Preparation of TiB$_2$ and ZrB$_2$. influence of a mechano-chemical treatment on the borothermic reduction of titania and zirconia

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TiB$_2$ and ZrB$_2$ have been synthesized by a mechano-chemical treatment of a mixture of titania or zirconia powder and amorphous boron followed by a relatively low temperature annealing (1100 °C). Both the temperature and the kinetics of the borothermic transformations are affected by the mechano-chemical treatment when the size of the particles obtained after thermal annealing of the sample milled for a short time remains in the sub-micron range. The reaction paths are different for TiB$_2$ and ZrB$_2$ with the formation of TiBO$_3$ and Ti$_2$O$_3$ as intermediate compounds in the case of the borothermic reduction of titania, while in the zirconia/boron system a direct borothermic reduction of zirconium oxide is observed.

1. Introduction

A range of interesting properties makes TiB$_2$ and ZrB$_2$ useful materials for commercial applications. They exhibit extreme hardness, high electrical conductivity, good thermal shock resistance, high melting point, chemical inertness and durability. Their applications are found in many areas: TiB$_2$ is used as ballistic armour, coating for cutting tools and also, together with ZrB$_2$, in the electrolytic production of aluminium due to superior cathode quality compared to carbon. Other uses are found in the foundry or refractory industries and in steel refining, particularly in the case of ZrB$_2$.

The most common processes to produce TiB$_2$ and ZrB$_2$ are via borothermic and carbothermic reductions of the respective oxides. The main drawback from the commercial point of view is that these reactions require very high temperatures, i.e. 2000 and 1400–1700 °C, respectively, temperatures which lead to a size of the particles of the metal borides in the micrometre range.

There has been a continuous effort to try to find improved sample preparation methods, keeping in mind that, as was mentioned in the Annual Minerals Review of the American Ceramic Society Bulletin [1], market expansion is expected to be assisted by the introduction of a lower-cost, readily sinterable, technical grade of TiB$_2$, the same scenario applying to ZrB$_2$. Few approaches such as the polymer-precursor routes [2], the use of alkoxides [3] and the borothermic reduction of TiO$_2$ or derived polymers in the presence of amorphous boron [4] have produced

powders in the submicron range with a decrease in the reaction temperature. Indeed none of these reactions were completed at a temperature below 1300 °C.

The use of mechanical energy to produce metal borides could provide an alternative processing route. It is known that a mechanical treatment of solids leads to an increase in the reactivity of the powder particles [5]. This higher reactivity allows, in some cases, a solid state reaction to occur during the course of grinding while in other cases only a mechanical activation is observed with the advantage of greatly reduced reaction temperature. Direct formation of TiB$_2$ by mechanical alloying of titanium powder and boron powder has already been obtained [6, 7] but the cost of the starting materials, principally pure titanium metal, precludes the development of this process at the commercial scale. Starting from TiO$_2$ would provide a better option. In this sense, we have looked at the influence of a mechano-chemical treatment on the borothermic reduction of titania and zirconia.

2. Experimental procedure

TiO$_2$ (> 99%, Fluka, Structure anatase, particles size in the range 0.2–0.3 μm), ZrO$_2$ (99%, Hopkin and Williams Ltd, average particle size $\cong$ 2 μm) and amorphous boron (amorphous 92%, Johnson Mattey Electronics, particles size in the sub-micrometre range 0.2–0.4 μm) were used as the starting materials. They were introduced, in the ratio M : B = 1 : 4 (M : Ti or Zr), into a high energy ball mill (Uni-Ball-Mill) [8]. The ball to powder weight ratio was kept constant at 40 : 1.

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The milling process was performed under vacuum and a high energy mode was selected (i.e. high number of impacts of high velocity). The structural evolution of powder upon milling and annealing was monitored using X-ray diffractometry (XRD) using CoK$_\alpha$ radiation. Thermal properties were studied using a Shimadzu DTA-50 thermal analyser (temperature range 25–1100 °C) and the average size of the particles was estimated by using a scanning electron microscope (SEM, Jeol 6400). The B_2O_2 by-product was removed as in [4] by washing the annealed sample in hot water.

3. Results
3.1. Titania–boron system

The XRD patterns of the sample milled for 25 and 140 h are presented in Fig. 1a and b. It is observed that after a short milling time (Fig. 1a) all the peaks still corresponded to the anatase structure of TiO_2. The XRD peak broadening and the small intensity observed are due to the very fine crystallite size and are characteristic of typical structures observed after milling. Interestingly, the XRD pattern of the same sample milled for 140 h (Fig. 1b)) indicates a phase transformation from the anatase structure (which is stable below 700 °C) to the rutile structure. Such a mechanically induced phase transition has already been reported in the literature [9].

Fig. 2 shows the DTA traces of the sample milled for (a) 25 h and (b) 140 h. As can be seen for the sample milled for 25 h (Fig. 2a), three exothermic peaks are present. An XRD analysis of a sample (Fig. 1c) obtained after continuous heating and holding for 2 min at 785 °C under argon, followed by fast cooling, allowed characterization of the first reaction. This peak is due to the reaction of TiO_2 with amorphous boron leading to the formation of a mixture of $TiBO_3$ and Ti_2O_3. It was not possible to separate the contribution of the peaks forming the broad exothermic peak in the temperature range 785–1000 °C. Nevertheless, the XRD of a sample heated to 1050 °C shows a full transformation of TiO_2 to TiB_2, together with the formation of the amorphous compound B_2O_2 (Fig. 1d). The influence of a longer milling time is outlined Fig. 2b, where a small shift of the first exothermic peak to a lower temperature is observed. The second broad peak represents a more complicated feature. Several overlapping peaks, indicating the presence of at least three reactions, are clearly visible in a temperature range slightly lower than the previous case. However, the XRD pattern of the sample after annealing in the DTA at 1050 °C indicates the same phase transformation and the formation of TiB_2. In order to check if this difference in the DTA traces could be correlated with the different structures of the milled samples i.e. anatase or rutile, rutile was used as starting TiO_2 material and milled under the same conditions for 25 h. As indicated on the DTA trace presented in Fig. 2c, the different relative intensity of the exothermic peaks is the only main feature compared to Fig. 2a. The shape of the curves is similar which provides evidence that the different DTA trace
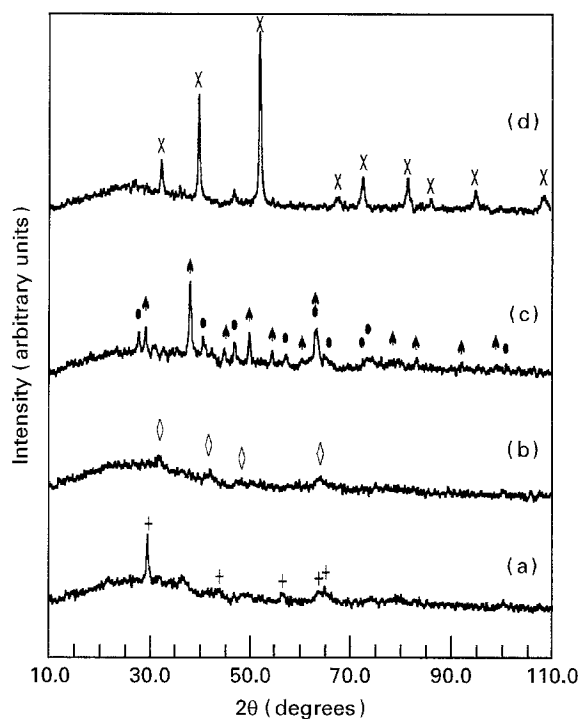

Figure 1 XRD patterns of TiO_2 + amorphous boron: (a) milled for 25 h; (b) milled for 140 h; (c) as (a) and annealed at 785 °C for 1 min in the DTA and (d) as (a) after DTA at 1050 °C. Phases are marked by the following symbols: TiO_2 anatase (+), TiO_2 rutile ($\Diamond$), $TiBO_3$ ($\blacktriangle$), Ti_2O_3 ($\bullet$) and TiB_2 ($\times$).
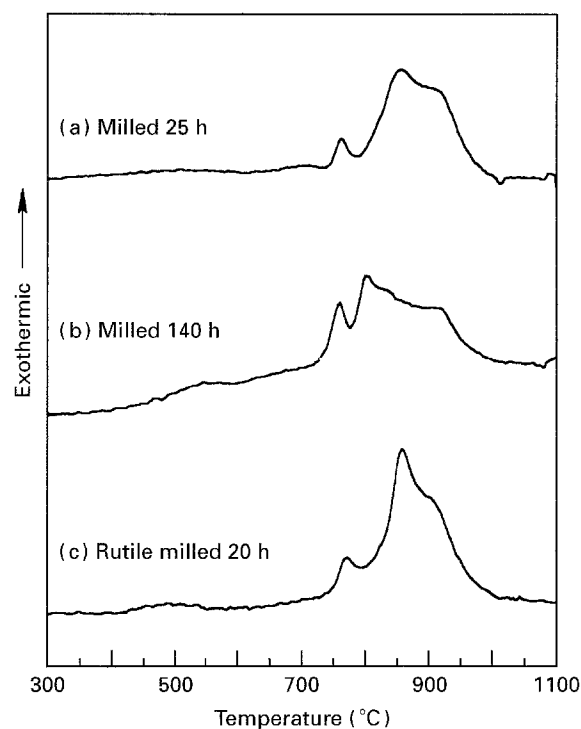

Figure 2 DTA curves of TiO_2 (structure anatase) milled with amorphous boron for (a) 25 h and (b) 140 h; (c) same as (a) when TiO_2, structure rutile, is used as starting material. (Continuous heating under argon, 20 °C min^{-1}, sample mass $\cong$ 25 mg.)

obtained for the sample milled for 140 h is not due only to a structural factor.

A SEM analysis of the samples milled for 25 and 140 h is presented in Fig. 3. The particles for the sample milled 25 h are very small with an average size
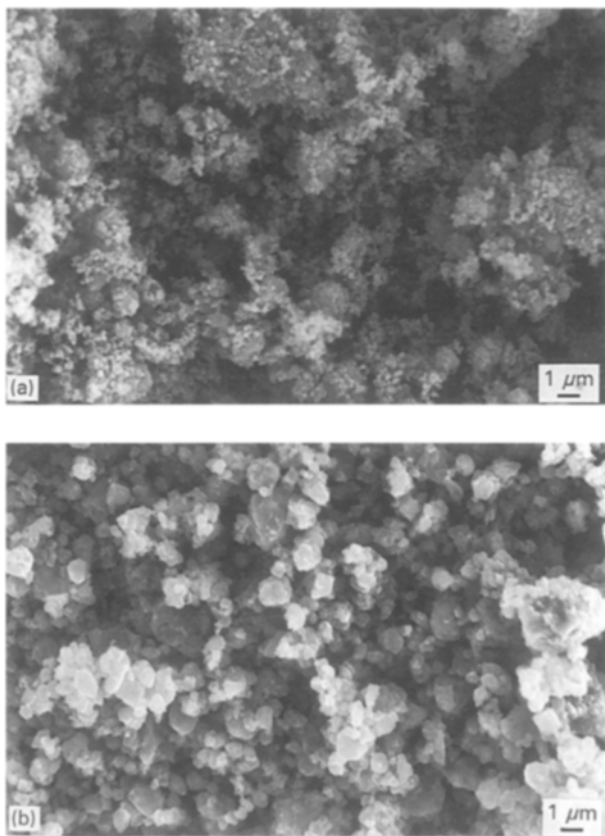
Figure 3 SEM micrographs of TiO$_2$ + amorphous boron: (a) milled for 25 h and (b) milled for 140 h.

Figure 4 XRD patterns of ZrO$_2$ + amorphous boron: (a) milled for 20 h; (b) milled for 70 h; (c) as (b) and annealed at 800 °C for 1 min in the DTA and (d) as (a) after DTA at 1100 °C. ZrO$_2$ monoclinic (0), ZrO$_2$ cubic (♦), ZrB$_2$ (▽).

of 0.2 μm (Fig. 3a). Spherical agglomerates of size ranging between 1–2 μm are also observed. Interestingly, as it is shown in Fig. 3b, the particle sizes of the sample milled for 140 h are much bigger with a size now in the range 0.5–1.5 μm. This fact is presumably due to a welding effect which occurs during the course of milling.

3.2. Zirconia–boron system

Fig. 4a presents the XRD pattern of a sample milled for 20 h. All the peaks correspond to zirconia of the baddeleyite structure and the broadening is a result of a decrease in the crystallite size during milling. In the case of a sample milled for a longer period (70 h), the intensity of the peaks (Fig. 4b) is greatly reduced and additional peaks are observed corresponding to a cubic ZrO$_2$ phase (the Joint Committee on Powder Diffraction Study file no. 27–997 seems to give the best agreement with the experimental pattern). Such a phase transition, from the monoclinic to the cubic structure, induced by mechanical treatment has been previously reported for zirconia milled with various oxide additives [9, 10].

The DTA traces presented in Fig. 5 show a different feature compared to the previous TiO$_2$/B system. Two exothermic peaks are observed for both short and long milling times. The first one, very weak for the sample milled for 20 h (Fig. 5a), but much more pronounced for the sample milled for 70 h (Fig. 5b), corresponds to the crystallization of the cubic ZrO$_2$ phase. An XRD analysis of the sample milled for 70 h
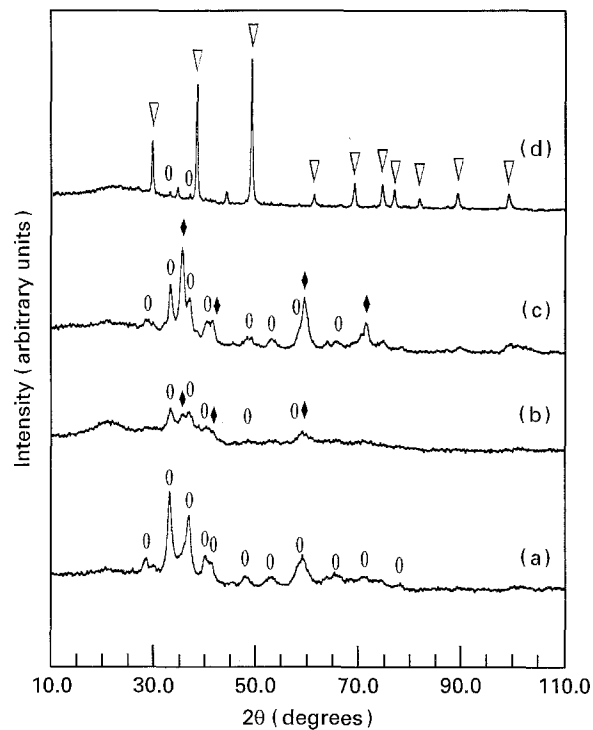
and then subsequently heated in the DTA at a temperature above the first exothermic peak clearly confirms this observation. As can be seen in Fig. 4c, there is a great similarity with the spectrum of the milled sample (Fig. 4b); the main difference is only the significant increase in the intensity of the peaks of the high symmetry phase. The XRD analysis of the sample milled for 25 h and then heated in the DTA above the second exothermic peak, i.e. 1100 °C is shown in Fig. 4d. Most of the peaks correspond to ZrB$_2$, indicating a very high yield for the transformation. Very small peaks of ZrO$_2$ are still present together with two peaks which we are not able to match at present. It must be pointed out that two very weak peaks are also observed in the pattern in Fig. 1d. The presence of the main peaks of ZrO$_2$ may be due to an incomplete reaction, as the DTA curve Fig. 5a seems to indicate. The second exothermic peak in the case of the sample milled for a longer time (Fig. 5b) is much weaker and has shifted to a lower temperature. The XRD analysis indicates the same phase transformation. However, the presence of the main peaks of ZrO$_2$ suggests that the amount of boron may be insufficient to obtain full transformation. This could be due to the low purity of the starting amorphous boron powder. A chemical analysis of the annealed samples would clarify this point.

Fig. 6a shows the SEM micrographs of the samples milled for 20 h. The particle size distribution looks quite narrow, with particles in the range 0.2–0.4 μm. As in the previous system, the particle sizes also increased during milling. The welding effect is clearly observed in Fig. 6b with particles forming large agglomerates of a few micrometres diameter.
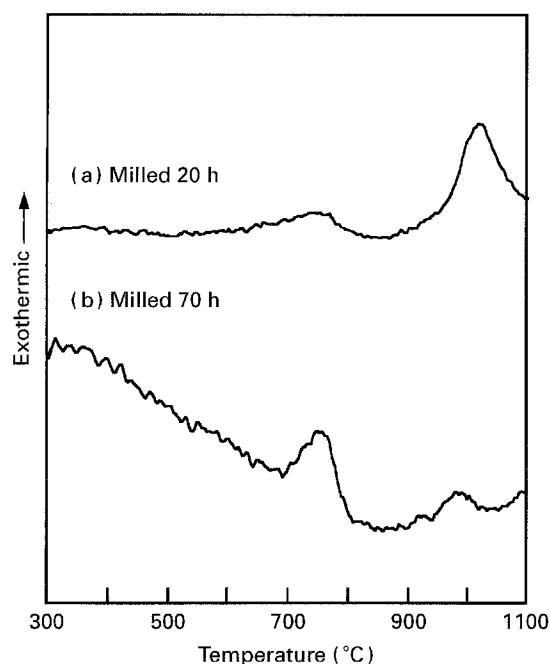
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Figure 5 DTA curve of ZrO_2 milled with amorphous boron for (a) 20 h and (b) 70 h. (Continuous heating under argon, $20°C\,min^{-1}$, sample mass $\cong 25$ mg.)

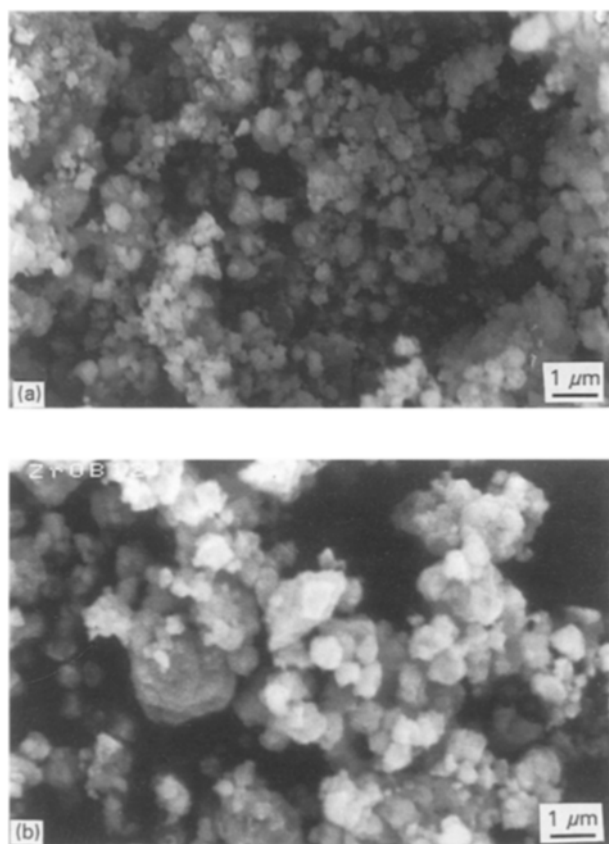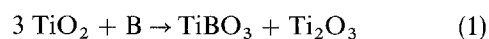*Figure 6* SEM micrographs of ZrO_2 + amorphous boron milled for (a) 20 h and (b) 70 h.

4. Discussion

If many of the physical properties of the titanium and zirconium borides are similar, this work provides clear evidence that the mechanism for the formation of these borides by mechanically activated borothermic

reduction of the respective oxides is different. For the titania/boron system, our experimental data confirm the following reactions sequence, proposed by Jiang and Rhine [4]:

$$3\,TiO_2 + B \rightarrow TiBO_3 + Ti_2O_3 \qquad (1)$$

$$2\,Ti_2O_3 + 14B \rightarrow 4\,TiB_2 + 3\,B_2O_2 \qquad (2)$$

$$2\,TiBO_3 + 8B \rightarrow 2\,TiB_2 + 3\,B_2O_2 \qquad (3)$$

The reactions (2) and (3) both contribute to the second broad exothermic peak observed on the DTA curve but it is not possible to distinguish which one occurs first. If the sequence of the reactions is similar the temperatures at which the transformations proceed are quite different compared to the classical borothermic reduction process. In our case the reaction (1) starts just above 700 °C and the overall reaction appears to be completed at 1000 °C. A slight decrease in the temperature of the reactions is observed for the sample milled for 140 h but this is not associated with a decrease in the size of the particles since the size actually increased.

In the zirconia/boron system, the borothermic reduction of ZrO_2 evolves through the following solid-state reaction:

$$ZrO_2 + 4B \rightarrow ZrB_2 + B_2O_2$$
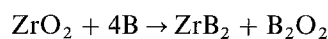
The main difference between the two reaction paths is the absence of the zirconium borate phase at the intermediate stage of the reaction. This fact is in agreement with the literature where it has not been possible to find any evidence that such a phase exists. The compounds annealed at 800 °C correspond to a mixture of monoclinic and cubic zirconia phases and the amount of the latter phase is higher in the compound milled for a longer time. This result shows the influence of a mechanical treatment on the structure of zirconia. The high energy milling activates this phase transformation which normally does not occur below 1100 °C. As was mentioned before, for the TiO_2/B system, the shift of the temperature of the borothermic reduction to a lower temperature for the sample milled for a longer time is not a consequence of the decrease of the particle size but most probably to partial phase transformation (anatase → rutile) morphology changes of the separate phases, or more intimate chemical mixing of boron with oxides.

For both systems, energetic grinding has proved to be an efficient way of decreasing the temperature of the solid-state formation of TiB_2 and ZrB_2. The reactions are completed at temperatures not exceeding 1100 °C. Such an activation is due to two main effects: (i) intimate mixing at the chemical level as a result of particle size reduction and impacts, and (ii) introduction into TiO_2, ZrO_2 grains during milling of lattice imperfections such as stacking faults, dislocations, vacancies which affect the mass transport upon further annealing. It must be pointed out that the milling time affects the state of the end-milled product in such a way that the longer milling time not only induces activation but also leads to polymorphic transformations involving the formation of rutile and cubic zirconia during grinding. Reaching such a state

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is not necessary to obtain the best activation since there is no evidence that the structure of the metal oxide has a noticeable influence on the temperature of the borothermic reduction (the same experimental procedure for the mixture of TiO_2 (structure rutile) and amorphous boron leads to similar results). However prolonged milling does lead to improved activation. The aim will be to find the right balance between activation and milling time.

The structural and compositional metastability created during the mechanical activation not only affects the temperature required for the solid-state reaction to occur but also strongly affects the kinetics of the transformation. Short annealing times (typically a few minutes at a temperature above the last exothermic peak on the DTA curve) were found to be sufficient to obtain complete reaction while preserving the small particle size obtained after milling. This acceleration of the borothermic reduction reaction, coupled with a wider temperature range within which it can proceed, should allow a better control of the grain growth and subsequently a better control of the sintering process. This last point is crucial for potential applications of these mechanically activated boride precursors.

This work confirms the efficiency of a mechano-chemical treatment to stimulate solid-state reaction as a method of preparing high technology ceramics. Actually, more complicated examples of the stimulation of solid-state reactions have been observed in the case of the borothermic reduction of ilmenite ($FeTiO_3$) to form TiB_2 directly from the mineral sand [12] and to form $TiB_2/ZrB_2/(Ti, Zr)B_2$ composites from a mixture of TiO_2, ZrO_2 and amorphous boron [13].

5. Conclusions

TiB_2 and ZrB_2 powders were synthesized by a mechano-chemical treatment of titania and zirconia powders with amorphous boron followed by a relatively low temperature annealing (1100 °C). The occurrence of polymorphic transformations has been observed versus milling time for both systems together with a decrease upon annealing of the temperature of the borothermic reduction reactions with increased milling time. This mechanical activation was not only a result of the reduction of the size of the particles since the particles size actually increased slightly during the course of milling, whereas the activation of the borothermic reduction reaction was actually increased. This latter fact may be associated with the increase in chemical mixing and defects concentrations in oxide grains during milling.

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