Study of the kinetics of spark plasma sintering of ultrafine-grained hard alloys WC-10%Co

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Abstract. The effect of carbon on the kinetics of spark plasma sintering (SPS) of submicron powder compositions WC-10wt.%Co is investigated. Free carbon in the form of graphite was added into submicron powders by mixing. The activation energy of solid-phase sintering under the conditions of isothermal hold and continuous heating rate sintering was determined. It was shown that an increase in the carbon content leads to a decrease in the volume fraction of particles of the η-phase and a shift of the shrinkage curve to the region of lower heating temperatures. It was established that an increase in the graphite content does not significantly affect the activation energy of sintering of submicron powders in the region of “average” heating temperatures, the value of which is close to the activation energy of grain boundary diffusion in cobalt. It has been shown that an increase in graphite content leads to a significant decrease in the activation energy of compaction of WC-Co powders in the region of “high” sintering temperatures due to a decrease in the concentration of tungsten atoms in the γ phase based on cobalt. The kinetics of sintering of fine-grained WC-Co hard alloys is limited by the intensity of the cobalt diffusion creep by Coble.

1. Introduction
Tungsten carbide based alloys containing a fusible metal binder, mainly cobalt, have a wide range of industrial applications [1-4]. Particularly widespread use of hard alloys as cutting tools [4]. Traditionally, the structure of these alloys represents grains of tungsten monocarbide α-WC surrounded by a plastic γ-phase, which is a solid solution of carbon and tungsten in cobalt [1-4]. Depending on the deficiency or excess of carbon in relation to the equilibrium concentration (C<sub>eq</sub> = 6.14 wt.%), in addition to the main two phases, in hard alloys WC-Co can form triple carbides (η-phase) or graphite, respectively. Therefore, the carbon content in the initial WC-Co powders exerts no less effect on the sintering kinetics and properties of hard alloys than the phase composition and particle size of tungsten carbide [1, 2].

Note that the carbon concentration significantly affects the growth of tungsten carbide grains during sintering of hard alloys. It was shown in [5] that an excess of free carbon (the presence of graphite) leads to coarsening of grains, while the structure of hard alloys with an excess of carbon is more uniform compared to the structure of a hard alloy having a carbon deficiency. It has been observed that carbides
with excess carbon are characterized by a more pronounced faceting of tungsten carbide grains, while grains with more carbon are more rounded [5]. The data obtained are also confirmed by other authors [6–11]. Note that the carbon content has a significant effect on the nature of the shrinkage of WC-Co powders during sintering. So, in [11], it was shown that in hard alloys with a carbon deficiency, shrinkage begins at lower temperatures than in alloys with an excess of carbon. Note that powders with a high carbon content sinter faster [9, 12], and an increase in the concentration of tungsten in cobalt leads to a decrease in its plasticity and a decrease in the intensity of spreading of the \( \eta \)-phase between \( \alpha \)-WC particles [11, 12]. It was suggested in [13–15] that the carbon concentration can strongly affect the diffusion creep of the \( \eta \)-phase, which can control the shrinkage intensity in the first stages of sintering of WC-Co hard alloys.

As is known, liquid-phase sintering is a standard technology for the production of hard alloys, accompanied by intensive grain growth according to the Ostwald dissolution-reprecipitation mechanism [16], which leads to a decrease in hardness and crack resistance. In recent decades, to obtain ultrafine-grained (UFG) hard alloys, hot (isostatic) pressing [17, 18], microwave [19], or spark plasma sintering (SPS) [20]. The SPS method, which consists in high-speed (up to 2500 \( ^\circ \text{C} / \text{min} \)) sintering of materials by passing millisecond high-current current pulses (up to 5 kA) through a graphite mold with powder placed in it, with the simultaneous application of pressure, can significantly limit the grain growth rate and form a homogeneous UFG structure at low compaction temperatures [21]. At present, the effect of cobalt amount, grain size, and SPS modes on the mechanical properties of WC-Co hard alloys has been studied in detail [22–24], but the kinetics of sintering of WC-Co submicron powders under conditions of high-speed heating has not been practically considered.

The purpose of the work is to study the mechanisms of shrinkage of powders of hard alloys in various temperature-time intervals of heating, as well as to study the effect of free carbon on the kinetics of SPS UFG of hard alloys WC-Co.

2. Methods and materials

The research objects were submicron powders of tungsten monocarbide \( \alpha \)-WC from Alfa-Aesar (initial particle size ~0.5 \( \mu \text{m} \)). Submicron powders \( \alpha \)-WC (carbon concentration in the powders \( C_{\text{WC}} = 6.40\% \)) and \( \beta \)-Co were mixed to obtain the composition WC-10\%Co, after which free carbon in the form of colloidal graphite was added to the resulting mixture. The maximum concentration of introduced free carbon was 0.5\%. The WC-Co powders were mixed in the FRITSCH - Pulverisette 6 planetary mill, in a grinding bowl with hard alloy lining, 1 mm diameter tungsten carbide balls in isopropyl alcohol for 16 hours at a speed of 150 rpm. Carbon was mixed into powder using a Heilscher UP200pt homogenizer in alcohol.

The samples were compacted with a diameter of 12 mm and a height of \( h = 3 \text{ mm} \) using the SPS method using the Dr. Sinter model SPS-625. A two-stage sintering regime was used: a low-temperature aging step at 700 \( ^\circ \text{C} \) to remove adsorbed oxygen from the surface of the powder particles (degassing) and heating at a given speed to the sintering temperature \( T_s \), followed by free-cooling. Exposure at a temperature \( T \) was absent. During heating, the shrinkage (L) and the shrinkage rate (\( S \)) of the powders were controlled. To take into account the contribution of thermal expansion of the mold, an experiment was performed on heating empty molds [25, 26]. Sintering was carried out with heating rates of 10, 25, 50, 100 \( ^\circ \text{C} / \text{min} \). Heating was carried out to temperatures corresponding to the region of solid phase (1100 \( ^\circ \text{C} \)) and liquid phase (1400 \( ^\circ \text{C} \)) sintering. The magnitude of the applied pressure (AP) was \( \sigma = 40, 70, 100 \text{ MPa} \). The accuracy of temperature determination is \( \pm 20 \text{ ^\circ \text{C}} \).

The structure of the samples was studied using a JEOL JSM-6490 SEM. The average grain size (\( d \)) was measured using the chord method with an accuracy of \( \pm 0.05 \mu \text{m} \). X-ray phase analysis (XRD) of the samples was carried out using a DRON-UM1 diffractometer. The accuracy of determining the volume fraction of particles of the \( \eta \)-phase (\( f_\eta \)) was \( \pm 2\% \). The density of the samples (\( \rho \)) was measured by hydrostatic weighing using an Sartorius CPA 225D laboratory balance. When calculating the relative density (\( \rho / \rho_b \)), the theoretical density of the WC-10Co alloy is taken to be \( \rho_b = 14.64 \text{ g/cm}^3 \).
3. Results
Figure 1a shows the microstructure of submicron powder WC-10%Co. The average particle size of α-WC is ~0.5-1 μm. An analysis of the XRD results shows that the initial composition contains hexagonal tungsten carbide α-WC and hexagonal β-Co (Figure 1b).

![Microstructure and XRD results](image)

**Figure 1.** Microstructure (a) and XRD results (b) of the powder WC-10%Co not containing free carbon

Figure 2 shows the dependence of shrinkage on the heating temperature L(T) for submicron powders WC-10%Co with different concentrations of free carbon. The L(T) dependences have a traditional three-stage character - the slow compaction stage (stage I) in the temperature range up to 800 °C, the intensive compaction stage (stage II) in the temperature range from 800-820 °C to 1000-1050 °C and stage III (more than 1050 °C) at which the powder shrinkage intensity is again low. As can be seen from figure 2, an increase in the concentration of free carbon leads to a shift in the dependence L(T) to a region of lower sintering temperatures and to a decrease in the characteristic temperatures T1 and T2 corresponding to the end of stage I and stage II, respectively.

![Shrinkage plots](image)

**Figure 2.** Shrinkage plots L(T) for submicron powders WC-10%Co with different free carbon content

Figure 3 shows typical photographs of the microstructure of sintered hard alloys obtained by heating at a rate of 50 °C/min to a temperature of 1100 °C (solid-phase sintering region) and 1400 °C (liquid-phase sintering region). There was no exposure at sintering temperature (1100, 1400 °C). Analysis of the results of electron microscopy studies shows that heating to a temperature of 1400 °C leads to intensive grain growth and the appearance of large anomalous grains in the structure of sintered alloys.
According to [16, 27], grain growth during liquid-phase sintering of WC-Co hard alloys is realized due to dissolution of tungsten and carbon atoms in liquid cobalt, their diffusion and reprecipitation on the most favorably oriented crystallographic planes of tungsten carbide particles. As can be seen from figure 3, the grain growth rate in the solid-phase sintering region is much lower, and the grains themselves retain a shape close to spherical. An increase in carbon concentration has practically no effect on the growth rate of carbide particles in the solid-phase sintering region (the average grain size is ~0.5 μm), leading to a decrease in the size of large (abnormal) grains in the liquid-phase sintering region from ~10 μm at C = 0.1% to ~2-5 μm with a carbon content of 0.5%C.

Figure 3. Microstructure of sintered to 1100°C (a) and to 1400 °C (b) hard alloys WC-10Co

An analysis of the XRD results shows that the samples sintered without the addition of free carbon contain α-WC phases, the γ-phase, which is a solid solution of tungsten and carbon in cobalt, and the η-phase, which is a cubic triple carbide W₃Co₃C. The volume fraction of the η-phase in alloys obtained at temperatures of 1100 and 1400 °C is 8% and 10%, respectively. With the addition of carbon, the intensity of the peaks of the η-phase decreases, and they completely disappear with the addition of 0.2 and 0.3% C in the case of solid-phase and liquid-phase sintering, respectively.

For further studies, the hard alloy WC-10Co-0.5C was chosen in which the possibility of the formation of the η-phase was excluded, which allows one to study the features of compaction of WC-Co powders under conditions of constant phase composition. The effect of the temperature of isothermal holding (from 750 to 1000 °C) and the AP (σ = 0, 70, 100 MPa) on the powder compaction intensity of WC-10Co-0.5C was studied. Results show that with an increase in the holding temperature, the shrinkage of powders increases. While holding at a temperature of 1000 °C for ~1200 s, the shrinkage of the powders stops and the density of the sample corresponds to the ρth. At a temperature of 950 °C, the sample is compacted to 100% of the theoretical density in a time of ~3600-4000 s. It should be noted that long exposures at temperatures of 900 and 850 °C lead to a noticeable increase in density, while the intensity of shrinkage at temperatures of 750 and 800 °C after exposure for ~2000-3000 s practically stops, reaching its stationary value. Also, it is worth noting that with an increased AP, the shrinkage and the shrinkage rate of WC-10Co-0.5C powders increase, at the same time at the stage of constant AP, the shrinkage rate, defined as the tangent to the dependence L(t), remains almost constant. This allows an analysis of the shrinkage rate from the value of the applied pressure and, in particular, to determine the compaction mechanism of powders (see below).

4. Discussion

4.1. Analysis of the kinetics of isothermal sintering of powders WC-Co
The kinetics analysis of the initial stage of sintering was carried out using a creep model, the choice of which was based on assumptions [14, 16, 27, 28]. It is traditionally assumed that the key mechanism of compaction of WC-Co powders at the initial stage of compaction is the creep process of the γ-phase based on cobalt. Note that there is currently no generally accepted notion of cobalt creep mechanisms during sintering hard metal WC-Co - in [15] validated that creep cubic cobalt has a dislocation nature, in [16] that the creep is controlled by bulk diffusion, and [12] it has been suggested that the driving force of creep is the Laplace force.

Suppose that at the initial stage of compaction, the creep rate (ε̇) is proportional to the rate of shrinkage (S), the value of which can be calculated from the slope of the dependence of shrinkage on the isothermal holding time L(t) for the steady-state stage. In accordance with the creep equation ε̇ = A(D/b2)(gΩ/kT)(σ/G)n [29, 30] (where A - dimensionless coefficient, D = Doexp(Q/kT) - the diffusion coefficient; k - constant of Boltzmann, b - Burgers vector, G - shear modulus, Ω - atomic volume, n - numerical coefficient). Note that a preliminary conclusion on the creep mechanism is made on the basis of the data on the activation energy Q and the coefficient n in the creep equation [30].

The activation energy can be estimated from the slope of the dependence ln(ε̇) - Tm/T, where Tm is the melting temperature (figure 5). The calculated activation energy for WC-10Co-0.5C powders is 7 ± 2 kTm (~78 kJ/mol), which is close to the activation energy of grain boundary diffusion in cobalt (~90 kJ/mol) [29]. To determine the coefficient n in the power creep equation, we analyzed data on the effect of applied pressure on the shrinkage rate (see figure 4b). The shrinkage rate was determined by the slope of the dependence L(t) at the stationary flow stage (at σ = const). The value of n can be determined from the angle of the dependence of the creep rate on the magnitude of the stress in the coordinates ln(ε̇) - ln(σ/G). For powders WC-10Co-0.5C, the coefficient is n = 1, which, in accordance with [29, 30], corresponds to the case of diffusion creep. This type of this creep can be controlled by volumetric creep (creep according to Coble) or grain-boundary (creep according to Coble) diffusion. Taking into account the proximity of the creep activation energy to the activation energy of grain boundary diffusion in cobalt, we can conclude that the kinetics of compaction of UFG WC-Co hard alloys at the initial stage of SPS is determined by the Coble diffusion creep intensity of cobalt.

4.2. Analysis of the kinetics of nonisothermal sintering of powders WC-Co

To analyze the kinetics of nonisothermal SPS sintering, we use the Young-Cutler model [32], which describes the initial stage of nonisotemic sintering of spherical particles under conditions of simultaneous processes of volume and grain boundary diffusion, as well as plastic deformation:

\[ \epsilon^2 \left( \frac{\epsilon}{\gamma} \right) = \left( 2.633 \gamma \Omega D_p \sigma / kT d^3 \right) + 0.7 \gamma 2b D_b / kT d^2 \left( Ape^2 D / kT \right), \]

where ε - shrinkage, t - time, γ - free energy, Dv - volume diffusion coefficient, Db - grain boundary diffusion coefficient, d - grain size, p - pressure, D - diffusion coefficient during plastic deformation.

In accordance with [32], the slope of the temperature dependence of shrinkage in the coordinates ln ln(Tε̇/εT) - Tm/T corresponds to the activation energy of the nonisothermal sintering process. From figure 6 it can be seen that this dependence has a two-stage character with a maximum corresponding to a heating temperature of 900-1000 °C. We note that the presence of a maximum in the ln ln(Tε̇/εT) - Tm/T dependence indicates a change in the powder compaction mechanism during SPS [33]. Table 1 presents the values of the activation energy of the first stage of nonisothermal SPS (Q100). An analysis of the results shows that the concentration of graphite in the composition of the initial mixtures does not significantly affect the activation energy of the first stage of nonisothermal SPS of WC-10Co hard alloys. Note that the obtained value (Q100 ~8-11 kTm) is close to the activation energy of the initial stage of isothermal sintering (see above). This allows us to conclude that, at low temperatures (up to ~900-1000 °C), the SPS kinetics of powders WC-10Co is controlled by the intensity of the creep process of low-melting γ-phase based on Co, which agrees well with the data [28, 35].

In the high temperatures region the slope of the dependence ln(Tε̇/εT) - Tm/T (figure 6) becomes negative and other approaches must be used to estimate the sintering activation energy.
In accordance with [25, 26], the activation energy can be estimated using the model of diffusion dissolution of pores located near grain boundaries of UFG materials. To calculate the activation energy, the shrinkage value is first converted to the compaction value by the formula:

$$\rho(T) = \rho_{\text{exp}} L_{\text{max}}/(L_0 - L(T)),$$

where $L_0$ is the initial pressing height corresponding to a density of 50% of the $\rho_{\text{th}}$, $L_{\text{max}}$ is the total shrinkage sample after SPS, $\rho_{\text{exp}}$ - experimentally measured sample density by hydrostatic weighing.

**Figure 4.** The dependence of the shrinkage rate during isothermal hold on the inverse homologous temperature of the SPS

**Figure 5.** The dependence of shrinkage on the inverse temperature at different amounts of free carbon in a submicron hard alloy powder

**Figure 6.** The dependence of the density in double logarithmic coordinates on the reciprocal temperature for the hard alloy WC-10% Co sintered from a submicron powder with an amount of free carbon of 0.5 wt.% C

**Table 1.** The activation energies of the first and second stages of non-isothermal SPS powder WC-10% Co with different content of free carbon

| Content of free carbon in the powder, % | Activation energy of the first stage, kTm | Activation energy of the second stage, kTm |
|----------------------------------------|------------------------------------------|------------------------------------------|
| 0                                      | 10 ± 2                                   | 35 ± 2                                   |
| 0.1                                    | 11 ± 2                                   | 30 ± 2                                   |
| 0.2                                    | 9 ± 2                                    | 22 ± 2                                   |
| 0.3                                    | 8 ± 2                                    | 20 ± 2                                   |
| 0.4                                    | 9 ± 2                                    | 19 ± 2                                   |
| 0.5                                    | 9 ± 2                                    | 20 ± 2                                   |

The activation energy of the second stage of non-isothermal sintering $Q_{\text{II}}$ is determined by the slope of the dependence $\rho(T)/\rho_{\text{th}}$ in the coordinates $\ln[\ln(\alpha\rho/\rho_{\text{th}}/(\rho/\rho_{\text{th}} - 1))] - T_m/T$, where $\alpha = 0.5$ is the compaction coefficient of the compact (figure 6). Analysis of the data presented in table 1 shows that an increase in the concentration of graphite in the composition of WC-10Co leads to a decrease in the
activation energy \( Q_s \) from 35 to 25 kT\(_m\) for submicron powders. The obtained values correlate well with the data [12, 14], and are also close to the activation energy of grain boundary diffusion of cobalt [31]. Important to note that the decrease in the sintering activation energy \( Q_s \) with increasing carbon content is in good agreement with the detected shift of the shrinkage curves \( L(T) \) to the region of lower heating temperatures (see figure 2).

Thus, we should discuss the reasons for the change in the mechanism of the SPS of powders WC-10Co at the stage of non-isothermal heating. In our opinion, a change in the sintering mechanism may be due to the onset of the formation of \( \eta \)-phase particles, the presence of which significantly affects the concentration of tungsten and carbon atoms in the \( \gamma \)-phase and, as a consequence, the intensity of diffusion processes in the hard alloy [29].

Since the temperature of the change in sintering mechanisms (900–1000 °C) is too low for the onset of intense diffusion processes in tungsten carbide, it can be assumed that the second stage of non-isothermal sintering is also controlled by the intensity of diffusion creep of cobalt. From this point of view, the decrease in the activation energy \( Q_s \) with increasing carbon content (see Table 1) is due to the onset of dissolution of tungsten and carbon atoms in cubic cobalt in this temperature range [1, 16, 29]. This leads to an increase in the concentration of carbon atoms in cobalt and, as a consequence, to an increase in the intensity of their diffusion mass transfer through the \( \gamma \)-phase: \( I = - I = -D \cdot \text{grad}C_i \), where \( \text{grad}C_i \) is the concentration gradient of the diffusing substance (C). An increase in carbon concentration decreases the solubility of tungsten in cobalt and increases the stability of tungsten monocarbide - it reduces the tendency of \( \alpha \)-WC particles, which have a narrow homogeneity region in the W-C diagram, to decompose into free carbon and W\(_2\)C carbide, which, when interacting with cobalt, leads to the formation of the \( \eta \)-phase.

![Figure 7. The dependence of the position and broadening of the X-ray peak of cobalt in sintered up to 1400 °C samples of WC-10Co depending on the amount of free carbon in the initial powder.](image1)

![Figure 8. The dependence of the position and broadening of the X-ray peak of cobalt in samples of WC-10Co-0.5C depending on sintering temperature](image2)
0.077 Å) in cobalt. We note that with an increase in the SPS temperature, the cobalt X-ray peak [111] shifts to the region of lower diffraction angles 2Θ (figure 8), which indicates an increase in the concentration of tungsten atoms in the γ-phase with increasing temperature of the SPS. This result is in good agreement with the known effect of increasing the solubility limit of doping atoms with increasing temperature [1].

It should be noted that in accordance with [30], the release of particles of the second phase leads to an increase in the creep limit and an increase in the creep activation energy. Therefore, the second reason for the decrease in the activation energy of sintering with increasing carbon concentration (see table 1) may be a decrease in the volume fraction of particles of the η-phase (see table 1).

5. Conclusion
It was shown that, during SPS the temperature dependence of the compaction of submicron powders WC-10%Co has a three-stage character: insignificant compaction in the region of “low” heating temperatures (stage I), intense compaction in the region of “medium” SPS temperatures (stage II) and again a less intense compaction in the region of “high” sintering temperatures (stage III).

It was shown that an increase in the content of free carbon leads to a shift of the shrinkage curves to lower heating temperatures, to a decrease in the volume fraction of η-phase particles, and also to a decrease in the size of anomalously large grains in samples of WC-10Co hard alloys obtained by liquid-phase SPS. The solid phase SPS method was used to obtain samples of WC-10Co hard alloys in which a uniform high-density ultrafine-grained structure is formed with a graphite content of more than 0.2-0.3 wt.%.

It was established that the compaction mechanism at the first stage of heating is a plastic flow process, the intensity of which is limited by the intensity of diffusion creep of cobalt. An increase in the concentration of free carbon in the composition of the initial mixture WC-10%Co does not affect the intensity of the compaction process and, accordingly, the activation energy of the SPS in the region of “average” heating temperatures. It is shown that the activation energy of isothermal and non-isothermal sintering in the region of “average” temperatures is close to the activation energy of grain boundary diffusion in cobalt.

It is shown that, in the region of “high” temperatures, the activation energy of non-isothermal sintering monotonously decreases with an increase in the concentration of free carbon in the WC-10%Co hard alloy. Using the methods of x-ray phase analysis, it was shown that the cause of the decrease in the activation energy of SPS can be a change in the concentration of tungsten and carbon atoms in the γ-phase.

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