Experimental study of the influence of different carbon content on the shrinkage kinetics and structure evolution of ultralow-cobalt hard alloys during spark plasma sintering

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Abstract. The features of the compaction of plasma-chemical WC - (0.3; 0.6; 1) %Co nanopowders with the addition of 0.3 and 0.5% graphite during high-speed spark plasma sintering have been investigated. It was shown that an increased concentration of oxygen adsorbed on the surface of plasma-chemical nanoparticles during mixing with graphite, as well as the effect of graphite itself, which leads to a decrease in the activation energy of sintering due to a decrease in the intensity of the formation of particles of the η-phase in the "oxidized" WC-Co nanopowders, are the main structure features of ultralow-cobalt hard alloys. Samples of fine-grained ultralow-cobalt hard alloys with increased hardness and fracture toughness were obtained (for a WC-0.6% Co-0.3% C hard alloy with an average grain size of ~ 1-1.5 μm, the hardness is Hv = 20.2-20.5 GPa with a minimum crack resistance coefficient KIC = 9.2-10.4 MPa·m1/2).

1. Introduction
Currently, the effect of carbon on the behavior of hard alloys with additions of 8-12 wt.% cobalt during high-temperature sintering has been studied in sufficient detail. It has been found that at a temperature of T > 900°C diffusion of carbon and tungsten into cubic cobalt occurs [1], while the diffusion coefficient of tungsten in cobalt (γ-phase based on Co) is several orders of magnitude lower than that of carbon in cobalt [2]. In this regard, an increase in the carbon concentration in the composition of the initial powders leads to a slowdown in the compaction processes of WC-Co powders, as well as a shift in the temperature of the onset of shrinkage to the region of higher values [3]. It is interesting to note the works [4, 5], which show that the compaction of powders and grain growth slows down in hard alloys with a reduced content of free carbon due to the increased concentration of tungsten in the cobalt γ-phase, the creep rate of which controls the process of solid-phase sintering of hard alloys, and when a liquid phase appears, it determines grain growth according to the Wagner-Lifshitz-Slezov theory or the Ostwald coalescence rate due to changes in its diffusion permeability [1].

The aim of this work is to study the effect of carbon on the kinetics of high-speed sintering of fine-grained hard alloys with small additions of cobalt, as well as to study the effect of carbon additions on the structure and properties of ultralow-cobalt hard alloys obtained by the spark plasma sintering (SPS) method.
2. Methods and materials

The research objects of this work were α-WC nanopowders obtained by the plasma-chemical method, in which various concentrations of cobalt (0.3, 0.6, and 1 wt% Co) were deposited by the deposition method. Free carbon in the form of colloidal graphite was mixed into WC-Co nanopowders using a Fritsch-Pulverisette 6 planetary mill in a grinding jar with a hard alloy lining and tungsten carbide balls 1 mm in diameter. The powders were mixed in isopropyl alcohol for 2 h at a speed of 150 rpm.

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 a continuous heating mode, in vacuum (2-5 Pa) and heated at a given rate of 50 °C/min to the sintering temperature \( T_s \), followed by cooling in a free mode. There was no holding at a temperature \( T_s \). The value of the uniaxial pressure applied to the powders during heating was 70 MPa. The oxygen and carbon content was determined with an accuracy of ± 0.01 wt% using a LECO TC-600 analyzer.

The structure of the samples was studied using a JEOL JSM-6490 scanning electron microscope with an Oxford Instruments INCA 350 energy-dispersive microanalyzer. X-ray phase analysis (XRD) of the samples was carried out using a Shimadzu XRD-7000 diffractometer (CuK\(_\alpha\), scanning step 0.04, which corresponds to the exposure time 2 sec). Qualitative phase analysis was carried out using the Diffrac.EVA program. Quantitative analysis followed the Rietveld method. The accuracy in determining the volume fraction of α-WC and η-phase particles was ± 0.5%.

Sample density (\( \rho \)) was measured by hydrostatic weighing using a Sartorius CPA 225D scales. Hardness \( H_v \) and fracture toughness \( K_{IC} \) were measured using a Qness A60+ hardness tester with a load of 2 kg.

3. Results

From the obtained micrographs of the structure of the initial powders, it can be seen that the WC-Co nanopowders after the cobalt reduction operation contain single large agglomerates, which are absent in nanopowders with the addition of graphite. The size of the agglomerates depends on the cobalt content. In WC-0.3Co nanopowders the size of the agglomerates ranges up to 1–2 μm, while in nanopowders with 0.6 and 1% Co, it varies from 5 to 20 μm. The absence of agglomerates in WC-Co-C nanopowders is associated with the use of a mixing operation, during which the agglomerated regions are “broken” into smaller ones, which leads to a more uniform particle size distribution. Separately located cobalt particles were not detected in the structure of powder compositions, which allows us to conclude that ultrathin cobalt layers are uniformly deposited on the surface of α-WC nanoparticles.

The process of mixing nanopowders in a planetary mill leads to an increase in the oxygen concentration from 0.514 to 0.748 wt%, from 0.475 to 0.605 wt%, and from 0.469 to 0.623 wt% for nanopowders with the addition of 0.3, 0.6, and 1% Co respectively. A decrease in the oxygen concentration in WC-0.6% Co and WC-1% Co nanopowders as compared to WC-0.3% Co nanopowders is due to the larger volume fraction of cobalt, which has a lower oxygen concentration as compared to the α-WC tungsten monocarbide nanopowder.

XRD results show that the nanopowders contain hexagonal tungsten carbide α-WC, as well as cubic and hexagonal phases of cobalt. No peaks corresponding to the W\(_2\)C phase, WO\(_x\), and α-W oxides were found. The peaks corresponding to tungsten monocarbide α-WC are broadened and partially overlap with each other in the region of large diffraction angles. After mixing, the X-ray peaks of cobalt are practically invisible, which, in our opinion, indicates its uniform distribution over the surface of tungsten monocarbide nanoparticles. Note also that the mixing process led to a decrease in intensity and additional broadening of the peaks of tungsten monocarbide, which may indicate deagglomeration of WC-Co nanopowders during grinding, as well as the formation of additional internal stresses in α-WC nanoparticles [1].

Figure 1 shows the dependence of shrinkage \( L \) and shrinkage rate \( S \) on the heating temperature (\( T \)) of plasma-chemical WC-Co nanopowders with different carbon content. The character of the \( L \) (\( T \)) dependence for WC-0.3%Co nanopowders has a three-stage character: insignificant compaction (Stage
Figure 1. The dependence of shrinkage $L$ (a, c, e) and shrink rate $S$ (b, d, e) on temperature $T$ of nanopowders WC-0.3%Co (a, b), WC-0.6%Co (c, d) and WC-1%Co (e, f).

I) at low temperatures (up to 700-800°C), Stage II, at which intense shrinkage is observed in the region of medium temperatures (from 700-800°C to 1100°C) and, finally, the Stage III region of high temperatures (over 1100°C) in which the shrinkage rate decreases. It is noticeable that the addition of graphite to WC-0.3%Co nanopowders leads to a decrease in the temperature of the onset of stage III towards lower temperatures. The maximum shrinkage values for WC-0.3%Co nanopowders with the addition of graphite are lower than for the initial nanopowder without the addition of graphite, as can be seen from fig. 1a, the maximum shrinkage for WC-0.3%Co nanopowder after heating to a temperature of 1300°C is $L_{\text{max}} = 7.67$ mm, while for WC-0.3Co-0.3C and WC-0.3Co-0.5C nanopowders it is $\sim 6.6$-6.7 mm after heating to a temperature of 1200°C. Note also that the shrinkage curves $L(T)$ for WC-0.3%Co nanopowders with the addition of graphite at the stage of intensive compaction are non-monotonic, which suggests a two-stage nature of the stage of intensive compaction of WC-0.3Co-C nanopowders. As can be seen from figure 1, the inflection in the $L(T)$ curves is observed at a temperature of $\sim 1000°C$. 
4. Discussion

4.1. Influence of C on the structure and properties of ultralow-cobalt hard alloys

Analysis of the data shows that with an increase in the content of graphite in the composition of plasma-chemical WC-Co nanopowders, a decrease in the absolute and relative density of hard alloys obtained by the SPS method is observed. With an increase in the graphite content from 0 to 0.5%, the relative density of ultralow-cobalt hard alloys decreases by ~ 2-3% at all cobalt contents. The result obtained is in good agreement with the results of studies of the effect of graphite on the sintering kinetics of WC-Co nanopowders - the introduction of graphite leads to a decrease in the maximum shrinkage of nanopowders \( L_{\text{max}} \) and a simultaneous "shift" of the \( L(T) \) dependences towards lower heating temperatures. This allows us to conclude that the introduction of graphite leads to a simultaneous slowdown of shrinkage and a shift in the characteristic temperatures of the end of the stage of intense shrinkage (Stage II) to a lower temperature region.

The results of electron microscopic studies of the microstructure of hard alloys showed that with an increase in the content of C in the composition of plasma-chemical WC-Co nanopowders, the intensity of the formation and growth of abnormally large grains of tungsten carbide decreases. For all three cobalt concentrations (0.3, 0.6, and 1 wt%), it was found that an increase in the graphite content from 0 to 0.5 wt% leads to a decrease in the average grain size from ~ 8 μm to 1–2 μm. This allows us to conclude that the introduction of free carbon stabilizes the grain structure of ultralow-cobalt hard alloys, thereby making the grain size distribution more homogeneous.

Analyzing the data, it can be seen that an increase in the graphite addition from 0.3 to 0.5% leads to a decrease in the microhardness and an increase in the minimum crack resistance of sintered specimens by an average of 2-3 GPa and 1-2 MPa\( \cdot m^{1/2} \), respectively. We assume that this is due, first of all, to a decrease in the volume fraction of the \( \eta \)-phase particles in the structure of sintered hard alloys, which, as is known [1], negatively affects their physical and mechanical properties.

4.2. Analysis of sintering mechanisms

To analyze the kinetics of compaction of nanopowders at the stage of intense shrinkage, we use the Young – Cutler model [6], which describes the nonisothermal process of sintering of spherical particles under conditions of simultaneous grain-boundary and/or bulk diffusion and/or plastic flow. In accordance with [6, 7], the slope of the dependence of the relative shrinkage (\( \varepsilon \)) on temperature in the coordinates \( \ln (T \frac{\partial \varepsilon}{\partial T}) - T_m / T \) corresponds to the effective activation energy of the SPS (\( mQ_s \)). Figure 2a shows the dependences \( \ln (T \frac{\partial \varepsilon}{\partial T}) - T_m / T \) for plasma-chemical nanopowders WC-Co with different contents of cobalt and graphite. The \( \ln (T \frac{\partial \varepsilon}{\partial T}) - T_m / T \) dependencies for WC – Co nanopowders with a content of 0.6% and 1% cobalt have the usual two-stage character with a maximum, which, according to [8], indicates a change in the sintering mechanism. The temperature corresponding to the maximum of the \( \ln (T \frac{\partial \varepsilon}{\partial T}) - T_m / T \) dependence decreases from 1050°C to 950°C with an increase in the cobalt concentration from 0.3 to 1 wt%. The value of the coefficient \( m \) can be taken equal to \( m = 1 \), which corresponds to the case of plastic flow of cobalt [8, 9]. The performed estimates show that the activation energy of SPS of WC-0.3%Co nanopowders at the stage of intense shrinkage is \( Q_s \sim 11 kT_m \). The activation energy of SPS of WC-0.3%Co nanopowders with an addition of 0.3 and 0.5% graphite, determined from the slope of the \( \ln (T \frac{\partial \varepsilon}{\partial T}) - T_m / T \) dependence near the first maximum, is \( \sim 7 \) and \( \sim 8 kT_m \), respectively. Similar values of the activation energy of SPS for Stage II were obtained for hard alloys with 0.6% and 1%Co.

The result obtained allows us to conclude that the shrinkage rate at Stage II is determined by the rate of plastic flow of cobalt. The influence of graphite manifests itself by changing the phase composition of the \( \gamma \)-phase – an increase in the concentration of carbon in cobalt and a decrease in the volume fraction of the \( \eta \)-phase particles, which prevent the plastic flow of the \( \gamma \)-phase based on cobalt.
The beginning of the third stage of ultralow-cobalt hard alloys sintering begins when the density reaches ~ 75-80%, at which, according to [10], the porosity becomes closed, and the pores themselves are located mainly at grain boundaries or at triple joints of tungsten carbide grain boundaries. This makes it possible to calculate the activation energy of this sintering stage using a model describing the diffusion dissolution of pores located near grain boundaries [11]. The activation energy within this model can be found from the slope of the dependence \( \ln(\ln(\alpha \cdot \rho/\rho_{th}/(\rho/\rho_{th}-1))) \) on the inverse homologous temperature \( T_m/T \), where the value of \( \rho \) can be calculated using the formula \( \rho(T) = \rho_{max}L_{max}/(L_0-L(T)) \) (here \( L_0 \) is the initial pressing height, \( L_{max} \) is the maximum shrinkage of the sample, \( \rho_{max} \) is the experimentally measured density of the sample).

Figure 2b shows the dependences in coordinates \( \ln(\ln(\alpha \cdot \rho/\rho_{th}/(\rho/\rho_{th}-1))) - T_m/T \) for WC-0.6%Co nanopowder compositions with different carbon and graphite contents. Dependences \( \ln(\ln(\alpha \cdot \rho/\rho_{th}/(\rho/\rho_{th}-1))) - T_m/T \) for ultralow-cobalt hard alloys have a two-stage character, and the slopes of this dependences in the regions of "low" temperatures (Stage III-1) and in the region of "high" temperatures (Stage III-2) differ markedly. Analyzing the calculated values of the activation energy, it can be concluded that the addition of carbon increases the activation energy sintering at Stage III-1 by approximately ~ 5-6 kT_m for hard alloys with 0.6 and 1% Co, and by ~ 20 kT_m for hard alloy WC-0.3%Co. Energy of activation of SPS at the final stage of compaction (Stage III-2) turns out to be noticeably lower and with an increase in the graphite concentration it decreases by ~ 2-3 kT_m for all ultralow-cobalt hard alloys.

5. Conclusions

It is shown that the introduction of graphite leads to the formation of a fine-grained structure (suppression of anomalous grain growth) and a decrease in the intensity of the formation of \( \eta \)-phase particles. It is noted that the formation of particles of the \( \eta \)-phase of the composition \( \text{Co}_3\text{W}_3\text{C} \) is observed in the surface layer of the sintered samples, while in the central layers of the samples by XRD, particles of the "low-temperature" \( \eta \)-phase of the composition \( \text{Co}_6\text{W}_6\text{C} \) were found. It has been suggested that the formation of particles of the \( \eta \)-phase of composition \( \text{Co}_6\text{W}_6\text{C} \) in hard alloys with the addition of graphite is due to a decrease in the characteristic sintering temperatures, as well as a decrease in the total duration of the sintering process as compared to the traditional vacuum annealing of plasma-chemical nanopowders.

Features of the evolution of the structure of ultralow-cobalt hard alloys with the addition of graphite are due to the simultaneous effect of (i) an increased concentration of oxygen adsorbed on the surface of plasma-chemical WC-Co nanoparticle during mixing, and (ii) the effect of graphite, which leads to a decrease in the activation energy of sintering due to a decrease in the intensity of \( \eta \)-phases particle
formation in "oxidized" WC-Co nanopowders, as well as the formation of a fairly uniform fine-grained structure.

It is shown that due to the combined use of the technology of plasma-chemical synthesis of tungsten carbide nanoparticles, the chemical-metallurgical method of obtaining nanocomposite WC-Co particles and the technology of spark plasma sintering, samples of ultralow-cobalt hard alloys with the addition of graphite were obtained, which have a homogeneous fine-grained structure (average grain size \( \sim 1-2 \) \( \mu \)m), increased density (not less than 98\%) and enhanced mechanical properties. For a specimen of hard alloy WC-0.6\%Co-0.3\%C, the hardness value is \( H_v = 20.2-20.5 \) GPa with the value of the minimum crack resistance coefficient \( K_{IC} = 9.2-10.4 \) MPa-m\(^{1/2}\).

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