Structural-phase features of WC-based ceramics obtained by the spark plasma sintering method

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Abstract. Ceramics obtained by spark plasma sintering of tungsten carbide powder were studied by X-ray diffraction layer-by-layer analysis. The surface of the ceramic samples was mechanical ground and polished in several stages. The distribution of crystal phases by the depth of ceramics was investigated.

1. Introduction

WC-based hard alloys produced by sintering [1] of powders are promising materials for use as metal cutting tool. It is characterized by high hardness, high wear resistance, high melting point, chemical resistance to corrosion and oxidation. At the same time, pure tungsten carbide ceramics are characterized by low flexural strength [2].

Original WC powders are sintered with various additives to improve the physical and mechanical properties of hard alloys. The addition of cobalt increases the crack resistance and strength of WC-based hard alloy [1].

Improvement of the hard alloy physical properties is also associated with the formation of a homogeneous high-density fine-grained structure in them [3]. In this regard, the most promising method for manufacturing of hard alloys is spark plasma sintering (SPS) of powders. The method consists in heating the powder at a high rate up to the sintering temperature in a vacuum under pressure [4]. The powder is poured into a hollow cylindrical graphite mold and fixed with graphite punches.

Previously, an X-ray diffraction layer-by-layer analysis of samples of the hard alloy WC + 10% Co revealed the heterogeneity of the phase composition over the depth of the sample [5]. It was established that the brittle η-phase (Co3W3C) appears in the studied samples at a depth of ≥ 100 µm. The observed effect indirectly confirms the hypothesis of carbon diffusion from graphite punches contacting the surface of sintered samples. Thus, the carbon deficiency was replenished in the surface layers of the samples with preventing the formation of the η-phase.

It is known that carbon not only prevents the formation of brittle phases in the sintering process (W2C in WC ceramics and the η-phase (Co3W3C) in WC – Co hard alloys), but also dissolves in cobalt. Therefore, for a detailed study of the discovered phenomenon, it was necessary to consider the original system – WC.

The purpose of the work is to determine the degree of homogeneity of WC ceramics obtained by the SPS method by the approach of X-ray diffraction layer-by-layer analysis.
2. Materials and techniques
Industrial WC powder with an average particle size of 3 μm (produced by JSC “KZTS”) was used as a raw material for the manufacture of ceramic samples. The content of carbon in the original powder was 6.13 ± 0.01% wt., where free carbon was 0.05 ± 0.01% wt.

SPS of WC powder was performed on the “Dr. Sinter model SPS-625” (SPS Syntex, Japan). Sintering was carried out in a vacuum in a graphite mold with an internal diameter of 12 mm.

The objects of the study were 2 ceramic samples. Sample 1 was obtained in the following mode: heating speed was 50°C/min, pressure was 70 MPa, sintering temperature was 1690°C.

Before sintering sample 2, punches and a mold were coated with BN to isolate the sintering powder from the surfaces of carbon parts. Otherwise, the sintering conditions for samples 1 and 2 were the same.

The surface of the sintered ceramic samples was mechanical grinded with diamond discs and sequentially mechanical polished with diamond paste to a roughness level of 1 μm. The operation of mechanical grinding was carried out on a “Struers Secotom-10”, polishing – on a “Buehler Automet 250”.

There were conducted 5 stages, each consisted of grinding and subsequent polishing. The thickness subtracted at each stage was 60, 70, 40, 140, 460 μm for sample 1 and 100, 100, 120, 180, 380 μm for sample 2. The height of the sample was controlled using a micrometer.

Phase composition of the original powder and sintered ceramic samples was studied by X-ray powder diffraction. X-ray diffraction experiments were performed on a diffractometer “XRD-7000” (Shimadzu, Japan) in the “wide slit mode” using CuKα-radiation (λ = 1.54 Å) in the range of angles 2θ = 30 – 80° with a scanning step of 0.04° and an exposure time of 2 s.

Quantitative phase analysis was carried out by the reference intensity ratio method using integral intensities of the analytical diffraction peaks of crystal phases detected in the studied samples [6]. The analytical peak of α-WC was peak (101) and W2C was peak (111).

Vickers hardness (HV) was measured using a “Struers Duramin-5” with 2 kg load.

3. Description of experimental results
Quantitative X-ray phase analysis of the original WC powder demonstrated the presence of 2.5 ± 0.2% wt. of W2C. This explains the introduction of free carbon into the WC powder by the manufacturer.

Figure 1 shows the results of X-ray diffraction experiments of ceramic samples 1 and 2. The numbers of X-ray diffraction patterns correspond to the number of the layer-by-layer analysis stage. Thus, 1 – diffraction pattern of the surface layer of the sample subjected to primary surface treatment, 5 – diffraction pattern of the layer closest to the center of the sample (at a depth of ~ 900 μm from the surface layer).

Significantly lower content of W2C – 0.8 ± 0.1% wt. is fixed in both samples after the first stage of surface treatment (up to 100 μm depth) than in the original powder. The recovery of W2C to α-WC can take place only due to carbon [7].

![image](image-url)
Figure 1. X-ray diffraction patterns of WC ceramic samples at the different stages of surface treatment: a) sample 1 (without BN covering of graphite parts of the mold), b) sample 2 (with BN covering of graphite parts of the mold).

The similar character of the diffraction patterns of both samples after the first stage of their surface treatment, and also the mentioned results on WC + 10% Co, allow us to draw a conclusion that the recovery of W₂C to WC on the surface occurs most likely due to the carbon diffusion from graphite punches.

Subsequent layers of both samples (at a depth of ≈ 200 μm) contain 3.0 ± 0.2% wt. of W₂C that slightly exceeding the content of W₂C in the original powder. The constant content of W₂C = 1.7 ± 0.2% wt. is fixed from a depth of 300-400 μm (see figure 2). An increasing in hardness Hᵥ is also observed with increasing degree of sample homogeneity in deeper layers.

The detected heterogeneity of the phase composition over the sample depth may be related to the features of the WC powder sintering process. So, adsorbed oxygen on the WC powder surface at heating reacts with WC, which leads to partial decarburization of WC particles with the formation of gases CO and CO₂, and therefore with the formation of new W₂C particles.

But the free carbon introduced into the original WC powder to achieve the equilibrium carbon value (6.13% wt.) is insufficient to suppress both the existing W₂C and the W₂C formed by decarburization during heating.
It should also be noted that the sample is heated from the mold. This leads to an uneven sintering process and prevents the formation of a homogeneous structure in the sintered sample.

4. Conclusion
The result of this study is the detection of the phase composition heterogeneity of WC-based ceramics obtained using a promising technology – spark plasma sintering of powder. It was found that at a depth of 100-300 μm, the content of W₂C reaches its maximum. This maximum is closer to a depth of 200 μm for a sample without BN and for a sample with BN – around 300 μm. In this case, the coating of the mold with a layer of BN did not affect the characteristic values of the W₂C phase content of the ceramic sample within the error limits. Thus, it was shown that in order to further study the sintering mechanisms of WC-based ceramics it is necessary to take into account the temperature distribution inside the sample.

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