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ScienceDirect
Ceramics International 37 (2011) 1895–1904
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Mechanochemical synthesis of $Ti_{1-x}Zr_xB_2$ and $Ti_{1-x}Hf_xB_2$ solid solutions

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Received 10 January 2011; received in revised form 9 February 2011; accepted 11 February 2011
Available online 19 February 2011

Abstract

Solid solutions of TiB_2–ZrB_2 and TiB_2–HfB_2 were obtained under an inert atmosphere by high-energy ball-milling mixtures of Ti/Zr/B and Ti/Hf/B, respectively. Milling promoted mechanically induced self-sustaining reactions (MSR), and the ignition time was dependent on the initial composition of the mixture. The stoichiometry of $Ti_{1-x}Zr_xB_2$ and $Ti_{1-x}Hf_xB_2$ solid solutions was controlled by adjusting the atomic ratio of the reactants. The solid solutions were characterised by X-ray diffraction, transmission electron microscopy, electron diffraction, and energy dispersive X-ray spectroscopy. The results revealed that TiB_2–ZrB_2 possessed a nanometric microstructure and good chemical homogeneity. However, in the TiB_2–HfB_2 system, an inhomogeneous solid solution was obtained when a Ti-rich mixture was employed. The solid solutions showed good thermal stability; thus, can be used as raw materials for the development of technological materials for structural applications.

Keywords: A. Milling; B. X-ray methods; D. Borides; E. Structural applications

1. Introduction

Diborides of group IVB transition metals (TiB_2, ZrB_2, and HfB_2) are useful compounds for the development of advanced materials for high-temperature technological applications because these compounds display high melting points (greater than 3000 °C), high hardness and strength at high temperatures, good thermal and electrical conductivities, low thermal expansion coefficients, chemical inertness, wear and oxidation resistance, and high thermal stability [1]. Group IVB diborides are currently employed in specialised applications, such as impact resistant armours, cutting tools, wear resistant coatings, molten metal crucibles, high temperature electrodes, and refractories for high-temperature manufacturing processes. Group IVB diborides are also potential candidates for the development of materials that can withstand ultra-high temperatures and extreme environments [2–4].

TiB_2, ZrB_2, and HfB_2 possess a hexagonal AlB_2-type crystal structure (space group P6/mmm, number 191), which can be depicted as honeycomb layers of boron separated by hexagonal closed-packed transition metal layers. The unit cell parameters of metal diborides can be attributed to the interatomic bond lengths of B–B and M–B bonds [5]. The length of the *a*-axis is primarily determined by the strength of covalent B–B bonds, and minimal changes in the *a*-axis are observed when different metal atoms are applied. However, cohesive forces in the *c*-direction are primarily due to M–B contacts, which increase with an increase in the M/B radius ratio and promote large changes in the *c*-axis.

When the differences in the atomic radii of metals are not extremely large, complete solid solubility occurs readily in isomorphous transition metal diborides due to the ability of the AlB_2-type structure to host a wide variety of metals along the *c*-direction. Thus, interest in diboride solid solutions would increase if their physical, chemical, or structural properties could be improved by controlling their stoichiometry. For example, Paderno et al. [6] have shown that the lattice parameters and B–B distance of the diboride phase of $(Ti, Zr)B_2$ solid solutions can be adjusted, which improves the perfectness and number of regularities in the microstructure of directionally crystallised MeB_6–MeB_2 eutectic composites. Mroz [7] demonstrated that $(Ti, Zr)B_2$ solid solutions exhibited increased mechanical properties (parabolic relationship) compared to those of end-member compositions. Moreover, in a previous study [8], a TiB_2–TaB_2 solid solution was formed to limit TiB_2 grain growth in ceramic matrix

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0272-8842/$36.00
doi:10.1016/j.ceramint.2011.02.004

composites and improve the mechanical properties of the materials.

Despite the scientific and technological interest in the formation of solid solutions, few studies have focused on reliable syntheses [9–13], and only restricted compositions have been evaluated. Nevertheless, some authors have reported the formation of solid solutions during the high-temperature processing of composite materials, including two different transition metal diborides [14–16]. However, due to the high refractoriness of these compounds, the materials are difficult to manufacture. Specifically, most of the proposed synthetic methods are characterised by high energetic requirements and are not suitable for the production of solid solutions.

The refractoriness and high stability of transition metal diborides are due to the high negative Gibbs free energy of formation, which is strongly correlated to the enthalpy of formation. Therefore, the synthesis of these compounds from a mixture of elements is an extremely exothermic process, and combustion-like methods can be employed as a practical means for their production. For instance, TiB_2, ZrB_2, and HfB_2 can be obtained by self-propagating high-temperature synthesis (SHS) [17–20]. Mechanochemical processes referred to as mechanically induced self-sustaining reactions (MSR) [21] are similar to thermally ignited SHS methods and also require highly exothermic chemical reactions [22]. Thus, the formation of TiB_2, ZrB_2, and HfB_2 by milling mixtures of elemental powders occurs through MSR [23,24].

MSR is a simple, low-energy procedure that produces a fine, homogeneous powder. With MSR, complex solid solutions can be obtained in a consistent and easy manner, and the chemical composition and microstructure of the materials can be controlled [25,26]. In a recent study [27], we demonstrated that ZrB_2–HfB_2 solid solutions could be synthesised by milling powder blends of hafnium, zirconium, and boron under an inert atmosphere. In the present investigation, MSR was used to obtain TiB_2–ZrB_2 and TiB_2–HfB_2 solid solutions, which present larger differences in atomic radii than that of ZrB_2–HfB_2. Moreover, the compositional range of each ternary system was investigated.

2. Material and methods

Titanium powder (99% pure, <325 mesh, Strem Chemicals, Newburyport, MA, USA), zirconium powder (<325 mesh, Alfa Aesar, Ward Hill, MA, USA), hafnium powder (99.6% pure, <325 mesh, Alfa Aesar, Ward Hill, MA, USA), and boron powder (95–97% pure, amorphous powder, Fluka, St. Louis, MO, USA) were used to synthesise the solid solutions.

A modified planetary ball-mill (model Micro Mill Pulverisette 7, Fritsch, Idar-Oberstein, Germany) was operated at a constant pressure by connecting the vial to a gas cylinder via a rotating union (model 1005-163-038, Deublin, Waukegan, IL, USA) and a flexible polyamide tube. In each milling experiment, 5 g of the powdered mixture and 7 tempered steel balls (d = 15 mm, m = 12.39 g) were placed in a 45-mL tempered steel vial (67 Rc) and were ball-milled under 6 bars of high-purity helium gas (H_2O < 3 ppm, O_2 < 2 ppm, and CnHm < 0.5 ppm, Air Liquide, Paris, France). The vial was purged with helium several times, and the pressure was selected prior to milling. The powder-to-ball mass ratio (PBR) was set to 1/17.35, and a spinning rate of 600 rpm was employed.

The occurrence of ignition during milling (a MSR process) was ascertained by monitoring the pressure of helium with an SMC solenoid valve (model EVT307-5DO-01F-Q, SMC Co., Tokyo, Japan). At ignition, the exothermic reaction provokes an instantaneous increase in the total pressure of the system due to an increase in the temperature. Thus, the ignition time (t_{ig}) of the mixtures was obtained from the time–pressure record. After ignition, milling was continued for 30 min to obtain a homogeneous product.

X-ray powder diffraction diagrams were obtained with a Philips X'Pert Pro instrument (Eindhoven, The Netherlands) equipped with a θ/θ goniometer, Cu Kα radiation (40 kV, 40 mA), a secondary K_β filter, and an X'Celerator detector. The diffraction diagrams were scanned from 20° to 150° (2θ) and 48° to 73.5° (2θ) in step-scan mode at a step of 0.017° and a counting time of 175 s/step and 2742 s/step, respectively. *In situ* high-temperature X-ray powder diffraction diagrams were recorded on the aforementioned instrument, which was equipped with an Anton Parr high-temperature attachment (HTK 1200). The diffraction patterns were obtained under a flow of helium at temperature intervals of 50 °C, and a maximum temperature of 1150 °C was investigated. The heating rate was set to 5 °C/min, and a scanning rate of 5.4° min^{-1} was applied. In total, the 2θ range was scanned from 20° to 80° for 12 min and 18 s.

Using the FULLPROF computer program, the lattice parameters were calculated from the peaks in the XRD diagram by assuming hexagonal symmetry [28]. The Williamson–Hall method [29] was used to separate the effects of domain size and microstrain on line broadening. The method assumes that the following mathematical relationship between the integral breadth (β), the size of the coherent crystalline domain (D), and the lattice distortion or microstrain (e) is applicable:

$$\frac{\beta\cos\theta}{\lambda} = \frac{1}{D} + 2e\left(\frac{2\sin\theta}{\lambda}\right)$$

A plot of $\beta\cos\theta/\lambda$ versus $2\sin\theta/\lambda$ was constructed, and the microstrain and the domain size were obtained from the slope and the intercept, respectively.

Transmission electron microscopy (TEM), electron diffraction (ED), and energy dispersive X-ray (EDX) experiments were performed on a 200 kV Philips CM-200 microscope (Eindhoven, The Netherlands) equipped with a supertwin objective lens, a LaB_6 filament, a ±45 tilt side-entry specimen holder (point resolution = 0.24 nm), and an EDS detector (EDAX Inc., Mahwah, NJ, USA). Powder samples were dispersed in ethanol and were deposited onto a holey carbon grid.

To study the thermal stability of the solid solutions, pellets of the milled samples were preformed by uniaxial pressing (12 MPa) and were annealed in a vertical tube furnace (Severn Furnaces Ltd., Bristol, England) at 1300 °C for 2 h (heating rate