Int. Journal of Refractory Metals and Hard Materials 29 (2011) 244–249

Contents lists available at ScienceDirect

Int. Journal of Refractory Metals and Hard Materials

journal homepage: www.elsevier.com/locate/IJRMHM

Mechanochemical synthesis of Al_2O_3–TiB_2 nanocomposite powder from Al–TiO_2–H_3BO_3 mixture

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ARTICLE INFO

Article history:
Received 5 October 2010
Accepted 7 November 2010

Keywords:
Al_2O_3–TiB_2
Nanocomposite
Mechanochemical
MSR reaction

ABSTRACT

Alumina–titanium diboride nanocomposite (Al_2O_3–TiB_2) was produced using mixtures of titanium dioxide, acid boric and pure aluminum as raw materials via mechanochemical process. The phase transformation and structural characterization during mechanochemical process were utilized by X-ray diffractometry (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and thermogravimetric analyses (TG–DTA) techniques. A thermodynamic appraisal showed that the reaction between TiO_2, B_2O_3 and Al is highly exothermic and should be self-sustaining. XRD analyses exhibited that the Al_2O_3–TiB_2 nanocomposite was formed after 1.5 h milling time. The results indicate that increasing milling time up to 40 h had no significant effect other than refining the crystallite size.

1. Introduction

Titanium diboride has an attractive combination of high Vickers hardness, electrical conductivity, excellent chemical resistance to molten nonferrous metals and relatively low specific gravity [1,2]. However, titanium diboride has poor mechanical properties such as fracture toughness and impact strength. The composites of TiB_2 such as TiB_2–Al_2O_3 improve those mechanical properties. Therefore, TiB_2–Al_2O_3 composites are useful in variety of applications such as cutting tools, wear-resistant substrates, and lightweight armor [3–5].

Titanium diboride and its composites can be produced by several techniques, which include reduction of the metal oxide with carbon [3], self propagating high temperature synthesis (SHS) [6], pressureless metal infiltration (PRRIMX) [7], mechanical alloying [8], direct metal oxidation method (DIMOX) [9], borothermic reduction of metal oxide and boron oxide [10], reaction between elemental powders [11], and magneziothermic or aluminothermic reduction of metal oxide–boron oxide mixture [12]. Recently, mechanical activation and mechanical milling have been extensively used for preparing and synthesis of composites powders as well as advanced materials [13–16]. Mechanochemistry is concerned with the physical and/or chemical changes of materials caused by mechanical energy. During mechanical milling repeated welding and fracturing of powder particles increase the area of contact between the reactant powder particles due to a reduction in particle size and allow fresh surfaces to come into contact repeatedly; this allows the reaction to proceed without the necessary diffusion through the product layer which enhances the formation of new compounds, amorphization of the crystalline structures, phase transformation and formation of chemical reaction (mechanochemistry process) [17–19].

Since the level of contamination increases if the powder is milled for times longer than required, it is advantageous that the powder mixture is milled just for the required duration. Recently, Al_2O_3–TiB_2 nanocomposite was produced after 60 h of milling [8], while in this research, the possibility of mechanochemical synthesis of Al_2O_3–TiB_2 nanocomposite during short milling times using raw materials of titanium dioxide, acid boric and pure aluminum is discussed.

2. Experimental procedures

Titanium dioxide (TiO_2, Merck, 99% purity–mean particle size 3–5 μm), aluminum powder (Al, Merck, 99% purity–mean particle size between 50 and 30 μm) and acid boric (H_3BO_3, Merck, 99.95% purity–particle size between 30 and 20 μm) were used as raw materials. The mixture of raw materials was prepared in accordance with the stoichiometry given by the following reaction:

$$2H_3BO_3 \rightarrow B_2O_3 + 3H_2O \qquad (1)$$

$$3TiO_2 + 3B_2O_3 + 10Al \rightarrow 3TiB_2 + 5Al_2O_3 \qquad (2)$$

A planetary type ball milling was used in milling experiments. Preliminary experiments indicated that the following conditions were appropriate: 600 rpm, five 20 mm diameter high Cr-Steel balls in a high Cr-Steel milling chamber gave a ball-to-powder weight ratio

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0263-4368/$ – see front matter
doi:10.1016/j.ijrmhm.2010.11.001

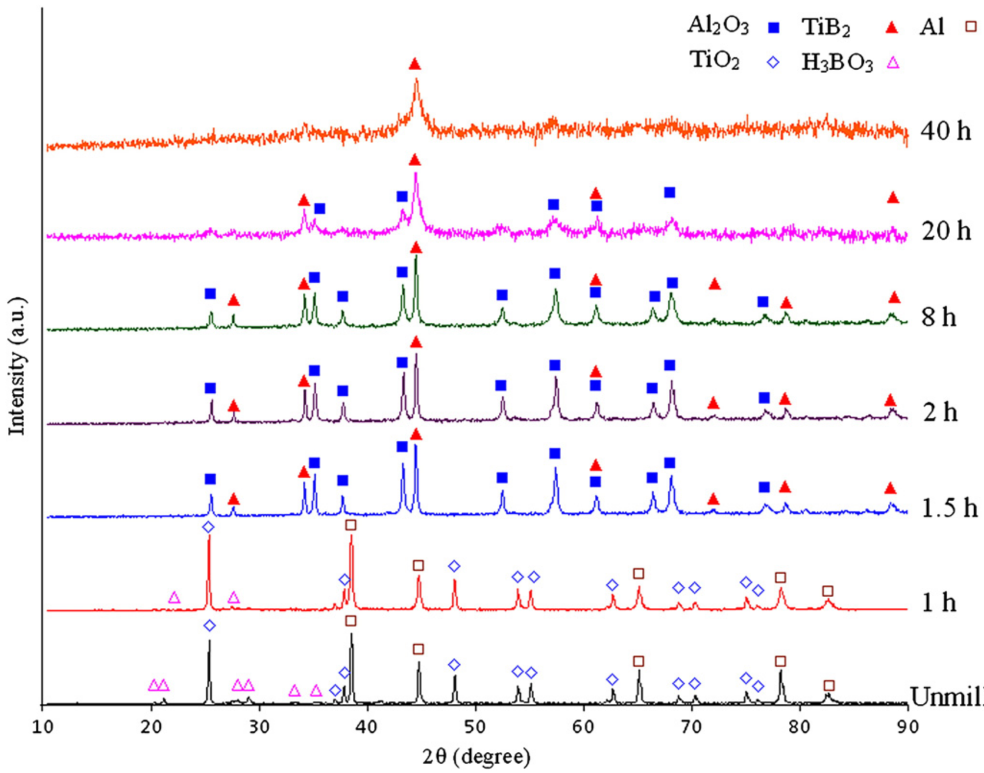

Fig. 1. The XRD patterns of the unmilled sample and a stoichiometric mixture of Al–H_3BO_3–TiO_2 milled for 1, 1.5, 2, 8, 20, and 40 h.

(BPR) 20:1. The milling runs were undertaken in an argon atmosphere (99.9% purity). Phase analysis was performed XRD using *Cu Kα* radiation with a step size of 0.05° and a scan rate of 3 s. An LEO 435VP scanning electron microscope was used. The sample for TEM was prepared by suspending the powder sample in ethanol and subjecting it to ultrasonic vibration. A drop of the suspension was then placed on a carbon-coated copper grid and dried. The powder sample mounted on the copper grid was studied using a 100 kV Philips CM10 transmission electron microscope. The physio-chemical change of synthesis systems during heating was studied by thermal analyses (TG–DTA; model STA 409 PC LUXX) under argon atmosphere with 30 ml/min argon flow and a heating rate of 5 K/min.

3. Results and discussion

3.1. Phase analysis and structural features (XRD analysis)

Fig. 1 shows the XRD patterns of the unmilled and milled samples for 1, 1.5, 2, 8, 20 and 40 h. Only sharp characteristic peaks of TiO_2 (JCPDS; 01-084-1286), Al (JCPDS; 01-085-1327) and H_3BO_3 (JCPDS; 00-033-0596) could be detected in an XRD pattern of unmilled and powder mixture milled for 1 h.

According to the XRD profile, the products of mechanochemical process after 1.5 h of milling were Al_2O_3 (JCPDS; 00-011-0661) and TiB_2 (JCPDS; 00-035-0741) phases. The peaks related to Al_2O_3 and TiB_2 phases are almost narrow and sharp especially in low angle diffraction ($2\theta<60°$). This suggests that the temperature reached during the reaction was sufficient to induce crystallization of the products. In addition, the absence of any reactant peaks confirms that the reaction is completed within 1.5 h. Mohammad Sharifi et al. [8] have reported that the Al_2O_3–TiB_2 composite is produced after 60 h of milling (BPR: 10/1 and rotational speed of vial: 500 rpm). However, our experimental results confirm that after 1.5 h of milling (BPR: 20/1 and rotational speed of vial: 600 rpm) the outcome is high crystalline Al_2O_3–TiB_2 composite. This conspicuous variation is justified by milling conditions. For the synthesis of nanostructured materials via mechanochemical process, the transition of impact energy is vital. Increased milling energy, which is obtained by higher ball-to-powder weight ratio (BPR) and increased speed of rotation, introduces more strain and expansion the defect concentration in the powder, thereby leading more readily to amorphization. From another point of view, higher milling energies can also produce more heat, resulting in crystallization of the amorphous phase. A balance between these two effects will determine the nature of the final product phase [20]. Therefore, the milling speed and ball-to-powder weight ratio are important parameters which can affect the required time for the mechanosynthesis of the nanocomposites with low level of contamination and appropriate structural features.

To investigate the effect of milling time on the products, the milling runs were undertaken in different times. It is clear that increasing milling time beyond 2 h does not have any significant effect. Indeed, all peaks become less intense and broader as would be expected as the crystallite size becomes smaller with increasing milling time. Up to 2 h of milling, the major peaks for Al_2O_3 and TiB_2 decrease in intensity, so that peaks corresponding to Al_2O_3 disappear

Table 1
Average crystallite size and lattice strain of the powder mixture.

Sample	Milling time (h)	Crystallite size (nm)			Lattice strain (%)		
		Al	H_3BO_3	TiO_2	Al	H_3BO_3	TiO_2
I	Unmill	44	42	57	0.228	0.460	0.287
II	1	35	28	42	0.284	0.692	0.383