and other low-melting metal phases are used in mechanical engineering for the production of wire drawing dies, drill bits and other wear-resistant machine elements [1–4]. Tungsten carbide is characterized by high hardness and wear resistance, high melting point as well as chemical resistance to acids and alkalis [1,5]. The combination of these properties allows the use of WC-based ceramics at high temperatures and under heavy loads. However, binderless tungsten carbide has a low fracture toughness and bending strength [5]. New technologies for producing high-strength binderless WC ceramics attract researchers' attention for this reason [5–8].

Spark plasma sintering (SPS) is one of the most promising FAST (field-assisted sintering technology) methods of manufacturing high-density fine-grained ceramics and hard alloys [3–5,9,10]. The technology consists of high-speed heating of conductive mold filled with initial powder or green body by passing millisecond current pulses (up to 5000 A) with simultaneous application of uniaxial load [9,11–13]. High speed of heating



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). (up 2500 °C/min) is provided by the use of pulse mode. This approach makes it possible to reduce the sintering time and keep the grain size in ceramics close to the particle size of initial powder. The advantage of SPS is the ability to control and manage key technological parameters directly during the sintering process—the applied stress, the heating rate, the sintering temperature, the time of isothermal exposure, the cooling rate. This ensures effective control of microstructure parameters and performance properties of ceramics and hard alloys. Descriptions of the SPS features were considered in detail in previous studies [11–13]. The effectiveness of SPS technology use for sintering ceramics and hard alloys based on tungsten carbide was demonstrated in several studies [3–5,10].

The use of WC nanopowders for the production of ceramics and hard alloys provides additional opportunities to optimize their phase composition, microstructure parameters and improve mechanical properties. One of the most promising methods for producing WC nanopowders is the DC arc plasma chemical synthesis [14]. The method allows to obtain tungsten monocarbide ( $\alpha$ -WC) powders with an average particle size of 30–80 nm. Previous studies reported that binderless ceramics obtained by SPS of plasma chemical nanopowders WC are characterized by high hardness (up to 30 GPa) and fracture toughness (4–5 MPa m<sup>1/2</sup>) [5]. WC—Co hard alloys made by sintering of plasma chemical nanopowders WC also had high hardness [15].

Recent studies suggest that ceramics and hard alloys produced by spark plasma sintering of WC nanopowders have nonuniform microstructure [15–17]. The method of layer-by-layer X-ray diffraction analysis (XRD) is the most effective way to study this issue [16,17]. The XRD information depth is about 5  $\mu$ m at the CuK $\alpha$  wavelength ( $\lambda = 1.54$  Å) due to the high absorption of X-ray radiation in phases containing tungsten. Sequential removal of layers will allow to carry out phase analysis of ceramics at different distances from the surface. The distribution of  $\eta$ -phase (Co<sub>3</sub>W<sub>3</sub>C) over the depth of WC + 10% wt. Co hard alloys was investigated using the technique of layer-by-layer XRD. It was found that there is no  $\eta$ -phase (Co<sub>3</sub>W<sub>3</sub>C) in the surface layer about 300–350  $\mu$ m in thickness [17]. Similar results were obtained for binderless WC ceramics [16]. It is assumed that the surface layer heterogeneity of ceramics and hard alloys based on WC was due to the intense carbon diffusion from graphite foil and graphite mold used in spark plasma sintering [16,17]. The carbon contamination effect of the surface layers of ceramics during SPS was also described in several studies [12,18–20].

The carbon contamination is considered as a negative effect that affects many characteristics of different ceramics [12,19–23]. As a result of this effect, the optical properties of oxide ceramics can be reduced [20–23]. At the same time, carburization of the surface layers in ceramics and hard alloys based on WC can lead to a decrease in the content of undesirable phases and, as a result, contribute to an increase in hardness [17,24].

W–C system is characterized by the presence of a very narrow range of temperatures and concentrations corresponding to the area of stable existence of  $\alpha$ -WC phase [25]. Even a slight deviation of the carbon content from the stoichiometric composition (6.13% wt.) leads to the appearance of undesirable W<sub>2</sub>C phase in WC ceramics or to the formation of  $\eta$ -phases (Co<sub>2</sub>W<sub>4</sub>C, Co<sub>3</sub>W<sub>3</sub>C, Co<sub>6</sub>W<sub>6</sub>C, Co<sub>3</sub>W<sub>9</sub>C<sub>4</sub>) in WC–Co hard alloys [5,15,17,25].

Adsorbed oxygen is present on the surface of WC powder particles [26]. Tungsten carbide nanopowders are characterized by increased oxygen concentration [26,27]. Oxygen reacts with carbon in carbide particles to form carbon dioxide, W<sub>2</sub>C phase and/or tungsten oxide in the process of heating WC powder [27]. The problem of decarbonization is partially solved by introducing a small amount of graphite into the raw WC powder [15,17,27]. Carbon is also introduced into tungsten powders containing oxygen as an impurity [28,29]. This decision avoids the formation of undesirable phases and leads to an increase in the mechanical properties of ceramics and hard alloys. However, excessive graphite content in the raw WC powder can lead to rapid grain growth and negatively affects the mechanical properties of WC-based materials [5,15,17,30,31]. The exact determination of the required graphite content is a difficult task. The oxygen concentration may increase during long-term storage of the powder or working with it in an environment containing oxygen.

The purpose of the work is a detailed study of the heterogeneity of the surface layers of the binderless tungsten carbide ceramics produced by spark plasma sintering.

#### 2. Materials and Methods

Three tungsten carbide (WC) powders with different average particle sizes were used as raw materials. Nanopowder #1 was prepared by DC arc plasma chemical synthesis [14]. Powders #2 and #3 were industrial micron powders produced by Kirovgrad Plant of Hard Alloys, JSC (Kirovgrad, Russia). Carbon and oxygen content in the raw powders was determined using an analyzer CS 400 (LECO, MI, USA). The average particle size of the powders was estimated by the formula:  $R_0 = 6/\rho_{\text{th}} \cdot S_{\text{BET}}$ , where  $\rho_{\text{th}}$  is the theoretical density of  $\alpha$ -WC (15.68 g/m<sup>3</sup>),  $S_{\text{BET}}$  is the specific surface area of the powder particles obtained by the BET method using TriStar 3000 analyzer (Micromeritics Instrument Corporation, GA, USA). The characteristics of the WC powders are presented in Table 1.

Powder	1	2	3
Specific surface area, m <sup>2</sup> /g	4.04	0.48	0.13
Average particle size, nm	95	800	3000
Oxygen content, % wt.	$0.40\pm0.01$	$0.25\pm0.01$	$0.12\pm0.01$
Carbon content, % wt.	$6.32\pm0.01$	$6.14\pm0.01$	$6.13\pm0.01$
Content of $\alpha$ -WC, % wt.	$97.4\pm0.2$	$98.6\pm0.2$	$98.4\pm0.2$
Content of $W_2C$ , % wt.	-	$1.4\pm0.2$	$1.6\pm0.2$
Content of W, % wt.	$2.6\pm0.2$	-	-
Average particle Size, hitOxygen content, % wt.Carbon content, % wt.Content of $\alpha$ -WC, % wt.Content of W2C, % wt.Content of W, % wt.	$93$ $0.40 \pm 0.01$ $6.32 \pm 0.01$ $97.4 \pm 0.2$ - $2.6 \pm 0.2$	$\begin{array}{c} 0.25 \pm 0.01 \\ \hline 0.14 \pm 0.01 \\ \hline 98.6 \pm 0.2 \\ \hline 1.4 \pm 0.2 \\ \hline - \end{array}$	$\begin{array}{c} 0.12 \pm 0.01 \\ \hline 6.13 \pm 0.01 \\ \hline 98.4 \pm 0.2 \\ \hline 1.6 \pm 0.2 \\ \hline \end{array}$

Table 1. The characteristics of the WC powders.

The concentration of oxygen in Nanopowder #1 was elevated. Carbon was added in the form of graphite (0.3% wt.) by the manufacturer to the composition of powder #1 to eliminate the negative effects of oxygen. Powders #2 and #3 also contained 0.05% wt. of graphite.

The powders were poured into a graphite mold with an inner diameter of 12.8 mm, an outer diameter of 30 mm and a height of 30 mm. The uniaxial stress (70 MPa) was applied to the mold using two graphite punches. The punch diameter was 12 mm and the height was 20 mm. Graphite foil with a thickness of 200  $\mu$ m was used to reduce the clearance between the specimen and the inner surface of the mold. Two sheets of graphite foil were placed between the powder and the punch surface. Preliminary pressing of the powders in mold was carried out using a hydraulic press Sorokin (Sorokin, Moscow, Russia) at room temperature at a stress of 70 MPa.

Spark plasma sintering of the WC powders was conducted using Dr. Sinter model SPS-625 setup (SPS Syntex, Tokyo, Japan). Figure 1 shows schematic setup of SPS system.

Graphite mold was covered with graphite felt of 4 mm in thickness to ensure the homogeneity of the temperature field during sintering inside the mold. A hole with a diameter of 14 mm was cut into the graphite felt for the temperature control during SPS. The temperature was measured using an optical pyrometer IR-AHS2 (CHINO, Tokyo, Japan) focused on the height middle of the mold outer wall. The accuracy of temperature measurements was  $\pm 20$  °C. SPS of the WC powders was carried out in a vacuum (about 6 Pa) under a uniaxial compressive stress of 70 MPa. The powders were heated at the rate of 50 °C/min until the end temperature of the effective shrinkage of the powders: 1410 °C (powder #1), 1530 °C (powder #2), 1625 °C (powder #3). There was no exposure at the sintering temperature. Free cooling was used to cool the specimens.

The comparison objects were WC ceramics produced by sintering in graphite molds with a protective coating of boron nitride (BN). Solution of BN was applied to the inner surfaces of the graphite parts (mold, punches, foil) that contact with the powder during SPS.



Figure 1. Basic spark plasma sintering system configuration. Scheme.

The dependencies of the effective powder shrinkage ( $L_{eff}$ ) on the heating temperature were recorded during sintering using a built-in dilatometer of Dr. Sinter model SPS-625. Experiments on heating an empty mold were carried out to account for the contribution of thermal expansion of the graphite mold ( $L_0$ ). The true shrinkage (L) was determined by the formula:  $L = L_{eff} - L_0$ .

The initial heights of the ceramics did not exceed 6 mm. The specimen surface was sequentially ground with diamond discs and polished with diamond pastes. Grinding was carried out on the Secotom 10 machine (Struers, Copenhagen, Denmark). Polishing was performed on the AutoMet 250 machine (Buehler, Braunschweig, Germany). Eleven stages of the mechanical treatment of the specimen surface were carried out. Each stage consisted of grinding and polishing. The layer up to 50  $\mu$ m in thickness (stages #1–7) and the layer at least 200  $\mu$ m in thickness (stages #8–11) was removed from the specimen surface in each treatment stage. In total, the layer about 1100–1200  $\mu$ m in thickness was removed from the surface of each specimen. The height control of the specimens was carried out using a micrometer 34480-25\_z01 (ZUBR, Moscow, Russia) with an accuracy equal to 10  $\mu$ m.

X-ray diffraction (XRD) studies of the powders and ceramics were carried out on the XRD-7000 diffractometer (Shimadzu, Kyoto, Japan) in CuK $\alpha$  radiation ( $\lambda$  = 1.54 A). Scanning was performed in the Bragg–Brentano geometry in the range of angles  $2\theta = 30-80^{\circ}$ with the step of 0.04° and the exposure of 2 s. XRD experiments were carried out after each stage of the specimen surface treatment (stages #1–11). The XRD experiment of stage #0 was conducted before the mechanical treatment of the specimen surface. The calculated penetration depth of CuK $\alpha$  radiation into the surface of WC specimens did not exceed  $5 \,\mu$ m, which was much less than the thickness of the removed layer during the mechanical grinding (50–200 μm). Qualitative phase analysis was carried out using the PDF-2 database (ICDD, 2012): α-WC (PDF 00-051-0939), W<sub>2</sub>C (PDF 00-035-0776), W (PDF 00-004-0806), C (PDF 00-056-0159), WB (PDF 00-006-0541), BN (PDF 01-085-1068). Quantitative phase analysis was carried out by the reference ratio method using cif-files of the ICSD (2015):  $\alpha$ -WC (ICSD 43380), W<sub>2</sub>C (ICSD 159904), W (ICSD 76151). The diffraction peak (101) at  $2\theta = 48.3^{\circ}$  was chosen as the analytical peak of  $\alpha$ -WC phase during the quantitative analysis. The analytical peaks of  $W_2C$  and W phases were (101) at  $2\theta = 39.6^{\circ}$  and (110) at  $2\theta = 40.3^{\circ}$ , respectively.

The microstructure of the powders and ceramics was studied by scanning electron microscopy (SEM) on a microscope JSM-6490 (JEOL, Tokyo, Japan). The images of the powder microstructure were obtained in secondary electron imaging (SEI) mode, which is sensitive to the surface relief of the powder particles. The images of the ceramic microstructure were obtained in back-scattered electron contrast (BEC) mode, which is sensitive to

contrast. After the sixth stage of the mechanical treatment of the surface and removal of the layer of 150  $\mu$ m in thickness, the control specimens were cut in half, as shown in Figure 2a. The cross section was polished with diamond pastes. Figure 2b shows the areas under study. In particular, D area was located on the surface that was subjected to the mechanical treatment.



Figure 2. Cutting scheme (a) and location of cross section areas under study (b) of the WC ceramics.

In total, 9 ceramic specimens were sintered and studied. Powders #2 and #3 were sintered twice to control the reproducibility of the measurement results.

Specimens produced from powders #1, #2, #3 are referred to as ceramics #1, #2, #3. Specimen labeling Ceramic 2-1 means that the specimen #1 produced from powder #2 is described. Specimen labeling Ceramic 2-1-BN means that the specimen #1 produced from powder #2 using a protective coating of boron nitride is described. Such labeling of the specimens was used to demonstrate the reproducibility of the results. The result reproducibility was evaluated based on a comparison of the specimens sintered under the same conditions.

## 3. Results

## 3.1. Characterization of the WC Powders

Figure 3 shows the results of the SEM studies of the WC initial powders. Agglomerates of individual nanoparticles were observed in powder #1 (Figure 3a). The size of the agglomerates did not exceed 10  $\mu$ m. No agglomerates were found in powders #2 and #3 (Figure 3b,c). The average particle size of powders #2 and #3 was 1  $\mu$ m and 3  $\mu$ m, respectively. The specified values of the average particle size determined by the chord method were close to the average particle size according to Fischer, declared by the powder manufacturer (Table 1).



Figure 3. SEM images of WC powder #1 (a), #2 (b), #3 (c).

Figure 4 presents the results of the XRD studies of the WC powders. The diffraction peaks on the pattern of powder #1 corresponded to  $\alpha$ -WC and  $\alpha$ -W phases. The XRD peaks on the diffraction pattern of powder #1 were significantly broadened compared to the

XRD peaks on the patterns of powders #2 and #3. The mass fraction of tungsten in plasma chemical nanopowder #1 was 2.6  $\pm$  0.2% wt. (Table 1). The XRD peaks on the patterns of powders #2 and #3 corresponded to  $\alpha$ -WC and W<sub>2</sub>C phases. The mass fraction of W<sub>2</sub>C in powders #2 and #3 were 1.4  $\pm$  0.2 and 1.6  $\pm$  0.2% wt., respectively (Table 1).



**Figure 4.** XRD patterns of WC powders #1–3. The pattern number corresponds to the powder number (Table 1).

# 3.2. SPS of the WC Powders

Figure 5 shows graphical sintering diagrams of the ceramics sintered from powders #1-3 in the Process time (t)—Temperature (T)—Stress (P) coordinates. Stability and reproducibility of SPS process were ensured during the manufacture of specimens #2 and #3 (Figure 5b,c).





Figure 6 presents the temperature shrinkage curves L(T) of the WC powders. The L(T) curves had a conventional three-stage character for all powders: stage I—slight compaction at 600–1000 °C, stage II—intensive shrinkage at 1000–1400 °C, stage III—low shrinkage rate at above 1400 °C. The difference in the absolute shrinkage ( $L_{max}$ ) observed in Figure 6 was due to the difference in the bulk density of the powders under study. A previous investigation reported a detailed analysis of SPS process of these powders [15].



**Figure 6.** Temperature shrinkage curves *L*(*T*) of WC powders 1–3.

The effective density of ceramics #1, #2, #3 was determined by hydrostatic weighing: 99.2% ( $15.642 \text{ g/cm}^3$ ), 96.2% ( $15.168 \text{ g/cm}^3$ ), 96.0% ( $15.140 \text{ g/cm}^3$ ), respectively [15]. The specimens had no visible macrodefects such as chips, cracks or large pores. The specimens were not destroyed during the grinding and polishing process.

## 3.3. Layer-by-Layer Analysis of the WC Ceramics

Figure 7 shows images of ceramic #1 after different stages of the surface mechanical treatment. The characteristic appearance of the ceramics with untreated initial surface (stage #0) is presented in Figure 7a. Graphite foil residues were visible on the specimen surface. This layer was removed during the initial mechanical treatment of the specimens (stage #1, Figure 7b). The gray metallic color characteristic of binderless tungsten carbide appeared after the second stage of the mechanical treatment (stage #2, Figure 7c).



**Figure 7.** Appearance of ceramic #1 after various stages of the surface mechanical treatment: untreated initial surface—stage #0 (**a**), stage #1 (**b**), stage #2 (**c**). Graphite foil remains on the ceramic surface after sintering (**a**), which can only be removed by mechanical treatment.

Figure 8 shows the XRD patterns of ceramics #1–3 after each stage of the mechanical treatment, including the diffraction pattern of the untreated surface (stage #0, Figure 7a). The XRD peaks on the untreated surface pattern correspond to the  $\alpha$ -WC and graphite phases. The high-intensity XRD peak of graphite on the diffraction pattern at  $2\theta \approx 54^{\circ}$  was explained by the presence of graphite foil residues on the untreated surface of the specimens (Figure 7a). The graphite peak on the diffraction pattern was not observed after the second stage of the surface mechanical treatment of ceramic #1 (Figure 8a) and after the third stage of the treatment of ceramics #2 and #3 (Figure 8b,c).



(a)



(b)



Figure 8. XRD patterns of ceramic 1 (a), 2 (b), 3 (c) after every stage of the surface treatment.

The diffraction peaks corresponding to  $W_2C$  phase were observed on the patterns starting from the fourth stage of the mechanical treatment. The intensity of  $W_2C$  peaks increased with the total removed layer thickness (Figure 9a). These results were similar to those of ceramics 2 and 3 (Figure 9b,c).



**Figure 9.** Sections of the XRD patterns of ceramic #1 (a), #2 (b), #3 (c) after various stages of the surface treatment. The intensity of the  $W_2C$  phase peaks increases with increasing thickness of the removed layer.

Table 2 presents the results of the quantitative XRD of ceramics #1-3 after various stages of the surface mechanical treatment. It can be seen from the data in Table 2 that there was no difference (within the uncertainty) in the mass fraction of  $W_2C$  phase for the ceramics #2 and #3 sintered under the same conditions.

**Table 2.** Results of the quantitative XRD analysis of WC ceramics 1–3 depending on the stage of the surface treatment.

	Content of $W_2C$ , % wt.						
Stage	Ceramic #1	Ceramics #2		Ceramics #3			
	Sample #1	Sample #2-1	Sample #2-2	Sample #3-1	Sample #3-2		
#0–3	-	-	-	-	-		
#4	$0.9\pm0.2$	$1.6\pm0.2$	$1.0\pm0.2$	$2.1\pm0.2$	$1.4\pm0.2$		
#5	$0.7\pm0.2$	$1.6\pm0.2$	$1.2\pm0.2$	$1.8\pm0.2$	$1.7\pm0.2$		
#6	$1.3\pm0.2$	$3.1\pm0.2$	$3.5\pm0.2$	$3.9\pm0.2$	$4.1\pm0.2$		
#7	$1.5\pm0.2$	$2.6\pm0.2$	(*)	$3.9\pm0.2$	(*)		
#8	$2.1\pm0.2$	3.1 ± 0.2		$3.7\pm0.2$			
#9	$2.0\pm0.2$	$3.1\pm0.2$		$3.4\pm0.2$			
#10	$2.0\pm0.2$	$3.3\pm0.2$		$4.0\pm0.2$			
#11	$1.9\pm0.2$	$3.1\pm0.2$		$3.5\pm0.2$			

(\*) The surface treatment of the specimen has been completed. The specimen was cut in accordance with the scheme shown in Figure 2b to the SEM study.

Figures 10–12 shows the results of the SEM studies of ceramics 1–3. Ceramics 2-2 and 3-2 were examined according to the scheme shown in Figure 2.



Figure 10. Microstructure of ceramic #1. SEM.



(c)

Figure 11. Microstructure of ceramic #2 cross section: area A (a), area B (b), area C (c). SEM. Abnormally large grains are observed at the edges of the sample. The edges came in contact with a graphite foil during sintering.



Figure 12. Microstructure of ceramic #3 cross section: area A (a), area B (b), area C (c). SEM.

As can be seen in Figures 10-12, the surface layers of the ceramics were characterized by nonuniform distribution of grain sizes, including the presence of abnormally large grains. Areas with non-uniform grain size distribution had a clear boundary. The thickness of the layers was 50–100 µm. The size of abnormally large grains reached 50 µm. Abnormally large grains can be observed at the very edge of the specimen cross section (Figure 11c), which came in contact with a graphite foil during sintering. Additionally, there was another thin layer with a clear boundary, containing grains whose size exceeded the average one in the main volume of the specimens by 2–3 times (most prominently in Figure 11a,b). Despite the difference in the sintering temperatures, there was no difference in the surface layer depth in ceramics #2 and #3. The grains in the surface layer of ceramic #1 (Figure 10) were mostly elongated. The average size of the abnormally large grains in ceramics 1 was much smaller than the one in ceramics 2 and 3.

A number of researchers reported about abnormal grain growth in tungsten carbide at Spark Plasma Sintering [5,30,31]. Abnormal grain growth is also often detected in the study of WC–Co hard alloys [15,17,32–35]. Researchers note that increased concentration of carbon in powder is one of the key factors contributing to the appearance of large grains in fine-grained materials based on WC [32–35].

Thus, the analysis of the presented experimental results showed that the binderless tungsten carbide specimens obtained by SPS method have nonuniform microstructure and phase composition. It was presumed that the heterogeneity was due to the carburization of the surface layers of tungsten carbide.

#### 3.4. Influence of BN Coating on the Phase Composition and Microstructure of the WC Ceramics

To minimize the carburization effect of the surface layers, graphite molds with a protective coating of boron nitride on the inner surface were used. The protective coating was also applied to the graphite foil and to the punch surface. Figure 13 presents the temperature shrinkage curves L(T) of the WC powders sintered in the graphite molds with BN coating. A comparison of the curves L(T) shown in Figures 6 and 13 revealed that there was no effect of BN coating on the character of the curves L(T).



**Figure 13.** Temperature shrinkage curves *L*(*T*) of WC powders #1–3 sintered in the graphite molds coated with BN.

Figure 14 presents the XRD patterns of the untreated surface (stage #0) of ceramics #1–3 sintered in the graphite molds with BN coating. The XRD peaks of  $\alpha$ -WC phase, graphite, tungsten boride WB (ICDD PDF 00-035-0738), boron nitride BN (ICDD PDF 01-085-1068) were observed on the diffraction patterns of the specimens.



**Figure 14.** XRD patterns of the untreated initial surface (stage #0) of ceramics #1–3 sintered in the graphite molds coated with BN.

Traces of WB and BN phases were observed in all ceramics up to #3–4 stages of the surface mechanical treatment. At the same time, one of the most intense peaks of WB phase (at  $2\theta \approx 39.2^{\circ}$ ) overlapped with the most intense peak of W<sub>2</sub>C phase. In this regard, there

was no reliable evidence that  $W_2C$  phase was present in the ceramics at stages #1–4 of the surface treatment. Full XRD patterns of the ceramics #1–3 sintered in the graphite molds with BN coating are presented in Figure 15.



Figure 15. XRD patterns of ceramic #1 (a), #2 (b), #3 (c) sintered in the graphite molds coated with BN.

Figure 16 shows the results of the SEM investigation of microstructure at the edge of the lower face of ceramics #1-3 sintered in the graphite molds with BN coating.

Figure 17 presents the results of the SEM investigation (according to the scheme in



Figure 16. Microstructure of ceramic #1 (a), #2 (b), #3 (c). SEM.





Figure 17. Microstructure of ceramic #2 cross section: area A (a), area B (b), area C (c). SEM.

Areas with non-uniform grain size distribution were observed on the ceramic surface sintered in the mold with BN coating (Figures 16 and 17). The areas of non-uniform microstructure were found to have a clear boundary between the layers. The area thickness varied from 50 to 150 µm (Figure 17a,b). Cracks observed in the surface layer indicated a low fracture toughness of this layer (Figure 17c).

#### 4. Discussion

To analyze the results presented, it was necessary to consider the nature of the phase transformations in tungsten carbide-based ceramics at sintering previously. It is a widely held view that  $W_2C \rightarrow \alpha$ -WC phase change is possible only in the presence of excess carbon in accordance with the reaction [25,36]:

$$W_2C + C \to 2 \alpha - WC. \tag{1}$$

As mentioned in the introduction to the paper, adsorbed oxygen is present on the surface of WC powder particles [26]. Oxygen reacts with carbon in WC carbide particles to form carbon dioxide (CO<sub>2</sub>) in the process of heating WC powder:

$$2 \alpha - WC + O_2 \rightarrow W_2C + CO_2 (g). \tag{2}$$

This leads to a decrease in the carbon concentration in the carbide particles and the formation of  $W_2C$  phase particles. This process is also known as decarbonization [27,37].

As was pointed out in the introduction, the existence of  $\alpha$ -WC phase is a narrow carbon concentration range. The equilibrium carbon content in  $\alpha$ -WC is 6.13% wt. Even a slight deviation of the carbon concentration from its equilibrium value leads to the formation of  $W_2C$  particles [25,27,37].

Figure 18 shows the distribution of the mass fraction of  $W_2C$  phase over the specimen depth in ceramics #1–3. It was taken into account that at the first stages of the treatment, the graphite foil residues were found on the specimen surface. In this regard, the depth reference point correction by the thickness of the layer containing graphite was made.



**Figure 18.** Dependence of  $W_2C$  mass fraction on the distance from the ceramic surface #1 (a), #2 (b), #3 (c). The red vertical line indicates the distance from the surface where the  $W_2C$  phase peaks were indicated on the XRD patterns.

According to the results of the XRD studies, the layer with a thickness of at least 50  $\mu$ m that did not contain W<sub>2</sub>C phase on the ceramic surface. According to the results of the SEM

studies, abnormal grain growth processes were taking place in the surface layer. The phase composition of the specimens was a mixture of  $\alpha$ -WC and W<sub>2</sub>C phases in deeper layers. There was no significant difference in the mass fraction of W<sub>2</sub>C phase at a depth of more than 200–300  $\mu$ m.

As mentioned above,  $W_2C \rightarrow \alpha$ -WC phase change was possible only in the presence of "free" carbon (Equation (1)). It seems possible that the detection depth of  $W_2C$  phase corresponded to a rough estimation of the carbon diffusion depth into the ceramic surface. As can be seen from Figure 18, this value was at least 50  $\mu$ m.

Due to the classical equation (solution of Fick's law), the diffusion layer thickness increased with the square root of the sintering time:

$$x_C = \sqrt{tD^*} \tag{3}$$

*t*—the sintering time,  $D^*$ —the effective diffusion coefficient:

$$D^* = D_v + (\delta/d)D_b \tag{4}$$

 $D_v$ —the volume diffusion coefficient of carbon in WC,  $D_b$ —the grain boundary diffusion coefficient of carbon in WC,  $\delta$ —the grain boundary width ( $\delta \approx 5 \times 10^{-10}$  m), *d*—the average grain size.

The diffusion coefficient temperature dependence may be written in the form:

$$D_i = D_{0i} \exp(-Q_i / kT) \tag{5}$$

 $D_{0i}$ —the pre-exponential diffusion factor,  $Q_i$ —the diffusion activation energy (in  $kT_m$ ,  $T_m = 3143$  K—the melting point of  $\alpha$ -WC phase), *k*—the Boltzmann constant.

It was demonstrated that the volume diffusion depth of carbon (<sup>14</sup>C) of fine-grained tungsten carbide did not exceed 0.5 µm at temperature of 2370 °C (the exposure time ~60 h) [38]. Table 1 presents the comparison of available literature data for the carbon diffusion activation energy and pre-exponential factor in tungsten carbide. The estimation of the carbon diffusion depth in WC according to the presented literature data was performed for powder 1:  $T_1 = 1683$  K,  $t_1 = 28.2$  min,  $d_1 = 10^{-6}$  m.

The estimates of the carbon diffusion depth given in the paper (Figure 18) turned out to be significantly greater than the values calculated from the literature data (Table 3). Thus, it can be suggested that the effect of the abnormally deep carbon diffusion into tungsten carbide was observed in the spark plasma sintering process. The exact nature of this effect is not known.

Phase	Mechanism	$D_0,  { m m}^2/{ m s}$	$Q, kT_m$	References	<i>x</i> <sub>C</sub> , μm
α-WC	Volume	$1.9  imes 10^{-10}$	14.1	[20]	5
	Grain boundary	$4.6 imes10^{-2}$	11.4	- [30]	
	(*)	$10^{-8}$	9.3	[39]	1
W <sub>2</sub> C	Volume	$1.8  imes 10^{-3}$	14.6	[40]	2
	Grain boundary	$1.8  imes 10^{-8}$	11.0	- [40]	
	(*)	$6.7 imes10^{-4}$	11.9	[41]	16
		$2  imes 10^{-4}$	13.6	[42]	2
		0.1	16.0	[43-45]	4
		30	20.0	[46,47]	2

Table 3. Carbon diffusion parameters in tungsten carbide.

(\*) There is no clarification about the carbon diffusion mechanism in a number of studies [39,41–47]. In this regard, it is assumed that the effective diffusion coefficient is specified.

It seems possible that there were three main factors contributing to a significant acceleration of the carbon diffusion process during sintering of tungsten carbide.

Firstly, it should be noted that SPS process of tungsten carbide is accompanied by plastic deformation of particles by the mechanism of power-law creep [48]. The strain can accelerate the carbon diffusion in the surface layers of ceramics based on tungsten carbide.

The second factor was the multistage process of  $W_2C$  particle formation at sintering, which can lead to an increase in the error in determining the carbon diffusion depth. Two processes (decarbonization and carburization) occurred simultaneously during the sintering of WC-based ceramics. The decarbonization process led to an increase in the proportion of  $W_2C$ , and the carburization process caused a decrease in the proportion of  $W_2C$ . The rates of these processes may differ and have different activation energy values. As a result of the addition of the two processes, non-monotonic character of the estimated carbon diffusion depth from the temperature and time of SPS process can be obtained.

The third factor to be taken into account was nonuniform distribution of thermal and electric fields at SPS [11,49,50]. In particular, overheating of the specimen surface at increased heating rates may cause an increase in the carbon diffusion depth. However, it was difficult to expect a large difference in the temperatures of the central and surface layers during the sintering of tungsten carbide specimens. Therefore, it was assumed that the influence of this factor was insignificant.

#### 5. Conclusions

The phase composition homogeneity of tungsten carbide specimens obtained by spark plasma sintering was investigated. This study showed that the phase composition and microstructure of the specimen surface layer significantly differed from the phase composition and microstructure of the central layer. The ceramic surface layers contained increased carbon concentration, which prevented the formation of  $W_2C$  particles and caused intensive grain growth. There was no significant dependence of the carburized layer depth on the initial particle size and sintering temperature. According to the results of the X-ray diffraction studies, the carburized layer depth in the specimens was ~50 µm. The layer with a thickness of at least 50 µm with grains 10–50 times larger than the grain size in the main volume of the specimens was present near the surface. In the central layers of the ceramics, a uniform fine-grained microstructure and a homogeneous increased mass fraction of  $W_2C$  compared to the raw powders were observed.

It seems possible that changes in the phase composition and abnormal grain growth in the surface layers of tungsten carbide ceramics were due to abnormally deep carbon diffusion during sintering. The excess carbon source can be the material of a graphite mold and graphite punches, as well as graphite foil, which was used to reduce the clearance between the specimen and the inner surface of the mold. The current study found that the boron nitride coating did not completely eliminate the carburization effect of the surface layers of tungsten carbide ceramics.

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