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Low temperature synthesis of dense TiB_2 compacts by reaction spark plasma sintering

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ABSTRACT

In this study, the low temperature synthesis of dense titanium diboride (TiB_2) compacts by reaction spark plasma sintering (RSPS) of ball milled mixtures of titanium and boron powders is presented. The influence of milling time and sintering temperature on the in-situ reactive synthesis, densification, grain size and mechanical properties of TiB_2 was investigated. TiB_2 compacts with relative density above 99% have been obtained at a significantly low sintering temperature of 800 °C. X-ray diffraction analysis confirmed the formation of TiB_2 along with a small amount of secondary TiB phase. The effect of TiB on the grain size and the hardness and fracture toughness was investigated. TiB_2 compacts processed were found to have a nanohardness >26 GPa and an elastic modulus >570 GPa and indentation fracture toughness more than 3.30 MP a.m$^{1/2}$. It is shown that RSPS can be an attractive route for synthesis of ultrahigh temperature ceramics at low temperatures.

1. Introduction

TiB_2 has a high melting point of 3225 °C and exhibits attractive properties such as low density (~4.52 g·cm^{-3}), high hardness (25–35 GPa) and elastic modulus (>570 GPa) and excellent thermal conductivity (60–120 W·m^{-1}·K^{-1}) along with low electrical resistivity (10–30 × 10^{-6} Ω·cm), which makes it a candidate material for use as ultra high temperature ceramics (UHTCs) and in armour applications, cutting tools, electrode materials, heating elements and as a reinforcement in metal matrix and ceramic matrix composites [1–4]. TiB_2 has an $A1B_2$ type hexagonal crystal structure with *P*6/*mmm* space group ($a = b = 3.029$ Å, $c = 3.229$ Å; $\alpha = \beta = 90°$, $\gamma = 120°$) where titanium atoms are at (0,0,0) and boron atoms are located at (1/3,2/3,1/2) and (2/3,1/3,1/2) lattice points [1]. The anisotropy of thermal expansion co-efficient [5] and hexagonal symmetry impedes the material to achieve full density without the presence of microcracking [6,7]. The predominantly covalent nature of bonding along with the presence of oxides such as TiO_2 and B_2O_3 on the surface of TiB_2 powders and the low self diffusion co-efficient result in difficulties for achieving full densification during sintering [1,4,8]. As a result, commonly used processing techniques such as pressureless sintering, hot pressing, and hot isostatic pressing require a very high temperature (>1800 °C) and a long holding time (>45 min) to sinter TiB_2 which is often accompanied with grain growth [9].

In recent times, reaction spark plasma sintering (RSPS) has been identified as one of the effective techniques to synthesize UHTCs and their composites. Several researchers have studied reactive systems such as TiC–TiB_2, B_4C–TiB_2, $MoSi_2$, TiN–TiB_2, ZrB_2–SiC, and HfB_2–SiC_w, ZrC, TaC, TaC–B_4C and HfC to achieve dense composites and monoliths with fine homogeneous grain size and superior mechanical properties [7,10–19]. It has been reported that the self-propagating high temperature synthesis (SHS) reactions occur due to exothermic reactions between the reactants during RSPS which enhances the sintering and densification [10]. It has been empirically concluded that an adiabatic temperature of above 1800 K is necessary for self-sustaining the SHS reaction [20]. It has also been reported that an adiabatic temperature of 3300 K could be reached during the SHS reaction between elemental Ti + B mixture to produce TiB_2 [6,20,21]. Prior activation of reactants by means of mechanical milling has been found to enhance the kinetics of combustion synthesis by SHS reaction [22,23]. Mechanical milling is a popular method for alloying, where cold welding and fracture of particles continuously happen and the strain built up increases the reactivity of the milled powders for combustion synthesis [24]. It is reported that, to exhibit good mechanical properties including strength at elevated temperatures, the density of monolithic TiB_2 should be above 97% [2]. Metallic and non-metallic additives such as Ti, Cu, Co, Ni, Fe, B_4C, CrB_2, AlN, $MoSi_2$, and $TiSi_2$, have been added to obtain dense TiB_2 with improved properties [8,25–31]. However, metallic additives have been found to degrade the corrosion resistance and high temperature properties. Silicide based sinter additives have been found to be compatible with the borides in enhancing the densification achieved at low temperatures [32]. It is reported that densification of TiB_2 can be achieved only

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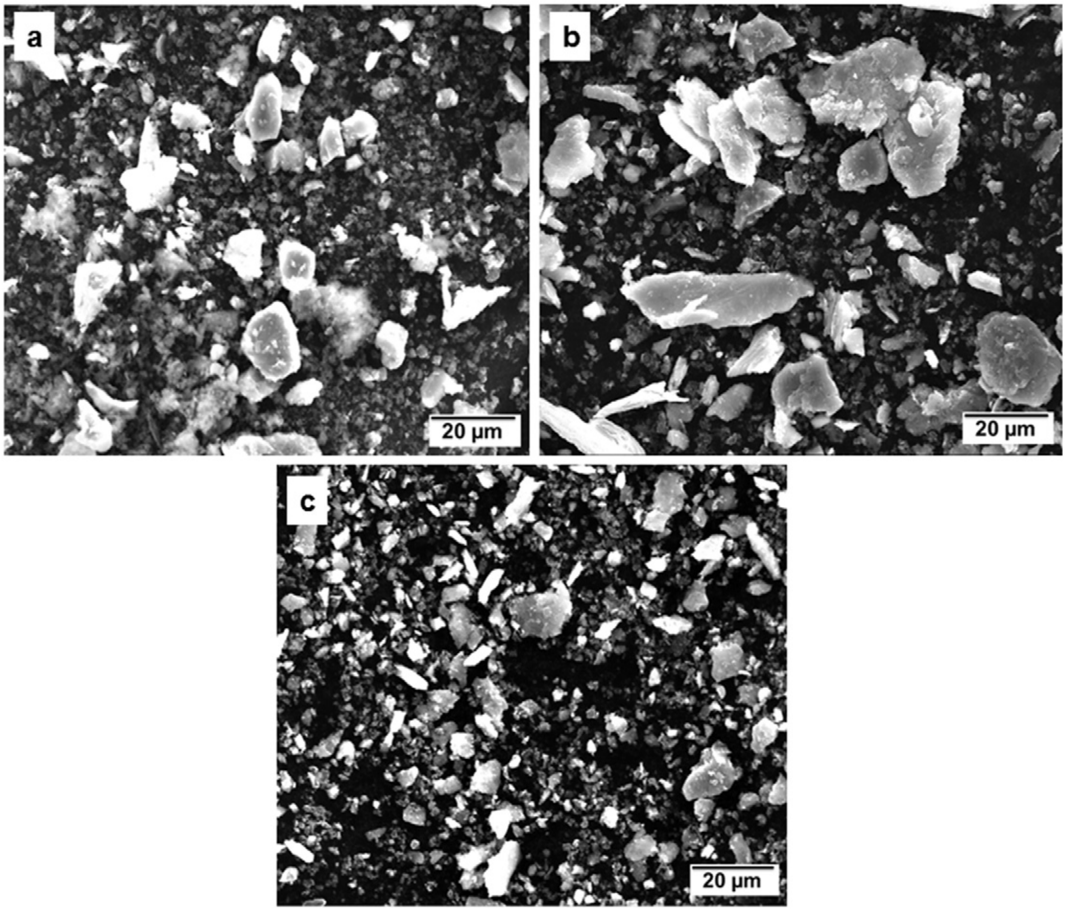

Fig. 1. Secondary electron images of Ti–B powder mixture after (a) 0.5 h, (b) 4 h, and (c) 8 h of milling.

above 1600 °C in Spark Plasma Sintering (SPS), but at this high temperature abnormal grain growth and formation of micro-cracks have been found to be unavoidable [28]. In a previously reported study, Salamon et al. used 1 h dry ball milled Ti–6Al–4V and boron powder mixture to synthesize dense monolithic TiB_2 in-situ during SPS. Two types of amorphous Boron powder (one containing Mg and the other without Mg) were used and it was concluded that addition of Mg and very high heating rate produces homogeneous monolithic TiB_2. The mechanical properties were found to be affected by unreacted boron [33]. However, there was no mention of what happens to Mg, Al and V in the material in this study. Li Gai et al. synthesized TiB_2–Fe composites utilizing elemental Ti–B–Fe powders by application of 450 MPa pressure just after the SHS reaction. They found that the grain size and hardness was affected by the volume fraction of Fe. Additionally, the Fe_2B intermetallic formed during the synthesis may deteriorate the mechanical properties of the composite [34].

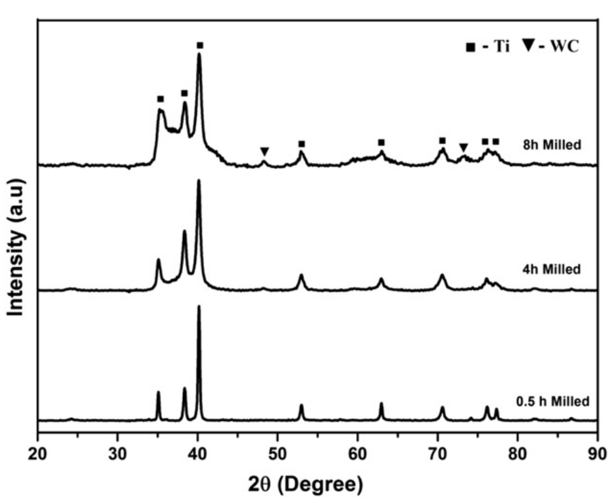

Fig. 2. XRD of mechanically milled Ti–B powders after 0.5 h, 4 h and 8 h milling.

It is observed from the existing literature that fully dense monolithic TiB_2 having good mechanical properties have not been achieved so far below a sintering temperature of 1400 °C with or without the addition of sintering aid. The idea of reaction spark plasma sintering (RSPS) has been originally proposed and patented by Munir and co-workers [33]. They have shown that dense $MoSi_2$ can be produced from elemental powders using this technique at a lower temperature. This approach has not been used for UHTCs to the authors' knowledge. So the aim of the present work was to study the feasibility of low temperature synthesis of TiB_2 using RSPS of elemental powders. Further, to improve reaction kinetics and sintering rates, the mixtures of Ti and B were mechanically activated by ball milling which has not been carried out earlier. This is the first study which shows that this RSPS is highly advantageous for the synthesis of dense TiB_2 having sub-micron grain size. The effect of milling time and sintering temperature on the

Table 1
Information obtained from analysis of XRD plots of the powders.

S no	Material/condition	Micro-strain (%)	a (Å)	c (Å)
1	Ti–B, 0.5 h milled	0.3	2.9510	4.6894
2	Ti–B, 4 h milled	0.8	2.9491	4.6950
3	Ti–B, 8 h milled	2.4	2.9483	4.6966