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Pressureless sintering of binderless tungsten carbide

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ABSTRACT

The aim of this study was to produce dense, single phase polycrystals. The research was carried out on the submicron tungsten carbide powder without additives, with either a carbon or tungsten additive and on the powder with both additives. The primary task of carbon was to reduce surface oxide impurities which passivate WC grains; tungsten in turn bounds free carbon in the WC. The authors manufactured fine-grained, dense (96–98% T.D.) and single-phase WC polycrystals, using the technique of pressureless sintering at the temperature not exceeding 2000 °C. A positive effect of carbon addition on tungsten carbide sinterability was observed, whereby a dense, fine-grained polycrystals can be obtained at 1900 °C. It was also observed that a significant excess of temperature of sintering process resulted in a strong abnormal grain growth of WC grains.

1. Introduction

Tungsten carbide is a well-known material. It has the high melting point (2785 °C), high hardness (20–25 GPa), low friction coefficient, good electrical and thermal conductivity, relatively high corrosion and oxidation resistance and moderate fracture toughness [1,2]. The high melting point and low self-diffusion coefficients are the main reasons of difficulties in sintering of tungsten carbide. The low interest in single-phase WC polycrystals results from the well-established production technology of sintered carbides, commonly called WIDIA. In this case, metallic additives such as Co or Ni are used as a WC grains binder. This method allows materials of high bending strength and fracture toughness to be obtained, in relatively low sintering temperatures (1400–1600 °C). Cemented carbides are usually used as cutting and drilling tools, abrasive materials or wear resistant elements [3,4].

Nevertheless, the addition of metallic phase results in lowered hardness as well as chemical resistance. The progress, observed in the recent years, in the techniques of sintering increased the interest in the production of the single-phase polycrystalline WC. There were numerous attempts to sinter WC powders without metallic additives by the use of hot pressing (HP) [5–7], hot isostatic pressing (HIP) [8,9], or high pressure-high temperature technique (HPHT) [10]. Moreover, due to good electrical conductivity of tungsten carbide, sintering enhanced by electric field, e.g. spark plasma sintering (SPS), was investigated, [11–22].

The main purpose of the application of external pressure (HP, HIP, HPHT) during sintering is to decrease sintering temperature and to obtain non-porous dense bodies. The use of fine powders allows dense sinters at lower temperatures to be obtained. Its high surface energy increases sintering driving forces, yet the forming of an oxide layer on their surface is intensified. The addition of carbon escalates densification of the material by a carbothermic reaction of oxide impurities reduction [7,8,17,20]. Nevertheless, the addition of carbon, use of nano- and submicron WC powders, too high sintering temperature or too long annealing time may cause the abnormal grain growth effect (AGG) [7,8,17,20,23]. AGG manifests itself in the form of growth of certain grains to the size of even 1000 times larger than in the starting powder. AGG may lead to an increase in fracture toughness (bridging effect) and reduction in hardness and bending strength of the material. To avoid an unfavorable AGG effect, two approaches were proposed. SPS method allows sintering time a from few hours to be shortened to a few minutes and elimination of annealing time. High current (up to 3000–5000 A), used in this method, led to the occurrence of plasma at the grain boundaries which helps to remove oxide layers from the grain surface. As a result, it is possible to obtain dense sinter with fine microstructure in relatively low temperatures (1600–1800 °C), and then avoiding AGG. However, the spark plasma sintering is very expensive and only small, simple-shaped sinters can be achieved. Another way is to use grain grown inhibitors, such as TiC, ZrC, VC or Cr_3C_2, [5,24,25]. Nonetheless, it requires the application of expensive pressure-assisted sintering at temperatures above 1950 °C. The

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Table 1
Characteristics of powders: WC, W and resin (data provided by the powder manufacturer).

WC (ABCR GmbH & Co. KG)	W (AEE)	Resin – source of carbon (Organika; Sarzyna)
Amount of oxygen: 0.21–0.40 mass% Amount of total carbon: 6.08–6.18 mass% Amount of free carbon: 0.06–0.08 mass% Amount of impurities (Co, Fe, Mo): <700 ppm d_{fisher} = 0.5–0.7 μm	Grain size: −325 mesh Purity: 99.9mass%	Type Novolac After pyrolysis the resin leaves 50mass% in the form of amorphous carbon

main disadvantage of complex and energy-consuming sintering techniques described above is the inability to produce different shapes of samples, in contrast to the simplest sintering technique, which is pressureless sintering. Applying this method, the authors of this study sintered fine (submicron) WC powders successfully [26,27]. In this research, carbon was the only addition introduced into the sintering powders, in order to reduce oxide contaminants, present at the surface of the tungsten carbide grain. Moreover, this additive allows sinters to retain its single-phase nature.

The aim of the work was to obtain dense, fine-grained and single-phase WC polycrystals by means of pressureless sintering without metallic additives, such as cobalt or nickel. Carbon or tungsten or both of them were used simultaneously as sintering additives. Both additives guarantee that the sintered material will be single phase. On the basis of the performed studies, such as density measurements, sintering dilatometric analysis, XRD phase composition analysis, qualitative and quantitative microstructure analysis, the attempts to determine the influence of additives on submicron WC powder sintering were made.

2. Experimental

2.1. Powders

In the following research the commercial submicron tungsten carbide powder (d_{fisher} = 0.5–0.7 μm) was used (ABCR GmbH & Co. KG Cat. No. AB173079). Carbon was introduced as an alcoholic solution of phenol-formaldehyde resin (type Novolac – Nowolak MR; Organika; Sarzyna), which leaves 50 mass% of amorphous carbon after pyrolysis. Purity of tungsten was 99.9% and average grain size was 44 μm. (AEE Cat. No. WP-104) (Table 1).

2.2. Preparation and sintering

Calculations of the amount of carbon needed to reduce oxide impurities passivated on surface of carbide grains, were based on carbothermic reactions of the oxide impurities reduction (Eqs. (1) and (2)):

$$WO_3 + 4C = WC + 3CO\uparrow \quad (1)$$

$$WO_2 + 3C = WC + 2CO\uparrow \quad (2)$$

The results of calculations are presented in Table 2.

The powders were homogenized in the following compositions:

- tungsten carbide without additives (WC),
- WC + 0.2 mass% of carbon (WC + 0.2%C),
- WC + 0.4 mass% of carbon (WC + 0.4%C),
- WC + 0.5 mass% of tungsten (WC + 0.5%W),

Table 2
Calculations of amount of carbon additive.

	Carbon additive [mass%]		
	Min.	Max.	Mean value
Reaction (1)	0.21	0.40	~0.40
Reaction (2)	0.24	0.45	

- WC + 0.2 mass% of carbon + 0.5 mass% of tungsten (WC + 0.2%C + 0.5%W),
- WC + 0.4 mass% of carbon + 0.5 mass% of tungsten (WC + 0.4%C + 0.5%W).

The amount of carbon addition was determined as the minimum and maximum amount needed to reduce the oxide impurities (Tables 1 and 2). The amount of tungsten additive was similar to the maximum amount of carbon additive and to the amount of tungsten required to bind free carbon in the WC (Table 1). All the samples were prepared using the same procedure. The powders (WC, W and resin powder) were weighted and then homogenized by wet mixing in ethanol in the ball mill for 12 h. Then, the alcohol was evaporated from the slurry under IR radiator. The obtained mixtures of powders were granulated by sieving in a perlon sieve. Next, the granulates were used for molding raw samples by the uniaxial, two-side pressing technique (p = 150 MPa) in a matrix made of zirconium oxide. The raw samples were additionally compacted by cold isostatic pressing under 250 MPa. The samples had a diameter of 13 mm and height ranging from 2 to 3 mm. Green density was 55–60% T.D. of tungsten carbide. The water solution of polyvinyl alcohol (5.0 mass%) was used as a binding phase in the amount of 0.5 mass% for pure tungsten carbide batches and the samples composed of WC and 0.5 mass% W.

The initial (T_0) and end (T_S) temperatures of sintering were defined on the basis of $\Delta d/d_0 = f(T)$ curves (linear shrinkage of samples vs. temperature), which were recorded in the high-temperature dilatometer. The presence of "plateau" at sintering curves and occurrence of minor changes in the dimensions of samples were considered to be the end of sintering.

Pressureless sintering was carried out at the following temperatures 1800 °C; 1900 °C; 2000 °C and 2100 °C. Sintering temperatures were close to T_S, which was determined according to the dilatometric measurements. The samples were pressurelessly sintered in a high-temperature Thermal-Technology reactor, in argon flow with a heating rate 10 °C per minute.

2.3. Density and phase compositions

Apparent density measurements were performed by the Archimedes method in water immersion. The phase composition of sintered bodies was conducted with the X-ray diffraction method. Quantitative phase composition of polycrystals was determined by the Rietveld method. Relative density of samples was counted on the basis of theoretical density, which was calculated by the rule of mixtures, assuming densities of 15.68 g/cm^3 for WC and 17.16 g/cm^3 for W_2C.

2.4. Qualitative and quantitative analysis of polycrystals microstructure

The samples were polished (Struers Rotopol 25) and chemically etched in molten alkali salts (25% KNO_3 + 75% KOH; 480 °C) in order to perform observations of the material microstructure. The microstructure of samples was observed by the SEM microscope (Nona Nano SEM 200, FEI Company) and the optical microscope (Nikon Ephiphot 300). The method of observation depended on size of the observed grains. Microstructures were analyzed by Aphelion

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