Processing and characterization of CrB2-based novel composites

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Processing and Characterization of CrB_2-Based Novel Composites

Abstract: This paper presents the results of investigations carried out on processing and characterization of CrB_2-based novel composites. Niobium metal powder was used as additive to form new composites. Hardness and fracture toughness of chromium boride increased by addition of niobium. CrB_2 composites were prepared by addition of 2.5, 10 and 20 wt.% Nb. Density of higher than 95% ρ_{th} was achieved in all the samples. Hot pressed samples were analyzed to contain reaction products of NbB_2, Cr_2B_3 and Cr_3B_4 phases along with CrB_2. Hardness of CrB_2 composite was increased from 18.46 GPa to 21.89 GPa by increasing the Nb content from 2.5 to 10 wt.%. Fracture toughness of composites prepared by addition of 2.5 and 10% was measured as 3.11 and 3.38 MPa.m$^{1/2}$ respectively. Addition of 20% Nb resulted in increased fracture toughness of 4.32 MPa.m$^{1/2}$.

Keywords: CrB_2, densification, niobium, hardness, fracture toughness, hot pressing

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Introduction

CrB_2 is a potential candidate for structural applications, which requires high temperature strength and stability under severe conditions [1]. It has high melting point (2,200°C), high hardness (~20 GPa) and good wear resistance [2, 3]. Chromium diboride has considerable potential for hard coatings on cutting tools and as a protective coating for material exposed to wear and corrosion [4, 5]. It fulfills the function of a protective layer in chromium alloys and stainless steels [5, 6]. CrB_2 is also used as additive for improvement in properties of high performance ceramic materials like borides and carbides [7–9].

Most of the literature on CrB_2 is related to thin film formations [10–12], whereas literature on bulk processing of CrB_2 is very limited. In bulk form borides can be processed by powder metallurgy route. Chromium borides can be synthesized by (a) reaction between elemental boron and chromium powder [1, 13] (b) borothermic reduction of Cr_2O_3 [14] (c) boron carbide reduction of Cr_2O_3 [15].

Usually, densification of boride powders is extremely difficult due to presence of covalent bonding and low self-diffusivity. High temperature and external pressure is required to get dense shapes of borides. Pressureless sintering and hot pressing of CrB_2 have been studied by Iizumi et al. [16] Hiroki et al. [17] have studied sintering of CrB powder by hot isostatic pressing. In this study, investigations were carried out on processing and characterization of CrB_2-based composite. Niobium metal powder was used as additive to form new composites. Nb had been used as sinter additive to ZrB_2 and was found to increase the mechanical properties of boride [18]. As per author's knowledge, there is no report on effect of Nb addition on microstructure and properties of CrB_2.

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Experimental

Starting material

In-house synthesized CrB_2 (D_{50}: 6.7 μm, "C": 0.9 wt.%, "O": 0.6 wt.%) and commercial Nb (99.7% pure) powder were used as starting materials. CrB_2 powder was prepared by boron carbide reduction of Cr_2O_3 in presence of carbon. Preparation details of CrB_2 powder are presented elsewhere [15]. Figure 1 presents the XRD pattern of the starting powders.

Densification and characterization

For densification, weighed quantities of fine chromium diboride and Nb powder were mixed thoroughly using a motorized mortar and pestle in dry condition for 1 h to obtain samples of different compositions. Figure 2(a) and (b) presents the particle size distribution of CrB_2 and Nb

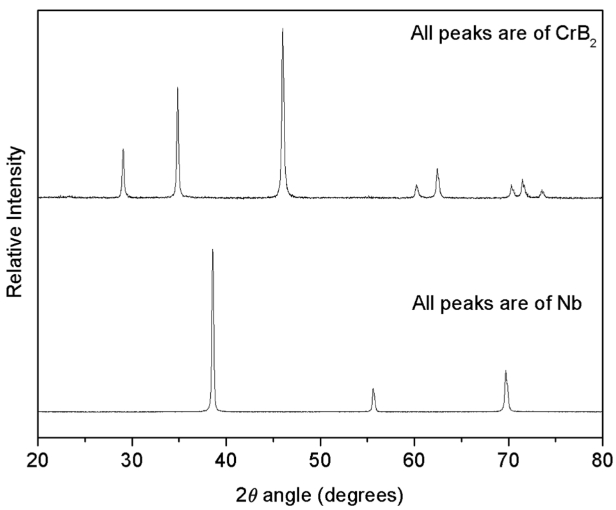

Figure 1: XRD pattern of starting CrB_2 and Nb powder.

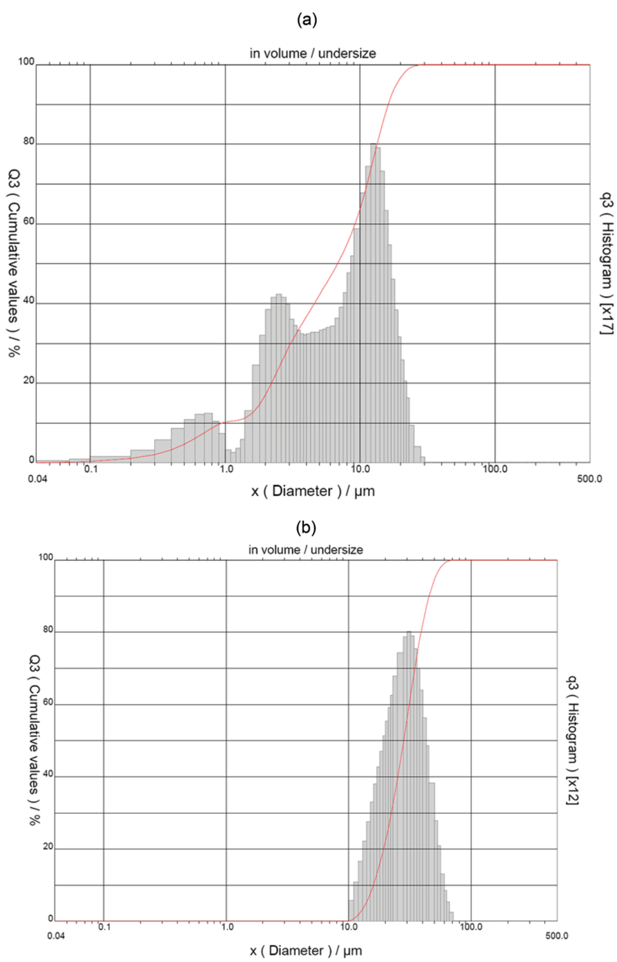

Figure 2: Particle size distribution of (a) CrB_2 and (b) Nb powder.

powders respectively. CrB_2 powder has tri-modal distribution and particle size in the range of 0.1 µm to 20 µm. Median particle diameter was measured as 6.79 µm. Distribution of Niobium powder was monomodal and the particle size ranges from 10 µm to 70 µm. Median particle diameter was measured as 28.16 µm.

The powder mixtures were then loaded in a high density graphite die (12 mm dia) and hot pressed at a temperature of 1,600°C under a pressure of 35 MPa for 2 h in a high vacuum (1×10^{-5} mbar) chamber. The pellets were ejected from the die after cooling and the density measured by liquid displacement method. Densified samples were polished to mirror finish using diamond powder of various grades from 15 to 0.25 µm in an auto polisher (Laboforce-3, Struers). Microhardness was measured on the polished surface at a load of 100 g and dwell time of 10 s. The indentation fracture toughness (K_{IC}) data were evaluated by crack length measurement of the crack pattern formed around Vickers indents (using 10 Kg load), adopting the model formulation proposed by Anstis et al. [19],

$$K_{IC} = 0.016(E/H)^{1/2} P/c^{3/2}$$

where E = Young's modulus, H = Vickers's hardness, P = Applied indentation load, c = Half crack length.

Elastic modulus of the samples was measured by ultrasonic method. The reported value of hardness and fracture toughness are the average of five measured values. Polished and fractured surfaces of dense pellets were analyzed by scanning electron microscope and energy dispersive spectroscopy (EDS). X-ray diffraction was also used for phase analysis.

Results and discussion

Densification

Table 1 summarizes the results of densification experiments carried out by hot pressing. CrB_2 powder containing 0, 2.5, 10 and 20 wt.% Nb was hot pressed. A density of higher than 95% ρ_{th} was achieved in all the composites consolidated by hot pressing at 1,600°C and 34 MPa pressure. For monolithic CrB_2, only 89.42% density was obtained under similar hot pressing condition. The enhanced densification by addition of Nb could be due to reaction sintering caused by reaction between CrB_2 and Nb which resulted in formation of NbB_2. More details of the reaction are discussed in Section “Phase Analysis and Microstructure”. Iizumi et al. [16] have reported that chromium borides (Cr_2B, CrB and CrB_2) obtained by solid state reaction of Cr and B in the temperature range of 1,400 to 1,500°C. These powders [16] could not be consolidated by pressureless sintering process and were densified by hot pressing at about 1,700°C.

Table 1: Effect of Nb addition on densification and properties of CrB_2.

Sample	Temperature (°C)	Pressure	Density	Hardness (GPa)	K_{IC} (MPa.m$^{1/2}$)	Elastic modulus (GPa)
CrB_2	1,600	34 MPa	89.42	11.45	3.10	481
CrB_2 + 2.5% Nb	1,600	34 MPa	98.66	18.46	3.11	510
CrB_2 + 10% Nb	1,600	34 MPa	98.32	21.89	3.38	559
CrB_2 + 20% Nb	1,600	34 MPa	96.9	17.34	4.32	570

Phase analysis and microstructure

XRD patterns of sintered CrB_2 pellet processed with different content are shown in Figure 3. It indicates the presence of crystalline CrB_2 and the reaction products such as Cr_2B_3, Cr_3B_4 and NbB_2. The presence of NbB_2 in XRD pattern indicates that niobium is converted into niobium boride. Niobium boride formation takes place due to reaction of niobium with chromium boride. Required boron to form NbB_2 will be obtained from the matrix CrB_2. As a result, boron-deficient chromium boride such as Cr_2B_3 and Cr_3B_4 is formed. The formation of NbB_2, Cr_2B_3 and Cr_3B_4 can be explained by following possible reactions:

$$CrB_2 + Nb \rightarrow NbB_2 + Cr \quad (1)$$

$$Cr + 2CrB_2 \rightarrow Cr_3B_4 \quad (2)$$

$$Cr + 3CrB_2 \rightarrow 2Cr_2B_3 \quad (3)$$

$$7CrB_2 + 2Nb \rightarrow 2NbB_2 + 2Cr_2B_3 + Cr_3B_4 \quad (4)$$

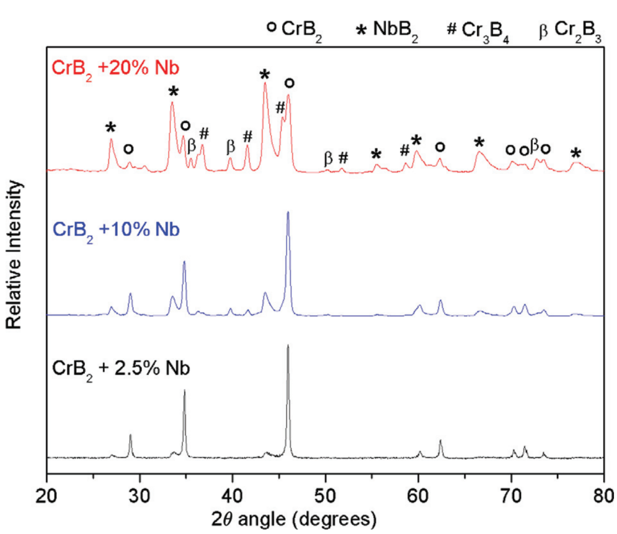

Figure 3: XRD pattern of hot pressed CrB_2 composites prepared by addition of Nb.

Reaction (1) is thermodynamically feasible at hot pressing temperature of 1,400°C in vacuum (1×10^{-5} mbar). Gibbs free energy change obtained using FactSage database for reaction 1 is presented in Figure 4. It shows that free energy change is negative for all the temperature. Elemental chromium, which formed as per reaction (1), reacts with CrB_2 and forms Cr_3B_4 (reaction 2) and Cr_2B_3 (reaction 3). Simultaneously, CrB_2 and Nb can react and result in formation of NbB_2, Cr_2B_3 and Cr_3B_4 as per reaction (4). Thermodynamic calculations for reactions (2 to 4) could not be computed as data for Cr_3B_4 and Cr_2B_3 are not available.

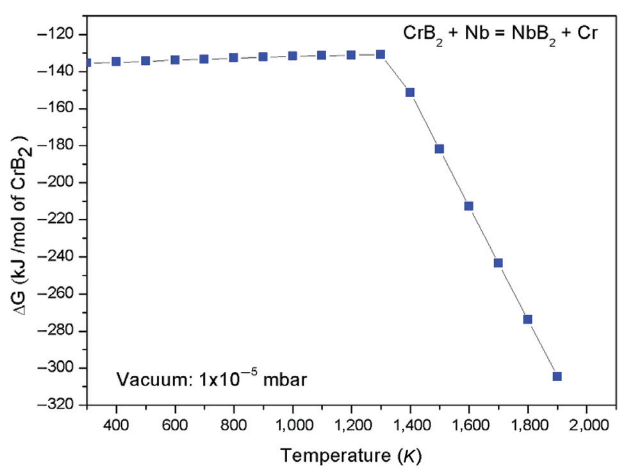

Figure 4: Free energy change for reaction between CrB_2 and Niobium (calculated using FactSage software).

From XRD pattern, it is observed that as the percentage of niobium increases in chromium boride, the intensity of niobium boride is higher in composite material.

Figure 5 presents the BSE image of CrB_2-based composite prepared by addition of 20% Nb, which shows the presence of gray matrix and in which, second phase (lighter shade) is dispersed. In EDS spectra, the gray matrix was analyzed to contain only Cr and B indicating that, it is CrB_2. The lighter shade was analyzed to contain mainly Nb in which very little amount of Cr (~4 atom %) is present. Chromium, which formed as per the reaction (1), could be diffused into Nb. Other phases such as Cr_3B_4 and Cr_2B_3 could not be seen in microstructure, due to

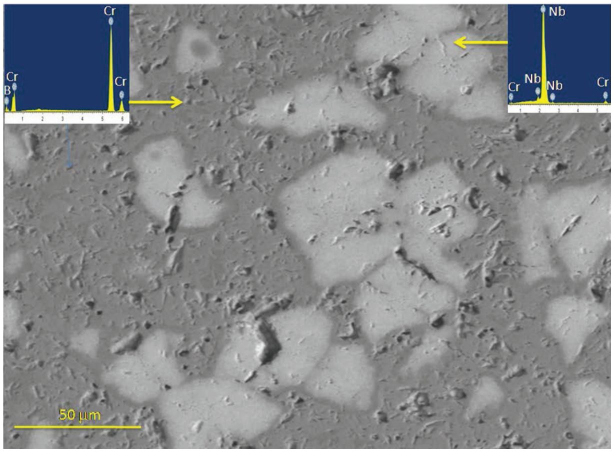

Figure 5: SEM image and elemental analysis of different phases in CrB_2 composite prepared by addition of 20% Nb.

difference in atomic number is not sufficient to distinguish the contrast of different chromium boride phases.

Mechanical properties and fractography

Measured Vickers hardness, fracture toughness and elastic modulus of CrB_2 composites are presented in Table 1. Hardness of CrB_2 prepared with 2.5% Nb was measured as 18.46 GPa which increases to 21.89 GPa with increasing Niobium content to 10 mass%.This could be due to the higher hardness (25.5 GPa) of NbB_2 phase as compared to monolithic CrB_2(22 GPa) [2]. Further increase of Nb content decreased the hardness to 17.34 GPa. This could be attributed to the formation of Cr_2B_3 and Cr_3B_4 phases in significant amounts. Hardness of monolithic CrB_2 was measured as 11.45 GPa. The low hardness obtained is due to the lower density (89.42%) of the sample. Microhardness of single crystal CrB_2 has been reported as 22.6 GPa (1N load) by Okada et al. [20]. Sonber et al. [15] have reported hardness of hot pressed CrB_2 as 22 GPa.

Fracture toughness of monolithic CrB_2 was measured as 3.10 $MPa.m^{1/2}$. Fracture toughness of composites prepared by addition of 2.5 and 10 wt.% Nb was measured as 3.11 and 3.38 $MPa.m^{1/2}$ respectively. Addition of 20% Nb resulted in increased fracture toughness of 4.32 $MPa.m^{1/2}$. The increase in the fracture toughness is due to presence of second phase. Figure 6 presents the fracture surfaces of CrB_2 composites. Dense surfaces were observed in all the composites. The mode of fracture is observed to be transgranular.

Reinforcement of metallic particles in ceramic material enhances fracture toughness of ceramics. Addition of Nb

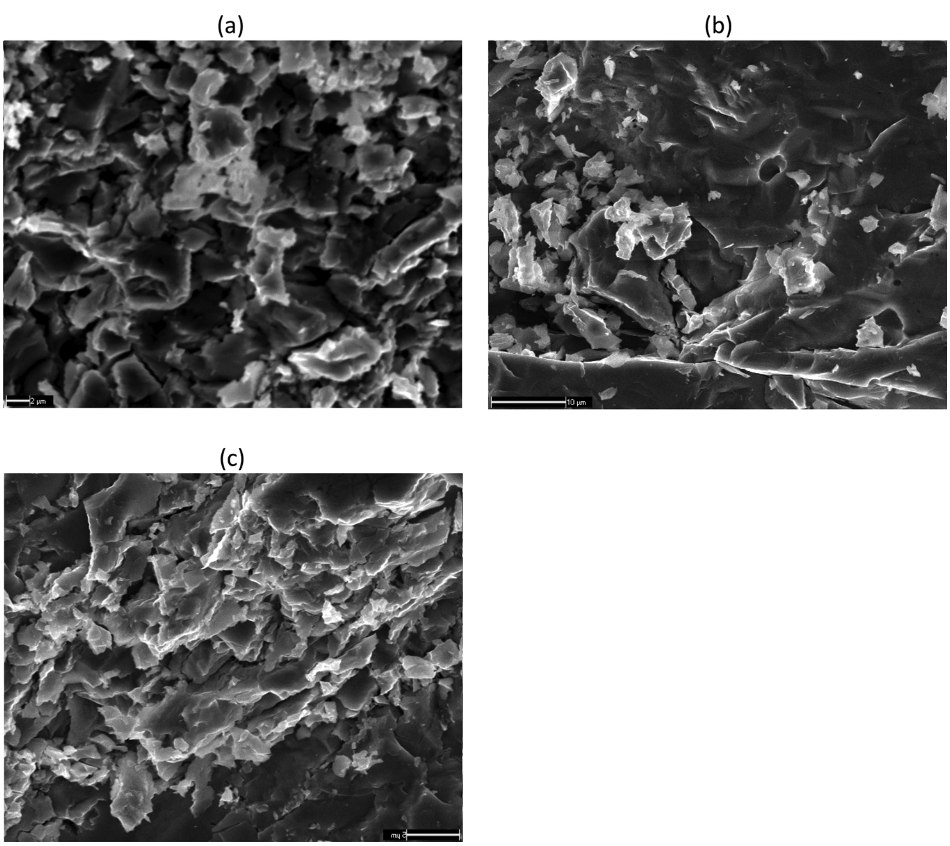

Figure 6: Fracture surface of CrB_2 composites prepared by addition of (a) 2.5% Nb (b) 10% Nb (c) 20% Nb.

and Mo into ZrB_2 has been reported to result in increased fracture toughness [18, 21]. This enhancement is due to plastic deformation of metals which consumes available energy. In the present study, Niobium metal was added to CrB_2 matrix to form new composite. During hot pressing, Nb has reacted with CrB_2 and formed NbB_2 and thus in composite, ductile Nb metal is not present. However, presence of NbB_2 resulted in enhancement of hardness and fracture toughness but effect is not as high as achieved by Nb addition in ZrB_2 by Sun et al. [18].

Conclusion

CrB_2-based novel composite has been developed by addition of Niobium powder. Hot pressing of CrB_2 + Nb mixture at 1,600°C and 34 MPa pressure resulted in a density higher than 95% ρ_{th}. Monolithic CrB_2 was densified to 89.42% under similar hot pressing condition. The enhanced densification of CrB_2 by addition of Nb is attributed to reaction sintering. During hot pressing, Nb reacts with CrB_2 and results in the formation of NbB_2, Cr_2B_3 and Cr_3B_4. Hardness of CrB_2 composite prepared by addition of 2.5% Nb was measured as 18.46 GPa which increases to 21.89 GPa by increasing Nb content to 10%. Fracture toughness of composites containing 2.5 and 10% Nb was measured as 3.11 and 3.38 MPa.m$^{1/2}$ respectively. Addition of 20% Nb resulted in increased fracture toughness of 4.32 MPa.m$^{1/2}$.

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