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Synthesis of TiB_2 by electric discharge assisted mechanical milling

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Abstract

In this study, synthesis of titanium diboride from elemental powders of Ti and B by electric discharge assisted mechanical milling technique was investigated. This recently developed technique has the following advantages: rapid reaction rate, controlled reaction, direct reaction between Ti and B without adding another element into the system and cost effectiveness. TiB_2 samples were prepared using an in-house built reactor with an ac high voltage transformer, generating impulses within kV/mA range. The structures of reaction products were characterized by X-ray diffractometry, and powder morphologies by SEM. X-ray diffraction studies showed that the milling product was TiB_2 with small fraction of TiB.
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1. Introduction

Titanium diboride (TiB_2) is an advanced ceramic material with relatively high strength and durability as characterized by high melting point, hardness, strength to density ratio, and wear resistance. It can withstand an oxidizing atmosphere up to 1000 °C [1–3]. TiB_2 is tough enough to be used as military armor and improves the fracture toughness of ceramic cutting tools and other components. It is also use as a cathodes material in the electro-chemical reduction of alumina to aluminum metal.

TiB_2 maybe hot-pressed (HP) or hot isostatic pressed (HIP) into desired shapes or electro-discharged machined due to its electrical conductivity.

The TiB_2 powders are generally prepared by a borothermic reduction of titania, fused-salt electrolysis, solution phase processing, gas combustion synthesis technique using the gas phase flame reaction and self-propagating high temperature synthesis (SHS) technique [4–8].

In the present work we describe rapid synthesis of TiB_2 using novel electric discharge assisted mechanical milling method (EDAMM) [9].

2. Experimental procedure

Titanium powder of particle size <250 μm and minimum purity of 99.9% was mixed with amorphous boron powder of particle size <50 μm (purity 99.8%) to give composition of TiB_2. Before electric discharge milling experiments Ti and B powders were pre-mixed for 1 h, under high purity argon in conventional laboratory ball mill. Electric discharge milling was performed in a modified vibrational laboratory rod mill. The mill was designed to produce a milling mode combining a repeated impact of a hardened curved rod end on powder particles, placed on a vibrating hemispherical container under electrical conditions of pulsed arc discharges (Fig. 1). The electric discharges were generated during milling in the gaps between the vibrating mill base, the powder particles and a loosely suspended conducting plunger. The power supply used in this study was connected through an ac high voltage transformer, generating impulses within the kV/mA range. During vibration, small gaps between the stainless steel rod and the chamber wall resulted in an arc discharge (Fig. 1). The localized temperature of reacting powder increased by Joule heating generated simultaneously by the electric arc discharge and mixing by the vibrating electrode. Milling was carried in a high purity Ar flowing with the rate 3 m^3/min.

In all experiments we used milling times 2, 5 and 10 min. XRD analysis of the as-milled powders was performed using a Phillips PW1730 diffractometer with a graphite monochromator and Cu Kα radiation. Phase identification was carried out using the International Centre for Diffraction Data (JCPDS-ICDD 2000) powder diffraction files (PDF).

The crystallite size of the powders was estimated using the method of integral breadths as described by Varin et al. [10]. The full width at half maximum (FWHM) values were corrected for instrument broadening using Warren's correction [11–13]:

$$B^2 = B_t^2 - B_i^2 \qquad (1)$$

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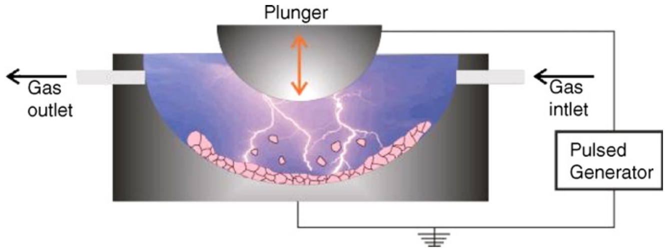

Fig. 1. Schematics of electrical discharge milling device used in this work.

where B is the corrected peak broadening, B_t the total broadening and B_i is the instrumental broadening. The instrumental broadening was determined using the strongest peak from the XRD pattern of a silicon reference sample.

Powder morphologies were characterized using scanning electron microscope (SEM).

3. Results and discussion

Fig. 2 shows the X-ray diffraction patterns of α-Ti and B powders milled for 2, 5, and 10 min (Fig. 2b–d). Diffraction pattern of pre-mixed, starting powder is shown in Fig. 2a. The peaks in this pattern give an excellent match with the International Centre for Diffraction Data powder diffraction file (PDF) card 05-0682 which corresponds to α-Ti. Surprisingly this XRD pattern do not show any boron XRD peaks. The absence of any boron XRD peaks could be due to amorphous nature of the boron powder. The absence of clearly define crystalline structure and much lower mass absorption coefficient of boron in comparison with Ti makes boron very difficult to detect by XRD analysis in the presence of titanium.

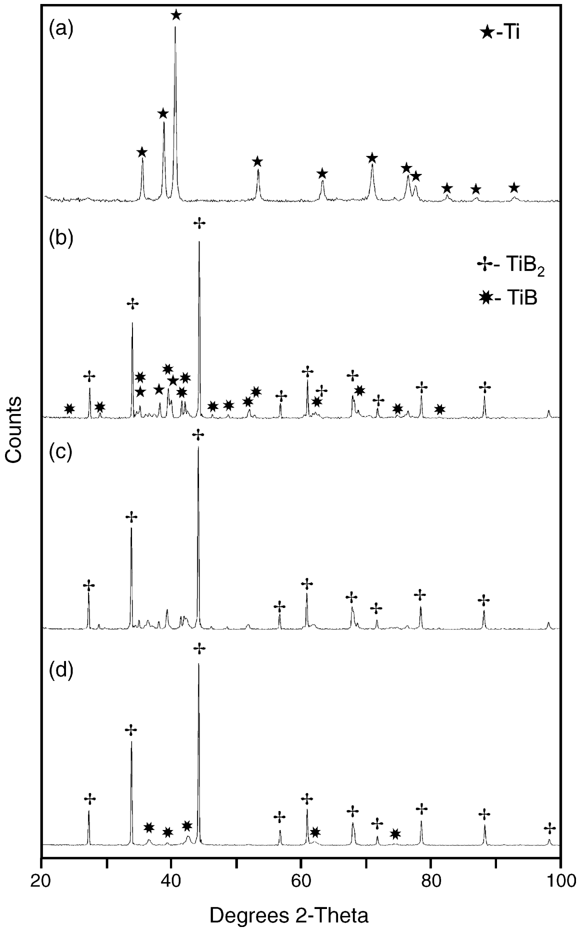

Fig. 2. X-ray diffraction patterns of (a) pre-mixed starting powder, and electric discharge milled for (b) 2 min, (c) 5 min, and (d) 10 min.

Fig. 2b shows that after 2 min of milling the XRD pattern contains strong TiB_2 peaks and weak peaks corresponding to TiB phase and unreacted α-Ti. After milling for 5 and 10 min (Fig. 2c and d) there are only strong TiB_2 and weak TiB peaks. Interestingly TiB peaks become less intense and broader after 10 min of milling indicating nanostructural character of TiB phase. The peak broadening analysis indicates that the TiB crystallite size estimated to be approximately 80 nm.

Fig. 3 shows SEM micrographs of starting powder (Fig. 3a) and milled after 2, 5 and 10 min (Fig. 3b–d). Fig. 3a illustrates microstructure of mixture of irregular large Ti particles and small boron particles. After 2 min of milling the size of Ti particles becomes smaller—below 100 μm. Fig. 3c and d shows powder morphology after 5 and 10 min of milling. One can notice that between 5 and 10 min of milling powder fracturing is much slower than within the first 2 min of milling. Prolonged milling time up to 10 min causes formation of large number of particles about 2 μm in size (Fig. 3d) predominantly in the form of agglomerates.

The phase diagram of the TiB system shows presence of TiB, Ti_3B_4 and TiB_2 phases. Our work shows that TiB_2 phase can be rapidly formed as a result of direct reaction between Ti and B powders.

When the high intensity electric discharge acts on the material, it creates a plasma channels with the localized high temperature areas as a result of Joule heating. The high temperatures in plasma channels accelerate diffusion and in consequence lead to fast reaction between Ti and B within short times. Subsequent rapid quenching in these areas induces supersaturaion of reactants which in turn, leads to formation of compounds with desired chemistry and formation of fine powders as a combined effect of fracturing caused by moving plunger and vapor condensation.

The XRD pattern revealed very low intensity and broad XRD peaks corresponding to TiB phase. Small intensity of these peaks indicate of presence of small volume of this phase.

Broad shape of these peaks indicate nanoscale grain size and/or effect of high lattice strain concentration. We believe that TiB_2 particles are formed as a result of direct diffusion between Ti and B particles. As the process progresses more TiB_2 particles surround Ti particles and towards the end of reaction there are small number of particles that are not in direct contact with Ti surfaces which may lead to formation of TiB areas as a result of much slower diffusion of Ti through TiB_2 phase. If TiB areas are formed within TiB_2 particles with different coefficient of thermal expansion value this may lead to additional generation of internal lattice strain which may contribute to the XRD peak broadening.

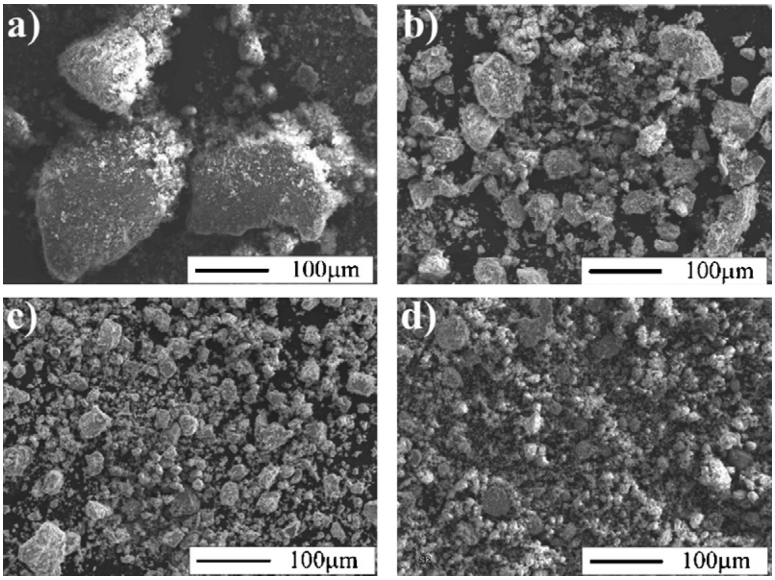

Fig. 3. Scanning electron micrographs of (a) pre-mixed starting powder, and electric discharge milled for (b) 2 min, (c) 5 min, and (d) 10 min.

4. Conclusions

It was found that milling of Ti and B elemental powders, in electric discharge assisted milling device, results in almost complete transformation into TiB_2 after milling for 10 min. This demonstrate that application of electric discharge in mechanical milling dramatically enhance reaction rate presumable to high local temperatures generated by electric discharges which in consequence speeds up diffusion. XRD peaks intensities indicate presence of large volume of TiB_2 and small volume of TiB phases in nanocrystalline form. Prolonged milling time up to 10 min causes formation of large number of particles about 2 μm in size predominantly in the form of agglomerates.

Acknowledgement

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