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Fractographical assessment of densification mechanisms in hot pressed ZrB_2-SiC composites

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Abstract

The controlling densification mechanisms of hot pressed monolithic ZrB_2 ceramics and ZrB_2-based composites, containing 15 and 30 vol% SiC, at different consolidating temperatures were investigated, based on scanning electron microscopy micrographs of fracture surfaces, relative densities, and average grain size of ZrB_2. For the hot pressed samples at 1700 °C, particles fragmentation in the composite samples, mechanical interweaving, and rearrangement without sizeable chemical bonding were appointed as dominant densification mechanisms. Neck formation between ZrB_2/ZrB_2 was observed at 1850 °C and plastic deformation of ZrB_2 grains was nominated as controlling densification mechanism. Reduction of porosity in the hot pressed specimens at 2000 °C was related to grain boundary diffusion mechanism. Colossal grain growth in monolithic ZrB_2 ceramic proposed the occurrence of detrimental mechanisms such as grain coarsening and evaporation/condensation. Presence of intergranular SiC particles between ZrB_2 grains impeded extremist grain growth.

Keywords: A. Hot pressing; B. Composites; D. Borides; D. SiC

1. Introduction

Zirconium diboride is striking for its ultrahigh melting temperature (3245 °C) as well as its hardness, elastic modulus, low electrical resistivity, and resistance to chemical attack. As a result, it has been proposed for a variety of structural applications including armor, cutting tools, steel processing, molten metal containment, and electrodes. It is also considered to be an ultrahigh temperature ceramic and is a candidate for use as leading edges and propulsion components in hypersonic aerospace and advanced reusable atmospheric reentry vehicles. Because of strong covalent bonding and low grain boundary self-diffusion coefficient, high temperatures and external pressures are required to densify ZrB_2 [1–3].

In historic studies, nominally monolithic ZrB_2 ceramic had only been densified by hot pressing at 2000 °C or higher, with pressures of 20–30 MPa, or at lower temperatures (~1800 °C), with much higher pressures (800–1500 MPa). Pure ZrB_2 with starting particle sizes of 5–10 μm requires hot pressing above 2000 °C to achieve full density. It was found that hot pressing of coarse ZrB_2 powder (20 μm) at 2000 °C, under a pressure of 20 MP, achieved only a relative density of 73%. Particle size reduction decreased the consolidating temperature necessary to achieve full density to 1900 °C, pressed under 32 MPa. Minimization of grain growth was attributed to lower sintering temperatures and reduced starting particle sizes [1,4,5].

Oxide impurities (e.g. B_2O_3 and ZrO_2) on the surface of starting powder restrain densification and encourage grain growth in ZrB_2-based ceramics and composites. Recently, use of commercial ZrB_2 powders has typically included non-reactive additives such as SiC, the most common additive for ZrB_2-based composites, to improve densification through producing a secondary phase and decreasing oxygen impurities content [5]. The high hot pressing temperatures and pressures of historic studies are not necessary with the finer starting powders and additives that minimize grain growth [1,6,7]. The introduction of submicron α-SiC powder (0.8 μm) was

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recognized as a key factor that enabled both the control of ZrB_2 grain growth and the achievement of full density by hot pressing at 1900 °C under 50 MPa [8]. Furthermore, the addition of ~22 vol% nano-sized SiC, with particle sizes ranging from 40 nm to 0.6 μm, sharply reduced the consolidating temperature necessary to achieve full density to 1650 °C under 60 MPa [5]. Study of the hot pressed samples with starting powder sizes of 2 and 0.7 μm for ZrB_2 and SiC, respectively, showed that the grain size decreased from 6 μm for ZrB_2 to 3 μm in ZrB_2–SiC composites. Hence, SiC acts as a grain growth inhibitor in ZrB_2-based composites [9]. Microstructure of ZrB_2 (with powder size of 2 and 6 μm) containing 30 vol% SiC (with powder size of 0.7 μm) has been studied at different hot pressing temperatures. Relative densities ranged from 97% to 100% and average grain size of ZrB_2 particles varied from 2.2 to 4.7 μm [10]. Investigation on the effect of SiC powder size, ranging from 0.45 to 10 μm, on the microstructure of ZrB_2–30 vol% SiC composites showed that the smaller the starting SiC powder, the better the densification and the finer ZrB_2 grain size [11]. In a ZrB_2-based composite containing 20 vol% nano-sized β-SiC powder (30 nm), which was hot pressed at 1900 °C under 30 MPa, the grain growth of ZrB_2 was effectively suppressed by SiC particles [12].

The processing temperature was a major variable in the investigation of densification of HfB_2 in high pressure hot pressing. The initial stages of densification occurred by particle fragmentation and rearrangement, but the final stages of densification in hot pressing of fine particle size HfB_2 occurred by viscous flow, diffusion, or creep by dislocation movement [13]. The densification of spark plasma sintered ZrB_2–25 vol% SiC composites has been divided into a two-stage process with a transition temperature of 1750 °C; first, a slow stage by a sintering based mechanism on the basis of reduction of starting powder surface and second, a fast stage as a forging step where creep and pressure remove porosity, after the initial grains have been shaped [14]. Recently, the dominant densification mechanisms for hot pressing of ZrB_2–20 vol% SiC composite at different temperatures and pressures were identified. For hot pressing at 1700 °C, it was found to be mechanically driven particle fragmentation and rearrangement only, whereas at 1850 °C a plastic flow mechanism started to take place. At 2000 °C, the dominant mechanism changed from plastic flow to grain boundary diffusion [15].

Although in recent times, ZrB_2 based composites have been densified by other techniques, including pressureless sintering [6,16–18], reactive hot pressing [4,19–21], and spark plasma sintering [14,22–26]; hot pressing is still a popular method in consolidating research cases. The purpose of this paper is to describe the densification mechanisms in ZrB_2–SiC composites, hot pressed under a relatively low pressure. Field emission scanning electron microscopy micrographs of fracture surfaces of the samples are used to study the evolution of microstructure as a function of consolidating temperature and SiC content. In addition, density and porosity of the samples together with average grain size of ZrB_2 are compared to deduce the effects of hot pressing temperature and presence of SiC.

2. Experimental procedure

2.1. Processing

ZrB_2 (particle size ~2 μm, purity ~99.9%, Leung Hi-tech Co., China) and α-SiC (particle size ~2 μm, purity >99%, Carborundum Universal Limited, India) powders were the starting materials. Powder samples of ZrB_2 with 0, 15 and 30 vol% SiC were mixed at 120 rpm for 1 h in zirconia cups and balls. Then, samples were loaded into a graphite die and boron nitride spray was applied to all graphite surfaces. Hot pressing was completed in a graphite resistance-heated vacuum hot press furnace (made by Shenyang Weitai Science & Technology Development Co. Ltd., China). In each hot pressing experiment, 10 MPa pressure was applied as soon as the final isothermal temperature cycle started. Samples were initially heated at a rate of 12 °C/min up to 1000 °C, given a dwell isotherm at 1000 °C for 30 min in order to remove volatile materials contained in the samples, then heated again at a rate of 10 °C/min up to the designated temperatures. Above 1000 °C, the temperature of the graphite die was monitored using an infrared temperature sensor (Model IT-6). Hot pressing was carried out at different temperatures (1700, 1850 and 2000 °C), given a dwell isotherm for 30 min. Finally, the hot press furnace was cooled down naturally. One billet, with a diameter of 25 mm and thickness of 5 mm, was prepared for each experiment.

2.2. Characterization

Bulk density of samples was measured using the Archimedes' technique with distilled water as the immersing medium, and the relative density was calculated with respect to the theoretical density. The theoretical density was estimated using rule of mixtures, based on starting compositions of the samples and following pure component densities ZrB_2: 6.1 g/cm^3 and SiC: 3.2 g/cm^3. Microstructural characterization was carried out by a scanning electron microscope (Mira3 Tescan, Czech Republic). Chemical analysis was performed simultaneously with SEM, using energy dispersive spectroscopy (EDS). The grain size was determined from fracture surfaces micrographs, using an image analysis software (ImageJ 1.44p, Wayne Rasband, National Institutes of Health, USA).

3. Results and discussion

3.1. Fractographical investigation

The microstructures of fracture surfaces of hot pressed ZrB_2-based samples with various SiC contents and different consolidating temperatures are shown in Fig. 1. Fractographical examinations by SEM exhibit grained microstructures with ZrB_2 particles as a matrix and a distribution of SiC in the composite.

Fracture surfaces of all hot pressed samples at 1700 °C (Fig. 1a, d and g) show a fully intergranular fracture state, due to the fact that the sintering process was not significantly