Ultralow-cobalt hard alloys obtained by spark plasma sintering

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Abstract. The features of spark plasma sintering (SPS) of plasma-chemical nanopowders WC-(0.3, 0.6, 1) wt.% Co were studied. The SPS process of ultralow-cobalt hard alloys can be sequentially represented as a change of the following mechanisms: rearrangement of particles at lower temperatures (Stage I) → sintering of WC-Co particles due to Coble diffusion creep of cobalt, the intensity of which is determined by the grain boundary diffusion rate (Stage II) → sintering due to diffusion creep, the rate of which is limited by the bulk diffusion in cobalt (Stage III-1) → sintering of tungsten carbide particles along the intergranular boundaries of WC/WC under conditions of intensive grain growth (Stage III-2). Samples with a high density (96.4-98.4%) and high mechanical properties were obtained (for the WC-0.3% Co hard alloy: \(H_v \sim 20.5\) GPa, \(K_{IC} = 7.1\) MPa \(\cdot m^{1/2}\)).

1. Introduction

Hard alloys WC-Co currently play an important role in industry due to their unique physical and mechanical characteristics: high hardness, especially at elevated temperatures, and, at the same time, high crack resistance, wear resistance and corrosion resistance [1]. The physical properties of pure tungsten carbide [2], as well as carbides with the addition of a large volume fraction of a low-melting metal binder [3], are well studied. Recently, much attention has been paid to the methods of high-speed solid-phase sintering of hard alloys [4-6], which make it possible to ensure the formation of a homogeneous high-density structure with the smallest possible grain size and, as a consequence, with increased physical and mechanical properties. One of the promising materials for machine tool and special machine building are ultralow-cobalt hard alloys, which can combine the high hardness inherent in pure tungsten carbide and the increased crack resistance characteristic of conventional hard alloys with a cobalt content of 8-12 wt.%. Such materials are promising for creating a new generation of metal cutting tools and special applications.

Note, there are few data in the literature on sintering ultralow-cobalt hard alloys. Therefore, the purpose of this work is to study the features of high-speed sintering of ultrafine-grained (UFG) ultralow-cobalt hard alloys and, in particular, to analyze the effect of the cobalt content on the microstructure parameters and physical and mechanical properties of new hard alloys.
2. Methods and materials

The objects of study in this work were tungsten monocarbide nanopowders α-WC, obtained by the plasma-chemical method with subsequent reduction annealing in hydrogen at a temperature of 1050°C (3 h) [7]. Various concentrations of cobalt were added to tungsten carbide nanopowder with an initial particle size of 95 nm by precipitation from an alcohol solution of CoCl₂·6H₂O salts: 0.3, 0.6, and 1 wt% Co. Powder of pure tungsten carbide is No.1, powders with 0.3, 0.6 and 1 wt% cobalt addition are No.2, 3 and 4, respectively.

The compacting of samples with a diameter of 12 mm and a height of h = 4 mm was carried out by the method of spark plasma sintering (SPS) using the Dr. Sinter model SPS-625 (Japan). Sintering of nanopowders was carried out in vacuum (2-5 Pa). During the experiments, the dependence of shrinkage (L) of powders on the heating temperature and isothermal holding time was monitored. The structure of the samples was investigated using a JEOL JSM-6490 scanning electron microscope with an Oxford Instruments INCA 350 energy-dispersive microanalyzer. Qualitative phase analysis was carried out using the Diffrac.EVA program. Quantitative analysis was determined by the Rietveld method. The accuracy of determining the volume fraction of particles of α-WC, W₂C, and η-phase was ±0.5%. Sample density (ρ) was measured by hydrostatic weighing using a Sartorius CPA 225D analytical laboratory balance. Hardness H, and fracture toughness K_c on sintered specimens were measured using a QnessA60 + microhardness tester. The measurements were carried out with a load of 2 kg.

3. Results

The SEM images of pure tungsten carbide nanopowders and nanopowder compositions WC-Co with various cobalt content show that nanoparticles are collected in agglomerates, the average size of which is the same for all samples and is ~2-3 μm. The structure of pure tungsten carbide contains rather large agglomerates several tens of microns, which are practically absent in the WC – Co nanopowder composites. Analysis of the XRD results shows that the powder compositions contain hexagonal tungsten monocarbide α-WC and cobalt in two modifications - with a cubic and a hexagonal lattice. Figure 1a shows the dependence of shrinkage L of WC-Co nanopowders on the continuous communication temperature. It is seen that the dependence of shrinkage on the system for nanopowders has a three-stage character.

![Figure 1. Shrinkage plots L(T) of the powders (a) and XRD results of sintered samples (b)](image-url)

The microstructure photographs of the surface layers of sintered hard alloys show that in pure tungsten carbide can provide a fairly uniform UFG structure with an average grain size of ~ 0.2–0.3 μm. In the structure of the obtained ceramics, single coarse elongated grains with a size of ~ 1-3 μm are visible. In samples containing cobalt, individual inclusions of cobalt up to 1 μm in size were found.

Figure 1b shows XRD results of the surface layers. It is seen that in the composition of ultralow-cobalt hard alloys, in addition to the α-WC phase, there is a phase of ternary carbide η-Co₃W₂C, the volume fraction of which is less than 0.5 vol.%. The structure of the central layers of ultralow-cobalt
hard alloys also contains particles of the η-phase of the composition Co₃W₃C, the amount of which increases from ~1.6 to 3.6% with an increase in the content of cobalt in the composition of the initial nanopowders from 0.3 to 1 wt%, respectively. We emphasize that the bulk η-phase for particles in some samples of ultralow-cobalt hard alloys is several times larger than in the surface layers. The hardness of the surface layer obtained in the continuous mode with an increase in the cobalt content from 0.3 to 1 wt% decreases from 20.5 GPa to 15.4 GPa. A fairly noticeable spread in hardness is observed, which may indirectly indicate an unequal distribution of cobalt in the structure of sintered hard alloys. Crack resistance of the surface layer of ultralow-cobalt hard alloys with 0.3 and 1% Co is 7-8 MPa·m^1/2. The hardness of the center hard alloy is slightly different from that of the hard surface layer.

4. Discussion

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

Generalization of the results at figure 2a shows that with an increase in the concentration of cobalt, the absolute and relative values of the density of the sintered specimens decrease. The result obtained, in our opinion, is a consequence of an increase in the volume fraction of the η-phase particles in hard alloys, which have a lower theoretical density (14.48 g/cm^3 for Co₃W₃C). An analysis of the data on the hardness and crack resistance of the sintered specimens is shown in figure 2b. It is seen that there is a decrease in the hardness of the surface layers from 28.8 GPa to 20.5 GPa and an increase in KIC from 4.8 to 7.1 MPa·m^1/2 with an increase in the cobalt content from 0 to 0.3%. A further increase in the cobalt content leads to a significant decrease in the hardness to 11.4, but does not lead to a noticeable change in the crack resistance of the sintered specimens. This may be due to the non-uniform distribution of cobalt in the process of solid-phase sintering of hard alloys, in which the propagation of cobalt between WC particles occurs only with the help of plastic deformation (viscous flow).

4.2. Analysis of sintering mechanisms

The generalization of presented in figure 1b dependences of shrinkage on heating temperature shows that the dependences L(T) have a traditional three-stage character. To analyze the kinetics of non-isothermal sintering of powders at the stage of intense shrinkage (Stage II), we use the Young – Cutler model [8], which describes the initial stage of nonisothermal sintering of spherical particles under conditions of simultaneous processes of volume and grain boundary diffusion. In accordance with [8], the slope of the shrinkage (ε) dependence on temperature in the coordinates ln (εεT − T₀) - Tଶ / T corresponds to the effective activation energy of the non-isothermal sintering process mQs. It should be noted that the value of the coefficient m depends on the type of the dominant diffusion mechanism under non-isothermal sintering conditions (m = 1/3 for grain boundary diffusion, m = 1/2 for bulk diffusion, m = 1 for viscous flow [8]).

For ultralow-cobalt hard alloys with 0.3, 0.6, and 1 wt% Co, the effective activation energies at Stage II are mQs ~ 11 kTm, 10 kTm, and 9 kTm, respectively. The values obtained in the case m = 1 (see [9])
are quite close to the activation energy of diffusion creep of cobalt, limited by the rate of grain boundary diffusion (Coble creep) [10]. We also note that in [9], the activation energy of SPS for plasma-chemical nanopowders with an increased cobalt content WC-Co, calculated using the Young-Cutler model, was $Q_{S2} \sim 7-8 \text{kTm}$, which is in good agreement with the results obtained in this work. Similar values of the activation energy for diffusion creep were obtained in [10]. The decrease in the activation energy of sintering at Stage II is probably due to the increased volume fraction of the interphase boundaries "tungsten carbide WC – γ-phase (Co)", through which the process of diffusion of carbon and tungsten atoms occurs.

5. Conclusion
The samples obtained by the SPS method have a high density (96.4-98.4% of the theoretical value), a fine-grained structure and high mechanical properties: the hardness of the WC-0.3% Co hard alloy is $\sim 20.5 \text{ GPa}$, and the Palmquist fracture toughness coefficient is $K_{IC} = 7.1 \text{ MPa m}^{1/2}$. The result obtained indicates, in our opinion, the efficiency of the combined use of the SPS technology and the chemical-metallurgical method of applying ultrathin layers of the metal phase on the surface of the synthesized tungsten carbide nanoparticles.

It is shown that the process of high-speed sintering of ultrafine-grained ultralow-cobalt hard alloys can be represented as a sequential change of the following mechanisms: rearrangement of particles at low temperatures (Stage I) $\rightarrow$ sintering of WC-Co particles due to diffusion creep of cobalt according to Coble, the intensity of which is determined by the rate of grain boundary diffusion (Stage II ) $\rightarrow$ sintering due to diffusion creep, the rate of which is limited by the rate of bulk diffusion in cobalt (Stage III-1) $\rightarrow$ sintering of tungsten carbide particles along the WC / WC grain boundaries under conditions of intensive grain growth (Stage III-2).

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