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Low temperature synthesis of dense and ultrafine grained zirconium diboride compacts by reactive spark plasma sintering

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ABSTRACT

Dense (>98%) submicron sized monolithic zirconium diboride (ZrB_2) was fabricated by reactive spark plasma sintering (RSPS) of 8 h ball milled Zr and B elemental mixtures at 1200 °C. During RSPS, ZrB_2 formed in-situ and the densification takes place by a two-step process. Plastic flow of ZrB_2 resulting from application of higher pressure enhanced densification significantly. Improvement in nanohardness, elastic modulus and indentation fracture toughness were observed with increased sintering pressure.

Zirconium diboride (ZrB_2) has very high melting point of above 3245 °C and crystallizes into hexagonal crystal structure of type $A1B_2$. It has excellent properties such as moderate density (6.11 g cm^{-3}), high elastic modulus (489 GPa), hardness (23 GPa) and metal like electrical (1.0×10^7 S m^{-1}) and thermal conductivity (60 W m^{-1} K^{-1}) [1]. ZrB_2 is being considered for ultra-high temperature applications such as thermal protection systems of re-entry vehicle, leading edges of scramjet powered hypersonic vehicles, rocket nozzles and furnace elements [2–5]. Densification of ZrB_2 requires high temperatures due to its covalent bonding nature and low self diffusion coefficient. Presence of oxide impurities such as B_2O_3 and ZrO_2 on powder surface also retard low temperature densification and promote grain growth [4]. To address this issue, reaction sintering methods such as reactive hot pressing (RHP) and reactive spark plasma sintering (RSPS) has been adopted over conventional hot pressing and pressureless sintering in the recent times. Chamberlin et al. [5] have fabricated dense (~99%) ZrB_2 at 2100 °C by RHP utilising 4 h milled elemental powders. The RHP process involved a multi stage sintering process which caused grain growth up to ~12 μm and subsequently reduced flexure strength. RSPS has been used to synthesise and densify simultaneously in a single step several materials such as TiB_2 [6], TaB_2 [7] and ZrB_2 [8] from elemental mixtures. Hu et al. [8] have synthesized dense (>95%) ZrB_2 by RSPS of 20 h ball milled Zr and B elemental mixture at 1800 °C. Licheri et al. [3] have reported similar work using RSPS. They have reported that dense compacts can be fabricated at the processing temperature of 1850–1900 °C. Previous studies show that temperatures greater than 1800 °C are required to produce dense ZrB_2. In the present study, in situ synthesis and densification of monolithic ZrB_2 compacts has been achieved by RSPS of elemental mixtures at the lowest sintering temperature of 1200 °C. The phase evolution, densification mechanism, pore size shrinkage and mechanical properties have also been evaluated.

Elemental powders of Zirconium (99% pure sponge fines ranging between 5 and 30 μm obtained from Nuclear Fuel Complex, Hyderabad, India) and Boron (amorphous, LobaChemie, India) were taken in stoichiometric ratio and milled for 8 h in a planetary ball mill (Fritsch Pulverisette-5, Germany). Tungsten carbide vials and 10 mm diameter WC balls were used and toluene was used as a process control agent. Ball to powder ratio was 10:1 and 300 RPM was chosen during the mechanical milling. Sintering was carried out at temperatures 800–1400 °C with a heating rate of 100 °C min^{-1} and a hold time of 10 min at peak temperature and a pressure of 50 MPa. Based on the results, two more samples were prepared at pressure of 80 and 100 MPa at 1200 °C. Cylindrical pellets of 20 mm dia. and 5 mm thickness were prepared. The sample shrinkage, temperature and pressure were recorded during RSPS and analysed. Samples synthesised at 800–1400 °C with 50, 80 and 100 MPa were named as Zr-B-800C50, Zr-B-1000C50, Zr-B-1200C50, Zr-B-1400C50, Zr-B-1200C80 and Zr-B-1200C100 with sintering conditions as mentioned in Table 1. Density was measured by water immersion method. Mercury intrusion porosimetry (MIP) (Micromeritics, AutoPore IV 9500, USA) was used to determine the pore size distribution.

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Table 1
Relative density and mechanical properties of RSPS samples.

Sample identification	Relative density (%)	Grain Size (μm)	Elastic modulus (GPa)	Nanohardness (GPa)	Indentation fracture toughness (MPa $m^{1/}$)
Zr-B-800C50	61.0	–	–	–	–
Zr-B-1000C50	76.0	–	–	–	–
Zr-B-1200C50	89.6	0.38 ± 0.19	538 ± 29	24.3 ± 3.0	2.7 ± 0.4
Zr-B-1400C50	95.4	0.94 ± 0.20	549 ± 28	29.0 ± 2.8	3.2 ± 0.3
Zr-B-1200C80	94.5	0.32 ± 0.14	552 ± 24	26.1 ± 2.4	2.8 ± 0.2
Zr-B-1200C100	98.4	0.35 ± 0.16	582 ± 28	30.2 ± 2.5	3.1 ± 0.3

X-ray diffractometer (Panalytical, The Netherlands) was used to characterise the phases formed after RSPS. A scanning electron microscope (FEI Quanta 400, USA) was used to study fracture surface of the processed samples. Nanohardness and elastic modulus was measured using Hysitron Triboindenter (TI 950, Hysitron, USA) using a Berkovich indenter at a maximum load of 8000 μN and using the Oliver and Pharr method [9]. The mean and standard deviation of at least 20 values were reported. Indentation fracture toughness was measured using Vickers indentation done at a load of 3 kg. Anstis' equation [10] was used to calculate the indentation toughness. At least 6 tests were carried out and the mean and standard deviation were reported.

Fig. 1(a–e) show the shrinkage curves during sintering. It is seen that at temperatures between 400 and 600 °C, an abrupt displacement was observed in all the samples. This sudden displacement was observed along with a flash of light emanating from top and bottom parts of the die. The reaction $Zr + 2B = ZrB_2$ is highly exothermic in nature ($\Delta H = -323$ kJ mol^{-1} at 25 °C [5]) and is responsible for the sudden emission of light. It is reported that an adiabatic temperature of above 3000 °C is obtained during the reaction which is sufficient to form 100% ZrB_2 [5]. The formation of ZrB_2 results in sudden shrinkage which has been observed during the simultaneous synthesis and densification of UHTCs [3,6,11,12]. This is the first stage of densification and contributes towards major fraction of the total density. A sudden surge in pressure inside the SPS chamber was observed and the plots showing the variation are provided in Supplementary materials. For the Zr-B-800C50 and Zr-B-1000C50 samples, no significant was displacement observed after the in situ reaction. It is observed from Fig. 1(c and d) that an additional densification process gets activated between 1100 and 1300 °C and there is no significant shrinkage beyond 1300 °C. This second stage is attributed to plastic flow of ZrB_2 at high temperatures as discussed subsequently. The relative densities of the samples are listed in Table 1. The relative density of the Zr-B-1000C50 sample was found to be 76% while that of the Zr-B-1200C50 sample was 89.6% indicating that second stage of densification is necessary for removing porosity. It was found that even the Zr-B-1400C50 sample was not fully dense.

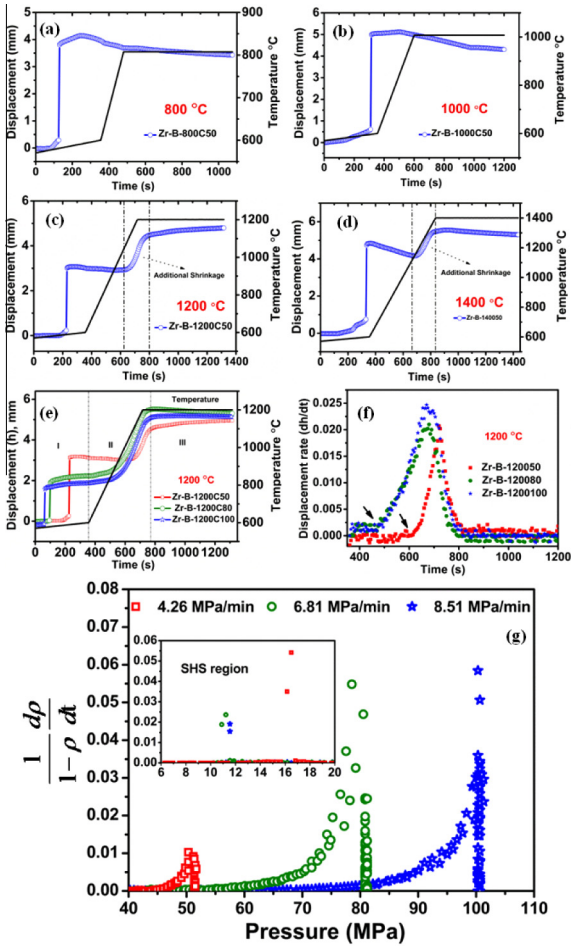

Fig. 1. Shrinkage curves of RSPS samples (a) Zr-B-800C50, (b) Zr-B-1000C50, (c) Zr-B-1200C50, (d) Zr-B-1400C50. (e) and (f) show the shrinkage curves and displacement rate curves, respectively, for samples sintered at 1200 °C with 50, 80 and 100 MPa pressure. (g) Shows the plot of the densification rate as a function of pressure for 1200°C sintered samples at 50, 80 and 100 MPa pressure (increased loading rates as mentioned in the legend) with the inset showing the SHS region.

The effect of pressure on the density was studied for sintering temperature of 1200 °C. Fig. 1(e) shows the punch displacement for the 50, 80 and 100 MPa cycles at 1200 °C and Fig. 1(f) shows the displacement rate. The densification curves shift towards lower times at high pressures. It can be clearly observed that the SHS reaction took place in Zr-B-1200C80 and Zr-B-1200C100 at lower temperatures than Zr-B-1200C50. It indicates that higher pressure can bring the elemental powders closer and aid in faster reaction. The chamber pressure vs. time plots for Zr-B-1200C50, Zr-B-1200C80, Zr-B-1200C100 and Zr-B-1400C50 provided in the Supplementary materials indicate sudden increase in chamber pressure during in-situ reaction. Fig. 1(f) shows that the maximum shrinkage rate was observed ~1100 °C for Zr-B-1200C80 and Zr-B-1200C100, whereas in Zr-B-1200C50 sample, the maximum shrinkage rate was observed around ~1200 °C. Higher pressures thus accelerated the second stage of densification by aiding plastic flow.

Munir et al. [13] have provided a general model for densification rate with pressure as given in Eq. (1) which has been modified for the present condition where the pressure is increased linearly.

$$\left(\frac{1}{1-\rho}\right)\left(\frac{d\rho}{dt}\right) = B\left(g\frac{\gamma}{x}+P\right) = C_1\left(e^{-\frac{Q_A K_2}{RPK_1}}\right)\left(g\frac{\gamma}{x}+P\right) \quad (1)$$

where ρ is relative density, t is time, B is a diffusion controlled term, g is geometric parameter, γ is surface energy, x is related to particle size, P is pressure, C_1 is a constant, Q_A is the activation energy, R is the universal gas constant and K_1 and K_2 are constants as explained in Supplementary data. This expression shows that displacement rate should vary nonlinearly with applied pressure. Fig. 1(g) plots the densification rate vs. pressure and it clearly shows a nonlinear behaviour with pressure. It is observed that the maximum sintering