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Reaction spark plasma sintering of niobium diboride

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ABSTRACT

Niobium diboride (NbB_2) is synthesized and consolidated by the spark plasma sintering technique. Elemental reactants such as niobium (Nb) and boron (B) were subjected to two stage heat treatment, initially at 1200 °C for synthesis and followed by densification at the temperatures in the range of 1700 °C to 1900 °C. High dense NbB_2 (~97.7%ρ_{th}) is obtained at 1900 °C after 15 min holding period. Load application during heat treatment stage is found to improve the sinterability of the niobium diboride compacts. Hardness, elastic modulus and indentation fracture toughness of the high dense NbB_2 are measured as 20.25 GPa, 539 GPa and 4 MPa $m^{1/2}$ respectively.

1. Introduction

Transition metal borides are the class of materials that are the focus of many researchers for diverse engineering applications due to their attractive properties like high hardness, high elastic modulus, high melting point, chemical inertness, etc. The literature reported properties of selected transition metal borides are summarized in Table 1. One such transition metal boride is niobium diboride (NbB_2), which received less research attention among other boride counterparts (MB_2; M: Ti, Zr, Hf, and Ta). To date, the prime research on NbB_2 was only focused on its superconducting behavior, even though it possesses good mechanical, chemical and thermal properties like other boride systems. The main concern for not exploiting NbB_2 for high temperature application is due to its low melting metal oxides (Nb_2O_5 ~1512 °C and NbO_2 ~1915 °C) [1–4].

Matsudaira et al. have synthesized single phase niobium diboride powder by heat treating a mixture of elemental niobium (Nb) and amorphous boron (B) powder and sintering it separately to high density (~98%ρ_{th}) using high pressure and high temperature process [5]. Iizumi et al. demonstrated the preparation of NbB_2 powder by mechanical alloying technique using Nb and B as reactants [6]. Peshev et al. have reported the formation of NbB_2 by borothermic reduction of Nb_2O_5 in vacuum [7]. Matsumoto et al. synthesized NbB_2 by melting a mixture of Nb_2O_5 and B in argon plasma arc [8]. Yeh and Chen have prepared niobium borides (NbB and NbB_2) by self propagation of high temperature synthesis from its elemental powders [9]. Other reports on NbB_2 were limited to single crystal growth [10] and thin film formation [11]. Even though many methods are available on the formation of NbB_2, the synthesis from the elemental route will ensure the formation of pure products.

The present study focuses on the processing of bulk NbB_2 ceramic in a single step from its elemental powders using spark plasma sintering technique and also studying its mechanical properties (hardness, elastic modulus and fracture toughness).

2. Experimental details

Stoichiometric amounts of elemental niobium (Nb, purity: 99.5%, particle size D_{50}: 28.2 μm) and amorphous boron (B, purity: 98%, particle size D_{50}: 38.8 μm) powders were considered for the in situ processing of NbB_2 ceramic by spark plasma sintering as per reaction (1).

$$Nb + 2B \rightarrow NbB_2 \quad (1)$$

Both niobium and boron powders were characterized for phase identification by XRD (Cu–Kα, XRG3000, Inel, France) and particle size analysis by the Laser Scattering Particle Size Analyzer (1064 liquid, Cilas, France). The starting materials were mixed and milled in a tungsten carbide lined motorized mortar pestle for 2 h. Fig. 1 shows the particle size distribution of starting elemental powders and composite powder mixture after milling operation. The mean particle diameter of milled mixture was measured to be 18.1 μm showing a tri-modal distribution. The milled mixture was filled into the high density graphite die and loaded in the spark plasma sintering chamber. At room temperature, the chamber was evacuated to 10^{-3} mbar and the mechanical pressure of 10 MPa was applied onto the powder. Current of the order (700–2000 A) was passed through the graphite plunger and die assembly during processing. The on–off cycle of pulsed direct current was maintained as 20 ms–2 ms respectively throughout the experiments.

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Table 1
Literature reported crystal structure, melting point and some mechanical properties of selected transition metal diborides [1–4].

Material	Crystal structure	Density (g/cm^3)	Melting point (°C)	Hardness HV (GPa)	Elastic modulus E (GPa)
TiB_2	Hexagonal	4.52	3225	25.5	551
ZrB_2		6.10	3245	17.9	500
NbB_2		6.97	3036	20.9	637
HfB_2		11.19	3380	21.2	500
TaB_2		12.54	3037	25.6	551

Temperature was measured by optical pyrometer by focusing on the graphitic plunger whose schematic is shown elsewhere [12]. Heating rate of 100 °C/min was maintained above 1000 °C. Since the minimum temperature measured reproducibly by the pyrometer used was 1000 °C, the measurement below 1000 °C was not recorded.

The samples were heat treated in SPS chamber under two different temperature regimes, (1) at 1200 °C (low temperature regime), with holding time of 1 min and 15 min under load and no load conditions, respectively, and then (2) the same samples were heat treated at high temperature regime in the range of 1700 °C to 1900 °C with the interval of 100 °C for 15 min duration under load of 12.5 kN which is equivalent to 50 MPa mechanical pressure. Fig. 2 shows the typical schematic of heat treatment sequence of the reaction sintering operation followed in the present study. This two stage heat treatment was allowed to synthesize and consolidate NbB_2 ceramic in a single process by spark plasma sintering. Also, few experiments were carried out at 1900 °C under different load conditions, 30 MPa, 50 MPa and 70 MPa.

The sintered samples were measured for density by liquid displacement method, phase analysis by XRD, and elastic modulus by ultrasonic pulse-echo technique (UT 340 pulser receiver system, UTEX Scientific Instrument Inc., Canada) using 15 MHz normal beam probe. Hardness and fracture toughness were measured based on Vickers indentation technique using 0.1–5 kg load for 15 s (Nexus 4304, Eseway, UK). Anstis methodology [13] was adopted for fracture toughness calculations. Elastic modulus measured in the present study was used in the calculation of fracture toughness (K_{IC}) measurement. Fracture surface analysis was carried out by scanning electron microscope (SEM; MB 2300 CT/100, CAMSCAN, UK). All the reported data points represent the average of five measured values.

3. Results and discussions

The enthalpy ($\Delta H^\circ_{1200\ ^\circ C} = -244$ kJ/mol) [14] and Gibb's free energy data ($\Delta G^\circ_{1200\ ^\circ C} = -237$ kJ/mol) [14] for reaction (1) confirm that the formation of NbB_2 by the elemental route is highly exothermic and feasible at the processing temperature adopted in the present study. The samples heat treated in SPS at the low temperature regime (1200 °C) for both 1 min and 15 min holding period resulted in the

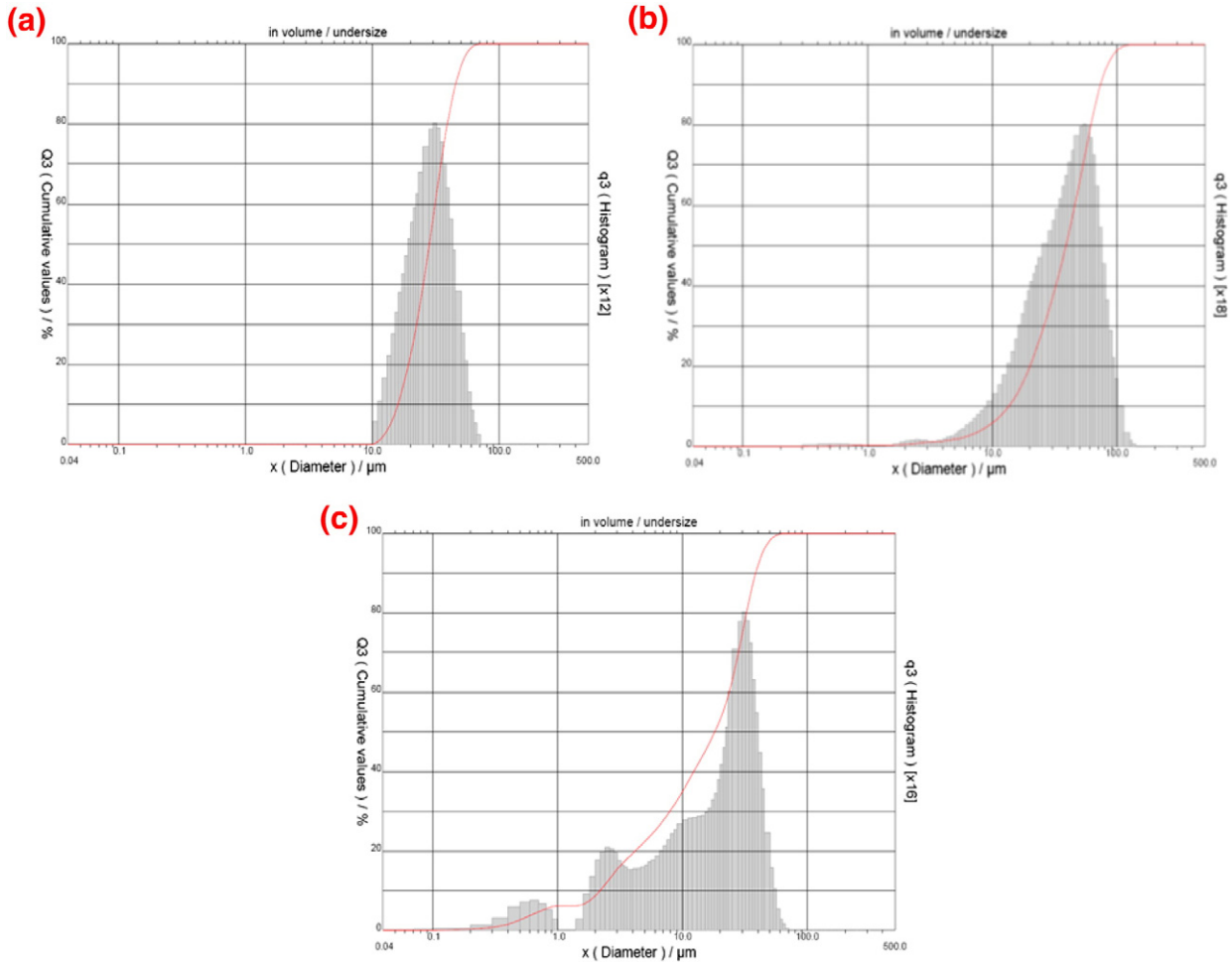

Fig. 1. Particle size distribution of the initial starting powders: [a] niobium, [b] boron and [c] mixture of both niobium and boron powders after milling.