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Short communication

Significance of hot pressing parameters on the microstructure and densification behavior of zirconium diboride

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In this study, microstructure–densification relations were investigated for zirconium diboride ceramics. Billets of ZrB_2 were densified by hot pressing at 1700, 1775 or 1850 °C for 30, 60 or 90 min under 8, 12 or 16 MPa. SEM micrographs of polished and fracture surfaces as well as density and porosity measurements were used to study the influences of hot pressing parameters (temperature, dwell time and applied pressure) on the final microstructure and densification behavior of ZrB_2. A design of experiment approach, Taguchi methodology, was used to optimize the hot pressing of ZrB_2. In this way, an L9 orthogonal array procedure, which comprises the signal to noise ratio and the analysis of variance, was employed. The significances of temperature, dwell time, pressure as well as unknown parameters, affecting the mean ZrB_2 grain size, were recognized about 56, 33, 1.5 and 9.5%, respectively. The controlling densification mechanisms were shown to vary from ZrB_2 particles rearrangement to diffusion-based mechanisms with increasing hot pressing factors. In addition, by approaching the optimal hot pressing conditions, the fracture surfaces of the samples changed from intergranular to transgranular state, dominantly.

1. Introduction

Zirconium diboride, generally known as a member of ultrahigh temperature ceramics group, has exceptional combined characteristics of high melting point, chemically stable crystal structure, high conductivity (electrical and thermal), and strange chemical inertness. On account of these superior properties, it has been used for refractory linings, molten metal crucibles, hypersonic vehicles, re-entry shuttles, cutting tools, steel processing, and high-temperature electrodes. Despite that, low mechanical properties (eg., fracture toughness) and deficient oxidation resistance are still the obstacles for monolithic ZrB_2 ceramics to be exploited over a wide area. Due to the strong covalent bonding, surface oxide impurities, large starting particle sizes and low self-diffusion coefficient of zirconium diboride, it is difficult to produce a fully dense ceramic without addition of any reinforcement phases (eg. SiC and C) or sintering aids (eg., Si_3N_4 and $MoSi_2$). However, progress has been made in the awareness of the sintering of ZrB_2 while decreasing second phases which may be harmful to its high-temperature characteristics [1–5].

The relative density of a pressureless sintered monolithic ZrB_2 ceramic remained at 60% for processing temperatures up to 1950 °C. Its relative density, improved, but only arrived 78% after sintering at 2100 °C for 120 min [6]. Pure ZrB_2 ceramic requires an elevated hot pressing temperature (2100 °C), with pressures of 20–30 MPa, or a temperate temperature (1800 °C), with extra high pressures (800–1500 MPa) to be densified completely [7]. Generally, sintering mechanisms can be categorized into those which promote densification and those that cause grain coarsening without significant densification [8]. When sintering at elevated temperatures, densification process is usually accompanied by an unwelcome grain growth. For example, the grain size of a ZrB_2 ceramic, hot pressed at 1850 °C, is coarser than that of densified at 1700 °C, by a factor of ~1.6 [9]. Minimization of grain growth is associated with lower process temperatures and reduced starting powder sizes [1].

Surface oxide impurities have an important effect in the sintering of non-oxide ceramics by activating evaporation–condensation mechanisms, which lead to coarsening without remarkable densification proceeding [8,10]. Probable oxide impurities (B_2O_3 and ZrO_2) on the surfaces of starting ZrB_2 powder not only prevent the densification process, but also lead to grain growth since B_2O_3 exists as a liquid or vapor phase which provides a rapid diffusion path [7]. The densification of sintered ZrB_2 ceramic could be improved by decreasing the oxygen contaminations of starting material. For example, it is reported that oxide impurities on the surface of ZrB_2 powder could be eliminated through etching in a dilute hydrofluoric solution. Milling process (eg., attrition or planetary milling) may be also useful as an early treatment technique for the densification of zirconium diboride. High-energy

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ball-milling can prepare ZrB_2 with an exceptional sinterability which is not able to be achieved by the normal technique of wet attrition milling [8,11,12]. Study of the densification process of a bimodal micron/nano-sized ZrB_2 ceramic disclosed that a relative density of 99.2% is able to be achieved applying a two-step hot pressing (step 1: 1300 °C; step 2: 1900 °C) as the processing method [13].

We have reported heretofore the effect of process parameters (temperature, dwell time and pressure) on density and hardness of monolithic ZrB_2 ceramic during hot pressing [14]. In this paper, the influence of the mentioned parameters on the densification behavior of ZrB_2 was studied using Taguchi method. This method employs signal to noise (S/N) ratio to quantify the quality traits divergence from the desired values. S/N ratio exhibits the relation between useful result (signal) and deviation of measured values (noise). In addition, this relation simplifies the optimization processes, because the larger S/N ratio, the best result is achieved [15,16].

2. Experimental procedure

A commercially available ZrB_2 powder (Leung Hi-tech Co., China) with a purity of 99% was chosen as raw material. Based on the supplier's datasheet, oxygen content was 0.55 wt.% and other impurities were 0.2 wt.% C, 0.1 wt.% N, 0.05 wt.% Fe and 0.1 wt.% Hf. The SEM morphology of the starting ZrB_2 powder reveals that the particles are regular globular shape with an average particle size of ~2 μm [14].

Experiments were designed based on the Taguchi method to infer the effect of process factors on the densification behavior (density and grain size) of ZrB_2. In this way, an orthogonal array (L9) with nine incorporations of input factors was employed. The prepared L9 orthogonal array, the levels of each factor and the nine combinations of the hot pressing parameters are itemized in Table 1.

Achieving a denser ZrB_2 is worthwhile; hence, the statistical density analysis is carried out with the "higher is better" option. The S/N ratio for the mentioned option is estimated as per Eq. (1):

$$\frac{S}{N} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right). \tag{1}$$

On the other hand, obtaining a fine-grained microstructure is beneficial; therefor, the statistical analysis for ZrB_2 grain size is fulfilled with the "smaller is better" option. The S/N ratio for this option is evaluated according to the following equation:

$$\frac{S}{N} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}y_i^2\right) \tag{2}$$

where y_i (i = 1, 2 …n) are the response values and n is the number of reiterations [15,16]. Analysis of variance (ANOVA) is accomplished to appraise the significance of each hot pressing parameter to the final density as well as ZrB_2 grain size. The data analysis is carried out using Qualitek-4 software (Automatic design and analysis of Taguchi experiments, Nutek Inc., Michigan, USA).

Five billets, with a diameter of 25 mm and thickness of ~5 mm, were prepared for each experiment. In this way, the powders were loaded into a graphite die coated with boron nitride and lined with a thin graphite foil. Hot pressing was completed in a graphite resistance-heated vacuum hot press furnace (made by Shenyang Weitai Science & Technology Development Co., Ltd., China). The hot pressing procedures for all the experiments were illustrated in Fig. 1, and the detailed processing conditions were reported elsewhere [14]. Nine runs were conducted in vacuum atmosphere (5×10^{-3} Pa) as described in Table 1.

Bulk density of the samples was measured using the Archimedes' method with distilled water as the immersing medium, and the relative density was calculated with respect to the theoretical density of pure ZrB_2 (6.1 g/cm^3). The calculated relative density for each hot pressing condition is the average value of the measured bulk density of the 5 billets consolidated at that condition.

The microstructure of each billet was characterized using a scanning electron microscope (SEM: Mira3 Tescan, Czech Republic). Specimens were prepared for microstructural characterization by a four-step mechanical polishing to 0.25 μm, using diamond abrasive. The grain size was determined from fracture surface micrographs, using an image analysis software (ImageJ 1.44p, Wayne Rasband, National Institute of Health, USA).

3. Results and discussion

The density outcomes and the mean ZrB_2 grain sizes obtained from the examined combinations of hot pressing parameters are presented in Table 1. The main effect plots, displaying the change in S/N ratios with hot processing factors, are depicted in Fig. 2. Fig. 2a exhibits an increase in density of ZrB_2 with temperature, dwell time, and also pressure. On the other hand, as it can be seen in Fig. 2b, a fine-grained microstructure is achievable at the lower levels of the hot pressing temperature/dwell time. Based on this figure, the applied pressure does not have a critical effect on the mean ZrB_2 grain size.

The analysis of variance supplies the influences of hot pressing factors on the density and the mean ZrB_2 grain size with rank. The ANOVA analyses of the density are reported elsewhere [14] and of the grain size are summarized in Table 2, which identify the hot pressing temperature as the critical parameter having consequential effects on the density and grain size of zirconium diboride. The significances of temperature, dwell time, pressure, and other/error (unknown or uncontrolled parameters) on the density are about 54, 21, 11 and 14%, respectively. This result is logical as diffusion mechanisms, which need higher processing temperatures/times, are expected to provide a major contribution to densification at relatively lower applied pressures. The optimal hot pressing conditions, which lead to a better

Table 1
Experimental values and corresponding S/N ratios for density and grain size of hot pressed ZrB_2 ceramics.

Trial No.	Hot pressing conditions			Density		Grain size	
	Temperature (°C)	Dwell time (min)	Pressure (MPa)	Value (g/cm^3)	S/N ratio	Value (μm)	S/N ratio
t-1	1700	30	8	4.878 ± 0.004	13.764	7.6 ± 1.9	−18.108
t-2	1700	60	12	4.994 ± 0.003	13.968	9.2 ± 2.2	−19.744
t-3	1700	90	16	5.415 ± 0.008	14.670	15.4 ± 2.4	−23.961
t-4	1775	30	12	5.110 ± 0.012	14.168	8.3 ± 1.3	−18.585
t-5	1775	60	16	5.184 ± 0.010	14.296	10.1 ± 2.9	−20.769
t-6	1775	90	8	5.159 ± 0.008	14.252	16.2 ± 3.6	−24.593
t-7	1850	30	16	5.388 ± 0.024	14.627	17.5 ± 3.6	−25.221
t-8	1850	60	8	5.450 ± 0.017	14.727	19.8 ± 2.7	−26.094
t-9	1850	90	12	5.493 ± 0.003	14.794	22.2 ± 3.6	−27.148
Grand average				5.230	14.363	14.0	−22.691