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TiB_2/TiC nanocomposite powder fabricated via high energy ball milling

Jianlin Li *, Fei Li, Keao Hu, Yong Zhou

Department of Materials, Institute of Composite Materials, Shanghai Jiaotong University, 1954 Huashan Road, Shanghai 200030, PR China

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Abstract

TiB_2/TiC nanocomposite powder was fabricated via high-energy ball milling processing, and microstructure development of the powder mixtures was monitored by X-ray diffraction, transmission electron microscopy. Ball milling B_4C and elemental Ti powder mixture at ambient temperature resulted in the formation of TiC prior to the formation of TiB_2. The bulk of TiC and TiB_2 formation accomplished after 5 h of milling. The final product consisted of nanosized TiC particles and microscale TiB_2 particles.

Keywords: Milling; Nanocomposites; Powder preparation; TiC; TiB_2

1. Introduction

TiB_2 is representative of refractory compounds with very high melting points and high hardness. Researches have shown that fine-grained TiB_2 possesses extraordinary resistance to plastic deformation at high temperatures. Further more, the fracture toughness of 5 Mpa $m^{1/2}$ is also encouraging. In contrast, TiC deforms plastically over the range 1000–1500°C. TiC, however, can be precipitation hardened by TiB_2 at high temperatures. This combination of extreme resistance to plastic deformation, high melting point precipitation hardening, and the high-temperature plasticity of the TiC phase suggests that a TiB_2–TiC composite should be attractive as a high-temperature structural ceramic.[1–3]

Transient plastic phase processing (TPPP) has been introduced recently by Barsoum et al.[4] as a technique for net-shape fabrication of fully titanium carbide–titanium boride composites at relatively low temperature. However, it usually takes a long time to finish this processing, i.e. 4 h at 800°C followed by 4 h at 1600°C . The evolution of the microstructure in the processing is governed by the diffusion of carbon and boron into titanium, therefore using powders after high-energy ball milling for the proper time as raw materials might be helpful.[4,5] On the other hand, Nihara and many researchers have demonstrated that ceramic materials with fine microstructures, especially nanocomposites, exhibit improved mechanical properties.[6] As we know, nanocomposite powders are needed to fabricate bulk materials with a fine microstructure. Thus, it is meaningful if nanocomposite TiB_2/TiC powders could be prepared via high-energy ball milling.

Recently, high-energy ball milling (mechanical alloying) has been widely used to produce supersaturated crystalline solid solution, amorphous phases, nanocrystalline solids, and compounds through in situ solid–solid, gas–solid, and liquid–solid reactions. Furthermore, high-energy milling can be designed as an intermediate step to promote reactions that can be completed at high temperatures. Munir et al. have investigated the synthesis of carbides, silicides, nitrides and borides by this processing.[7–12] Le and Wu also studied the syntheses of nanocrystalline TiC by mechanical alloying using Ti and C as starting materials.[13–15]

Here we report on the reactions in the 3:1 Ti/B_4C starting composition in high-energy ball milling processing.

2. Experimental

The raw materials used in this study were 99.9% pure Ti powder with a sieve size −400 mesh and 98% pure B_4C powder with an average particle size 4 μm.

* Corresponding author.
E-mail address: lijinlin2000@263.net or jfli@maill.sjtu.edu.cn (J. Li).

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Powder mixtures consisting of a B_4C:Ti molar ratio of 1:3 were ball milled in a GN-1 high-energy ball milling machine (Shengyang Science Equipment Factory, China). The milling was conducted using hardened steel balls with a diameter of 5 mm. The ball-to-powder weight ratio was 10:1, and the milling speed was 360 rpm. The hardened steel canister was evacuated to 0.2 Pa and flushed with Ar gas.

The time when the self-propagating reaction occurred was determined by monitoring temperatures of the canister. Temperatures that the canister had reached during per milling period (1 h) were estimated by checking the rubberized fabric glued on the canister. After different times of milling, such as 3, 4, 5 and 6 h, the rubberized fabric was checked and another piece of rubberized fabric was glued onto the canister. In order to separate the heat contributions from the milling machine and from a self-propagating reaction, milling runs were interrupted for 15 min whenever powder mixtures were milled for 1 h. During the interruptions, the temperature of the canister would reduce to room temperature and the heat contributions from the milling machine would be eliminated.

After milling for selected times, ball milled powder mixtures were taken out in Ar for analysis. The powders were characterized by X-ray diffraction (XRD, CuK_α radiation: $\lambda = 0.154$ nm). XRD peak broadening was used to determine the crystallite size d. By plotting $\beta\cos\theta$ (β the line width at half-maximum intensity and θ the Bragg angle) again $\sin\theta$, a straight line was obtained from which the crystal size d was obtained from the intercept. The as-milled powders were also investigated by transmission electron microscopy (TEM, Hitachi H800). The operating electron voltage was 200 kV.

3. Results and discussion

3.1. Reaction in premilling period

X-ray diffraction (XRD) patterns of the powder mixtures after different milling times are shown in Fig. 1. After 2 h of milling, B_4C peaks disappear completely, but no TiC or TiB_2 is detected in the powder mixture (Fig. 1b). It is suggested that B_4C are broken into very small pieces among fine Ti grains. Metal Ti, therefore, block out the reflections of B_4C. A similar phenomenon was reported by Wu when he milled Ti and C. In his experiments, Wu found that C peaks disappeared due to hindrance of Ti, and no TiC was detected by XRD at the same time.[14]

With increasing milling time, the diffraction peaks of crystalline Ti becomes broader and of less intensity, but their positions do not shift. After 3 h of milling, the average diameter of Ti grains is around 30 nm by Scherrer formula.

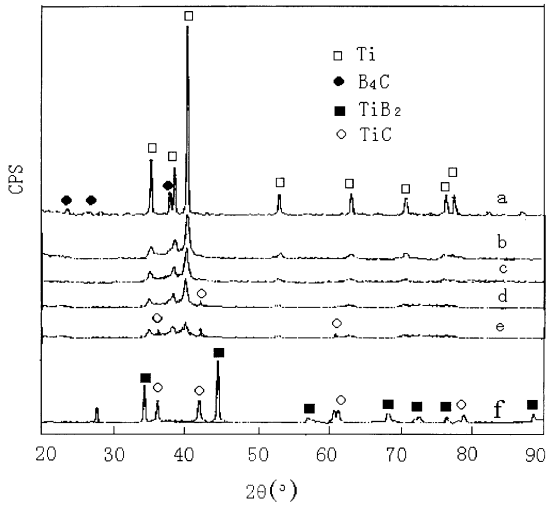

Fig. 1. XRD patterns of the powder mixtures milled for different times, (a) before milling, (b) 2 h, (c) 3 h, (d) 4 h, (e) 4.5 h and (f) 5 h.

After 4 h of milling, TiC peaks appear, but no TiB_2 is found (Fig. 1d). The lattice parameter of TiC is found to be 0.432 nm, which does not change during the subsequent milling process. Fig. 2 shows some nanosized TiC particles.

Researchers have demonstrated that Ti and C will react during high energy ball milling by MRS (self-propagating reaction).[13] However, dilution of reactants increases the ignition temperature for explosion reaction. Consequently, the reaction velocity can be remarkably reduced, and the explosion reaction will be suppressed. As a result, products are usually to be nanosized particles.[16,17]

In this experiment, the outer shell of some B_4C particles would decompose into B and C due to the heavy impact of milling balls and reduction of Ti around these B_4C particles. C and B atoms then diffuse into Ti. Although the powders are more loosely dispersed in the vial during ball

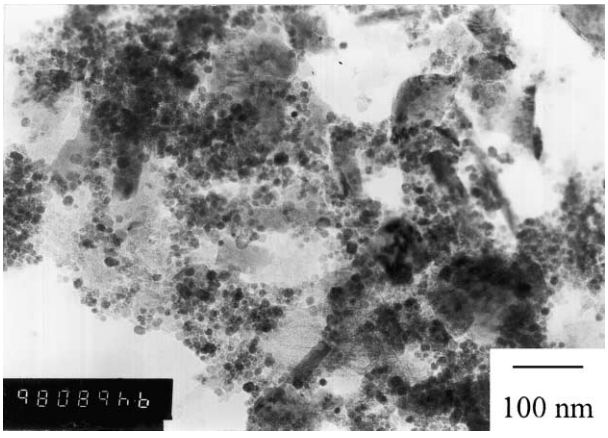

Fig. 2. TEM image of the powder mixtures milled for 4 h, showing nanosized TiC particles (dark spots).

milling, the mixing of the reactants on a nanometre scale and many defects in Ti induced in milling processing favor mass transfer and the diffusion path length is considerably reduced. In addition, the diffusivity of carbon is significantly greater than that of boron, according to the literature data.[4] The diffusivity of carbon in titanium is approximately three orders of magnitude higher than that of boron in titanium. Therefore, TiC is easier to form than that of TiB_2, but the rest Ti and B_4C will dilute the reactants Ti and C, then suppress the explosion reaction of Ti and C. Thus, TiC will appear in the form of superfine particles (Fig. 2). On the other hand, the XRD patterns (Fig. 1c–e) show that the positions of Ti reflections do not shift. C atoms, therefore, diffused mainly along Ti grain boundaries. Wu also reported that C diffused along Ti grain boundaries before the formation of TiC.[15] This indicates that the decomposition of outer shell of some B_4C particles is a must before TiC formed.

Barsoum et al.[4] reported that when Ti reacted with B_4C at elevated temperature, carbon diffused rapidly from B_4C areas into titanium during the initial stages, form $TiC_{0.5}$ and leave behind areas of high boron activity. $TiC_{0.5}$ was one of the intermediate phases. In this experiment, however, TiC, not $TiC_{0.5,}$ was detected. Thus, it is assumed that the impact of milling balls trigger reaction between Ti and C near B_4C particles where C content is high enough. But the reaction cannot self-propagate due to the dilution of reactants by Ti. The fine TiC particles formed are moved away quickly in milling processing, so they remain nanosized.[16,17]

3.2. Self-propagating reaction (MSR) after premilling period

With further milling up to 5 h, the abrupt formation of TiB_2 occurs. Only TiB_2 and TiC are detected by XRD (Fig. 1f). It was found that the temperature of the canister raised rapidly when the powder mixtures were milled for nearly 5 h. Namely, B_4C reacted with Ti and gave off a large amount of heat to ignite the MSR.

TiC peaks become of intensity after 5 h of milling (Fig. 1f), due to the formation of larger TiC particles by MSR (Fig. 3a). Some nanosized TiC particles are located in TiB_2 grains (Fig. 3a). The nanosized TiC formed prior to the formation of TiB_2, and they were wrapped in when TiB_2 formed rapidly by MSR. Fig. 3c shows the nanosized TiC particles formed previously. On the other hand, the temperature during MSR was very high, and C atoms diffused rapidly in Ti. TiC or TiB_2 then formed at different sites. As a result, few TiC or TiB_2, particles formed by MSR are wrapped in TiB_2 or TiC grains.

3.3. Reaction mechanism in high energy ball milling

In summary, the evolution of the powder mixture during milling processing is as follows.

During 0–4.5 h, a small part of B_4C decomposes and reacts with Ti. Namely, reaction (1) takes place at almost the same time.

$$Ti + B_4C \rightarrow Ti + 4B + C \rightarrow TiC + 4B \quad (1)$$

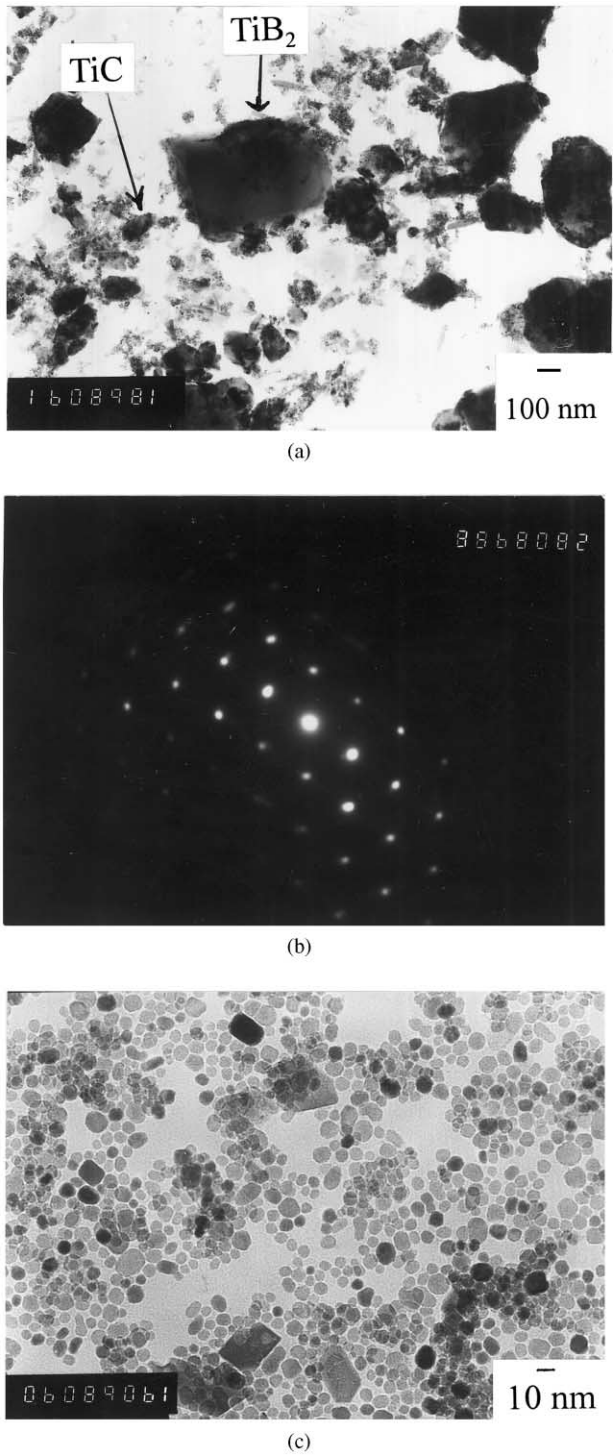

Fig. 3. TEM images of powders milled for 5 h, showing (a) large TiC and TiB_2 grains, (b) electron diffraction pattern of TiB_2 [0001], and nanosized TiC particles (c).

Table 1
Typical reactions in high energy ball milling processing

Reaction	Heat of formation (kJ mol^{-1})	Adiabatic temperature, (K)	Mode of reaction
$Mo+2Si \rightarrow MoSi_2$	−138	1900	Combustive
$Ti+2B \rightarrow TiB_2$	−342	3190	Combustive
$Ti+C \rightarrow TiC$	−183.8	3210	Combustive
$4A1+3C \rightarrow Al_4C_3$	−215.8	1200	Gradual
$Si+C \rightarrow SiC$	−67	1800	Gradual
$W+2Si \rightarrow WSi_2$	–	1500	Gradual

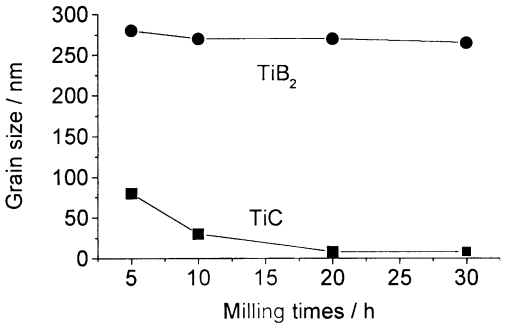

Fig. 4. Effect of time on TiC and TiB_2 grain size, TiC grain size was determined from the breadths while TiB_2 grain size were determined by TEM.

During 4.5–5 h, reaction (2) takes place.

$$Ti + B_4C + B \rightarrow TiC + TiB_2 \quad (2)$$

The XRD patterns (Fig. 1f) demonstrate the overall reaction (3):

$$3Ti + B_4C = TiC + 2TiB_2 \quad (3)$$

Researches have shown that the adiabatic temperature, which is the maximum temperature achieved under adiabatic conditions as a consequence of the evolution of heat from the reaction, should be above 1800 K[7,14] in thermally ignited systems. Some typical reactions in high energy milling process are summarized in Table 1.[7,14,18] The heat involved in reaction (3) is about −780 kJ at 300 K. The adiabatic temperature is, therefore, much higher than 1800 K. Namely, the bulk of TiC and TiB_2 can form by MSR though reaction (3). On the other hand, the present investigation shows that the ignition of the combustion reaction (3) requires an initial premilling period (incubation) during which ball milling leads to a change in the factors determining the critical combustion condition.

In general, the reaction rate in the powder system is dependent on particle size.[16,17] This is because refinement of particle size increases the reaction interface area

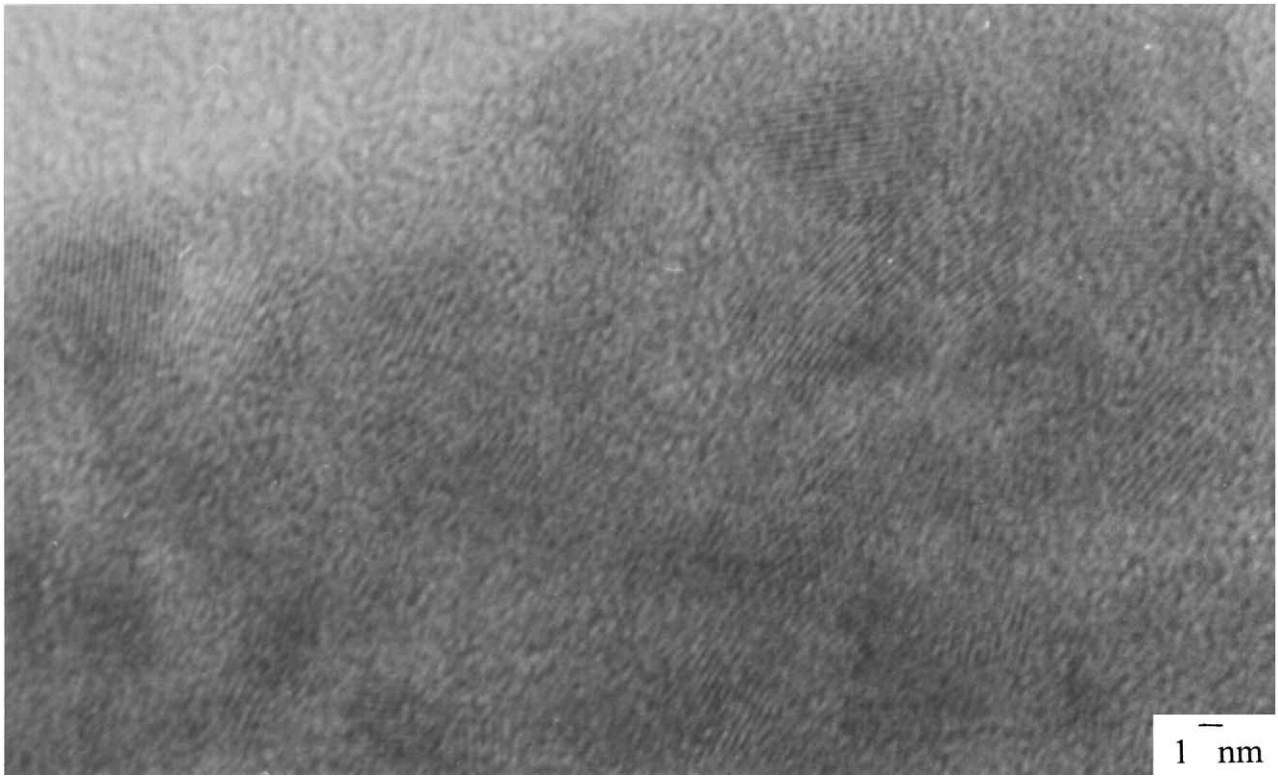

Fig. 5. HRTEM images of powders milled for 30 h, showing nano-sized TiC particles with a diameter of 6–7 nm.

and the activities of the reactants. Hence, some researchers have proposed that there exist a critical particle size for ignition of the combustion reaction during the course of high energy ball milling processing. In the current experiment, an initial premilling period (incubation) is at least 4.5 h in order to ignite the combustion reaction (3). Although nanosized TiC particles formed during the premilling period 4.5 h, the bulk of TiC and TiB_2 could not form by MSR because the B_4C particles were not fine enough at that time. With further milling up to about 5 h, the combustion reaction is accelerated by the refinement of B_4C particle, and the bulk of TiC and TiB_2 formed abruptly. In this work, it was found that reaction (3) was accomplished within 0.5 h. In fact, reaction (3) may be accomplished in a few minutes. Previous studies have demonstrated that MRS reactions can accomplish during high energy ball milling process in a few minutes.[7,17,19]

3.4. Effect of milling time on microstructure of products

Structure evolution with milling time was followed with X-ray diffraction and TEM and HRTEM. Further milling leads to no other new phases. The TiB_2 peaks did not change their intensities or positions, which shows that the TiB_2 grains remain microscale size. The broadening of the TiC peaks indicates that the average grain size of TiC decreases to about 8 nm after 30 h (Fig. 4). Few TiC particles above 30 nm in size were found after 30 h of milling. Most nanosized TiC particles stick to the surface of TiB_2 particles. The electron diffraction pattern can be indexed on the basis of TiB_2 and nanocrystalline TiC. Since the hardness of TiB_2 is higher than that of TiC, it is assumed that a large number of TiB_2 particles act as small milling balls in further milling process.

HRTEM image shows that there is no obvious defects or lattice strain in TiC particles (Fig. 5). The grain size of TiC is about 6–7 nm, in agreement with the result 8 nm by Scherrer formula. Namely, TiC particles, in this experiment, are milled into nanosized particles instead of nanocrystalline TiC.

The TiB_2/TiC nanocomposite powder prepared in this work is micro-scale TiB_2 particles incorporated with nanosized TiC particles. It is relatively an ideal composite powder; further research is being carried out.

4. Conclusion

TiB_2/TiC nanocomposite powder has been prepared via high-energy ball milling processing. The formation of TiC occurs prior to that of TiB_2 during milling processing, due to the faster diffusion of carbon, relative to boron, in titanium matrix. The bulk of TiC and TiB_2, form abruptly by MRS after 5 h of milling. The final product is composed of nanosized TiC and micro-sized TiB_2 particles. Some nanosized TiC particles are located in TiB_2 grains.

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