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Binderless tungsten carbides with an increased oxygen content obtained by spark plasma sintering

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Abstract. The features of spark plasma sintering (SPS) of plasma-chemical nanopowders with an increased oxygen content are investigated. It is shown that the process of shrinkage of nanopowders during SPS is limited by the rate of grain-boundary diffusion with anomalously low values of the activation energy. It has been established that a decrease in the activation energy of SPS may be due to the effect of oxygen on the diffusion permeability of grain boundaries of tungsten carbide at the stage of intense compaction, as well as anomalous grain growth at the stage of high-temperature sintering. The SPS kinetics of WC-W₂C-WO₃-W nanopowder compositions at the stage of intensive compaction is controlled by the rate of sintering of oxide particles with their simultaneous transformation into W_2C particles, and then, at the stage of high-temperature sintering, by the process of plastic flow of W_2C particles in the presence of tungsten particles. Ceramic samples with high density (98-99%), ultrafine-grained structure (average grain size less than 0.3 µm), having increased hardness were obtained by the SPS method. $H_v = 30.5$ GPa at Palmquist crack resistance ~ 6.5 MPa \cdot m^{1/2}.

1. Introduction

Currently, hard alloys based on tungsten carbide are one of the most frequently used materials in the machine tool industry, which imposes ever higher demands on the physical and mechanical properties and performance characteristics (strength, hardness, crack resistance and wear resistance) of metal cutting tools [1-3]. At the same time, it should be noted that although the use of a low-melting metal binder phase allows an increase in crack resistance and bending strength, it inevitably leads to a decrease in the hardness of tungsten carbide, as well as to a decrease in the maximum allowable temperatures in the cutting zone, which imposes significant restrictions on the cutting speed. This circumstance determines the attempts to develop a new group of structural ceramics based on pure tungsten carbide [4, 5] for ceramic metal-cutting tools intended for finishing and semi-finishing machining of viscous structural materials.

Analysis of the literature data shows that one of the promising methods for producing ceramics is the technology of high-speed electric pulse ("spark") plasma sintering (SPS) [4, 6]. Ultrafine-grained ceramics obtained by the SPS method have both high density, increased strength, hardness and crack resistance [4-6]. In [4, 7], it was shown that the combined use of the SPS technology and the technology

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of plasma-chemical synthesis of nanopowders [8] makes it possible to obtain samples of tungsten carbide with high density, hardness, and crack resistance. One of the features of plasma-chemical nanopowders of tungsten carbide is an increased concentration of oxygen adsorbed on the surface of nanoparticles [9, 10], the amount of which monotonically increases with increasing storage time [9].

The aim of this work is to study the features of high-speed sintering of tungsten carbide nanopowders with an increased oxygen content, obtained by plasma-chemical synthesis, as well as to study their structure and physicomechanical properties.

2. Methods and materials

The objects of the study were nanopowders of tungsten monocarbide α -WC with different contents of oxygen, carbon and impurity phases (semi-carbide W₂C and tungsten α -W) obtained by the plasmachemical method [7, 8, 11]. Nanopowders of the W-C system were obtained by the process of reductive synthesis from tungsten trioxide WO₃ and methane in nitrogen-hydrogen (H₂ + N₂) arc thermal plasma. The resulting powders are a mixture of W₂C, WC_{1-x} (β -WC), α -W, oxides of tungsten and carbon with a predominance of W₂C semi-carbide in the resulting mixture (~ 65 vol.%). The synthesis of tungsten monocarbide was carried out in a hydrogen atmosphere at a temperature of 950-1050°C for 3-5 hours. By varying the temperature and time of annealing in hydrogen, the oxygen concentration and the volume fraction of particles (W₂C, α -W) in the synthesized nanopowders were varied. The description of tungsten carbide nanopowders is given in Table 1.

 Table 1. Characteristics of powders.

Group			Ι			II		III				
Powder No.		1	2	3	4	5	6	7	8	9	10	11
VDD	α-WC	100	100	100	99	99	99	70.6	70.2	73.2	79.4	70.6
AKD	W_2C	-	-	-	<1	<1	<1	2.3	3.5	3.6	2.4	3.8
vol.%	α-W	-	-	-	-	-	-	3.3	4.3	2.1	0.8	4.9
	WO _x	-	-	-	-	-	-	23.8	22	21.1	17.4	20.7
Carbon, %		6.26	6.14	6.08	6.22	6.08	6.05	5.34	5.28	5.24	5.18	5.03
Oxygen, %		1.30	1.57	1.57	1.31	1.32	1.26	4.35	4.2	4.82	5.17	4.76
S_{BET} , m^2/g		7.98	7.98	8.32	10.45	8.53	8.86	а	а	а	а	а
R_0 , nm		47	47	46	36	44	43	а	а	а	а	а

^a due to the presence of powders with different initial particle sizes in the composition of Group III compositions, the average specific gravity has no physical meaning

All synthesized powders were divided into three groups. The first (I) group includes nanopowders (No. 1-3) of tungsten monocarbide with different carbon content (6.08-6.26 wt.%), the second (II) group includes nanopowders (No. 4-6) with a low content of W_2C particles and different carbon contents (6.05-6.22 wt.%), and the third (III) group contains nanopowders (No. 7-11) with a high content of oxides and an increased concentration of oxygen, in which, in addition to W_2C particles, α -W particles and oxide particles are present.

The measurement of the specific surface area of the powders (S_{BET}, m^2 / g) was carried out on a Micromeritics TriStar 3000 analyzer. The S_{BET} determination accuracy was $\pm 0.02 \text{ m}^2 / g$. The average initial particle size (R₀, nm) was calculated by the formula: R₀ = $6 \cdot 10^3 / (\rho_{WC} \cdot \text{SBET})$, where $\rho_{WC} = 15.77 \text{ g} / \text{cm}^3$ is the theoretical density of tungsten monocarbide. The oxygen and carbon content was determined using a LECO TC-600 analyzer. The accuracy of determining the concentration of carbon and oxygen was $\pm 0.01 \text{ wt\%}$.

The compaction of samples with a diameter of 12 mm and a height of h = 3 mm was carried out by the SPS method using a Dr. Sinter model SPS-625. Sintering was carried out in a vacuum (4 Pa) by passing millisecond (3.3 ms) high-power direct current pulses (up to 5 kA) through a graphite mold. The sintering was carried out by heating at a predetermined rate (50°C / min) to the sintering temperature T_s

= 1500°C, followed by cooling in free mode. The applied load was 70 MPa. There was no holding at the sintering temperature (t = 0).

The structure of the samples was studied using a JEOL JSM-6490 scanning electron microscope with an Oxford Instruments INCA 350 energy dispersive microanalyzer. The average grain size (d) was measured by the chord method with an accuracy of $\pm 0.1 \,\mu$ m. X-ray phase analysis (XRD) of the samples was carried out using a Shimadzu XDR-7000S diffractometer (CuK_a radiation, scanning rate 0.25 rpm). The phase composition of the samples was determined by the method [12], in the program "Diffrac.EVA".

Sample density (ρ) was measured by hydrostatic weighing using a Sartorius CPA 225D analytical laboratory balance. The error in determining ρ was 0.01 g / cm³. When calculating the relative density (ρ / ρ_{th}) of samples with different initial contents of semi-carbide W₂C and tungsten (α -WC + W₂C + α -W), the density of the W₂C phase was taken to be 17.15 g / cm³, the density of tungsten is 19.25 g / cm³, and the density tungsten oxide - 7.3 g / cm³.

Vickers hardness (H_v) was measured using a Struers Duramin-5 microhardness tester (load 2 kg). The minimum fracture toughness coefficient $K_{IC\,(min)}$ was calculated by the Palmquist method, along the length of the maximum crack. The measurement accuracy of H_v and K_{IC} was \pm 0.1 GPa and \pm 0.2 MPa m^{1/2}, respectively.

3. Results

Analysis of the SEM data shows that the nanopowders of groups I and II are rather uniform in their particle size distribution. Agglomerates 50-100 μ m in size found in the structure were easily destroyed by preliminary pressing in a graphite mold.

The initial dependences of shrinkage L (T) of nanopowders were recalculated into compression curves ρ/ρ_{th} (T) using the procedure described in [4, 13]. From the calculated compaction dependences ρ/ρ_{th} (T) shown in Figure 1, it can be seen that with high-speed heating, two different types of compaction of tungsten carbide nanopowders are observed - the compaction curves for nanopowders of groups I and II are quite close to each other, while the dependences ρ/ρ_{th} (T) for nanopowders with an increased content of oxides (group III) have a more complex character, apparently due to the multistage nature of baking different powders to each other, as well as the multistage nature of the chemical reactions occurring during sintering in the W-C-O system. The stage of intensive shrinkage for nanopowders of groups I and II ends at temperatures of ~ 1400-1420°C, the temperature of the end of the stage of active shrinkage for nanopowders of group III lies in the range from 1220°C to ~ 1300°C.



Figure 1. The dependence of the relative density of the sintered samples on the heating temperature during the SPF: (a) - group I, (b) - group III.

Figure 2 shows an analysis of the results of XRD for samples sintered at different temperatures. It can be seen that when group III nanopowders (for example powder No. 7) are heated to 900°C, the WO₃

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oxide is converted to WO₂ without significant changes in the total volume fraction of oxides and tungsten monocarbide in the sintered composition (~ 24-25% and ~ 74%, respectively). When heated to 1000°C, the volume fraction of tungsten oxides in the samples becomes less than the detection limit by XRD, and the volume fraction of tungsten α -W sharply increases to ~ 61-62% with a simultaneous decrease in the volume fraction of tungsten monocarbide to ~ 41%. Further heating to 1500°C leads to a decrease in the volume fraction of tungsten monocarbide and α -W to ~ 32% and ~ 2%, respectively, and an increase in the volume fraction of the W₂C phase to ~ 66%. Note that at temperatures of 1100°C and 1200°C, corresponding to the temperatures of the change in the slope of the ρ/ρ_{th} (T) dependences at the stage of intense shrinkage (Stage II), the volume fraction of tungsten particles is quite large and amounts to 61.5% and 23.7%, respectively.



Figure 3. The SEM results of the sintered ceramic from powder No.3 (Group I).

Figure 4. The SEM results of the sintered ceramic from powder No.8 (Group III).

The phase composition, density, microstructure parameters and physical and mechanical properties of sintered tungsten carbide samples are given in Table 2, from which it can be seen that the obtained samples are characterized by high relative density (96.74-98.61%) and small - submicron - average grain size (0.17-0.24 μ m). Sintered samples of group I ceramics are characterized by high hardness (more than 30 GPa) and increased crack resistance (5.1-5.5 MPa \cdot m^{1/2}), which makes it possible to consider the obtained materials as structural ceramics.

The results of electron microscopic studies show (Figure 3) that in the structure of group I samples obtained from nanopowders with a low carbon content and an increased oxygen content (samples No. 2, 3), there are abnormally large grains, the average size (length) of which can reach 3-5 μ m. The XRD

results show that the structure of sintered samples contains W₂C semi-carbide particles, the volume fraction of which varies from 5.0 to 11.4 vol%. Note that the volume fraction of W₂C particles, determined by the XRD method, with a good degree of accuracy corresponds to the volume fraction of anomalously large grains in the structure of sintered samples. This suggests that the reason for the appearance of W₂C particles in tungsten carbide is the increased concentration of oxygen in the initial nanopowders - during heating, the oxygen adsorbed on the surface of α -WC nanopowders chemically reacts with the carbon contained in tungsten monocarbide to form carbon dioxide (2WC + O₂ \rightarrow W₂C + CO₂). This leads to the decomposition of tungsten monocarbide particles and the formation of W₂C semi-carbide particles, which will be the nuclei for abnormally large grains. As can be seen from table 2, this process will proceed most intensively during sintering of nanopowders, the carbon content of which is below the equilibrium value (C₀ = 6.14 wt% [1]).

Group			Ι			II			III				
Powder No.		1	2	3	4	5	6	7	8	9	10	11	
עע	α- WC	94.7	95	88.6	91.4	89.7	91.7	32	19.9	24.7	16.1	15.3	
results	$egin{array}{c} W_2 \ C \end{array}$	5.3	5	11.4	8.6	10.3	8.3	66.1	78.2	71.4	82.3	81.3	
, vol %	α-W	-	-	-	-	-	-	1.9	1.9	3.9	1.6	3.4	
V01.70	WO	-	-	-	-	-	-	-	-	-	-	-	
	х	08.0	07.6	067	08.6	08.2	08.5	08.8	07.0	07.8	077	08.6	
ρ/ρ_{th}	, %	98.0 9	4	90.7 4	98.0 1	98.2 8	1	98.8 6	97.9	4	3	98.0 9	
d, µ	m	0.17	0.18	0.24	0.16	0.23	0.21	1.5	1.8	1.2	2.4	1.7	
H _v , GPa		29.9	30.3	30.5	30.2	30.5	29.9	22.9	21.3	21.8	21.2	21.8	
$K_{IC}, MPa \cdot m^{1/2}$		5.3	5.1	5.5	4.1	6.5	6.1	4.9	3.9	4.9	5.2	6.5	

Table 2. Characteristics of sintered ceramics.

Group II nanopowders initially contained less than 1 vol% of W_2C particles, but had a lower oxygen concentration at a comparable carbon concentration (see table 1). In our opinion, the lower oxygen concentration in the initial nanopowders makes it possible, under conditions of high-speed heating, to reduce the rate of decomposition of tungsten monocarbide and the formation of the W_2C phase and, as a consequence, to ensure the production of high-density samples, the phase composition and microstructure parameters of which are close to the samples sintered from group I nanopowders (see table 2).

The results of the XRD study show that group III powders contain an increased volume fraction of tungsten oxides (17.4–23.8 vol.%), as well as particles of semi-carbide W₂C and tungsten α -W. During sintering, tungsten oxide interacts with tungsten monocarbide α -WC to form semi-carbide according to the previous presented formula. The occurrence of these chemical reactions determines the absence of oxide particles and the presence of an increased volume fraction of the W₂C phase in sintered samples of tungsten carbide. Note also that the volume fraction of tungsten particles decreases slightly (see table 2), which is probably due to the occurrence of the chemical reaction W + WC \rightarrow W₂C. The increased density of sintered specimens (density is ~ 16.5-16.8 g / cm³) is a consequence of the presence of tungsten particles in ceramics (density 19.3 g / cm³), which indirectly confirms the correctness of the XRD results. The relative density of the sintered ceramics varies from 97.73% (sample No. 10 with the maximum volume fraction of W₂C) to 98.86% (sample No. 7 with the minimum volume fraction of W₂C particles). The microstructure of most of the sintered specimens is heterogeneous - as can be seen from figure 4, against the background of a microcrystalline structure with an average grain size of ~ 2-3 µm, there are large spherical particles, which are obviously tungsten particles and oxide particles transformed into semi-carbide W₂C. The structure of sintered ceramics contains regions of anomalously

large grains, which are, apparently, regions of the W_2C phase. Note that micron-sized W_2C particles transformed from oxides are also located in the region of abnormally large grains. The hardness of the sintered ceramics of group III turns out to be much lower than the hardness of samples of groups I and II, but at the same time, for some samples, it is possible to provide sufficiently high values of the crack resistance coefficient corresponding to the K_{IC} value for samples of the first two groups. In our opinion, this is due to the positive effect of tungsten metal particles on the retardation of brittle cracks propagating in ceramics.

4. Discussion

The dependences ρ/ρ_{th} (T) for nanopowders of pure tungsten monocarbide (group I) and nanopowder with a low content of W₂C particles (group II) have a classical three-stage nature, similar to analogous dependences for compaction of fine-grained single-phase ceramics [14]: stage I up to a heating temperature T₁ ~ 850°C, the intensity of compaction at which is very low, the stage of intense shrinkage (stage II) in the temperature range T₁ < T < T₂ ~ 1400-1420°C, and, finally, stage III (at T > T₂), at which the density of the material already exceeds 90 % and intensive grain growth is observed.

As noted above, the ρ/ρ_{th} (T) dependences for nanopowder compositions of group III with an increased content of tungsten oxides, W2C and α-W particles are of a more complex nature, determined by the kinetics of chemical reactions during sintering, as well as by the intensity of the processes of sintering powders to each other. of various composition. As seen from figure 1, at the first stage of sintering $(T < T_1 \sim 820-850^{\circ}C)$ the intensity of compaction is low and practically does not depend on the composition of the sintered nanopowder composition. The stage of intense shrinkage in the first approximation can be divided into two substages (Stage II-1, II-2), differing in the temperature interval and the slope of the ρ/ρ_{th} (T) dependences. In the temperature range from 820-850°C to 1050-1080°C (Stage II-1), in our opinion, tungsten oxide decomposes and W_2C particles are formed ($WO_2 + WC \rightarrow$ $W_2C + CO_2$). Thus, at Stage II-1, the transformation of the initial powder composition of the composition $[\alpha$ -WC + WO₃ + W₂C + α -W] into a nanopowder composition with a predominant tungsten content (~ 50-60%), in which particles W₂C and α- WC. At Stage II-2, in the temperature range from 1050-1080°C to $T_2 \sim 1210-1240^{\circ}$ C, sintering of W₂C particles (their volume fraction is ~ 60%), as well as the chemical interaction of tungsten particles with carbon, which is part of the crystal lattice tungsten monocarbide $(W + WC \rightarrow W_2C)$. At stage III, upon heating to temperatures exceeding the temperature T₂, in our opinion, diffusion dissolution of pores and active growth of grains in ceramics with a predominant W₂C content occur.

Let us determine the diffusion mechanisms that control the process of compaction of nanopowders at each stage.

The analysis of the kinetics of compaction of nanopowders at Stage II can be carried out using the Young-Cutler approach [15, 16], developed to analyze the compaction curves of fine-grained powders in a continuous heating mode. This model [15] describes the initial stage of nonisothermal sintering of spherical particles under conditions of simultaneous processes of volumetric and grain-boundary diffusion, as well as plastic deformation:

$$\varepsilon^{2} \frac{\partial \varepsilon}{\partial T} = \left(\frac{2.63\gamma \Omega D_{\nu}\varepsilon}{kTd^{3}}\right) + \left(\frac{0.7\gamma \Omega b D_{b}}{kTd^{4}}\right) + \left(\frac{Ap\varepsilon^{2}D}{kT}\right),\tag{1}$$

where ε is the relative shrinkage of the powder, *t* is the sintering time, γ is the free energy of the surface, D_v is the bulk diffusion coefficient, D_b is the grain-boundary diffusion coefficient, *d* is the grain size, *p* is the applied pressure, *D* is the diffusion coefficient during plastic deformation. In accordance with [14], the slope of the temperature dependence of shrinkage in coordinates $\ln(T\partial\varepsilon/\partial T) - T_m/T$ corresponds to the effective activation energy of sintering mQ_{s2} , where *m* is the coefficient depending on the dominant sintering mechanism (m = 1/3 - for the case of grain-boundary diffusion, m = 1/2 - for bulk diffusion and 1 for viscous flow (creep)).

The dependences $\ln(T\partial \epsilon/\partial T) - T_m/T$ for the studied powders are shown in Figure 5. Average values of the effective activation energy of sintering at Stage II (mQ_{s2}) are presented in Table 3. In the region of high heating temperatures, after a small "transitional stage" at which the intensity of change in the

value of $\ln(T\partial \epsilon/\partial T) - T_m/T$ is very small, the slope of the dependence becomes negative (Stage III). This means that to estimate the activation energy of sintering at Stage III, it is necessary to use other approaches. The accuracy of determining the effective activation energy mQ_{s2} is ± 0.3 kT_m. Analysis of the graphs shows that there are three different types of dependences of the shrinkage rate on the heating temperature in semi-logarithmic coordinates. For ceramics of group I (figure5a), the presented dependences have a classical two-stage character with a maximum, the temperature of which is close to the temperature of the maximum shrinkage rate $S_{max} = S$ (T = T_{max}). The effective activation energy at the second stage is $mQ_{s2} \sim 2.2-2.6 \text{ kT}_{\text{m}}$ and slightly increases with a decrease in the carbon content in the initial nanopowder (table 1) and, as a consequence, with an increase in the content of the W_2C phase in the sintered ceramic. Note that at m = 1/3 the value of the effective activation energy at Stage II turns out to be quite close to the activation energy at the third stage of sintering (Table 3). This allows us to conclude that the dominant mechanism that determines the intensity of compaction of tungsten carbide nanopowders at the second and third stages of sintering is grain boundary diffusion. The obtained conclusion is in good agreement with the data of works [4, 17]. It should be noted that at m = 1/3, the value of the activation energy of sintering for Stage II will vary from 6.6 kT_m (167 kJ / mol) to 7.8 kT_m (198 kJ / mol). This is a rather low value of the activation energy, since traditionally the activation energy of grain-boundary diffusion of carbon in tungsten monocarbide varies from 9.1 kT_m (240 kJ / mol) to ~ 11.4 kT_m (~ 300 kJ / mol). Note that the density of the sintered material at Stage II is not high (less than 80%) and, therefore, low activation energies cannot be explained by the migration of grain boundaries, which leads to a decrease in the activation energy of grain boundary diffusion [4]. We emphasize that similar values were previously obtained in the works of other authors [17-19], but the question of the reasons for the decrease in the activation energy at Stage II remains open.



Figure 5. The dependence $\ln(T\partial \epsilon/\partial T) - T_m/T$ for tungsten carbide powders No.1-6 (a) and No.7-11 (b).

Compaction plots in coordinates $\ln(T\partial \epsilon/\partial T) - T_m/T$ at the second stage of sintering for samples No.4-6 are qualitatively similar to analogous dependences for nanopowders of group I. The effective activation energy of group II nanopowders at the second stage is $mQ_{s2} \sim 2.0-2.3$ kTm and is close to the activation energy of compaction of group I nanopowders.

The $\ln(T\partial\epsilon/\partial T) - T_m/T$ dependences for group III nanopowders, presented at Figure 5b are more complex and exhibit two maxima - the first maximum is observed in the sintering temperature range $T_m / T \sim 2.4$ (~ 1000-1050°C), the second the maximum is observed at a temperature $T_m / T \sim 2.1$ (~ 1200°C). The two-stage nature of the compaction suggests that the sintering kinetics of group III nanopowders is controlled by two simultaneous processes of different intensities. The nature of the first maximum in these dependences is due to the sintering of tungsten particles to each other in the presence of W₂C and α -WC particles. The temperature of the second maximum is close to the temperature at which the

formation of W₂C carbide occurs in vacuum. Note also that the effective activation energy of sintering mQ_{s2} near the second maximum, at m = 1/3, varies from 10.5 kT_m to 21.0 kT_m (from 266 kJ / mol to 532 kJ / mol). The estimates obtained turn out to be close to the activation energy of diffusion in W₂C [20]. This conclusion is confirmed by the XRD results, which indicate a significant volume fraction of W₂C particles in sintered ceramics. Thus, it can be concluded that the second maximum in the ln(T $\partial \varepsilon/\partial T$) – T_m/T dependence for group III nanopowders is caused by the sintering of W₂C particles to each other.

In accordance with [13], the estimation of the activation energy at Stage III can be carried out using the model of diffusion dissolution of pores located near the grain boundaries of ultrafine-grained (UFG) materials. The correctness of the application of this procedure was previously demonstrated in [4, 7]. The activation energy of the stage of nonisothermal sintering Q_{s3} is determined from the slope of the ρ (T) / ρ_{th} dependence in double logarithmic coordinates $\ln(\ln(\alpha \cdot \rho/\rho_{th}/(\rho/\rho_{th}-1))) - T_m/T$, where α is the compacting coefficient of the compact ($\alpha = 0.33$ for α -WC nanopowders). The average accuracy of determining the activation energy Q_{s3} is $\pm 1 \text{ kT}_{\text{m}}$. Analyzing compaction at Stage III, we note that the dependence $\ln(\ln(\alpha \cdot \rho/\rho_{th}/(\rho/\rho_{th}-1))) - T_m/T$ at this stage can be represented by two straight lines (Stage III-1, III- 2), the tilt angle of which is slightly different. With a decrease in the carbon content in nanopowders, the activation energy of sintering at sub-stages III-1 and III-2 decreases (Table 3). At sub-Stage III-1, the activation energy turns out to be slightly higher than in sub-Stage III-2. In our opinion, the main reason for the decrease in the activation energy with a decrease in the carbon content and with an increase in the heating temperature (during the transition from sub-Stage III-1 to sub-Stage III-2) is the growth of grains, which, in accordance with [4], can lead to a noticeable decrease in the activation energy of sintering. In particular, as can be seen from table 2, with a decrease in the carbon content in the tungsten monocarbide nanopowder, an increase in the volume fraction of W₂C particles is observed, which, in accordance with [4], are "nuclei" of abnormally large grains in sintered structure of sintered ceramics. As noted above, the volume fraction of W₂C particles, determined by the XRD method, correlates with a good degree of accuracy with the volume fraction of abnormally large grains found in the electron microscopic study of the structure. Thus, a decrease in the carbon concentration in the initial nanopowders will promote more intensive grain growth during ceramic sintering and, as a consequence, a decrease in the activation energy for sintering tungsten carbide. Note that an increase in the heating temperature will also contribute to a more intense grain growth and, apparently, a decrease in the activation energy of sintering at sub-Stage III-2.

Group			Ι		II			III					
Powder No.		1	2	3	4	5	6	7	8	9	10	11	
Stage II	II-1							2.4 ^a	2.6 ^a	3.9 ^a	6.5 ^a	3.8 ^a	
$(mQ_{s2}),$ kT _m	II-2	2.2	2.3	2.6	2.1	2.3	2	3.5 ^b	4.2 ^b	5.8 ^b	7 ^b	4.7 ^b	
Stage III	III- 1	12. 5	11. 7	10.3	12	10. 9	11. 4	-	-	-	-	-	
$(Q_{s3}), \mathrm{kT}_{\mathrm{m}}$	III- 2	9.4	8.7	6.7	8.4	7.5	7.2	5.7	7	5	5.7	6	

 Table 3. Activation energies of the SPS process.

^(a) - During calculations, the melting temperature of the material was taken to be equal to the melting temperature of tungsten ($T_m = 3695$ K)

^(b) - During calculations, the melting temperature of the material was taken to be equal to the melting temperature of tungsten carbide W_2C ($T_m = 3073$ K)

As can be seen from Table 3, the activation energy for the samples of group I and II varies from 10.3 kT_m to 12.5 kT_m (from 261 kJ / mol to 317 kJ / mol) for sub-Stage III-1 and from 6.7 to 9.4 kT_m (from 170 kJ / mol up to 238 kJ / mol) for sub-Stage III-2. These values are close to the known data on grain-boundary diffusion of carbon in tungsten monocarbide [21] and, therefore, it can be assumed that at the

final stage of heating the compaction process is controlled by the mechanism of grain-boundary diffusion.

The dependences $\ln(\ln(\alpha \cdot \rho/\rho_{th}/(\rho/\rho_{th}-1)) - T_m/T$ at Stage III for group III nanopowders are rather complex. If the average activation energy of SPS at Stage III is determined by the slope at this dependence, then the value of Q_{s3} will vary from ~ 5 kT_m (127 kJ / mol) to ~ 7 kT_m (177 kJ / mol) (table 3). These are rather low values of the activation energy of SPS, which are lower than the activation energies of sintering at sub-Stage III-2 for nanopowders of groups I and II. It is rather problematic to answer the question about the reasons for such low values of the activation energy of SPS at Stage III for plasma-chemical nanopowder compositions W₂C-WC-W. We only note that the values of the effective activation energy at Stage II (mQ_{s2}) and the activation energy at Stage III (Q_{s3}) are quite close to each other.

5. Conclusion

It is shown that the kinetics of high-speed sintering of tungsten monocarbide nanopowders with an increased oxygen content and a low presence of W_2C particles has a two-stage nature, the intensity of which is determined by the intensity of carbon diffusion along the grain boundaries. Low values of the effective activation energy of sintering at the stage of intense compaction are primarily due to the increased oxygen concentration and the presence of nanothick oxide layers on the surface of the synthesized nanoparticles. This probably changes the diffusion along the grain boundaries of tungsten carbide. An insignificant decrease in the activation energy of sintering at the final stage of compaction is due to anomalous grain growth, for which the W_2C particles act, which are initially present in the nanopowder or formed during sintering of the oxidized nanopowder.

The kinetics of SPS of nanopowders with an increased content of oxides and tungsten particles at the stage of intensive compaction is controlled by the rate of sintering of tungsten particles with their simultaneous transformation into W_2C particles, and then, at the stage of high-temperature sintering, by the process of plastic flow of W_2C particles in the presence of tungsten particles.

Samples of ceramics sintered from nanopowders with an increased oxygen content are characterized by close to theoretical density, UFG structure (grain size less than 0.3 μ m), high hardness (more than 30 GPa) and increased crack resistance (5.1-5.5 MPa·m^{1/2}). A good combination of high hardness and fracture toughness was achieved by SPS of nanopowders with an initial carbon content of 6.08%, oxygen 1.32%, and a small (less than 1%) volume fraction of W₂C particles - the obtained samples have a high density (98.28%), ultrafine-grained structure (average grain size 0.23 μ m), increased Vickers hardness H_y = 30.5 GPa with a minimum crack resistance of ~ 6.5 MPa m^{1/2}.

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