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EFFECT OF MILLING TIME ON MECHANOCHEMICAL SYNTHESIS OF NANOCRYSTALLINE ZIRCONIUM DIBORIDE

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Abstract. Zirconium diboride (ZrB_2) is the material suitable for high performance applications. It has high melting point and high hardness value. On the other hand, recently, mechanical activation and mechanical milling have been extensively used for synthesis of advanced materials. In this present research, nanocrystalline ZrB_2 was produced using mixtures of zirconium dioxide, boric acid and pure magnesium as raw materials via mechanochemical process. The phase transformation and structural evolution characterization during process were utilized by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. A thermodynamic appraisal showed that the reaction between ZrO_2, H_3BO_3 and Mg is highly exothermic and should be self-sustaining. XRD analyses exhibited that the nanocrystalline ZrB_2 was formed after 60 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

Zirconium diboride (ZrB_2) is the material suitable for high performance applications. It has high melting point (3250°C) and high hardness value (36 GPa) [1]. This material also has high resistance to oxidation at elevated temperatures, an excellence chemical resistance. It has several applications such as in nose caps, rocket nozzle inserts, air-augmented propulsion system compounds, evaporation boats, cutting tools, cathode material for Al extraction, etc. [2].

One possible route for producing the fine and homogenous distribution of hard particles in composite microstructure is the mechanochemical processing in which ball milling promotes the reaction in a mixture of reactive powders.

Enhanced reaction rates can be achieved during high-energy milling as a result of microstructural refinement and mixing processes accompanying repeated fracture, cold welding and deformation of particles during collision events [3, 4]. This technique can lead to formation of interpenetrating phase composites with nano-sized microstructures. An important characteristic of such phases is that they exhibit very improved properties and performance over their conventional microcrystalline counterparts [4, 5].

Hence, in view of the advantages and applications of ZrB_2 powder and the successful application of mechanochemical processing for preparing nanocrystalline powders, it is meaningful to study if nanocrystalline ZrB_2 powder can be synthesized by this process. Here, we report the preparation of ZrB_2 powder via mechanochemical reaction between ZrO_2, H_3BO_3 and Mg which has not been previously studied. This article demonstrates the formation of ZrB_2 by ball milling a mixture of oxides and pure magnesium with the stoichiometry of reaction (1):

$$ZrO_2 + 2H_3BO_3 + 5Mg = ZrB_2 + 5MgO + 3H_2O \uparrow, \qquad \Delta H^{\circ}_{298} = -957.7 \text{ kJ/mol} \qquad (1)$$

The negative value of ΔH°_{298} suggests that this reaction is exothermic and should be self-sustaining [6].

2. Experimental

The starting materials consisted of ZrO_2 (Merck Chemicals, 99 % pure), H_3BO_3 (Merck Chemicals, 99 % pure) and Mg (Merck Chemicals, 99 % pure).

The powders were mixed in the stoichiometric ratio based on the following reaction (1). Ball milling of powder mixture was carried out in a planetary ball mill at room temperature and under argon atmosphere. Milling medium was hardened chromium steel vial (150 ml) with seven hardened carbon steel balls (15 mm).

The ball-to-powder weight ratio and the rotational speed of vial were 15:1 and 300 rpm, respectively. The milling was interrupted at selected times and a small amount of powder was removed for further characterizations. Phase transformation during milling were determined by X-ray diffraction (XRD) in a Philips X'PERT MPD diffractometer using filtered Cu Kα radiation ($\lambda = 0.15406$ nm). The morphology and microstructure of milled powder particles were examined by SEM images in a Philips XL30 at an accelerating voltage of 30 kV.

The sample for transmission electron microscopy (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 EM208S transmission electron microscope. Crystallite size and internal strain of specimens were calculated from broadening of XRD peaks using the Williamson-Hall method [7].

$$\beta_s \mathrm{Cos}\theta = \mathrm{K}\lambda / \mathrm{d} + 2\varepsilon \mathrm{Sin}\theta, \qquad (2)$$

where θ is the Bragg diffraction angle, d is the average crystallite size, ε is the average internal strain, λ is the wavelength of the radiation used, and β is the diffraction peak width at half maximum intensity. The average internal strain can be estimated from the linear slope of β Cosθ versus 2 Sinθ while the average crystallite size can be estimated from the intersection of this line at Sin$\theta = 0$.

3. Results and discussion

XRD results of as-milled powders are shown in Fig. 1. XRD patterns of powder mixture up to 40 h of milling time were identified as a mixture of starting materials. No peak shift was observed for starting materials, indicating that no solid solution was formed during milling process [6].

This result indicates that ball milling up to 40 h had no effect on as-received powder mixture except broadening of Bragg peaks which is caused by reduction of the crystallite size as well as microstrain induced in the powder particles. Reducing the crystallite size to nanometer range and increasing the defect densities can promote the reaction kinetically by providing short circuit diffusion paths [4].

After 20 h of milling it is clear that the major phase present are the starting tetragonal zirconia (t-ZrO_2).

After milling for 60 h the reaction was apparently complete with only peaks for MgO and ZrB_2 present. The presence of ZrO_2 indicates that the reaction to form ZrB_2 was incomplete. In any process for the formation of ZrB_2 it would be necessary to ensure that all of the ZrO_2 is consumed by reaction as ZrO_2 is difficult to remove by dissolution.

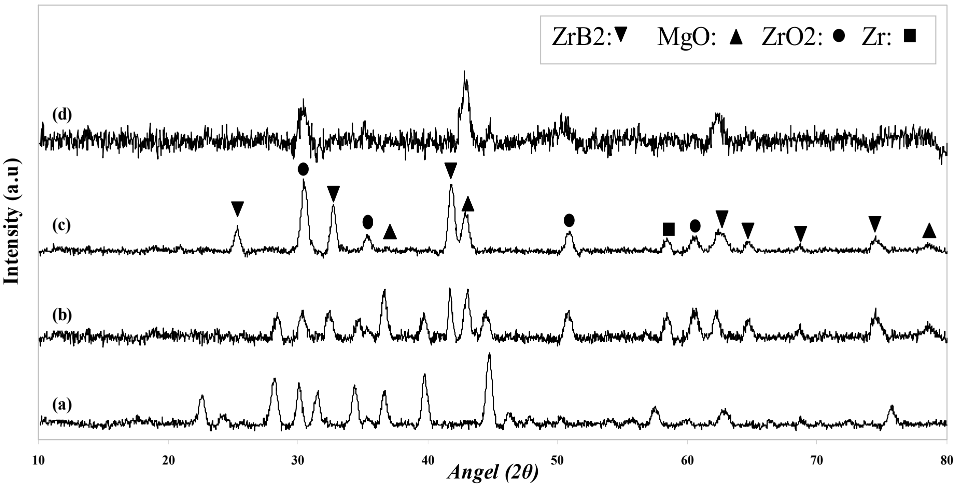

Fig. 1. XRD patterns taken from the mixtures after
(a) 20, (b) 40 h, (c) 60 h, and (d) 80 h of milling process.

This could be achieved by using a stoichiometric excess of both Mg and H_3BO_3 in any process [8].

At the beginning of the milling process, the ductile powders (Mg and ZrO_2) got flattened by milling media collisions, while the brittle particles (H_3BO_3) got fragmented and comminuted.

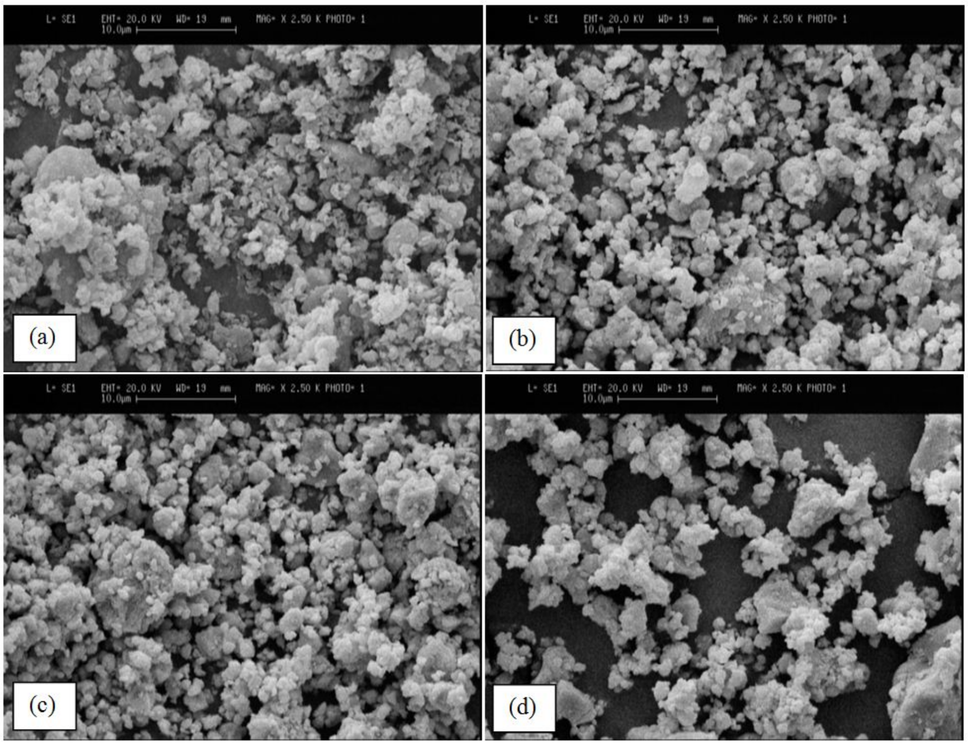

Fig. 2. SEM micrographs of starting powders particles after
(a) 20 h, (b) 40 h, (c) 60 h, and (d) 80 h of milling times.

Figure 2 shows morphology of powder particles after different milling times. Figure 2a shows that after 20 h of milling time, the magnesium and zirconia powder particles are extensively flattened.

After 40 h (Fig. 2b), the powder particles became nearly equiaxed in shape with a wide size distribution of 2-8 μm. By increasing milling time to 60 h, due to work hardening of starting powders, the rate of fracturing increased and as a result the size of powder particles decreased. At this stage, the morphology of powder particles was almost equiaxed (Fig. 2c).

The powder particles after 80 h of milling time are large agglomerates of ultrafine particles ranging from 800 nm to 8 μm (Fig. 2d). Further milling up to 80 h led to a significant decrease in agglomerate and particle sizes because of fragmentation of the brittle constituent phases, MgO and ZrB_2.

The leaching process tests were carried out by using a solution of 2 M HCl at a temperature of about 90 ºC for 30 min. It could be observed that with a complete MgO elimination, a small amount of ZrB_2 is also dissolved which could be due to its small crystallite sizes [9, 10]. MgO dissolution reaction in HCl acid solution is shown in Eq. (3):

$$MgO + 2HCl = Mg^{2+} + 2Cl^{-} + H_2O. \tag{3}$$

The solution was filtered after leaching and the purified products were washed by distilled water for several times to eliminate extra HCl acid until the pH value is about 7.
At the end, the products were dried in air oven at 353 K for 1 h.

The average crystallite size of ZrB_2 in the microstructure of the best sample (the mixture which was milled for 60 h) was calculated 65.7 nm that were confirmed by transmission electron microscopy (TEM) images.

The TEM images of milled powders (after 60 and 80 h respectively) are shown in Figs. 3 and 4. It is observed that, the products are made up of nanosized particles ranging from 70 to 120 nm.

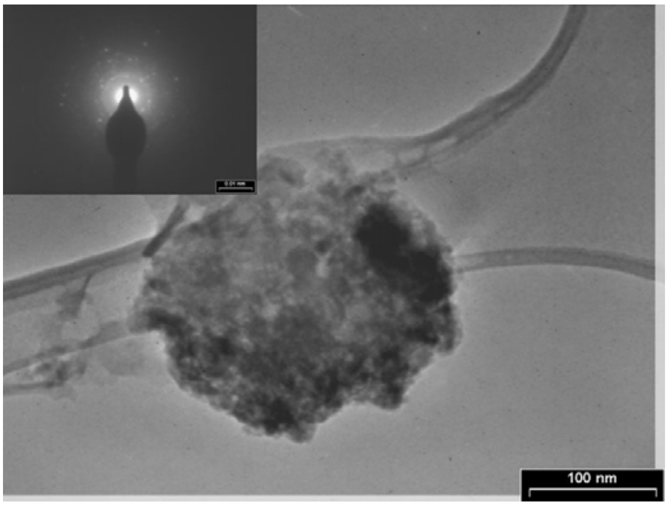

Fig. 3. TEM image of starting powders particles after 60 h of milling time**.**

As can be seen, a relatively good agreement exists between the grain size of the phases estimated from TEM observation and that of XRD analysis using Williamson–Hall method.

It also shows presence of agglomeration of spherical particles and the particle size increases with increasing of milling time. The corresponding selected area diffraction patterns (SADP) show presence of mirror images of dots (inset of Fig. 3 and Fig. 4), which indicate that the formation of nanocrystalline particles.

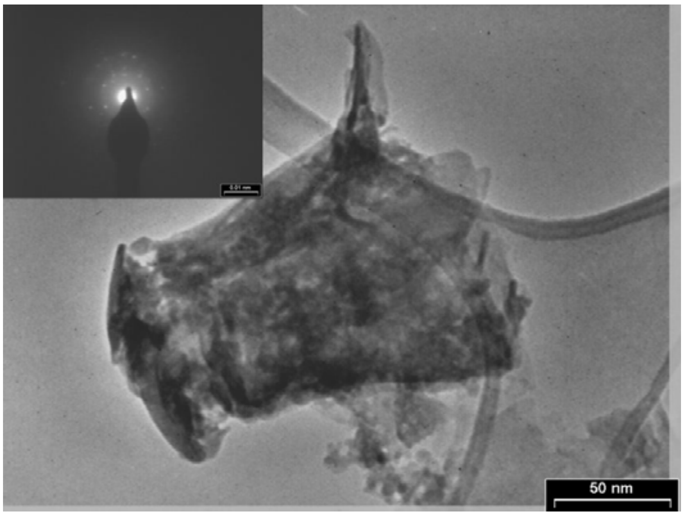

Fig. 4. TEM image of starting powders particles after 80 h of milling time.

4. Conclusions

Zirconium diboride has been synthesised by a low temperature solid-state reaction between zirconium dioxide, boric acid and elemental magnesium. The reaction was found to occur during ball milling in a tumbling mill with a gradual conversion from ZrO_2 to ZrB_2 during milling. The results indicate that increasing milling time up to 40 h had no significant effect other than refining the crystallite size. The conversion was almost complete after 60 h milling and the concomitantly formed MgO was selectively separated by a simple acid leaching step leaving behind an essentially pure ZrB_2.

Acknowledgments

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