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# Formation of zirconium diboride (ZrB<sub>2</sub>) by room temperature mechanochemical reaction between ZrO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and Mg

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#### Abstract

A mixture of magnesium, boric oxide and zirconium dioxide were mechanically milled under argon for up to 15 h in a laboratory scale ball mill. X-ray diffraction showed that there was an increasing conversion of  $ZrO_2$  to  $ZrB_2$  with milling time with >98% reaction after 15 h. Differential thermal analysis revealed there were multiple, overlapping reactions all of which seemed to be formation of  $ZrB_2$ . The energy evolved decreased with milling time and the sample after 15 h milling showed no thermal reaction. After milling, separation of the  $ZrB_2$  from the coproduct MgO was easily achieved by a mild acid leaching leaving essentially pure  $ZrB_2$  with a crystallite size of ~75 nm. © 2005 Elsevier B.V. All rights reserved.

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## 1. Introduction

The diborides of titanium (TiB<sub>2</sub>) and zirconium (ZrB<sub>2</sub>) are materials suitable for high performance applications. They have high melting points (3200 and 3250 °C) and high hardness values (30.0 and 36.0 GPa), respectively. These materials also have high resistance to oxidation at elevated temperatures, an excellence chemical resistance to HCl and HF and are stable in metal melts (Al, Cu, Mg, Zn, Cd, Fe, Pb), cryolite and nonbasic slags [1–3]. Composites using zirconium diboride with alumina have mechanical strengths similar to that of a titanium diboride–alumina composite [4,5] but are resistant to higher temperatures.

The self-propagating-high temperature synthesis (SHS) process is one advanced method which has been used extensively for preparing refractory materials such as carbides, silicides, nitrides and various composite materials [6,7]. Mishra et al. synthesised a zirconium diboride–alumina composite by SHS process of a milled and pelletised mixture of zirconium oxide, aluminium and boron oxide [3]. Radev and Klissurski used pure elemental zirconium and boron to synthesis zirconium diboride by SHS [8]. However, the use of elemental Zr and B is much more expensive than using the oxides due to the high cost of extracting metals from the minerals. A similar argument regarding costs can be made for recent processes which use complex polymeric metal alkoxides or air and moisture sensitive materials, such as borazine, as the precursors [9,10]. These preparations also require pyrolysis before the required phases are formed.

Recently, there have been a number of studies on ambienttemperature reduction reactions which occur during extended ball milling to form ceramic products [11–13]. Welham synthesised <200 nm, single crystal particles of titanium diboride after 15 h of milling of a mixture of titanium dioxide, boron oxide and pure magnesium [14]. The use of magnesium as the reactant instead of aluminium allowed acid leaching of the unwanted oxide product leaving behind a pure boride phase. As there was no product at 10 h but complete reaction at 15 h the reaction was thought to have required an incubation time before becoming self-propagating. The particles formed were clearly faceted crystals which implies a high temperature must have been present in the mill during reaction.

This article demonstrates the formation of zirconium diboride by ball milling a mixture of oxides and pure magnesium with the stoichiometry of reaction (1):

$$ZrO_2 + B_2O_3 + 5Mg = ZrB_2 + 5MgO$$
$$\Delta H = -957 \text{ kJ at } 25 \text{ }^{\circ}\text{C}$$
(1)

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The highly exothermic nature of the reaction could be used to monitor the progress of the reaction by measuring the vial temperature as a function of time. The temperature would be expected to change regardless of reaction, primarily due to friction and impact energy transfer due to the motion of the balls. By this mechanism, the temperature would be expected to rise until heat loss by conduction (along the drive shaft), convection (natural and due to mill rotation) and radiation were equal to the physical energy generated. This would be expected to be a fairly constant rise.

For a self-propagating reaction, a single large temperature spike would be expected after the required incubation time as all exothermic energy would be evolved within a few seconds. For the 7.0 g of reactant mixture used a total of 21.7 kJ of energy would be release by the complete reaction. If this energy is used to adiabatically heat the product and milling vial ( $\sim 2.5$  kg) from 25 °C, the equilibrium temperature would be 44.3 °C. However, if the reaction proceeds at a constant rate, then there would be no spike, simply more rapid attainment of an equilibrium temperature.

### 2. Experimental

Mixtures of raw materials were prepared in accordance with the stoichiometry given by reaction 1 (39.2 wt.%  $ZrO_2$ , 22.1 wt.%  $B_2O_3$  and 38.7 wt.% Mg). Seven grams was loaded into the mill with five 25.4 mm diameter stainless steel balls giving a ball to powder mass ratio of 43:1. The vial was evacuated to  $10^{-2}$  Pa then backfilled with argon to prevent oxidation of the magnesium and placed onto the mill drive where it was run at 165 rpm for up to 15 h. An infrared thermometer was used to monitor the temperature of the milling vial.

After milling, samples were heated to  $1000 \,^{\circ}$ C in an alumina crucible at  $20 \,^{\circ}$ C/min under a flowing argon ( $100 \,$ mL/min) atmosphere using a differential thermal analyser (DTA). Simultaneous thermogravimetry revealed no mass losses were associated with the experiments.

The magnesium oxide and any residual magnesium and/or boron oxide were removed by leaching the as-milled powder in 10% hydrochloric acid for 1 h. The solution was decanted after leaching and deionized water was added to wash the solids and the residue dried in air. All of the products were analysed by XRD using Co K $\alpha$  radiation over a range of 20–80° 2 $\theta$ , using a step size of 0.1° and 3 s counting time per step.

# 3. Results and discussion

The temperature of the vial with increasing milling time is shown in Fig. 1. Apart from the expected underlying increase the major feature is a rise at 115 min, clearly, there is an exothermic reaction occurring, although the temperature rise of just over  $3^{\circ}$ C implies the reaction was relatively minor. Samples were milled for 115 and 130 min and the products analysed by XRD. However, no discernible differences between these traces were observed indicating the reaction was relatively minor. After this peak there are no more clearly defined thermal events which imply that the majority of the reaction was gradual rather than self-propagating as in the case of TiB<sub>2</sub>.

The DTA data presented in Fig. 2 shows that there were no thermal events in the sample milled for 15 h, clearly, the reaction was at its maximum extent after milling. The sample milled for 8 h showed an exotherm starting at around 400 °C, XRD of the residue showed a greater conversion of  $ZrO_2$  than in the as-milled powder, but the reaction was still incomplete. This is



Fig. 1. Milling vial temperature as a function of time.

slightly surprising as there is no apparent endotherm at 650 °C where any residual Mg would melt. The 2 h milled sample also shows an exotherm starting around 400 °C but it was somewhat wider than that after 8 h milling, this is a complex exotherm indicating that the conversion of ZrO<sub>2</sub> was not a simple process. The reaction was clearly slowing above about 520 °C but reignited around 650 °C, this was probably due to an increase in interfacial reaction area due to the melting of Mg. A final exotherm is also evident above ~750 °C. XRD of the residue showed increased conversion of ZrO<sub>2</sub> compared with the as-milled powder, but less than the 8 h as-milled powder. In all cases, the residue after heating contained both monoclinic and tetragonal ZrO<sub>2</sub>, with tetragonal becoming increasingly dominant with milling time.

It has been shown previously [14,15] that a self-propagating reaction results in a narrow and very intense exothermic peak during DTA due to the near instantaneous combustion of the entire sample. In Fig. 2, the presence of multiple, broad, relatively small exotherms is indicative of a system which reacted



Fig. 2. Differential thermal analysis of the as-milled powders. Data has been normalised to the same mass and then offset for clarity.



Fig. 3. XRD traces of powders milled for up to 15 h. Also shown are traces for 15 h milled samples heated to  $1200 \,^{\circ}$ C and as-milled powder leached for 1 h in 0.1 M HCl.

gradually and therefore would not be expected to undergo selfpropagation since the rate of release of energy is too low to heat any nearby reactants beyond the temperature required for ignition.

XRD traces of as-milled powders are shown in Fig. 3. After 2 h of milling it is clear that the major phases present are the starting tetragonal zirconia (t-ZrO<sub>2</sub>) and elemental magnesium. The absence of peaks for B<sub>2</sub>O<sub>3</sub> is not unexpected as the starting B<sub>2</sub>O<sub>3</sub> showed no discernible peaks, just a broad peak around 30° indicating a glassy phase. There was a small peak at 50.3° due to MgO, however, this could have formed by oxidation of the milled magnesium on exposure to atmosphere after milling. The presence of peaks for ZrB<sub>2</sub> at 29.6°, 38.6° and 48.8° indicate that some reaction had occurred.

Extending the milling time to 8h showed the reaction was more extensive with peaks for the starting phases weakening as those for ZrB<sub>2</sub> and MgO intensified. After milling for 15 h the reaction was apparently complete with only peaks for MgO and ZrB<sub>2</sub> present. XRD of the sample heated to 1200 °C, Fig. 3, showed narrowed and intensified peaks for the product phases. Also present were a weak peak at  $33^{\circ}$  due to t-ZrO<sub>2</sub> and a slightly stronger peak at 35.3° which can be attributed to monoclinic m-ZrO<sub>2</sub>. The latter polymorph of  $ZrO_2$  is formed by thermal transformation of the tetragonal form, this transformation may have been enhanced by the smaller crystallites formed during milling [16-20]. The presence of ZrO<sub>2</sub> indicates that the reaction to form ZrB<sub>2</sub> was incomplete. The absence of a melting endotherm for Mg in the 15 h DTA trace in Fig. 2 implies there was insufficient Mg to complete the reduction of ZrO<sub>2</sub>. In a practical application of this process excess Mg and B<sub>2</sub>O<sub>3</sub> would be used to account for this.

The absence of any unattributed peaks in the XRD traces would imply that the reaction occurred by reaction (1) without any formation of intermediate phases.

Profile fitting using Powder Cell [21] was carried out for the three milling times and the relative abundances of the four phases (ZrO<sub>2</sub>, Mg, ZrB<sub>2</sub> and MgO) determined. From the data for zirconium phases the fraction of Zr present as ZrB<sub>2</sub> was estimated



Fig. 4. Fraction of zirconium present as ZrB<sub>2</sub>.

and this data is presented in Fig. 4. This graph reinforces the gradual nature of the reaction with conversion of  $ZrO_2$  to  $ZrB_2$  being a direct function of milling time.

The non-zero intercept of the linear fit indicates that in the early stages there is a disproportionate rate of formation of  $ZrB_2$ . This not entirely unexpected since in the early stages particles of  $ZrO_2$ ,  $B_2O_3$  and Mg are more likely to react as the particle surfaces will be fresh. After some time the particle surfaces will be composed primarily of product thereby decreasing the probability of reaction.

The gradual nature of this reaction is clearly different to the analogous formation of  $TiB_2$  from  $TiO_2$  reported previously [14]. The milling equipment and conditions were identical yet  $TiB_2$  formed by a high temperature process while  $ZrB_2$  formed gradually.

Thermodynamically, reaction (1) has a free energy of -3.0 kJ/g and an enthalpy of -3.0 kJ/g, the same reaction for TiO<sub>2</sub> has a free energy of -3.8 kJ/g and enthalpy of -3.9 kJ/g all at 25 °C. Thus, for the same mass of starting mixture, TiO<sub>2</sub> is more favourable and produces more energy than ZrO<sub>2</sub>, yet the rate determining step is apparently different. If it is assumed that the energy generated by reaction (1) is used to heat the reactants, then a temperature of >1000  $^{\circ}$ C is obtained for both TiO<sub>2</sub> and  $ZrO_2$  systems. For TiO<sub>2</sub> this is above the ignition temperature of 1 h milled powder [14] and above the exotherms for ZrO<sub>2</sub> shown in Fig. 2. Consequently, once initiated, the reaction could be expected to be self-propagating, leading to a near instantaneous reaction within the mill. Therefore, it seems that for the TiO<sub>2</sub> system the ignition temperature for the mixture was attained but not in the ZrO<sub>2</sub> system. However, it could be argued that there was a minor stage of self-propagation where the mill heated up, as shown in Fig. 1, however, the extent of this reaction remained low and the remaining ZrO<sub>2</sub> reacted gradually.

Dissolution of the residual Mg and product MgO was readily achieved using 0.1 M HCl, the XRD trace of the leached product after 15 h milling is shown in Fig. 3. Clearly, the major phase present in the solid residue is ZrB<sub>2</sub>, although the small peak at 33.3° is due to unreacted ZrO<sub>2</sub>. Determination of the unit cell size of the ZrB<sub>2</sub> formed was made on the peaks up to  $2\theta = 80^{\circ}$  using UnitCell [22], the obtained values, with error in parentheses, were a = 0.31655(1) nm and c = 0.35265(1) nm. These are slightly smaller than the published values of 0.316870(8) and 0.353002(10) nm [23] which are used in the Powder Diffraction File. Crystallite size determination using the Scherrer equation indicated a size of ~75 nm.

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. This could be achieved by using a stoichiometric excess of both Mg and  $B_2O_3$  in any process. A previous attempt to make MgB<sub>2</sub> by magnesium reduction of  $B_2O_3$  was unsuccessful with no reaction evident even after heating a 50 h milled sample to 1200 °C so any excess of these phases would remain once the  $ZrO_2$  had been consumed and be dissolved along with the MgO product.

The mill used in these investigations is known to be extremely inefficient and a more efficient device would be expected to lead to a substantially shorter milling time. This has recently been demonstrated [24] with milling times of around 1 h required to achieve the same result as between 10 and 15 h milling in the mill used here [14]. Thus, it seems probable that formation of  $ZrB_2$  can be achieved more rapidly than in this paper. It may also be that a more rapid induction of  $ZrB_2$  observed in the TiB<sub>2</sub> system.

# 4. Conclusions

Zirconium diboride  $(ZrB_2)$  has been synthesised by a low temperature solid-state reaction between zirconium dioxide, boron oxide 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 conversion was almost complete after 15 h milling and may have been hindered by a slight sub-stoichiometry in Mg. The concomitantly formed MgO was selectively separated by a simple acid leaching step leaving behind an essentially pure  $ZrB_2$  powder.

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