Effect of initial particle size and various composition on the spark plasma sintering of binderless tungsten carbide

E A Lantsev, N V Malekhonova, V N Chuvil’deev, A V Nokhrin, M S Boldin, P V Andreev and K E Smetanina

Lobachevsky State University of Nizhny Novgorod, 23 Prospect Gagarina (Gagarin Avenue), Nizhny Novgorod, 603950, Russia

E-mail: elancev@nifti.unn.ru

Abstract. The results of studies of the kinetics of high-speed spark plasma sintering (SPS) of plasma-chemical nanosized and industrial micron tungsten carbide powders are described. During SPS the carburization of the surface layer of tungsten carbide samples takes place, which leads to differences in the phase composition and hardness of the surface and central regions of sintered ceramics. The process of SPS of tungsten carbide can be sequentially represented as a change of the following mechanisms: rearrangement of particles at lower temperatures (Stage I) → sintering of particles due to grain boundary diffusion (Stage II) → sintering due to diffusion in the crystal lattice (Stage III-1) → sintering under conditions of intensive grain growth with an abnormally low diffusion activation energy (Stage III-2).

1. Introduction

Currently, tungsten carbide (WC) is widely used in mechanical engineering, mining, machine tool construction, etc. High wear resistance, chemical stability (corrosion resistance), melting point and hardness make it possible to use ceramics and hard alloys based on tungsten carbide as wear-resistant materials [1, 2]. Pure tungsten carbide has low fracture toughness and bending strength, as a result of which, plastic low-melting metals (cobalt, nickel, iron, etc.) are introduced into its composition, which reduce the sintering temperature and increase the physical and mechanical properties of ceramics. Usually, to obtain hard alloys, liquid-phase sintering is used, which makes it possible to obtain a homogeneous fine-grained structure with increased crack resistance [3]. Note that low-melting metal additives reduce the hardness and corrosion resistance of the hard alloy, especially at elevated operating temperatures. As a result, the attention of scientific groups is focused on new technologies for obtaining powders of pure tungsten carbide and new methods of compacting them [4]. Much attention is paid to the problem of high-speed solid-phase sintering of nano- and submicron tungsten carbide powders, which make it possible to ensure high hardness of ceramics [4-6].

A promising method for the consolidation of tungsten carbide powders is the technology of electric pulse (spark) plasma sintering (SPS), which is a method of high-speed hot pressing [7, 8]. Due to the high heating rate, which is realized due to the transmission of millisecond current pulses, and the possibility of applying pressure, the SPS technology makes it possible to produce samples of tungsten carbide with close to theoretical density and high physical and mechanical properties [9-13].

The technology of plasma-chemical synthesis of refractory carbide nanopowders [14-16] has great prospects, which makes it possible to effectively control the granulometric and phase composition, as well as the carbon content in tungsten carbide nanopowders. Plasma-chemical nanopowders of tungsten...
carbide have a “core - shell” structure, in which the core of tungsten monocarbide $\alpha$-WC is surrounded by nanothick graphite-like layers of pyrolytic carbon [16], on the surface of which oxygen is adsorbed.

The aim of this work is to study the structure and properties of ceramics obtained by the method of electro-pulse (spark) plasma sintering of plasma-chemical nanopowders of tungsten monocarbide.

2. Methods and materials

The objects of the study were $\alpha$-WC monocarbide nanopowders obtained by plasma chemical synthesis followed by reductive annealing in hydrogen at different temperatures (1000°C, 1 h for nanopowders No. 3 and ~1050°C, 3 h for nanopowders No. 4). The lower temperature of the reductive annealing promoted the presence of $\alpha$-W tungsten particles in the composition of nanopowder No. 3. As objects of comparison, industrial micron powders of tungsten monocarbide $\alpha$-WC produced by the Kirovograd hard alloys plant (Russia) were used. Commercial powders had an average Fischer particle size of 3 microns (powder No. 1) and 0.8 microns (powder No. 2). The characteristics of the powders are presented in Table 1.

The compaction of samples with a diameter of 12 mm and a height of $h = 4$ mm was carried out by the SPS method using a Dr. Sinter model SPS-625. The samples were sintered in vacuum (2-5 Pa) in the mode of continuous heating. The applied load was 70 MPa. The samples were heated at a rate of 50 °C / min.

The carbon and oxygen content was measured using a CS-600 Leco instrument. The specific surface area of the powders was measured by the BET method ($S_{BET}$) on a TriStar 3000 analyzer (Micrometrics). The initial particle size ($R_0$) was calculated using the formula: $R_0 = 6 / (\rho \cdot S_{BET})$.

The hardness and fracture toughness of the ceramics were measured using a Qness A60+ microhardness tester. The structure was investigated using a JEOL JSM-6490 scanning electron microscope with an Oxford Instruments INCA 350 energy dispersive microanalyzer [17]. Qualitative phase analysis was carried out using the Diffrac.EVA program. Quantitative analysis was carried out by the Rietveld method. The accuracy of determining the volume fraction of phases was ~ 0.2%.

The density of the samples ($\rho$) is measured by hydrostatic weighing using a Sartorius CPA 225D balance. When calculating the relative density ($\rho / \rho_0$), the theoretical density of pure tungsten carbide was taken to be $\rho_0 = 15.77$ g / cm$^3$, the density of $W_2C$ carbide was taken to be 17.15 g / cm$^3$. The error in determining $\rho / \rho_0$ was ~0.2%, and the density was 0.05 g / cm$^3$. Studies of the structure and properties of ceramics were carried out on the surface layer, which was previously subjected to mechanical polishing to a depth of ~ 20 μm, and also at a depth of about 300 μm from the surface. Polishing was carried out using a Struers Secotom-10 grinding machine.

3. Results

3.1. Sintering of micron powders

The average particle size of tungsten carbide determined by the SEM method for powders is quite close to the average particle size according to Fischer, which for powders No. 1 and No. 2 is 3 and 0.8 μm, respectively. From the analysis of the SEM images it can be seen that the composition of the powders contains a fairly noticeable number of particles, the size of which is less than 3 microns for powder No. 1 and less than 0.8 microns for powder No. 2. No agglomerates are observed in powders. Characteristics of the powders are shown in Table 1.

Generalization of the XRD results shows that the composition of the initial powders contains hexagonal tungsten carbide $\alpha$-WC and a hexagonal phase of lower tungsten carbide $W_2C$. The volume fraction of $W_2C$ particles is ~2 vol.%.

Figure 1 shows the dependences of shrinkage L and shrinkage rate S of powders on the heating temperature at a constant rate of 50 °C / min. It can be seen that the character of shrinkage L (T) for micron powders No. 1 and No. 2 has a classic three-stage character: insignificant compaction at low heating temperatures (Stage I), intense shrinkage at medium temperatures (Stage II) and Stage III at high temperatures heating, at which the shrinkage rate decreases again. The analysis of the presented dependences L (T) shows that with a decrease in the initial particle size $R_0$, an increase in the shrinkage
of the powders is observed, and the process of intensive compaction itself shifts to the region of lower heating temperatures.

| Powder No. | 1    | 2    | 3    | 4    |
|------------|------|------|------|------|
| R₀, nm     | 3000 | 800  | 95   | 95   |
| Sintering temperature Tₛ, °C | 1690 | 1620 | 1480 | 1550 |
| Relative density, % | 96   | 96.1 | 98.81 | 99.2 |
| XRD results, vol.% | Surface α-WC | 100 | 100 | 100 | 96 |
|   | Central W₂C | - | - | - | 4 |
|   | Central α-WC | 97.1 | 96.3 | 100 | 96.6 |
|   | Central W₂C | 2.9 | 3.7 | - | 3.4 |

The results of electron microscopic studies show that the surface layer of ceramics obtained by the SPS method to a temperature of T = 1690°C from powder No. 1 with an initial particle size of R = 3 μm has a more homogeneous structure - the average grain size is ~ 4.5 μm. The surface layer of a ceramic sample obtained by the SPS method to a temperature of 1620 °C from powder No. 2 (R = 0.8 μm) has an inhomogeneous microstructure - abnormally large grains are visible on the thin section, the average size of which is ~ 34 μm.

Analysis of the microstructure of the central layers of ceramics after removing the surface layer 300 μm deep shows that there is no anomalous grain growth - the ceramics have a homogeneous microstructure, and rather large submicron pores are located at the grain boundaries. The average grain size in the central layers of ceramics sintered from powders No. 1 is d ~ 3 μm, and ceramics sintered from powder No. 2 - d ~ 0.8 μm. Thus, the average grain size in the central part of the sintered ceramics practically does not differ from the initial particle size of the powders. X-ray phase analysis of the surface layer of sintered samples showed that the composition of ceramics contains only hexagonal α-WC.

**Figure 1.** The dependence of the shrinkage L (a) and the shrinkage rate S (b) on the heating temperature (T) during the SPS of powders No.1-4
The results of studies of hardness and crack resistance for ceramics show the hardness of the surface layers of ceramics sintered from fine powders No. 1 and No. 2 is 14.6 and 13.5 GPa, respectively. Crack resistance of the surface layers of ceramics No. 1 and No. 2 was 10.5 and 7.6 MPa · m$^{1/2}$, respectively. The hardness of the central layer of ceramics sintered from powders No. 1 and No. 2 is 22 and 24 GPa, respectively, and crack resistance is 4.2-4.5 MPa · m$^{1/2}$. Thus, it can be stated that the surface layer of ceramics has a higher crack resistance, but lower hardness.

3.2. Sintering of plasma-chemical nanopowders

The average particle size of α-WC, calculated from the data on the specific surface area of $S_{\text{BET}}$, nanopowders No. 3 and No. 4 is ~ 95 nm. Tungsten carbide nanoparticles are fairly uniform in particle size distribution. The results of electron microscopic studies show that nanopowder No. 4 contains agglomerates ~ 2-10 microns in size. Generalization of the XRD results shows the composition of the powders contains tungsten monocarbide α-WC; the parameter $a$ of the α-WC unit cell is $a = 2.9057$ Å. Nanopowder No. 3 contains ~ 1 vol.% α-W.

Figure 1 shows the temperature dependences of shrinkage $L(T)$ and shrinkage rate $S(T)$ for plasma-chemical nanopowders of tungsten carbide. The analysis of which shows the kinetics of compaction of nanopowders has a three-stage nature and is similar to the kinetics of micron powders No. 1 and No. 2. Dependences $L(T)$ and $S(T)$ for tungsten monocarbide nanopowder No. 4 have a more complex character. As can be seen from Figure 1, an inflection is observed on the $L(T)$ dependence in the heating temperature range of 1100-1200 °C, accompanied by a decrease in the shrinkage rate of the nanopowder on the $S(T)$ dependence.

XRD analysis shows the surface layers of sintered ceramics No. 4, in addition to hexagonal tungsten monocarbide α-WC, there are particles of the α-W$\text{$_2$}$C phase. There are no X-ray peaks corresponding to the W$_2$C phase in the X-ray diffraction pattern of the surface layer of ceramic No. 3.

Figure 2. The SEM images of microstructure of the surface (a, b) and central (c, d) layers of nanopowders No.3 (a, c) and No.4 (b, d).
Figure 2 shows photographs of the microstructure of the surface and central layers of sintered ceramics. From the analysis of the presented data, it can be seen that the presence of tungsten particles in nanopowder No. 3 leads to the appearance of large elongated grains, the width of which is ~ 2-3 μm, and the length is ~ 7-8 μm. Note also that in the structure of ceramics No. 3, large micron pores are visible, located mainly in the volume of grains. Ceramics No. 4, sintered from tungsten monocarbide nanopowder, has a uniform ultrafine-grained structure of the surface layer with an average size of ~ 0.16 μm and single micron elongated grains. The method of scanning electron microscopy did not reveal large pores in the structure of ceramics No. 4. The results of electron microscopic studies of the microstructure of ceramics after removing the surface layer 300 μm thick showed that the structure of the central layer of ceramics sintered from the α-WC + 1% W nanopowder contains rather elongated large grains.

4. Discussion

The generalization of the research results shows the structure and properties of the surface and central layers of the sintered specimens differ. In particular, as can be seen from table 1, in the central part of the sample, at a distance of ~ 300 μm from the surface, there is an increased volume fraction of W2C particles, which are not detected by XRD on the surface of sintered ceramics. This, in particular, leads to the fact that the hardness of the central part of the samples is noticeably higher than the hardness of the surface layer.

As mentioned above, XRD showed that in the surface layer of ceramics sintered at temperatures of 1620-1690 °C (fine powders) and 1480-1550 °C (nanopowders) there are no particles of the W2C phase, which are present in the powder (~ 2%) and in the central part samples of ceramics (~ 3%). In our opinion, the absence of W2C particles in the surface layers of sintered ceramics is obviously associated with the diffusion of carbon from the graphite mold into the surface layers. The saturation of a thin surface layer with carbon leads to a synthesis reaction and transformation of W2C carbide into α-WC monocarbide [2].

Let us now determine the mechanisms of sintering tungsten carbide powders of various fineness at the stage of intensive compaction (Stage II) and the stage of high-temperature compaction (Stage III).

To analyze the kinetics of nonisothermal sintering of powders at Stage II, we use the Young-Cutler model [18, 19], which 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:

$$\varepsilon_2 \frac{d\varepsilon}{dT} = \left( \frac{2.633\gamma D_b\varepsilon}{kTd^2} \right) + \left( \frac{0.7\gamma bD_b}{kTd^4} \right) + \left( \frac{4pD^2}{kT} \right),$$

where $\varepsilon$ is the relative shrinkage of the powder, $t$ is the sintering time, $\gamma$ is the free energy of the surface, $D_b$ 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 [18], the slope of the temperature dependence of the shrinkage in coordinates ln(T∂ε/∂T) – Tm/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)).

Shown in figure 2a the dependences ln(T∂ε/∂T) – Tm/T for powders 1–3 have a two-stage character with a maximum. Note that, in accordance with [9], the presence of a maximum in this dependence may indicate a change in the dominant diffusion mechanism or plastic deformation, which determines the intensity of powder compaction during SPS.

Table 2 shows the values of the effective activation energy of the second stage of SPS of tungsten carbide powders ($mQ_{s2}$). This values for compaction of powders at Stage II are $mQ_{s2} \sim 4$ kTm for powder No. 1 and ~ 2.5-3 kTm for powder No. 2. The effective activation energy of sintering plasma-chemical nanopowder No. 3 is $mQ_{s2} \sim 3$ kTm. Note that at $m = 1/3$, the values of the activation energy of SPS at Stage II are 8-12 kTm (~ 210-310 kJ / mol) and turn out to be close to the activation energy of carbon.
diffusion along the grain boundaries of tungsten carbide (~ 300 kJ / mol [20]). Hence, it can be concluded that the second stage of sintering of α-WC powders is controlled by the mechanism of grain-boundary diffusion of carbon in tungsten carbide.

![Graph showing the dependence ln(T∂ε/∂T) – Tm/T for tungsten carbide powders No. 1-3 (a) and No. 4 (b).](image)

**Figure 3.** The dependence ln(T∂ε/∂T) – Tm/T for tungsten carbide powders No. 1-3 (a) and No. 4 (b).

Figure 3b shows the dependence ln(T∂ε/∂T) – Tm/T for nanopowder No. 4 synthesized at higher temperatures of annealing in hydrogen. It can be seen that the dependence in the indicated coordinates has two maxima - at a temperature of 1100-1150 °C and ~ 1400 °C. The values of the effective activation energy near these two maxima turn out to be close to each other (3.0-3.5 kTm), which at m = 1 / 3 gives the activation energy value of ~ 9-10.5 kTm (~ 230-274 kJ / mol). Thus, the activation energies of Stage II of intensive compaction are close for all studied powders.

| Table 2. Activation energy SPS. |
|----------------------------------|
| Powder No. | Stage II: Qs2, kTm (kJ/mol) | Stage III-1: Qs3(1), kTm (kJ/mol) | Stage III-2: Qs3(2), kTm (kJ/mol) |
|-----------|-------------------------------|-----------------------------------|-----------------------------------|
| 1         | 12 (305)                      | 14 (355)                          | 7 (180)                           |
| 2         | 9 (230)                       | 15 (380)                          | 7 (180)                           |
| 3         | 9 (230)                       | 15 (380)                          | 7 (180)                           |
| 4         | 9 (230)                       | 14 (355)                          | 6 (155)                           |

Let's move on to the analysis of the sintering mechanisms at Stage III. According to [21], the activation energy of sintering at this stage can be found using the model of diffusion dissolution of pores located near grain boundaries. To calculate the activation energy, the shrinkage value is recalculated into the compaction value (the dependence of the relative density on temperature) according to the formula \( \rho (T) = \rho_{\text{exp}} \cdot \frac{L_{\text{max}}}{L_0 \cdot (1 - T/T_m)} \), where \( L_0 \) is the initial pressing height, \( L_{\text{max}} \) is the maximum specimen shrinkage after sintering, \( \rho_{\text{exp}} \) is the experimentally measured density of the sample. In this model, the activation energy can be determined from the slope of the dependence ln(ln(\( \alpha \cdot \rho/\rho_{\text{th}}/\rho_{\text{th}}-1 \)) - Tm/T, where \( \alpha = 0.5 \) is the coefficient of compaction of the powder. Analysis presented in Figure 4 shows these dependences can be interpolated by two straight lines, the slope of which is different in the "low" temperatures (Stage III-1) and in the "high" temperatures (Stage III-2). The activation energy of sintering at Stage III-1 (14-15 kTm ~ 350-380 kJ / mol) turns out to be noticeably higher than the activation energy of SPS at Stage III-2 (6-7 kTm ~ 155-180 kJ / mol). Note that the activation energy of SPS at Stage III-1 corresponds to the activation energy of bulk diffusion (~ 368 kJ / mol [20]). The activation energy at Stage III-2 is quite typical for the activation energy of WC sintering in case of grain-boundary diffusion and intense grain growth [22, 23], and is also close to the activation energy of creep of tungsten carbide in this temperature range (250 kJ / mol [24]). Note that a decrease in the shrinkage rate in the case of intensive grain growth was previously described in detail in [25].
Figure 4. The dependence of the density in double logarithmic coordinates on the reciprocal temperature for all sintered ceramics.

The activation energy of sintering at Stages II, III-1 and III-2 weakly depends on the initial level of dispersion of tungsten carbide particles - the particle size has a significant effect on the duration of this stage, including the size of the density (shrinkage) at which the “transition” from one sintering stage to another.

5. Conclusion
Sintering of pure tungsten carbide powders consists of three stages: stage I - low-temperature compaction up to 50% relative density; stage II - compaction at medium heating temperatures up to 75-80% relative density; stage II - high-temperature compaction until the samples reach the maximum possible density. An increase in the size of the initial particles of tungsten carbide in the composition of powders, as well as the addition of 1% pure tungsten to the composition of plasma-chemical powders, shifts the temperature-time intervals of compaction towards higher temperatures, and also reduces the absolute value of shrinkage of compacts.

It is shown that the process of high-speed sintering of tungsten carbide can be sequentially represented as a sequential change of the following mechanisms: regrouping of particles at low temperatures (Stage I) → sintering of particles due to grain-boundary diffusion (Stage II) → sintering due to diffusion in the crystal lattice (Stage III-1) → sintering under conditions of intensive grain growth (Stage III-2). The process of decomposition of tungsten monocarbide particles into $\alpha$-W and W$_2$C is minimized due to the high heating rate and low oxygen concentration in the powders.

The activation energy of high-speed sintering weakly depends on the value of the initial size of the tungsten carbide particles, as well as on the phase composition of the initial powders - these parameters have the most significant effect on the duration and temperature-time interval of sintering stages, as well as on the density (shrinkage), at which there is a change in diffusion mechanisms that determine the intensity of shrinkage at each of the sintering stages. An increase in the particle size of tungsten carbide shifts the temperature-time intervals of compaction towards higher temperatures, and also reduces the maximum value of shrinkage and shrinkage rate of ceramics.

During high-speed electro-pulse plasma sintering, the surface layer of tungsten carbide samples is carburized, which leads to differences in the phase composition and hardness of the surface and central regions of the sintered ceramics. The generalization of the obtained results shows that in the central part of the specimen section, which has increased hardness and reduced crack resistance, there are W$_2$C particles. Carburization of the surface layer during SPS leads to an increase in the fracture toughness of ceramics, as well as the absence of W$_2$C particles.
Acknowledgments
The authors wish to thank the Russian Science Foundation (grant No. 18-73-10177)

References
[1] Fang Z Z, Koopman M C and Wang H T 2014 Cemented tungsten carbide hardmetal-an introduction Comprehensive Hard Materials (vol 1) ed V K Sarin (Oxford: Elsivier) chapter 1.04 pp 123-137
[2] Kurlov A S and Gusev A I 2013 Tungsten Carbides (Springer Series in Materials Science vol 184) (Cham: Springer International Publishing) p 242
[3] Panov V S and Chuvilin A M 2001 Technology and Properties of Sintered Hard Alloys and Products from Them [Tehnologiya i svoistva spechennih tverdih splavov i izdelii iz nih] (Moscow: MISIS) p 428 (in Russian)
[4] Sun J, Zhao J, Huang Zh, Yan K, Shen X, Xing J, Gao Y, Jian Y, Yang H and Li B 2020 Nano-Micro Letters 12 [13] 37
[5] Allibert C H 2001 Int. J. Refr. Met. And Hard Mat. 19 [1] 53
[6] Fang Z, Maheshwari P, Wang X, Sohn H Y, Griffio A and Riley R 2005 Int. J. Refr. Met. And Hard Mat. 23 [4–6] 249
[7] Tokita M 2015 Nanotechnologies in Russia 10 261
[8] Olevsky E and Dudina D 2018 Field-Assisted Sintering (Switzerland: Springer Int. Pub.) p 432
[9] Kumar A N, Watabe M and Kurokawa K 2011 Ceramics International 37 [7] 2643
[10] Demirskyi D, Borodianska H, Agrawal D, Ragulya A, Sakka Y and Vasylkiv O 2012 J. Alloys Comp. 523 1
[11] Cha S I and Hong S H 2003 Materials Science and Engineering: A 356 381
[12] Zhang G Z, Wang C, Zhang J X, Zhou M L and Zhou T X 2005 Rare Metals Cemented Carbides 33 [2] 12
[13] Girardini L, Zadra M, Casari F and Molinariet A 2008 Metal Powder Rep 63 [4] 18
[14] Tsvetkov Yu V and Panfilov S A 1980 Low-temperature Plasma in Recovery Processes [Nizkotemperaturnaya plazma v protsessakh vosstanovleniya] (Moscow: Nauka) p 359 (in Russian)
[15] Tsvetkov Yu V, Nikolaev S A and Panfilov S A 1980 Plasma Metallurgy [Plazmennaya metallurgiya] (Novosibirsk: Nauka) p 255 (in Russian)
[16] Blagoveshchenskiy V, Kishenov N and Zelensky V A 2018 Inorganic Materials: Applied Research 9 [5] 924
[17] Andreev P V, Smetanina K E and Lantsev E A 2019 IOP Conf. Series: Mater. Sci. Eng. 558 12003
[18] Young W S and Cutler I B 1970 J. Am. Ceram. Soc. 53 [12] 659
[19] Johnson D L and Cutler I B 1963 J. Am. Ceram. Soc. 46 [11] 541
[20] Buhsmer C P and Crayton P H 1971 J. Mat. Sci. 6 981
[21] Chuvil’deev V N, Boldin M S, Dyatlova Ya G, Rumyantsev V I, Ordan’yan S S 2015 Inorganic Mat. 51 [10] 1047
[22] Chuvil’deev V N et al 2017 J. Alloys Comp. 708 547
[23] Blagoveshchenskiy Yu V et al 2015 Inorganic Materials: Applied Research 6 [5] 415
[24] Lay S and Osterstock F 1984 Mat. Sci. Res. 18 463
[25] Kumar A N, Watabe M and Kurokawa K 2012 Philosophical Mag. 92 [32] 3950