High-energy ball milling of B-C-Ti mixtures for the fabrication of B$_4$C and TiB$_2$ nanocomposite powder

L. Nikzad, T. Ebadzadeh, M. R. Vaezi and A. Tayebifard

Nanotechnology and advanced material Division, Materials and Energy Research Center, Alborz, Iran

Ceramic Division, Materials and Energy Research Center, Alborz, Iran

Semiconductor Division, Materials and Energy Research Center, Alborz, Iran

The present work reports the effect of high-energy ball milling on B-Ti-C mixtures. The milling process was carried out for up to 70 h and then the milled powders were heat treated between 800 °C and 1200 °C for 1 h. The milled and heat treated powders were characterized by means of X-ray diffraction (XRD) and a scanning electron microscope (SEM). TiB$_2$ was characterized as the only crystalline phase after milling for 6 h. B$_4$C was formed after heat treatment of the milled powders above 1000 °C. The crystallite sizes of TiB$_2$ varied from 57.2 nm up to 7.5 nm after milling of powders from 6 to 70 h, respectively.

Key words: High-energy ball milling, B-Ti-C system, Boron carbide, Titanium diboride, Nanocomposite.

Introduction

Metal borides such as TiB$_2$, ZrB$_2$, CrB$_2$, … are promising high temperature materials due to their unique properties such as high melting point, high hardness, excellent wear resistance, high electrical conductivity and exceptional resistance to acids and molten metals [1-3].

Boron carbide possesses unique physical and thermal properties such as a high modulus, a high melting point, good chemical stability, a large neutron absorption cross section and also excellent mechanical properties such as high hardness and wear resistance [4, 5]. In spite of the excellent properties of B$_4$C, the use of it has been limited due to its high sintering temperature and susceptibility to brittle fracture [6].

It has been shown that a secondary phase such as a boride can improve the toughness and sinter ability of B$_4$C. Li et al. [7] reported that the toughness of B$_4$C with TiB$_2$ increased. Therefore, the advantage of both phases is usually obtained in composite structures.

Usually, TiB$_2$ has been produced by the reduction of TiO$_2$ and B$_2$O$_3$ with carbon and an active metal using the self propagating high temperature synthesize process [8-10]. Because of the high reduction temperature, the grain growth of TiB$_2$ is rapid and it is very difficult to obtain ultrafine grains. To produce fine TiB$_2$ particles, the use of mechanical alloying (MA) has been recommended. Recently a high-energy ball milling process has been widely used to produce supersaturated crystalline solid solutions, nanocrystalline solids, amorphous phase via in situ solid-solid, gas-solid and liquid-solid reactions. Furthermore, high-energy ball milling can be used as an intermediate step to promote reactions that can be completed at high temperatures. Some researchers [10-13] have investigated the synthesis of carbides, silicides, nitrides and borides by this process.

In the present study, we report the effect of high-energy ball milling on synthetic reaction in Ti-B-C system.

Experimental

The starting materials used in this study were Ti (96%) with a particle size of < 150 µm, B (99%) with a mean particle size of 2 µm and graphite (99.5%) with a mean particle size of 50 µm. A powder mixture of Ti, B and C in the molar ratio of 1 : 6 : 1 was milled in a high-energy ball mill. The ball to powder was in a molar ratio of 20 : 1 and the powder was milled for up to 70 h with a rotation speed of 350 rpm. To minimize oxidation and nitridation of the blended powder, the steel vial was filled with argon. The heat treatment process was carried out at temperatures between 800 °C and 1200 °C under an argon atmosphere.

After milling for selected times (1, 3, 6, 10, 14, 20, 26, 32, 50 and 70 h), the milled and heat-treated powders were characterized by means of X-ray diffraction (model Philips PW 3710) using CuK$_\alpha$ radiation and $\lambda = 0.154$ nm. XRD peak broadening was used to determine the crystallite size and lattice strain.
via the Williamson-Hall relation:
\[ \beta \cos \theta = \frac{0.9 \lambda}{D} + \varepsilon \sin \theta \] (1)

By plotting ‘\( \beta \cos \theta \)’ (‘\( \beta \)’ the width at half-maximum intensity and ‘\( \theta \)’ the Bragg angle) against ‘\( \sin \theta \)’, a straight line was obtained from which the crystal size ‘\( D \)’ (intercept) and lattice strain ‘\( \varepsilon \)’ (slope) were obtained.

The morphology of powders was characterized by SEM (Vega/Tescan and Philips XL30). A transmission electron microscope (FEG Philips CM200) study of the final powder was carried out by a 200 kev electron beam.

**Results and Discussion**

**Thermodynamic considerations**

Table 1 summarizes thermodynamic functions concerning the following reactions:

\[ \text{Ti} + 2\text{B} \rightarrow \text{TiB}_2 \] (2)
\[ 4\text{B} + \text{C} \rightarrow \text{B}_4\text{C} \] (3)
\[ \text{Ti} + 6\text{B} + \text{C} \rightarrow \text{B}_4\text{C} + \text{TiB}_2 \] (4)

Since the Gibbs energy changes of these reactions are negative at ambient temperature; they should be thermodynamically possible. \( \text{B}_4\text{C} \) has a very low adiabatic temperature of 1000 K, so it is very difficult to form by self-sustaining combustion synthesis. On the other hand, titanium diboride exhibits a large heat of formation (exothermic potential) and has a very high adiabatic temperature of 3190 K. Therefore, \( \text{TiB}_2 \) can be expected to be of great assistance in producing \( \text{B}_4\text{C} \) which has a small exothermic potential. From Table 1 it is observed that the reaction 3 has a medium heat of formation with about 2300 K as the adiabatic temperature (Fig. 1) [14].

**XRD analysis**

The XRD patterns of powder mixtures milled for different times are illustrated in Fig. 2. For the unmilled powder all the major peaks correspond to Ti and C. Although boron was amorphous, the small peaks observed in the 15° - 25° 2θ range are due to the presence of some crystalline boron. After 1h milling the sharp peak of C reduces remarkably and finally disappears for 3 h milled powders. Regarding graphite disappearance during milling different explanations are possible based on results reported in the literature related to B-C and Ti-C binary system. Lohse et al. [15] reported that amorphorization of Graphite during the milling of Ti-C mixture causes elimination of graphite peaks. Wu et al. [16] noticed that the absence of graphite peaks during milling of a Ti and C mixture is because of the location of C atoms at the grain boundaries of Ti as a consequence of milling. In an other study [12] it was reported that elimination of graphite peaks during milling of Ti and C are because of large difference between the mass absorption coefficient (MAC) of Ti and graphite and also the location of graphite as sandwiched in thin layers between Ti layers or at the junction of Ti grain boundaries. Ghosh et al. [17] concluded that this phenomenon maybe due to a transitional bonding state between C and Ti atoms as the crystallinity of pure graphite remained after 1h milling. Also in the milling of a B and C mixture it was noticed that the elimination of C peaks after 2 h milling of B-C mixtures is due to

![Fig. 1. Theoretical adiabatic temperatures for different mole ratio of \( \text{B}_4\text{C}/\text{TiB}_2 \) [14].](image1)

![Fig. 2. XRD patterns of powders milled for: (a) 0 h(unmilled), (b) 1 h, (c) 3 h, (d) 6 h, (e) 10 h, (f) 14 h, (g) 20 h, (h) 26 h,( i) 32 h,( j) 50 h and( k) 70 h.](image2)
the dissolution of C atoms in to B lattice to form supersaturated solid solution [18].

In this study it can be concluded that there are three possibilities for the elimination C peaks during milling a Ti-B-C mixture: 1) formation of a solid solution between B and C, 2) amorphization of C, 3) location of C atoms in Ti grain boundaries so because of the large difference between MAC of them, detection of C is difficult.

As observed, Ti and TiB$_2$ peaks are present in the powder milled for 6 h. This means that a part of TiB$_2$ has been formed after milling. After 10 h of milling, XRD reveals the sharp peaks of TiB$_2$ accompanied by small peaks of TiB (according to JCPDF number 06-0641). Over 14 h of milling, the resulting powder was fully composed of TiB$_2$. There are no peaks of B$_4$C and boron or graphite in powders milled up to 70 h. The obtained results suggest that carbon atoms dissolved in the lattice of B after milling to form a supersaturated solid solution. No peaks corresponding to graphite were detected as the result of refinement in the microstructure and peak broadening. Ramos et al. [18] detected intense peaks of an unknown structure accompanied by weak peaks of B from milling of the mixture of B and C for 90 h. They also reported that B$_4$C compound was not formed during ball milling. On the other hand, Dudina et al. [19] mechanically milled a mixture of Ti, B, and C powders according to 23 vol.% TiB$_2$ and 77 vol.% B$_4$C and in their study neither TiB$_2$ nor B$_4$C was formed during the milling process up to 16 h because of the low adiabatic temperature of this composition. The crystallite size and lattice strain of milled powders were calculated from the Williamson-Hall equation (Table 2). It can be seen that with increasing milling time the crystallite size of TiB$_2$ was decreased.

The XRD patterns of powders mechanically milled for 70 h and heat treated at 800 °C, 1000 °C and 1200 °C for 1 h are shown in Fig. 3. As this figure shows, B$_4$C was formed above 1000 °C. The crystallite size of TiB$_2$ is about 53 nm after heat treatment at 1200 °C.

**SEM and TEM analysis**

The morphology of powders at different milling times is shown in Fig. 4. In the initial stage of milling, the brittle powders are repeatedly fractured and it can be shown that with increasing milling time, the degree of agglomeration increases while the microstructure basically remains fine. As Fig. 4 shows a large amount of very fine particles with a rounded morphology was observed after milling for 70 h. Figure 5 shows the microstructure of powder milled for 70 h and heat treated at 1200 °C. Fig 6 shows TEM analysis of the powder milled for 70 h and heat treated at 1200 °C on two different parts of a grid. It can be seen that the distribution of grain size is very wide from 50 nm up to more than 100 nm. The EDAX analyses of points that
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are marked in Fig 6b are reported in Fig 7. EDAX of points 1 and 3 show B and C elements that confirmed these are from B$_4$C. For the grain that is marked with 2 Ti along with B and C are detected that shows this is TiB$_2$ grain with a size of less than 50 nm.

Synthesis mechanism
XRD data (Fig. 2) showed that the formation of TiB$_2$ was started at 6 h of milling; the amount of this phase gradually increased with an increase in the milling time, it can be concluded that a gradual diffusion reaction (GDR) is a possible mechanism that controls the formation of TiB$_2$. In most of the studies [20, 21] reported for the synthesizing of TiB$_2$, the mechanically induced self-propagating reaction (MSR) has been considered to be the mechanism of the formation of TiB$_2$; however Tang et al. [13] reported GDR as a dominant mechanism. According to the GDR mechanism [13], a thin TiB$_2$ layer may be firstly formed by the reaction between Ti and B during ball milling. The diffusion of the Ti and B atoms through the TiB$_2$ layer is necessary to complete the reaction, until the Ti (B) in the powder is completely converted to TiB$_2$. In this study it can be said that C acts as a diluent for the Ti-B system and gives rise to a reduction in the adiabatic temperature and heat of formation of the reaction. So this condition caused the formation of TiB$_2$ which was completed in a GDR mechanism.

Conclusions

The present study showed that:

1) TiB$_2$ nanocrystalline powder can be synthesized by ball milling of a Ti-B elemental powder mixture. The crystallite sizes of TiB$_2$ decrease with increasing
milling time and become about 7.5 nm after 70 h of milling. The formation of TiB$_2$ is controlled by the GDR mechanism.

2) In the B-C system, after 6 h of milling, nanometric B particles form, however, they cannot be detected due to peak broadening.

3) No B$_4$C compound is formed during milling up to 70 h; however it forms after heat treatment above 1000 °C.

References