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Hard polycrystalline eutectic composite prepared by spark plasma sintering

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Abstract

A polycrystalline eutectic B_4C–TiB_2 composite was prepared by spark plasma sintering. The starting eutectic powder was obtained by mechanical grinding of the directionally solidified eutectic B_4C–TiB_2 alloy. The microstructure of the polycrystalline composite exhibited randomly oriented eutectic grains with an average size of about 50–100 μm. Eutectic grains consisted of boron carbide matrix reinforced by titanium diboride inclusions. The secondary eutectic structure in the grain boundary is formed at sintering temperature higher than 1700 °C. XRD analysis revealed that the eutectic B_4C–TiB_2 composite consist mainly of B_4C and TiB_2 phases. The measured Vickers hardness was in the range of 32.35–54.18 GPa and the average fracture toughness of the samples was as high as 4.81 MPa $m^{1/2}$. The bending strengths of the composite evaluated at room temperature and at 1600 °C were 230 and 190 MPa, respectively.

Keywords: B. Composites; C. Hardness; D. Borides; Spark plasma sintering

1. Introduction

Due to their unique combination physical and mechanical properties, boron carbide based materials are increasingly used in several industrial sectors. The boron carbide crystal structure B_4C exhibits strong covalent bonding, which results in high hardness, augmented Young's modulus and elevated melting point [1]. Furthermore, boron carbide shows low density (2.53 g/cm^3). The boron carbide is semiconductor, however the presence of small amounts of metal impurities can affect significantly the electrical conductivity. The excellent strength-to-weight ratio makes boron carbide attractive materials to be employed in various fields such as tooling, high-temperature structural materials and thermoelectrics [2]. If compared to traditional refractory metals, such as W, Mo, Ta and Nb [3,4], the application fields of boron carbide ceramics are limited by its low fracture toughness.

Due to its brittleness, monolithic B_4C is not used as structural material. The B_4C toughness is enhanced by using various metallic additives as well as high-energy compacting methods [5]. The fibres reinforcement, realized by directional solidification of quasibinary eutectics of systems B_4C–RC (where RC – refractory compounds – TiB_2, ZrB_2, HfB_2, SiC, etc.) [6–10] represents one of the most effective method to enhance the fracture toughness. At present the directional solidification allows to obtain ceramic materials with strength above 4.5 GPa. Such high value is attributable to the highly oriented structure, elongated grains, good bonding between the phases and defect free crystals [11–13]. Unfortunately the directional solidification method results in limited size products (i.e. sample diameter 8 mm) and strong anisotropy of the mechanical properties due to the marked texturing of the grains.

Spark plasma sintering (SPS) is a rapid sintering technique which was recently developed for the rapid fabrication of dense ceramics and composites at low sintering temperatures compared to the conventional sintering methods as hot pressing (HP). Both SPS and HP are pressure assisted sintering method, an uniaxial pressure is applied across the specimen during the sintering process. However, SPS and HP differ significantly in the heating mode. Specifically, in HP an array of heating

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elements indirectly heats the punch/powder/die assembly by radiation and eventually by convection and/or conduction. The powder heating rate is controlled by the rate of radiation and/or convection and conduction. Conversely, in SPS, the punches transfer the pulsed current (typically a thousand amperes) and Joule heat directly to the powder. In the SPS, the current effects are not limited to Joule heating, thus other non-thermal effects as current enhanced mass transport, electroplasticity, and reactivity [14–18] have been identified. The applied pressure, in turn, indirectly aids in the densification process by increasing the surface energy driving force. Even if there is no direct evidence existence of plasma [19] during the sintering, the SPS has the well recognized ability to produce fully dense material which cannot be obtained by conventional sintering methods. The SPS permits to avoid grain coarsening whilst promoting densification due to the short heating and the cooling times [20–22].

In the present work, the SPS densification mechanisms of eutectic powder were investigated aiming to obtain an isotropic fibre reinforced B_4C–TiB_2 ceramic. As reported in Refs. [23,24], the pseudo-binary systems of borides produced by zone melting resulted in improved microhardness and fracture toughness if compared to the monophasic compositions (i.e. B_4C or TiB_2). The fracture mode of brittle polycrystalline materials at near room temperatures is dominated by transcrystalline mechanism [25], thus, randomly oriented eutectic particles consisting of boron carbide directionally reinforced by titanium diboride might contribute to increase the toughness of the isotropic ceramic material.

2. Experimental details

The eutectic powder with average grain size 50–100 μm was obtained by mechanical grinding of the directionally solidified eutectic B_4C–TiB_2 alloy in a steel mortar. The directionally solidified eutectic B_4C–TiB_2 composite was produced by a floating zone method based on crucibleless zone melting of the compacted powders as described in Ref. [26]. B_4C–TiB_2 particle size smaller than 50–100 μm is undesired, it results in the destruction of regular eutectic microstructure within the individual particles.

As shown in Fig. 1 the eutectic consists of 77 vol% of boron carbide matrix and 23 vol% of titanium diboride inclusions. The average TiB_2 inclusion diameter and interphase spacing are 0.5–1 and 1–1.5 μm, respectively. In order to remove the wear products of steel mortar, a magnetic separation was employed. The typical X-ray diffraction pattern of the B_4C–TiB_2 powder after magnetic separation is shown in Fig. 2(a). XRD analysis revealed that composite consisted of B_4C and TiB_2 phases. No other phase was identified.

Spark plasma sintering was carried out in an SPS apparatus (SPS-1050, SPS Syntex Inc., Japan) using a graphite die with an inner diameter of 10 and 20 mm. The temperature was controlled by an optical pyrometer focused on the non-through hole located on the surface of the graphite die. The sintering experiments were conducted in vacuum (1.3×10^{-3} Pa) atmosphere at different temperatures in the range of 1400–1900 °C and dwelling time of 1–20 min under a pressure of 50–100 MPa. The heating and

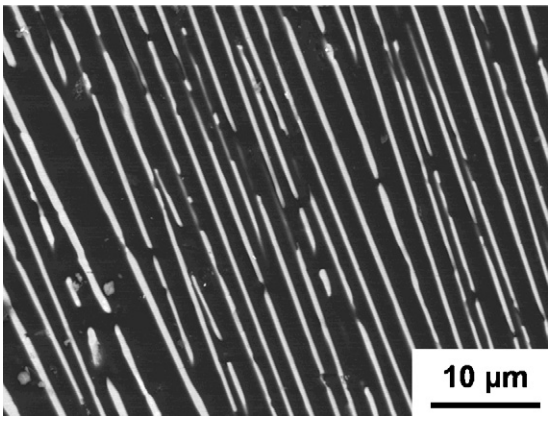

Fig. 1. Microstructure of the directionally solidified eutectic B_4C–TiB_2 alloy.

cooling rates were 100 °C/min. In order to decrease the radial temperature gradient inside the punch-sample-die assembly, an insulating felt was used. For easy sample extraction after sintering, a graphite paper was inserted between the powder and the die/punch. The sintered samples had diameter 10 and 20 mm. Densities and porosity of all sintered samples were measured using the Archimedes method with distilled water as the immersion medium.

The Vickers hardness and fracture toughness were measured using a standard indentation technique. Prior to indentation, the samples were polished with diamond abrasives to a 3-μm finish. Hardness tests (PMT-3, Russia) were performed at a load of 2 N and a holding time of 15 s. The fracture toughness, K_{IC}, was determined directly from the crack lengths produced by Vickers indentations (PMT-3, Russia) at 2 N load with a 15 s dwell time.

The fracture toughness values were calculated using Eq. (1) given by Niihara et al. [27] for the Palmqvist cracks in brittle materials:

$$K_{IC} = 9.052 \times 10^{-3} H^{3/5} E^{2/5} dl^{-1/2} \quad (1)$$

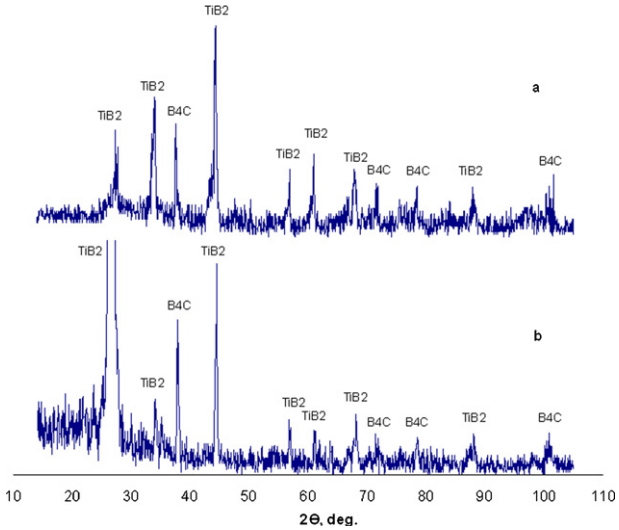

Fig. 2. X-ray diffraction patterns of the eutectic B_4C–TiB_2 powder (a) and sintered sample at 1800 °C for 20 min (b).