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The effect of heating rate and composition on the properties of spark plasma sintered zirconium diboride based composites

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ABSTRACT

Five different compositions of ZrB_2–SiC–ZrC were prepared and then processed by spark plasma sintering (SPS) to a maximum temperature of 2000 °C, with heating rates of 100 °C/min and 200 °C/min. Grain size, density, Rockwell hardness, flexural strength, and thermal conductivity were evaluated for the processed composites. Adding SiC up to 10 wt.% had a positive effect on densification and strength. Increasing the heating rate promoted densification and less overall grain growth for samples with SiC and ZrC above 15 wt.% each, and had a slight negative effect on densification when these values were at 10%.

1. Introduction

Ceramics, such as ZrB_2 and HfB_2, that can withstand temperatures above 3000 °C without melting are generally referred to as ultra-high temperature ceramics (UHTCs) [1]. The addition of secondary and tertiary phases has been shown to enhance the properties of these ceramics, such as increased strength and hardness. Several challenges are faced in the processing of ZrB_2-based UHTCs-namely poor sinterability, high temperature oxidation, and grain growth. To address these challenges, compositional control is coupled with an emerging sintering technique that applies an external electrical field and rapid heating rates, also known as spark plasma sintering (SPS). SiC is a commonly used additive that acts as a grain growth inhibitor, while ZrC is expected to increase resistance to ablation at high temperatures via the formation of a protective oxide layer on the surface of the composite [2–5]. The ZrB_2–SiC–ZrC multiphase system has been established as an interesting candidate for a variety of applications, including metal crucibles, leading edge materials, and hypersonic re-entry vehicles [6]. Electric field application during the sintering of these materials has resulted in better densification without many of the side effects that make conventional sintering processes less than ideal [7,8].

Powder consolidation aided by an electric field application was developed in the 1930s when Taylor sintered cemented carbides by resistance heating [9]. In 1966, Inoue developed a machine that used electric field application for powder sintering [10]. Since then, many metallic and non-metallic materials have been fully densified via methods based on this powder processing technique. These methods are similar to hot pressing, where the initial powders are loaded into a die and sintered under application of uniaxial pressure. In contrast to hot pressing, which uses an external heat source, temperature increase in the case of electrical field sintering is performed by Joule heating of the sample (if electro conductive), the die (fabricated from conductive graphite), or both. The specific techniques that involve simultaneous application of pressure and an electric field are often referred at as spark plasma sintering (SPS) [11], pulsed electric current sintering (PECS) [12], or field assisted sintering technique (FAST) [13]. The main factors that typify these types of sintering processes and make them suitable for consolidating a large variety of powders at lower temperatures than other methods are: (i) joule heating in the plungers/die, and in some cases, the powders, can provide rapid heating rates, and formation of large thermal gradients; (ii) enhanced mass transport via electromigration, and point defect generation [14]; (iii) processing time is greatly reduced, samples can be successfully sintered in minutes. Although it has been claimed in literature that there is plasma formation at the surface of the particles, which promotes densification through surface oxide cleaning, no distinct evidence of plasma formation has been offered so far.

A major advantage of SPS is the ability to obtain much higher heating rates than in conventional sintering or hot pressing. Electrical field application should enhance non-densifying mechanisms

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Table 1
Sample composition by weight percent.

Sample name	Composition (wt.%)		
	ZrB_2	SiC	ZrC
60-02-38	60	02	38
60-20-20	60	20	20
70-15-15	70	15	15
80-10-10	80	10	10
100-0-0	100	0	0

Table 2
Archimedes density data.

Sample name	2000 °C 100 °C/min [% theo. density]	2000 °C 200 °C/min
100-0-0	5.80 [95.3]	5.70 [93.8]
60-02-38	5.31 [85.7]	5.30 [85.4]
60-20-20	4.29 [81.3]	4.80 [90.4]
70-15-15	5.12 [94.3]	5.40 [99.0]
80-10-10	5.60 [99.5]	5.50 [97.0]

such as surface diffusion and evaporation–condensation [7,15]. This would lead to an increased grain growth tendency when sintering materials via these methods. Moreover, the coarsening tendency is increased for ultra-fine powders, which have a larger surface area per unit volume, leading to enhanced evaporation condensation and surface diffusion. The application of rapid heating rates has been reported as a way to limit coarsening, and therefore avoid fabrication of densified materials with inferior mechanical properties for materials that have higher activation energy for densification than for grain growth [16–21]. By employing a rapid heating rate, the time in the low temperature range, where the non-densifying mechanisms dominate, is shortened. Thus, the powder is brought quickly to high temperatures where densification occurs by grain boundary and volume diffusion, and the retention of a fine grain size is often possible. However, for other materials, which have an activation energy for densification that is lower than that for grain growth, this tendency seems to be challenged and the heating rate does not have the expected positive effects [22].

In this work we investigate the combined effect of heating rate and composition during SPS sintering of ZrB_2–SiC–ZrC at 2000 °C. To our knowledge there are few reports on investigations of heating rate effects in such systems. Two heating rates, of 100 °C/min and 200 °C/min, have been utilized. The composition of each phase was also varied to study their individual contributions to composite properties and elucidate their role in the sintering process. Density, average grain size, flexural strength, hardness measurements and thermal conductivity measurements were taken for each sample in order to understand the composition–microstructure–properties relationships in these composites.

2. Materials and methods

ZrB_2 (325 mesh), ZrC (100 mesh), and SiC (<1500 grit) purchased from Atlantic Equipment Engineers were used as starting powders. Five different compositions were prepared and will be referred to hereafter in terms of weight percent of each compound as shown in Table 1. The samples were mixed for ball milling in polyethylene bottles with 200 mL of hexane. The powders were milled using yttria-stabilized zirconia media at a weight ratio of 10 to 1 at 180 rpm for 15 h. After milling, the samples were immediately dried in a rotary evaporator at 70 °C, a vacuum pressure of 27 kPa, and a speed of 150 rpm. After drying, the samples were brushed from the walls of the flask and collected in glass vials. Particle size after milling was measured using transmission electron microscopy.

The milled powders were processed using a spark plasma sintering machine built in house by our collaborators at SPS Nanoceramics (Illinois, United States). The SPS processing was performed to a maximum temperature of 2000 °C with heating rates of 100 °C/min and 200 °C/min. A load of 60 MPa (~18 kN) was applied to a 19 mm die containing the green sample, and the samples were held at maximum temperature for 4 min in each experiment. The temperature was measured on the die surface by a pyrometer. No significant temperature overshoot was observed.

The surfaces of all samples were polished before any testing was done. The density of each sample was then measured by Archimedes' method. A 3-point bending test (Sintech 30/D digital tensile testing machine) was performed to measure the flexural strength of the samples. The SPS samples were used as discs for this test, as received after SPS processing. Before the test, the diameter and thickness of all samples were measured using a digital caliper. Thickness of all samples ranged from 2.90 mm to 3.40 mm (standard dev of 0.257) and the diameter of all samples was 19.06 mm. The span between the two supports was set to be 14.60 mm. Scanning electron microscopy (SEM) was performed on the fracture surfaces using a Philips XL40 SEM with accelerating voltage of 3.0 kV at a working distance of 10 mm. The surface of each sample was polished and the hardness was measured by the indentation method, on the Rockwell scale A, with a load of 60 kg for 10 s. Six measurements were taken for each sample, and the values reported here are averages of these measurements.

Thermal conductivity was measured using a transient photoacoustic (PA) technique that has been described in detail in previous work [23,24]. For a multi-layer structure, the PA technique can resolve bulk and component thermal resistances as well as thermal diffusivities of each layer. Using the acoustic signal in conjunction with the model based on a set of one-dimensional heat conduction equations, the thermal conductivity of the material was determined using the least-squares fitting method.

3. Results and discussion

For this study, each composition was processed via SPS to a maximum temperature of 2000 °C with heating rates of 100 °C/min and 200 °C/min. After SPS processing, the density of the composites were measured by Archimedes' method (Table 2). The densities of the composites are lower than the 6.17 g/cm^3, the true density value for ZrB_2 due to the addition of the lower density SiC phase (3.20 g/cm^3). The theoretical density of each composite was calculated using the rule of mixtures.

While several of the samples did not reach full density, the data suggests that an increase in SiC content leads to slightly greater densification, while the addition of ZrC results in a slight decrease in density. By carefully adjusting the secondary and ternary phase content of the composites, it is possible to obtain fully dense compacts. The presence of carbides in the samples is expected to lead to a reduction of oxide content and the formation of a secondary intergranular phase, which will enhance densification and grain growth inhibition [25–28].

The variations in density at different heating rates seem to be strongly dependent on slight modifications in composition. For pure ZrB_2, there is a slight decrease in density as the heating rate increases, which is in agreement with other studies [29]. ZrC additions appear to have a negative effect on densification, as seen for the 60-02-38 sample, which has a significantly lower density than the pure ZrB_2. The density values are not significantly affected by heating rate for this sample. This is somewhat expected as ZrC is known to have a poor sinterability given the inherent covalent character of the Zr–C bond. On the other hand, having equal percentages of 10% SiC and ZrC seem to lead to an increased density compared to pure ZrB_2, while increasing the heating rate led to a slight decrease