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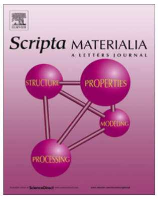

# Synthesis of nanosized zirconium diboride powder via oxide-borohydride solid-state reaction

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## ABSTRACT

A novel solid-state reaction was investigated to achieve nanosized $ZrB_2$ particles using $ZrO_2$ and $NaBH_4$ as starting materials, which were dry mixed and thermally treated at increasing temperatures and B:Zr molar ratio to get a complete oxide to boride conversion. X-ray diffraction analysis showed that the reaction was completed after 30 min at 900 °C. Field-emission scanning microscopy revealed $ZrB_2$ particles with dimensions around 100 nm. In this paper for the first time we propose the oxide-borohydride system as an alternative to synthesize metal borides to chemical and borothermic reactions.

**ZIRCONIUM** diboride ($ZrB_2$) has a high melting point (3250 °C), high hardness (22 GPa), good solid-state phase stability, high thermal and electrical conductivity. $ZrB_2$-based ceramics are expected to be potential candidate materials for ultra-high-temperature applications in the aerospace industry [1].

$ZrB_2$ powders can be synthesized by various methods such as solid-state reaction, electrochemical, mechanical alloying and self-propagating high-temperature synthesis [2–4]. The most common process is the solid-state reduction involving a metal oxide, boron oxide and a reducing agent such as carbon, aluminum, or magnesium [5] at temperatures above 1500 °C.

Otherwise, temperatures of 1100 °C and 1400 °C are required to get $ZrB_2$ if elemental boron [6] or boron carbide [7] are used instead of boron oxide, respectively. Many of these reactions have been re-proposed by replacing the traditional ceramic powders with polymer-derived ceramics in an attempt to obtain nanocrystallites of $ZrB_2$ [8–10]. Berthon et al. [11] and Reich and co-worker [12] independently synthesized $ZrB_2$ by chemical vapour deposition using $ZrCl_4$ and boron halides. Devyatkin researched electrosynthesis of zirconium boride from Cryolite-Alumina melts containing zirconium and boron oxides [13]. Andrievskii et al. obtained an amorphous powder of $ZrB_{2.76}$ with mean particle size 40 nm by thermolysis of $Zr(BH_4)_4$ at 573–623 °C [14].

To the best of the authors knowledge few studies were conducted on the synthesis of metal borides using sodium borohydride as boron source [15–20] and none of them combine it with zirconium oxide as zirconium source. In the present study, we propose for the first time the use of $ZrO_2$ and $NaBH_4$ to synthesize nanosized $ZrB_2$. The involved mechanisms were explained taking inspiration from the work of Rude et al. [21] who studied the thermal decomposition of $NaBH_4$, pure or mixed with $NaBF_4$.

Although the results here presented are still far from being optimized, the novel oxide-borohydride system represents a significant improvement in the state of the art for industrial application of $ZrB_2$ powders, with the possibility of extension to other transition metal oxides, such as $TiO_2$, $HfO_2$, $Ta_2O_5$ etc. The ability to control structure and properties of the metal oxide precursors at a nanosize level opens a new route towards the creation of metal-boride nanophases.

The following raw materials were used: Zirconia, $ZrO_2$ (Carlo Erba, analytical grade, main particles size ≅200 nm, molecular mass: 123.22 g), sodium borohydride, $NaBH_4$ (Sigma–Aldrich, >99% pure, molecular mass: 37.84 g) and Boron, B (<325 mesh, Aldrich, molecular mass: 10.81 g).

A mixture with composition 20% mol. $ZrO_2$ + 80% mol. $NaBH_4$ (corresponding to a B:Zr molar ratio 4:1) was dry ball-milled with zirconia grinding media ($d$ = 5 mm, 20 g) in a PE bottle for 4 h in air, at room temperature. The synthesis was carried out in an alumina tubular furnace (Nabertherm, Germany) under reducing atmosphere $Ar/H_2$ 4 vol.%, heating rate 3 °C/min, at 600, 900, 1100 °C for 30 min. The resulting black foam was crushed in Agate mortar for further characterization. The weight of the mechanically mixed powder mixtures was recorded before and after synthesis.

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A second set of experiments was carried out varying the mixture composition to 25% mol. $ZrO_2$ + 75% mol. $NaBH_4$ and 33.3% mol. $ZrO_2$ + 66.6% mol. $NaBH_4$ (corresponding to a B:Zr molar ratio of 3:1 and 2:1, respectively) and synthesis at 900 °C, in order to investigate the reaction yield. For the sake of comparison, another set of experiments was carried out replacing $NaBH_4$ with elemental boron, with the composition 20% mol. $ZrO_2$ −80% mol. B and synthesis at 900 °C and 1100 °C for 30 min. A summary of the experiments carried out is given in Table 1.

Pristine zirconia and synthesized products were analysed by X-ray diffraction (XRD) using a Bruker D8 Advance apparatus (Bruker, Karlsruhe, Germany). The powders morphology was analysed at different stages of reaction using a Field-emission scanning microscopy (FE-SEM) microscope (Carl Zeiss Sigma NTS Gmbh Öberkochen, Germany) equipped with energy dispersive spectroscopy (EDS, INCA Energy 300, Oxford Instruments, UK).

Fig. 1 shows XRD patterns of samples after synthesis at 600 °C–1100 °C of the 4:1 mixture, Table 1 experiment #1. After synthesis at 600 °C, broad reflections belonging to hexagonal $ZrB_2$ were identified, along with reflections from both monoclinic $ZrO_2$ (m-$ZrO_2$) and tetragonal $ZrO_2$ (t-$ZrO_2$). Additional reflections belonging to sodium zirconate, $Na_2ZrO_3$, were also recognized. After synthesis at 900 °C, reflections from $ZrO_2$ and $Na_2ZrO_3$ were no longer detected whilst those of $ZrB_2$ were much better defined. Moreover, only traces of meta-borate, $NaBO_2$, were found. Finally, at 1100 °C, the only crystalline phase observed was $ZrB_2$. FE-SEM/EDS analysis of the synthesized powders is shown in Fig. 2a-d, along with the starting $ZrO_2$.

The starting zirconia has a mean particle size of 200 nm, Fig. 2a. After synthesis at 600 °C, Fig. 2b, nucleation of ~50 nm particles, embedded in Na-B-Zr-O species was observed. SEM-EDS analyses are not conclusive about the identification of the newly formed particles, however it is interesting to note that their particle size is about four time smaller than the starting $ZrO_2$ ones. At 900 °C, particles with dimensions below 200 nm are recognized and only scattered pockets of spurious Na-B-Zr-O phases are observed (see arrow in Fig. 2c). According to EDS analyses $ZrB_2$ particles are recognized, even if some contamination from Na and O is still present (Fig. 2c). Finally, at 1100 °C, Fig. 2c, $ZrB_2$ grains grew up to about 500 nm.

**Table 1**
Summary of the experiments carried out.

| Synthesis | Reagents | B:Zr molar ratio | Temperature (°C) | Holding time (min.) |
|---|---|---|---|---|
| #1 | $ZrO_2$, $NaBH_4$ | 4:1 | 600–900–1100 | 30 |
| #2 | $ZrO_2$, $NaBH_4$ | 2:1, 3:1 | 900 | 30 |
| #3 | $ZrO_2$, Boron | 4:1 | 900–1100 | 30 |

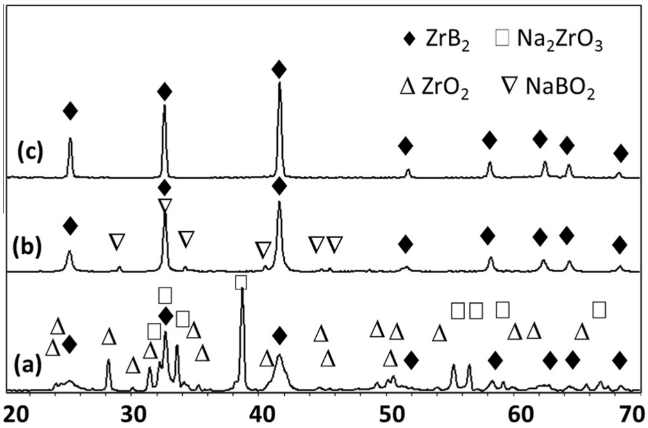

**Fig. 1.** XRD pattern of experiment #1, with B:Zr 4:1, at different temperatures, (a) 600 °C, (b) 900 °C, (c) 1100 °C.

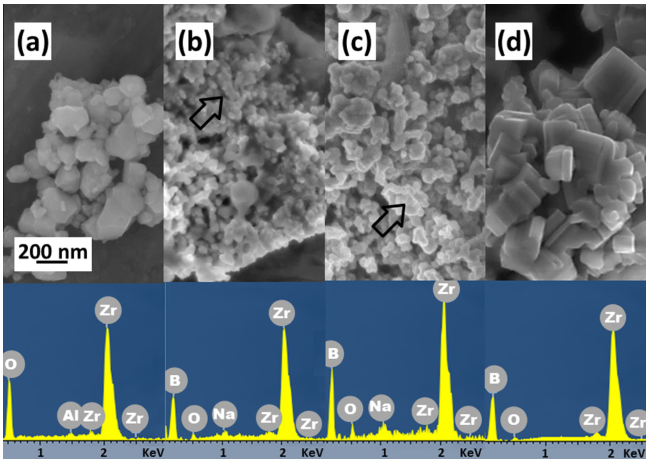

**Fig. 2.** Morphology of (a) starting $ZrO_2$, synthesized products after thermal treatment at (b) 600 °C, (c) 900 °C, (d) 1100 °C and corresponding EDS spectra. Al peak comes from the aluminum stub.

Further syntheses, varying the B:Zr molar ratio to 3:1 and 2:1, were carried out at 900 °C, XRD patterns of the powder after the reaction are reported in supplementary material in Fig. S1, according to conditions in Table 2, experiment #2). It can be appreciated that, different to the previous case, with B:Zr molar ratio 3:1 and 2:1, a considerable amount of unreacted $ZrO_2$ is still present (along with crystalline $NaBO_2$).

For the sake of comparison, we discussed the results achieved using the elemental boron in place of $NaBH_4$. Fig. S2 (supplementary material), refers to XRD patterns of the synthesized powders after the reactions at 900 °C and 1100 °C, according to conditions in Table 1, experiment #3. A considerable amount of unreacted $ZrO_2$ is still present at 900 °C and a temperature of 1100 °C is necessary to achieve complete conversion of $ZrO_2$.

Table 2 shows the list of all the experiments carried out, with indication of cases where the complete conversion of $ZrO_2$ in $ZrB_2$ occurred. The degree of conversion (estimated via the oxide/-boride peak intensity ratio in XRD pattern) increases with increase of the B:Zr molar ratio from 2:1 to 4:1. In the latter case, the synthesis is completed at a temperature of 900 °C. When elemental boron is used the complete conversion is observed only by increasing the temperature to 1100 °C. As for the weight loss, it can be observed that it increases with raising the synthesis temperature due to a volatilization of Na and $H_2$ products and for the same reason it decreases with decrease of the B:Zr ratio from 4:1 to 2:1. Conversely, no significant weight loss was observed for the borothermal reaction.

**Table 2**
Experimental details and weight loss of the synthesis carried out.

| N° | Synthesis | B:Zr (molar ratio) | Temperature (°C) | Weight loss (wt.%) |
|---|---|---|---|---|
| 1 | #1 | 4 | 600 | 11 |
| 2[a] | #1 | 4 | 900 | 26 |
| 3[a] | #1 | 4 | 1100 | 39 |
| 4 | #2 | 3 | 900 | 21 |
| 5 | #2 | 2 | 900 | 13 |
| 6[b] | #3 | 4 | 900 | <1 |
| 7[a,b] | #3 | 4 | 1100 | <1 |

[a] In this case the complete conversion was observed.
[b] $NaBH_4$ were replaced by elemental boron.