Int. Journal of Refractory Metals and Hard Materials 43 (2014) 193–199

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

Review

Hot pressing of tungsten carbide with and without sintering additives

Agnieszka Gubernat *, Paweł Rutkowski, Grzegorz Grabowski, Dariusz Zientara

AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Department of Ceramics and Refractories, 30 Mickiewicza Av., 30-059 Krakow, Poland

ARTICLE INFO

Article history:
Received 31 October 2013
Accepted 7 December 2013

Keywords:
Single-phase
Tungsten carbide
Hot-pressing
Thermal conductivity
Mechanical properties

ABSTRACT

This study presents the results of investigations concerning hot-pressing of submicron WC powders without sintering additives and with the addition of carbon or tungsten or both elements simultaneously. Dense polycrystals of diverse microstructures and phase compositions were obtained. Attempts were made to correlate a microstructure and phase composition of sinters with their thermal and mechanical properties. It was found that the presence of graphite nanolayers on grain boundaries in WC sinters with the addition of carbon favourably influences their thermal conductivity. All produced polycrystals are characterised by a high fracture toughness. The smallest scatter of K_{Ic} results is observed for compositions activated by a carbon addition. The presence of the graphite nanolayers as well as grain size in WC sinters with carbon additions reduce the polycrystal hardness. All WC polycrystals, regardless of introduced additives, are characterised by high bending strength and by high values of the Young and Kirchoff moduli. The tested polycrystals are not suitable for machining carbon steel of C45 grade.

Contents

1. Introduction

Polycrystalline tungsten carbide (WC) belongs to the group of materials called sintered carbides which might be defined in the following way: "A group of materials more commonly known as cemented carbides (hardmetals) consists of mixtures of one or more of finely divided tungsten, titanium, tantalum and vanadium carbides in a matrix of cobalt or nickel" [1]. From the material science point of view, sintered carbides are CMC in which mainly grains of tungsten carbide are bound by metallic matrix such as cobalt, nickel or manganese. Technologies of obtaining cemented carbides have been known since the 1930s [2]. The simple technology of producing cemented carbides of the required properties resulted in a small interest in single-phase tungsten carbide [3]. In addition, for years, a conviction that these substances are difficult to sinter was strengthened, which also contributed to this slim interest in single-phase polycrystals [4–6]. In recent years, the development of sintering techniques resulted in the appearance of studies concerning sintering of single-phase polycrystals of WC [7–13]. These studies [7–13] mainly concern obtaining polycrystals by electric field assisted sintering techniques. Authors obtain dense polycrystals, however, process parameters they give are significantly different. An addition of carbon (introduced on purpose) occurs in the discussed studies. The aim of carbon addition is to unify the phase composition, it means the reaction between carbon and W_2C carbide with the formation of the WC phase. Its influence on sintering is not discussed. According to the authors of papers [7–10], carbon contributes to a strong grain growth, due to which the hardness of sinters decreases which is accompanied by an insignificant increase in the fracture toughness. The other approach to the addition of carbon is presented in studies describing pressureless sintering of tungsten carbide [14–16], in which this addition is considered necessary for the formation of dense materials and influences favourably grain sizes in sinters. Carbon addition is required for reduction of oxide impurities located mainly as passivation layers on the

* Corresponding author. Tel.: +48 12 617 36 96; fax: +48 12 633 46 33.
E-mail address: gubernat@agh.edu.pl (A. Gubernat).

0263-4368/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ijrmhm.2013.12.002

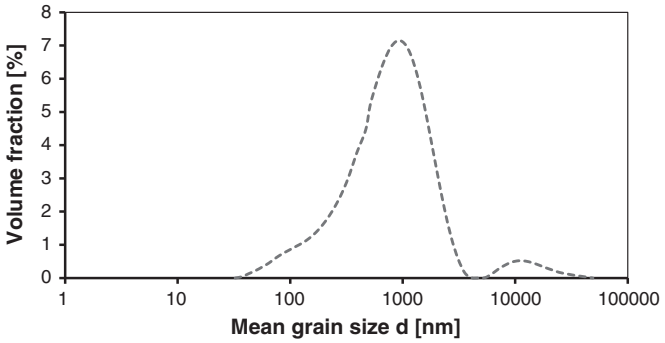

Fig. 1. Grain size distribution in WC powder.

surface of the carbide grains. Its addition is also required to create the unifying phase compositions, and it ultimately leads to obtaining single phase WC polycrystals.

The results of tests of hot-pressing of a commercial tungsten carbide powder of submicron grain sizes, into which additions of carbon, of tungsten or of both elements were introduced on purpose, are discussed in this study. Sintering tests were also performed for samples without any additions. Measurements of density and of a phase composition were performed on the obtained materials. Their microstructure was also observed. Measurements of mechanical, elastic and thermal properties with a special consideration of fracture toughness were also carried out. Machining tests of the produced polycrystals were additionally performed.

2. Preparation

From the commercial submicron WC powder (Fig. 1) (ABCR GmbH & Co. KG Cat. No. AB173079), metallic tungsten powder (AEE Cat. No. WP-104) and a carbon source: phenol-formaldehyde resin type Novolac (Nowolak MR; Organika; Sarzyna)—the following compositions were prepared:

- WC + 0.4% C + 0.5% W;
- WC + 0.4% C;
- WC + 0.5% W;
- Pure WC (WC + 0%).

Table 1 shows the characteristics of the powders used: WC, W and resin. It was taken into account, at the preparation of compositions, that after the thermal decomposition 50% of the resin mass remains in the form of amorphous carbon. The amount of carbon addition was calculated on the basis of the oxygen amount (0.21–0.40 mass%) in a WC powder and the carbothermal reduction of basic tungsten oxides WO_3 and WO_2 (Eqs. (1) and (2)). Data for the calculations of the carbon additive are presented in Table 2.

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

Table 1
Characteristics of the powders used: WC, W and resin.

WC	W	Resin (source of carbon)
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: 99.9 mass %	Type Novolac After pyrolysis the resin leaves 50 mass% in the form of amorphous carbon

Table 2
Carbon additive calculations.

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

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

The mean carbon content was 0.40 mass%. Tungsten was introduced in amounts similar to the calculated carbon amounts. The prepared compositions were homogenised in ethyl alcohol, in a ball grinder for 12 h. After evaporation of alcohol, the mixtures were rubbed through a perlon sieve, and the granulate ready for the hot-pressing was obtained. The main role of carbon additions during the sintering process, as it was mentioned above is the reduction of oxide passivation layers covering carbide grains. The Novolac resin addition – in the form of alcohol solutions – as a carbon source is desired for the creation of the uniform amorphous carbon layer covering all the carbide grains, which promotes the oxide layer reduction. Pressure assisted sintering was done in a matrix of a diameter ~51 mm, made out of high-strength graphite. Conditions for the hot-pressing process of individual compositions are given in Table 3.

The measurements of apparent density and porosity (Archimedes method) were performed on the obtained sinters and qualitative and quantitative analyses of their phase composition were carried out (XRD method; Rietveld method; Empyrean Panalytical). The relative density was also calculated. Table 4 presents the theoretical density of each composition. From the HP derived sinters the authors prepared samples for the measurements of bending strength (3-point bending test), fracture toughness (by the SNEB method), thermal diffusivity (the LFA method) and Young and Kirchoff moduli (ultrasonic method). The measurements of bending strength and fracture toughness were carried out by means of the testing machine Zwick/Roell 2.5 kN. Investigation speed in both cases was 0.1 mm/min. Thermal diffusivity was determined by the Netzsch LFA 427 analyser. Then the thermal conductivity coefficient λ was determined for individual measuring points. Elastic properties were measured by a UZP-1 (INCO-VERITAS) apparatus. Metallographic microsections were made on sample fragments and then their microstructure was observed using a scanning microscope Nova Nano SEM 200 of the FEI Company. These microsections were also chemically etched in a melted mixture of 75% KOH and 25% KNO_3, at a temperature of 480 °C. Due to this procedure, it was possible to observe grain shapes in sinters and the crack pathway initiated by the Vickers pyramid. The grain shape was determined by the aspect ratio (AR), defined as a ratio of the maximal chord to the minimal one passing through the grain [17]. The measurements of the Vickers hardness $HV_{3.0}$ and fracture toughness by means of the indentation method were made on non-etched metallographic microsections. The hardness tester Future-Tech Corp. FV-700 was used. The force of ~30 N was applied in all cases. The spectrum analysis by means of the Raman spectroscopy was carried out on samples into which carbon additions were introduced. Raman studies were carried out using Horriba Yvon Jobin

Table 3
Conditions for hot-pressing of WC polycrystals.

Composition	Pressure of hot-pressing	Sintering temperature and a holding time
WC + 0.5% W WC + 0% WC + 0.4%C + 0.5% W WC + 0.4% C	25 MPa	2150 °C/0.5 h 1950 °C/0.5 h