Original Research Paper

Formation mechanism of B_4C–TiB_2–TiC ceramic composite produced by mechanical alloying of Ti–B_4C powders

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A B S T R A C T

In this study, the B_4C–TiB_2–TiC composite powder was synthesized by mechanical alloying (MA) of Ti–B_4C powder mixture. For this purpose, four powder mixtures of Ti and B_4C powders with different molar ratios were milled. In order to study the mechanism of Ti–B_4C reaction during milling, structural changes and thermal analysis of powder particles were studied by X-ray diffractometry (XRD) and differential thermal analysis (DTA). Morphology and microstructure of powder particles during milling were studied by scanning electron microscopy (SEM). It was found that during MA, after decomposition of the outer layers of B_4C particles, first, C reacted with Ti and after that, B was diffused in Ti structure and TiC and TiB_2 phases were formed in gradual reaction mode. Also, the results of DTA and thermodynamic analysis confirmed the suggested mechanism for Ti–B_4C reaction.

1. Introduction

Boron carbide (B_4C) is the third hardest material after diamond and boron nitride at room temperature and its hardness is retained at high temperatures [1,2]. B_4C possesses unique physical and thermal properties such as high elastic modulus, high melting point, good chemical stability and high neutron absorption cross section. In addition, B_4C ceramics exhibit excellent mechanical properties such as high hardness and high wear resistance [3–7].

This material has also received attention for application in nuclear fusion reactors because the low atomic numbers of boron and carbon result in low X-ray absorption, and exposure to neutron irradiation does not cause radioactive decay [8–11]. B_4C is currently used in nuclear energy and high temperature thermoelectric conversion. However, their widespread application has been restricted mainly due to their low strength and fracture toughness as well as poor sinterability due to a low self diffusion coefficient. Several additives have been investigated in order to promote the sinterability and mechanical properties of B_4C [3].

B_4C ceramics with dispersed TiB_2 particles have been investigated in order to improve both strength and toughness [12–15]. The improvement of fracture toughness, which was achieved by TiB_2 addition, has been explained in terms of microcrack formation caused by the thermal expansion mismatch between dispersed

particles and the matrix [13,14]. TiB_2 has been proposed as a promising second phase for the improvement of B_4C properties [15–18]. Pairing B_4C and TiB_2 in a composite can be beneficial for the design of thermoelectric materials [19,20] and composites with increased fracture toughness and bending strength relative to pure boron carbide [3,21]. Also, TiB_2 was suggested as a possible grain growth inhibitor for B_4C [13].

In previous studies [22–24], some B_4C based composites, e.g. B_4C/TiB_2, B_4C/TiB_2/MB_2, B_4C/MB_2, B_4C/Al, B_4C/SiC, have been developed. Yamada et al. [3] fabricated B_4C–20 mol.% TiB_2 ceramic composites by reacting hot-pressing powder mixtures of B_4C, TiO_2 and carbon black at 2000 °C. They reported that the abnormal grain growth of B_4C was inhibited, and the fracture toughness was increased for some B_4C–TiB_2 specimens. It has been reported that this improvement in toughness was due to the formation of microcracks and the deflection of propagating cracks caused by the thermal expansion mismatch between TiB_2 particles and B_4C matrix.

Wang et al. [25] synthesized dense TiB_2/TiC composites by MA of Ti and B_4C powder blends and subsequent sintering. They indicated that diffusion played a major role in the formation of the TiC and TiB_2 phases. Also, TiC phase was formed earlier than TiB_2 phase, due to the higher diffusivity of C than B into the Ti matrix.

Li et al. [26] prepared TiB_2/TiC nanocomposite via MA of Ti and B_4C powders. It was found that the bulk of TiC and TiB_2 was formed abruptly by self-propagating reaction after 5 h of milling. The final product was composed of nano-sized TiC and micro-sized TiB_2 particles.

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Wang et al. [27] successfully prepared the TiB_2–TiC nanocomposite by MA of Ti and B_4C powder mixtures. They showed that the formation of TiC and TiB_2 was gradual. Also it was found that the decomposition of B_4C into amorphous B and C occurred during MA.

Preliminary estimates of TiC–TiB_2 composites fabricated from Ti and B_4C powders suggested that a 75% cost savings could be realized using B_4C as a reactant instead of elemental B and C [28]. Therefore, in this work, the MA of $3Ti + xB_4C$ ($x = 1, 2, 3, 4$) powder mixtures and the formation mechanism of B_4C–TiC–TiB_2 composite powder were studied.

2. Experimental

Ti and B_4C powders, with the purity of 99.5 and 99%, respectively, were used as starting materials. The Ti powder particles were irregular in shape with a size distribution of 50–100 μm and B_4C particles had a uniform angular shape with a size distribution of 150–200 μm. Ti and B_4C powders were mixed with different molar ratios according to the reactions (1)–(4). MA was carried out in a high energy planetary ball mill, nominally at room temperature and under Ar atmosphere. The ball and vial materials were hardened chromium steel. Ball to powder weight ratio and rotation speed of vial were 10:1 and 300 rpm, respectively. The total powder mass was 20 g. Samples were taken at selected time intervals and characterized by XRD in a Philips X' PERT MPD diffractometer using filtered Cu Kα radiation (α = 0.1542 nm). Morphology and microstructure of powder particles were characterized by SEM in a Philips XL30. The mean powder particle size was estimated from SEM images of powder particles by image tool software. Isothermal annealing was carried out to study the thermal behavior of milled powders. A small amount of powder was sealed and isothermally annealed at 1200 °C for 1 h in a conventional furnace and then cooled in air. The structural transitions occurring during annealing were determined by XRD. DTA was done in 30–1200 °C temperature range with 20 °C min^{-1} heating rate in order to study the thermal behavior of the milled powders.

3. Results and discussion

3.1. Structural changes

In order to study the formation mechanism of B_4C–TiB_2–TiC ceramic composite, MA of Ti–B_4C systems with different molar ratios was done according to the following reactions:

$$3Ti + B_4C = 2TiB_2 + TiC \tag{1}$$

$$3Ti + 2B_4C = B_4C + 2TiB_2 + TiC \tag{2}$$

$$3Ti + 3B_4C = 2B_4C + 2TiB_2 + TiC \tag{3}$$

$$3Ti + 4B_4C = 3B_4C + 2TiB_2 + TiC \tag{4}$$

3.1.1. MA of 3Ti–B_4C system

Fig. 1 shows XRD patterns of 3Ti–B_4C powder mixture at different milling times (according to the reaction (1)). As can be seen, after 5 min of MA, only Ti and B_4C peaks were seen. With increasing milling time up to 5 h, traces of TiC peaks appeared on XRD pattern. Also, one peak related to TiB phase was seen. After 10 h of milling, the intensity of TiC peaks was increased due to the gradual diffusion of C into the Ti structure to form TiC phase. Also, TiB_2 phase was formed and the intensity of its peaks was increased because of the gradual formation of it during MA. Wang et al. [25] synthesized dense TiB_2/TiC composites by MA and the subse-
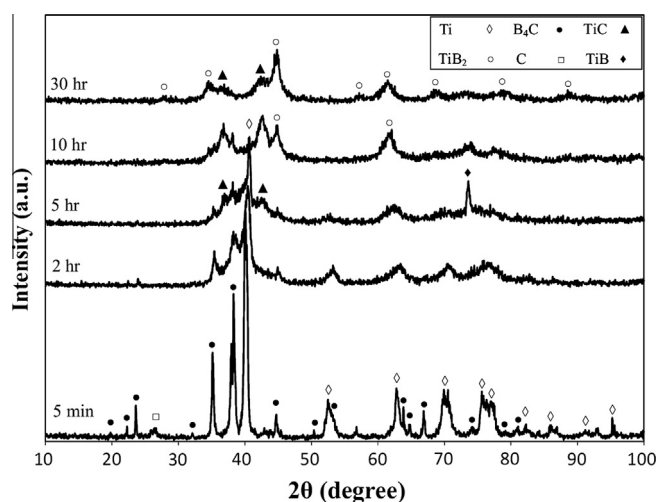

Fig. 1. XRD patterns of 3Ti–B_4C system at different milling times.

quent pressureless sintering and reported that the formation of TiC and TiB_2 compounds during MA was gradual in contrast to the conventional synthesis via the SHS reaction. At longer milling times, with more diffusion of B into the Ti structure due to the MA process, TiB phase was disappeared and transformed to TiB_2. After 30 h of MA, only TiB_2 and TiC peaks were seen, indicating the complete formation of TiB_2–TiC composite.

XRD patterns of 3Ti–B_4C system after 30 h of MA and subsequent heat treatment are presented in Fig. 2. As can be seen, with heat treatment, the intensity of TiC and TiB_2 peaks was increased due to the ordering of structure and strain removal. Also, Fe_2B phase was formed after heat treatment. The cause of Fe_2B formation is related to the presence of Fe in powder mixture due to the wear of steel bowl and balls with hard ceramic powders such as B_4C, TiC and TiB_2 and the reaction of Fe with B during heating.

3.1.2. MA of 3Ti–$2B_4C$ system

XRD patterns of 3Ti–$2B_4C$ system at different milling times are presented in Fig. 3. According to the reaction (2), it is expected that MA of this system can lead to the formation of B_4C–TiB_2–TiC ceramic composite powder. As can be seen, after 5 min of MA, just Ti and B_4C peaks are seen. With increasing the milling time up to 2 h, the height of Ti and B_4C diffraction peaks was decreased and simultaneously, the traces of TiC peaks were seen in XRD pattern due to the gradual reaction of Ti with B_4C during MA. With further
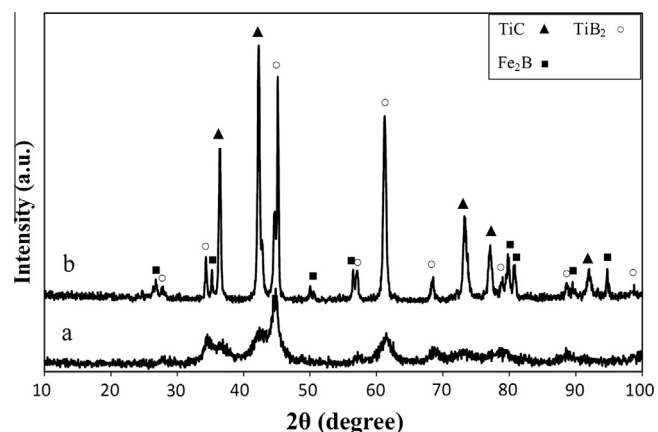

Fig. 2. XRD patterns of 3Ti–B_4C system, (a) after 30 h of milling and (b) after heat treatment at 1200 °C for 1 h.