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Characterization of the structure of TiB_2/TiC nanocomposite powders fabricated by high-energy ball milling

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Abstract

TiB_2/TiC nanocomposite powders were successfully prepared by high-energy ball milling of the powder mixtures of Ti and B_4C. X-ray diffraction analysis showed that the TiC phase was not produced until the milling time was up to 24 h and only a minimal amount of TiB_2 was generated, even after 48 h of milling. The critical grain size of Ti milled for the reaction between Ti and B_4C was 31.2 nm. Transmission electron microscopy clearly indicated that the resulting powder mixture obtained after milling for 48 h and annealing at 800 °C for 30 min was composed of nanosized TiC and TiB_2 particles.

Keywords: High-energy ball milling; TiB_2/TiC nanocomposite powder; X-ray diffraction; Transmission electron microscopy

1. Introduction

TiB_2 and TiC ceramics offer many desirable properties, such as high hardness, low density, high melting point, and high corrosion resistance. Furthermore, the high electrical and thermal conductivities of TiB_2 and TiC also suggest the potential utilization of TiB_2–TiC composites in high performance electrolytic systems, such as cathodes for Hall-Heroult cells [1–3]. However, TiB_2–TiC composites are very difficult to be fabricated by conventional sintering methods due to their high melting points (2980 °C and 3200 °C, respectively) and low self-diffusion coefficients [4]. Recently, it has caught the attention of many researchers that dense TiB_2–TiC composites from Ti–B_4C or Ti–B_4C–C compact reactants could be fabricated by the SHS reaction with hot isostatic pressing [5]. However, the shapes and size scales of such composites are limited by the hot isostatic pressing moulds, widely limiting their applications. High-energy ball milling can be designed as an intermediate step to promote reactions that can be completed at high temperatures [6]. Furthermore, nanosized powders, which can activate subsequent sintering processing and result in fine microstructures, can be prepared during the milling. The evolution of the microstructure in the processing is governed mainly by the sizes of mixture powders, therefore using powders after high-energy ball milling for the proper time as starting materials might be helpful. In fact, Nihara and many researchers have demonstrated that ceramic materials with fine microstructures, especially nanocomposites, exhibit improved mechanical properties [7,8]. Thus, the preparation of TiB_2–TiC nanocomposite powders via high-energy ball milling merits further study. Lee studied the synthesis of nanocrystalline TiB_2–TiC using high-energy ball milling of a mixture of Ti, amorphous B and C and Wu also studied the synthesis of nanocrystalline TiC by mechanical alloying using Ti and C as starting materials which have provided good basis for our studies [9,10].

In this paper, we used Ti and relatively inexpensive B_4C as starting materials to synthesize nanosized TiB_2–TiC powder mixtures by high-energy ball milling. The phase evolution with milling time was investigated by X-ray diffraction. The morphologies of the powder mixtures after milling for different time intervals were also observed by scanning electron microscopy and transmission electron microscopy, respectively.

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2. Experimental procedure and methods

The starting materials used in this study were titanium powder (>99%, purity) with a sieve size of 200–300 mesh, and B_4C powder (99%, purity) with an average particle size of 10.23 μm. In order to improve the milling efficiency, the starting materials were dried at 80 °C for 24 h inside a vacuum drying oven. They were then blended stoichiometrically according to the following reaction:

$$3Ti + B_4C = TiC + 2TiB_2 \quad (1)$$

High-energy ball milling experiments were conducted in a QM-WX4 planetary ball mill (Nanjing University Instrument Plant) using stainless steel jars with an internal volume of 500 mL and hardened stainless steel balls with diameters of 6, 10 and 20 mm. All the balls were used intentionally and the mass ratio of the different balls (φ20, φ10, and φ6) was 1:2:2. The resulting ball-to-powder mass ratio was 10:1. In order to minimize oxidation, the stainless steel jars were evacuated for 40 min and then were flushed with Ar gas (99.9%, purity). The milling speed was 500 rpm and the range of milling time investigated was 0–48 h.

After milling for selected time, the powder mixtures were taken out in Ar gas for analysis. The evolution of the phases in the powder mixtures with increasing the milling time was investigated by X-ray diffraction (XRD, PW3040/60) with Cu Kα radiation. XRD peak broadening was used to determine the critical grain size of Ti milled for the reaction between Ti and B_4C by the Scherrer formula. The morphologies of the starting materials and as-milled powders were investigated by means of scanning electron microscopy (SEM, SSX-550). The resulting powder mixtures obtained after milling for 48 h and annealing at 800 °C for 30 min were also analyzed using transmission electron microscopy (TEM, TecnaiG^{2}20) with energy dispersive spectrometry (EDS) and selected area diffraction pattern (SADP). The operating electron voltage was 200 kV.

3. Results and discussion

3.1. XRD analysis of powder mixtures

Changes in the XRD patterns reflecting the evolution with time of the phases during milling of the Ti–B_4C powder mixtures are shown in Fig. 1. The nature of the phases present and the general shape of the peaks depended on the milling time. The as-received material mainly contained Ti and B_4C, and no other phases existed in the mixture (Fig. 1). The initial sharp peaks of Ti were broadened due to the refinement of the crystalline size and the generation of strain with increasing the milling time. The intensities of B_4C peaks became relatively weak and even partially disappeared as the milling time increased, indicating the possible decomposition of B_4C into B and C. However, B and C were amorphous, and no traces of B or C were indicated in the Fig. 1. Although the intensities of the Ti peaks decreased significantly, the positions of these peaks were unchanged, indicating the possible dissolution of B or C into the Ti matrix, which is consistent with the results reported by Jianlin Li [11]. No

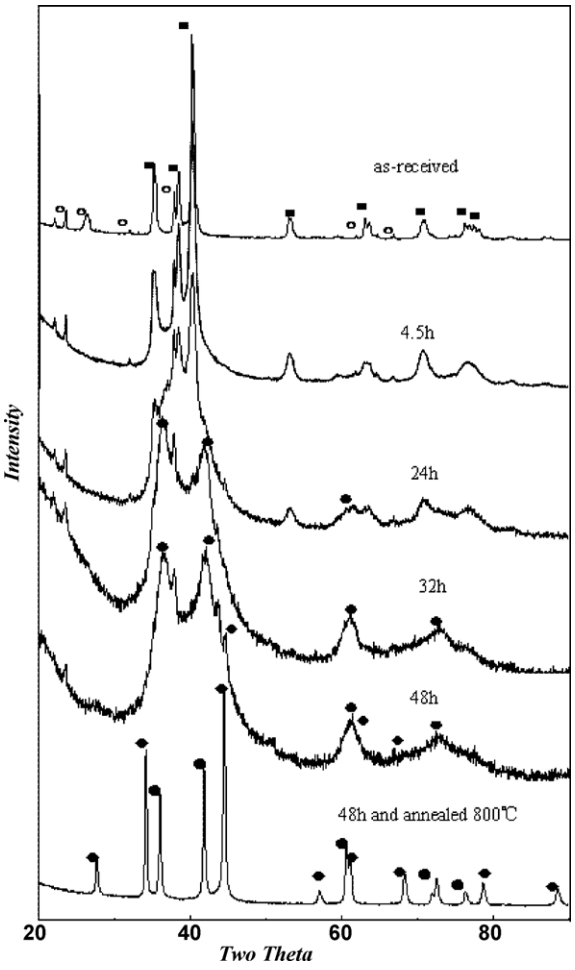

Fig. 1. XRD patterns of the powder mixtures milled for different lengths of time and the annealed powder mixture Ti (■); B_4C (○); TiC (●); and TiB_2 (◆).

evidence of the formation of TiC or TiB_2 was found until after 24 h of milling. It was obvious that TiC was formed prior to TiB_2 due to the higher diffusivity of C than that of B into the Ti matrix. According to Ref. [12], the diffusivity of C into Ti is approximately three orders of magnitude higher than that of B, making TiC is easier to form than TiB_2. Only a minimal amount of TiB_2 was produced, even if the milling time was extended to 48 h, indicating that no strong self-propagating reaction occurred during the milling, and therefore diffusion played a major role in the formation of TiC and TiB_2. Annealing was necessary in order to eliminate the structural defects and lattice stress in TiC and TiB_2 structures derived from the ball collisions during the milling. As shown in Fig. 1, the sharp diffraction peaks of TiC and TiB_2 were the only products after annealing at 800 °C for 30 min, indicating that subsequent heat treatment was an effective method of not only accelerating the complete phase transformation of TiB_2 but also promoting the formation of products with perfect crystal structures. Grain size analysis was performed on the XRD results of Ti peaks milled for up to 24 h, i.e. before the formation of the product phase (TiC). The changes in Ti grain size with increasing the milling time are shown in Fig. 2. A significant decrease occurred after milling for only 4.5 h. With further milling, the decrease became less

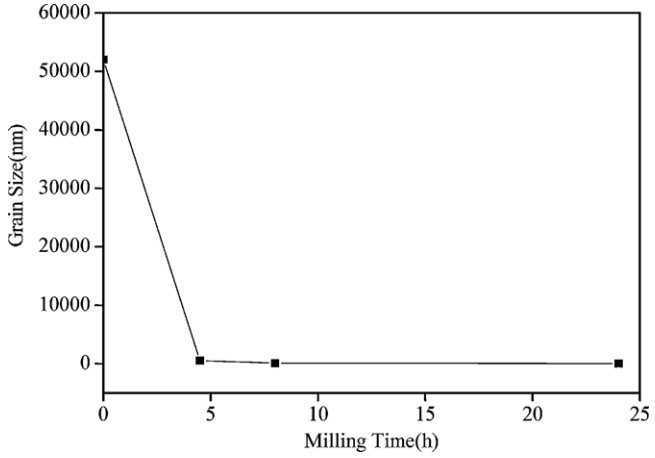

Fig. 2. Dependence of Ti grain size on the milling time.

significant, and was only marginal between 8 and 24 h. After milling for 24 h, the grain size of Ti was only 31.2 nm, as determined by the Scherrer formula, the smallest size achieved before the formation of TiC. In our experiments, the milling time for the formation of the resulting product phases was much longer than that reported by Jianlin Li which was only 4.5 h due to the larger particle size of the starting materials (Ti = 54 μm and B_4C = 10.23 μm) [11].

3.2. Microstructures of powder mixtures

The microstructural changes of the powder mixtures with increasing the milling time are shown in Fig. 3. The as-received powder mixture had the structures of coarse irregular polyhedrons; with increasing the milling time, their structures became spherical and fine. No significant decrease in the grain size of the powder mixtures occurred with further milling up to 24 h, which was in agreement with the results shown in Fig. 2. TEM was employed to observe the morphologies of the powder mixtures after the prolonged milling time. Fig. 4 shows the TEM images and selected area diffraction pattern (SADP) of the powder mixture which was milled for 48 h and annealed at 800 °C for 30 min. The {1 1 1} and {2 0 0} diffraction rings of TiC and {0 0 2} diffraction ring of TiB_2 were visible in the SADP shown in Fig. 4(c), confirming that the powder mixture consisted of TiC and TiB_2. From the bright field image (Fig. 4(a)), the grain sizes of the mixture powder were estimated to range in 30–50 nm when the milling time was increased to 48 h. The nanosized particles, composed of the TiC and TiB_2 phases, appeared to be wrapped together after annealing at 800 °C for 30 min (Fig. 4(b)). If the as-milled powder mixtures were impacted and sintered, TiB_2/TiC nanocomposites with superior properties are expected to be fabricated at relatively low temperatures. Further research on this is being carried out in our laboratory and will be reported in another paper.

3.3. Reaction mechanism during high-energy ball milling

In a conventional SHS reaction, the powder mixtures are pressed into pellets for propagation of combustion wave. Researchers have demonstrated that the value of $\Delta H_{298}/Cp_{298}$ should be above 2000 K for sustaining the combustion [13].

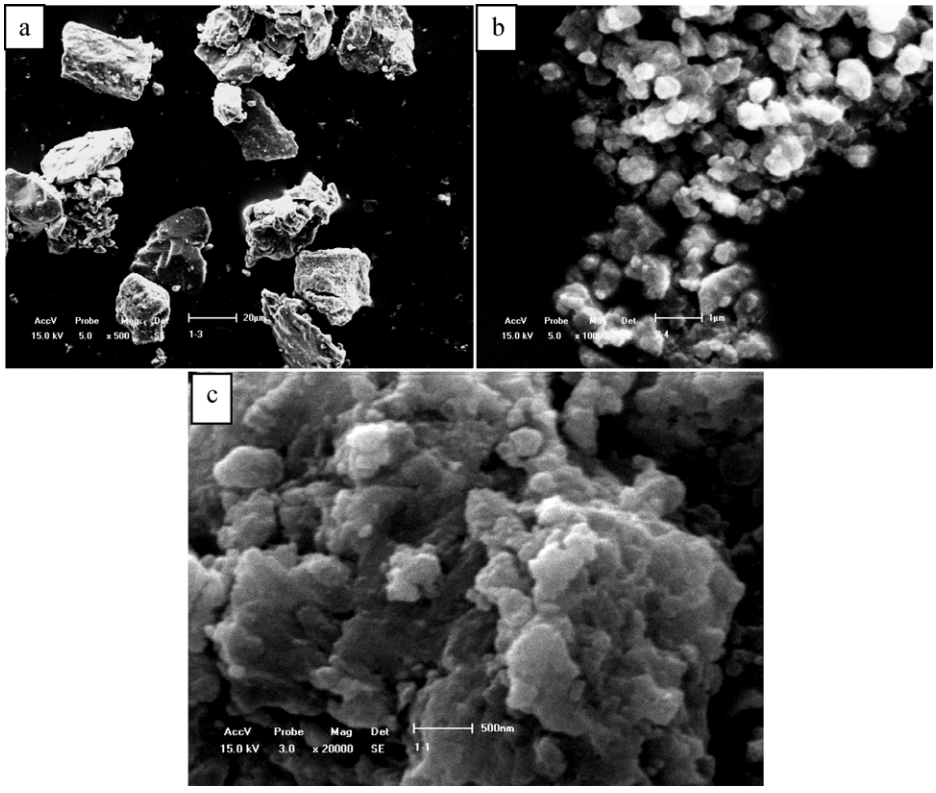

Fig. 3. SEM images of the mixture powders milled for different lengths of time a (0 h); b (4.5 h); and c (24 h).

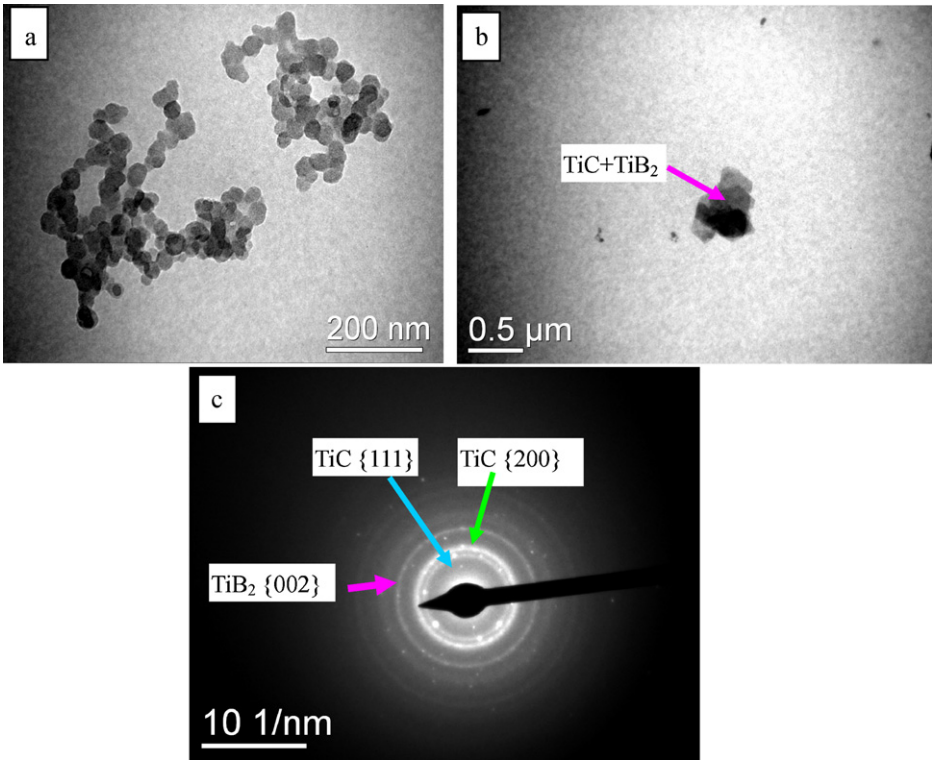

Fig. 4. TEM images of the powder mixtures milled for (a) 48 h, (b) annealed at 800 °C for 30 min and (c) the diffraction pattern of a selected area in (b) (the area marked by arrow).

Some typical combustion reactions are summarized in Table 1 [14]. As shown in Table 1, both the reaction between Ti and C and the reaction between Ti and B can take place the strong self-propagating reactions at high temperatures. In the present experiments, the outermost of the B_4C powder decomposed into B and C during the milling, which provided lots of reaction sources with Ti. Although the powder mixture was loosely dispersed in the vial during the milling, the nanometer reactants favored mass transfer and the diffusion path length was considerably reduced. Furthermore, the refinement of the particle size derived from the ball collusions during the milling could increase the reaction interface area and the activities of the reactants. As a matter of fact, the reaction rate in the system was also dependent on the particle size of the reactants. The ignition events in the powder mixture could be numerous; however, the strong self-propagating reaction did not occur because of a low heat of formation during the milling. Previous investigations show that ignition of the combustion reaction requires an initial premilling period during which ball milling leads to a change in the factors determining the critical combustion condition. Hence, some researchers have proposed that there exists a critical particle size for ignition of the combustion reaction during the high-energy ball milling [10,14]. The TiC phases were not produced until after 24 h of milling and the critical grain size of Ti milled for the reaction was 31.2 nm, which strongly confirmed the results reported above. The reaction for Ti and B_4C during the high-energy ball milling could be postulated as follows:

$$\mathrm{Ti} + \mathrm{B_4C} \rightarrow \mathrm{Ti} + \mathrm{B}\ \ (\text{amorphous}) + \mathrm{C}\ \ (\text{amorphous}) \quad (2)$$

$$\mathrm{Ti} + \mathrm{C}\ \ (\text{amorphous}) \rightarrow \mathrm{TiC} \quad (3)$$

$$\mathrm{Ti} + \mathrm{B}\ \ (\text{amorphous}) \rightarrow \mathrm{TiB_2} \quad (4)$$

Table 1
Typical reactions in high-energy ball milling processing.

Reaction	Heat of formation (kJ mol)	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	3200	Combustive
$4Al + 3C \rightarrow Al_4C_3$	−215.8	1200	Gradual
$Si + C \rightarrow SiC$	−67	1800	Gradual
$W + 2Si \rightarrow WSi_2$	–	1500	Gradual

4. Conclusions

TiB_2/TiC nanocomposite powders were successfully prepared via high-energy ball milling. The formation of TiC and TiB_2 is gradual, in contrast to the conventional synthesis by the SHS reaction. Diffusion played a major role in the formation of the TiC and TiB_2 phases. The formation of TiC appeared within 24 h of milling, earlier than that of TiB_2 because of C atoms diffuse more rapidly in the Ti matrix than do B atoms. Only a minimal amount of TiB_2 was produced even after 48 h of milling. Annealing could accelerate the final formation of TiB_2. The resulting products obtained were composed of nanosized TiC and TiB_2 particles.

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References

[1] D. Vallauri, I.C. Atlas Adrian, A. Chrysanthou, TiC–TiB_2 composites: a review of phase relationships, processing and properties, Journal of the European Ceramic Society 28 (2008) 1697–1713.

[2] I. Song, L. Wang, M. Wixom, Self-propagating high temperature synthesis and dynamic compaction of titanium diboride/titanium carbide composites, Journal of Materials Science 35 (2000) 2611–2617.

[3] G. Wen, S.B. Li, B.S. Zhang, Z.X. Guo, Reaction synthesis of TiB_2–TiC composites with enhanced toughness, Acta Materialia 49 (2001) 1463–1470.

[4] C.L. Yeh, Y.L. Chen, Combustion synthesis of TiC/TiB_2 composites, Journal Alloys and Compounds 463 (2008) 373–377.

[5] Xinghong Zhang, Chuncheng Zhu, Wei Qu, Xiaodong He, V.L. Kvanin, Self-propagating high temperature combustion synthesis of TiC/TiB_2 ceramic–matrix composites, Composites Science and Technology 62 (2002) 2037–2041.

[6] A.P. Radlinski, Calka, Mechanical alloying of high melting point intermetallics, Materials Science and Engineering A 134 (1991) 1376–1379.

[7] K.W. Nihara, New concept of ceramics–ceramics composites, Journal of the Japanese Ceramic Society 99 (10) (1991) 974–986.

[8] A.M. Locci, Roberto Orru, Giacomo Cao, Z.A. Munir, Effect of ball milling on simultaneous spark plasma synthesis and densification of TiC–TiB_2 composites, Materials Science and Engineering A 434 (2006) 23–29.

[9] J.W. Lee, Z.A. Munir, M. Ohyanagi, Dense nanocrystalline TiB_2–TiC composites formed by field activation from high-energy ball milling reactants, Materials Science and Engineering A 325 (2002) 221–227.

[10] N.Q. Wu, S. Lin, J.M. Wu, Mechanosynthesis mechanism of TiC powder, Materials Science and Technology 14 (4) (1998) 287–292.

[11] Jianlin Li, Fei Li, Keao Hu, Yong Zhou, TiB_2/TiC nanocomposite powder fabricated via high energy ball milling, Journal of the European Ceramic Society 21 (2001) 2829–2833.

[12] A.L. Lasker, J.L. Bocquet, F. Brebec, C. Monty, Diffusion in Materials, Kluwer, Dordre, Netherlands, 1990.

[13] Jianlin Li, Fei Li, Keao Hu, Yong Zhou, Formation of TiB_2/TiN/Ti(C_xN_{1-x}) nanocomposite powder via high-energy ball milling and subsequent heat treatment, Journal of Alloys and Compounds 334 (2002) 253–260.

[14] C.J. Smithells, Metals Reference Book, 5th edition, Butterworth, London, 1983.