The factors leading to abnormal grain growth during sintering of hard alloy

N V Isaeva¹, Y V Blagoveshchenskii¹, A V Terent’ev¹, V H Smirnova², V N Chuvil’deev², A V Nokhrin², M S Boldin², E A Lantcev² and A A Murashov²

¹Baikov Institute of Metallurgy and Materials Science RAS, 119334, Moscow, 49 Leninisky av., Russia
²Nizhny Novgorod State University. Department of Physical Material Studies
Nizhniy Novgorod, Russia

Abstract. This work investigated the sintering of the nanocrystalline tungsten carbide and cobalt composite powder. Vacuum sintering and spark plasma sintering (SPS) were used to consolidate powders into bulk nanocrystalline materials. In addition, two methods of the cobalt introduction were developed for making WC/Co compositions. The first one uses mechanical mixing in ball milling machine. The second one is based on a precipitation and reduction of the cobalt salt on the WC particle surface. The oxygen was always present in the produced powders. Therefore, a control of common carbon is necessary to produce bulk materials with correct chemistry. When vacuum sintering or SPS process are used for consolidation, the addition of grain growth inhibitor is necessary to minimize grain growth. Sintering hard alloys using the nanocrystalline WC-Co composite powders has unique properties and potential for commercial applications.

1. Introduction
The development of methods used for synthesizing nanoscale particles, in particular WC and Co nanoparticles [1-4], opens prospects for a significant increase in the mechanical properties of nanocrystalline WC-Co materials. However, the production of nanostructured (grain sizes <200 nm) hard alloys based on tungsten carbide remains an unresolved problem due to the rapid grain growth during sintering.

Rapid grain growth during the early sintering stage was detected in many nano-material systems, including sintered WC-Co [5].

It is well known that the coarsening of WC in WC-Co is suppressed in hard metals having low carbon contents and, consequently, high concentrations of tungsten dissolved in the binder. The study of WC-Co alloys with different carbon activity, ranging from graphite equilibrium to η-phase equilibrium, showed that as the carbon activity increases, the average WC grain size increases and the grain size distribution increases too [6]. The mechanism of suppressing the coarsening of WC in WC-Co hard metals with decreasing carbon content, according to the authors [7], is connected with the dissolution of carbon in a liquid binder. The limiting stage of coarsening WC can be self-diffusion of carbon in WC grains towards the WC-liquid interface in case of solid metals with very low carbon contents corresponding to the formation of the η phase. Also the limiting stage can be related to the processes of reprecipitation of W and C on WC grains from extremely rich W and depleted C of the binding phase.

The experimental approach to the quantitative calculation of the WC grain shape during sintering of WC-Co alloys as a function of the C and Co contents was used in [8]. Observation of the WC grain shape at heating process shows that the formation of the WC faces takes place in the solid state. At the
beginning of the sintering process in the solid state, the C content does not affect the shape of the WC grain. In the process of liquid-phase sintering, morphology develops as a function of composition. For a low Co content, the grains have a slightly less triangular shape from the edge enriched with C than from the W enriched side. They become much less elongated in alloys rich in C when the sintering time increases, while in W enriched alloys limited modification.

The authors of [9] believe that an effective means of preventing abnormal grain growth is preliminary solid-phase sintering.

The addition of carbide-inhibitors to the alloy is the most important way of slowing the grain growth during sintering. A number of works have been devoted to their influence on the sintering of fine-grained and nanopowders [10-13].

This paper is devoted to the study of these important factors affecting the process of sintering nanostructured hard alloys.

2. Experimental procedure
Nanoparticles of W-C system were produced by plasma-chemical synthesis in which metal oxide were used as a raw material. The temperature generated by DC plasma flame. The second stage is reduction in H₂ atmosphere in tube furnace (Naberterm R100/750/13). Carbon and oxygen content were analyzed by Leco equipment. The specific surface area was carried out by TriStar 3000 Micromeritics and XRD (Shimadzu XRD-7000) was used to determine the phase composition on different stages.

The powders were sintered in vacuum and in a SPS-625 spark plasma sintering system. The common carbon content and specific surface area as phase composition of the alloys were determined of the plasma-chemical synthesis conditions. As usual the carbon content is 6.07 – 6.45 mass%, the specific surface is 6-10 m²/g.

The preparation of a homogeneous composition of carbide with cobalt nanopowders is a difficult task due to the difference in the particle size of the powders. The standard cobalt powders used for hard alloy production have an average size of 1-2 μm, and tungsten carbide up to 1 μm. In our case, the average particle size of tungsten carbide is 40-60 nm. Traditionally, the industry uses a variant of canister ball mixers with a duration of about 72 hours. High-energy planetary mills or attritors are also used. Another option used in laboratory studies is the mixing of powders without balls in devices of the «Turbula» type. These methods are different in the energy characteristics of the effect on powders and lead to slightly different results in sintering.

Another variant of the WC-Co composition is the uniform deposition of the cobalt layer on the surface of tungsten carbide particles (cladding). The cobalt salt from the solution of the organic solvent is precipitated onto the carbide particles which are suspended while stirring. After drying, the precursor is reduced in hydrogen.

In our work, powder mixtures were prepared by these two methods - mixing powders in a planetary mill (Retsch PM-400) in carbide-tipped beakers with balls in a 4:1 ratio and precipitation of cobalt by the chemical-metallurgical process.

The initial tungsten carbide size was 7.19 m²/g. After the introduction of cobalt, the specific surface area changed to 6.12 m²/g and after milling to 8.82 m²/g.

It is characteristic of the nanopowders sintering that difficulty achieved a density as close as possible to the theoretical density. Such a density is achieved even in the solid phase by high-energy sintering (under pressure). For vacuum sintering, the process is required at temperatures somewhat higher than for industrial alloys.

It was shown that the relative density of compacts obtained by different methods is approximately the same (the effect of the initial compact density on the sintered samples was also studied). However, after sintering at 1430 °C, the sample density of powders with precipitated Co was appreciably higher than those obtained by mixing.
The sample density is close to the theoretical and was 14.97 g/cm\(^3\) for powders with precipitated Co and 0.94-0.96 from theoretical for milled powder.

3. Result and Discussion
The initial powder properties determine the quality of the material after sintering. The carbon and oxygen content in the powder and the uniformity of cobalt distribution in the material are the main ones. The behavior of oxygen in nanopowders is extremely important, since when it is heated it reacts with carbon and material is depleted. As it was shown in [15], the oxygen content does not exceed 0.1\% regardless of the specific surface area and air-holding time at the stage of plasmochemical synthesis of carbide particles (W-C mixture) (Fig. 1a).

![Fractional gas analysis for oxygen in nanopowders W-C, WC and WC-Co](image)

**Figure 1.** Fractional gas analysis for oxygen in nanopowders W-C, WC and WC-Co

The carbide particles are protected by very thin carbon films. Adsorbed oxygen is weakly bound to the surface and desorbed at heating. The oxygen which is registered as an oxide is chemical bonded with tungsten particles. The surface of tungsten carbide particles is freed from the graphite film at the stage of low-temperature synthesis of monocarbide (Fig.1b). More oxygen forms a strong bond when the powder contacts with air. The total oxygen content in the monocarbide powder reaches 0.25-0.35\%. The specific surface area does not change but the oxygen content increases significantly after precipitation of cobalt (Fig.1c) (up to 15\% by weight). Both the adsorbed and chemically bound oxygen content increases. As can be seen from Fig. 2, the average particle size is substantially less than 100 nm.
The initial stages of sintering are accompanied by a several physico-chemical processes.

There is a cleaning of the particle surface from adsorbed oxygen. Chemically bound oxygen begins to interact with carbon from carbide. The carbon in carbide lattice also restores oxidized cobalt. This results in a general depletion of carbon in the material. The grain growth, dissolution of tungsten in cobalt, the formation of an intermediate phases, the formation of a liquid eutectic, the growth of a tungsten carbide grain after recrystallization taken place during sintering even at relatively low temperatures.

Due to the local depletion of carbide, the reaction with oxygen generates the formation of double $W_xCo_yC$ carbides. At the same time, an appreciable anisotropic WC grains growth was noted under certain sintering conditions in the presence of a local carbon excess. The large, thin trigonal plates were formed preferentially than uniaxial trigonal prisms.

These plates can be traced up to 1150°C. They grow at high speeds in a stage where a significant residual porosity still prevails in a green material. This porosity (free space) proves to be necessary in advance for the growth of such large grains in the solid state which leads to the formation of plates up to 7 μm. Fig. 3 shows SEM of WC-10Co samples after vacuum sintering at 850 (a) and 1150 °C (b). It is seen that in the first case the growth of the carbide grain is not yet noticeable, and in the second case, the formation of twinned crystal micron-sized plates and a thickness of 100-200 nm is observed.

It is interesting how to change the phase composition of the material. There is a double $W_xCo_yC$ carbide in addition to the $\alpha$-WC and WC$_{1-x}$ phases in the initial nanopowder obtained by precipitation of cobalt according to XRD data. Samples sintered at 850 °C contain $\alpha$-WC, W, Co, and W$_2$C phases. At 1150 °C only $\alpha$-WC and beta-Co are already available. In powders mixed with cobalt, the phases of double carbides are formed at a higher temperature and a relatively low content of carbon in the material.
The structures with nanoscale tungsten carbide grains were obtained by solid-phase SPS (Fig. 4). The conditions of high heating rate (100°/min) and approximately the same temperature were used.

The abnormal grain growth is observed in the samples sintered by both vacuum and SPS. However, the shape and size of large carbide crystals depends on the initial powder composition. At a low carbon content, the characteristic shape is triangular plates with close length-to-width and height dimensions. This is typical for both large and small crystals. When the plates are formed (with a greater content of carbon), their height is much less than other dimensions.

Figure 4. The hard alloy structure obtained by solid phase SPS.

Smaller grains dissolve due to their higher dissolution potential (increasing chemical potential), while heavier grains grow as a result of reprecipitation of the substance, thereby reducing the interfacial surface of the system.

The density of WC-10Co and 1% Cr$_3$C$_2$ samples is 14.8 g/cm$^3$. 

Table 1. SPS conditions and WC-10Co, TaC, VC properties.

| $T_{sint}$, °C | Pressure, (MPa) | $\rho$, (g/cm$^3$) | HV (2 kg) | $K_{1C}$ (2 kg) |
|----------------|-----------------|--------------------|-----------|-----------------|
| 1253           | 25              | 14.74              | 17.2      | 9.5             |
| 1243           | 25              | 14.726             | 17        | 10.3            |
| 1200           | 25              | 14.732             | 17.6      | 8.7             |
| 1140           | 25              | 14.752             | 18.5      | 7.3             |
| 1160           | 25              | 14.747             | 18.1      | 8.9             |
| 1180           | 25              | 14.764             | 17.6      | 9.2             |
| 1157           | 100             | 14.768             | 19.5      | 6.4             |
| 1140           | 100             | 14.741             | 17.6      | 9.5             |
| 1140           | 100             | 14.759             | 18.3      | 7.6             |
| 1140           | 100             | 14.763             | 17.9      | 8.8             |

As can be seen in table 1, nearly 100% density and very high values of hardness and fracture resistance are achieved by SPS in a wide range of temperatures and pressures.

Table 2 shows the hard alloy properties obtained by SPS - without inhibitors and with two types of inhibitors - chromium and vanadium carbide and tantalum. Alloys without inhibitors have the highest density, lower hardness and higher fracture resistance. These are ultra-fine hard alloys. Alloys with chromium carbide have extremely high microhardness and the lowest fracture resistance. The grain size of such alloy is “neanano” and these are nanostructured alloys. The third alloy with tantalum and vanadium carbides as inhibitors has very high hardness and is also very fine-grained. In another series of experiments with the WC-10Co, 1VC composition the hardness ($HV_{20}$) was 17 GPa, the fracture toughness ($K_{1C}$) was more than 12.5 MPa·m$^{1/2}$. In the same series of experiments, the samples with $HV_{20}$ -15.6 GPa, $K_{1C}$-17.5 MPa·m$^{1/2}$ and $HV_{20}$ -12.3 GPa, $K_{1C}$-19.4 MPa·m$^{1/2}$ were obtained by changing the heating and sintering regimes.

Table 2. Hard alloy properties after SPS.

| Material                  | Properties | d, µm |
|---------------------------|------------|-------|
|                           | $\rho$, (g/cm$^3$) | HV (2 kg) | $K_{1C}$ (2 kg) |
| WC-6%Co                   | 15.176     | 18.9 | 6.7 | 0.2 – 3 |
| WC-6%Co-0.8%Cr$_3$C$_2$   | 15.17      | 18.4 | 6.9 | 0.2 – 3 |
| WC-6%Co-0.1%VC-2%TaC      | 15.038     | 24.7 | 4.2 | 0.1-0.5 |
|                           | 15.035     | 24.7 | 4.2 | 0.1-0.5 |
|                           | 15.091     | 24.6 | 4.4 | 0.1-0.5 |
| WC-6%Co-0.1%VC-2%TaC      | 14.181     | 21.7 | 5  | 0.1-1 |
|                           | 14.85      | 23.7 | 4.5 | 0.1-1 |
|                           | 14.901     | 23.8 | 4.9 | 0.1-1 |
4. Conclusions
Hard alloys obtained from WC-Co nanopowders by traditional and high-energy sintering methods have extremely high physical and mechanical properties (hardness and fracture resistance). Their quality depends on the sintering conditions but primarily on the properties of initial nanopowders. Oxygen in the nanopowder is chemically bonded and therefore at elevated temperature is a source of carbon loss. The conditions of carbide-cobalt mixing production are important for homogeneous mixture and also introducing oxygen into the material. To obtain tungsten monocarbide should be taken into account the probable loss of carbon when interacting with oxygen. Therefore, the content of free carbon in tungsten carbide should be more than 0.1-0.2 wt%.

Pre-sintering is applied at a temperature of 850-900 °C in vacuum for 0.5 hours for the complete removal of oxygen. The more accurate carbon content, the less is the possibility formation both abnormal large crystals and double carbides.

Vacuum sintering of nanopowders is carried out at temperature of 100 °C above the eutectic to achieve maximum density. The use of SPS provides a hard alloy without pores both in solid-phase and liquid-phase sintering with less than 100 nm carbide grain size in case solid-phase sintering. The heating rate, the time and application of the pressure in SPS determine the hard alloy properties. The obtained values of $H_v$ and $K_{IC}$ are extremely high.

Using nanopowder inhibitors (vanadium, chromium and tantalum carbides) prevented the grain growth of tungsten carbide during sintering. Their introduction in an amount of 0.7-1% provides the nanostructure in hard alloy. More than 80% of the particles have size less than 0.2 μm. Nevertheless, an abnormal grain growth is observed (particles 1-3 μm in size). Different effect of inhibitors is noted. For example, vanadium carbide sharply slows down the grain growth but tantalum and chromium carbides increase the physico-mechanical properties more strongly.

5. References
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