Mechanochemical Processing of Nanocrystalline Zirconium Diboride Powder

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Nanocrystalline ZrB_2 powder was prepared by mechanochemical processing of a zirconium (II) dihydride–boron mixture with subsequent annealing from 800°C to 1200°C. The crystallite size and morphology of the synthesized ZrB_2 powders were characterized by X-ray diffractometry, scanning electron microscopy, and transmission electron microscopy. The effects of annealing temperature on powder particle size and morphology were assessed. At 900°C or above, pure ZrB_2 powder was obtained without trace quantities of residual ZrH_2 . The synthesized ZrB_2 powder particles were spherically shaped, with a crystallite size between 5 and 40 nm. The crystallite size increased with increase of annealing temperature.

I. Introduction

Z IRCONIUM diboride (ZrB₂) is one of the most important members of a family of ultra-high temperature ceramic materials. It has an extremely high melting point (>3000°C), high thermal and electrical conductivities, chemical inertness against many molten metals, excellent thermal shock resistance, and relatively low density.^{1,2} As a result, ZrB₂ ceramics are being considered for a variety of high-temperature (>1800°C) thermomechanical and structural applications, including furnace elements, plasma-arc electrodes, rocket engines, and thermal protection structures for leading-edge parts on hypersonic re-entry space vehicles.¹⁻⁵ However, to meet the strict constraints of structural applications, ZrB₂ materials will require improved strength, fracture toughness, and resistance to oxidation. Studies of nano-grain size ceramic materials previously demonstrated that nano-powders had an excellent sinterability and nano-grained materials had improved strength, fracture toughness, resistance to oxida-tion, and creep resistance.⁶⁻¹¹ Hence, the motivation for this study was the development of nanocrystalline ZrB₂ powder and nano-grained ZrB₂ ceramic materials.

Currently, nanocrystalline ZrB_2 powder has been produced using two main synthesis routes: chemical routes and reactive processes. Chen *et al.*¹² synthesized nanocrystalline ZrB_2 powder (crystallite size: 10–20 nm) by reacting anhydrous chlorides with sodium borohydride at 700°C under pressure. Yan *et al.*¹³ prepared nanocrystalline ZrB_2 powder, averaging crystallite size 47 nm at 1500°C by a sol–gel method, using zirconium oxychloride, boric acid, and phenolic resin as

Manuscript No. 29487. Received March 22, 2011; approved July 27, 2011. [†]Author to whom correspondence should be addressed. e-mail: GUO.Shuqi@nims.go.jp sources of zirconia, boron oxide, and carbon, respectively. However, a small amount of oxygen and carbon was presented in the ZrB₂ lattice. Nanocrystalline ZrB₂ powder can also be prepared by the solid-state reaction of Zr and B. Camurlu and Maglia¹⁴ prepared nanocrystalline ZrB₂ powder with starting powders of Zr, B, and NaCl using self-propagating high-temperature synthesis (SHS). In addition, Chamberlain *et al.*¹⁵ employed a slow heating rate (~1°C/min) and extended isothermal holds (6 h at 600°C) to obtain a nano-grained ZrB₂ ceramic (grain size: 10 nm) by reacting an attrition-milled mixture of Zr and B powders.

Mechanical activation, also referred to as mechanochemical processing, is another attractive method for synthesizing materials.^{16,17} In the present study, nanocrystalline ZrB_2 powder was prepared by mechanochemical processing of a zirconium (II) dihydride–boron mixture and subsequent annealing. The microstructure of the resulting ZrB_2 powder was characterized by field emission scanning electron microscopy and transmission electron microscopy. Phases were identified by X-ray diffraction. Also, the effects of annealing temperature on the powder particle size and morphology were examined.

II. Experimental Procedure

The starting powders used in this study were: zirconium (II) dihydride (ZrH₂) powder (325 mesh, 99% pure, Sigma-Aldrich, Inc., Louis, MO), and amorphous boron (B) powder ($d_{50} = 0.8 \mu m$, 95.9% pure, H.C. Starck, Berlin, Germany). Figure 1 shows SEM images of as-received ZrH₂ and amorphous B powders. The ZrH₂ powder had large, irregular grains, whereas the B was composed of smaller, spherical particles. The starting powders were weighed in stoichiometric proportions according to the following reaction:

$$ZrH_2 + 2B \rightarrow ZrB_2 + H_2 \tag{1}$$

The ZrH₂ and B powders were mixed in ethanol using a silicon carbide media for 6 h. Subsequently, the as-received ZrH₂–B mixture was milled in a planetary ball-mill (Model P5; Fritsch Gmbh, Idar-Oberstein, Germany). Planetary milling was performed using hardened steel balls with a diameter of 9.5 mm and hardened steel vials with a 65 mm inner diameter and 45 mm inner height. A charge ratio (ball to powder weight ratio) of 20:1 was used. Before milling, each vial was filled with pure (99.999%) argon in a glove box. The milling speed was 300 rpm, and the milling times were 5 and 10 h. After milling, the powder was moved to an alumina crucible under an argon atmosphere in a glove box, to avoid ignition of a self-propagating reaction. The milled

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Fig. 1. Typical FE-SEM images of the as-received (a) ZrH_2 and (b) B powders.

powders were then annealed at different temperatures between 800°C and 1200°C with a heating rate of 10°C/min for 1 h in a flowing high-purity argon atmosphere. Field emission scanning electron microscopy (FE-SEM) was performed to characterize the particle size and morphology as a function of temperature. The microstructures of powders were investigated by transmission electron microscopy (TEM, JEOL JEM-2010F, Tokyo, Japan) operated at 200 kV. X-ray diffraction (XRD) was used to determine the phases present in the prepared powders. The average crystal size, d, was calculated using Scherrer's formula¹⁸:

$$d = \frac{0.9\lambda}{\beta\cos\theta},\tag{2}$$

where λ , β , and θ are the wavelength of CuK α radiation ($\lambda = 1.54056$ Å), the full width at half maximum (FWHM, unit: rad), and the Bragg angle (unit: rad), respectively.

Differential thermal analysis (DTA) and thermogravimetry (TG) of the as-received ZrH_2 -B mixture were performed (TGA/DTA, STA409 CD; Netzsch, Wolverhampton, Germany) up to 1300°C using a heating rate of 10°C/min in a flowing high-purity argon atmosphere.

III. Results and Discussion

(1) ZrB₂ Synthesis

Figure 2 shows the TG/DTA curve obtained on the as-received stoichiometric ZrH_2 -B mixture. The DTA trace reveals the presence of three significant endothermic peaks at 126°C, 418°C, and 696°C, with the maximum peak at 696°C. A few small endothermic peaks are also observed. Shemet *et al.*¹⁹ showed the presence of two weak endothermic peaks at 570°C and 830°C and a strong endothermic



Fig. 2. TG/DTA curve of the as-received stoichiometric $\rm ZrH_2\text{-}B$ mixture.



Fig. 3. XRD patterns of the powders prepared by ball milling for (a, b) 5 h and (c-g) 10 h and annealing from 800°C to 1200°C.

peak at 785°C for ZrH2 in argon atmosphere. They concluded that the process of thermal dissociation of ZrH₂ occurred at approximately 600°C-1000°C. Recently, Li et al.20 showed that there is a weak endothermic peak at 540°C and a strong endothermic peak at 730°C in argon as a result of decomposition of ZrH₂. Thus, the endothermic peaks observed at 126°C and 418°C in the DTA trace are not the result of ZrH₂ decomposition, but are presumed to be associated with the evaporation of the bound water and the melting of B₂O₃ impurities. The TG analysis showed that a weight loss began at 500°C and the loss continuously increased up to 800°C, indicating that the decomposition of ZrH₂ occurred between 500°C and 800°C. The decomposition process was completed at 1000°C as indicated by several distinguishable weak endothermic peaks in the DTA trace up to 1000°C. In addition, the DTA trace exhibited several exothermic peaks in the temperature range 500°C-1100°C, indicating that the reaction of ZrH₂ with B to form ZrB₂ occurred in multiple stages.

To synthesize a high-purity ZrB_2 powder, the post-milled precursor powders were annealed in a flowing high-purity argon atmosphere at different temperatures between 800°C and 1200°C. The XRD patterns for the annealed powders are presented in Fig. 3. The ZrB_2 phase is the primary crystalline phase and a trace amount of ZrO_2 is present in all the annealed powders. The trace quantities of ZrO_2 may be attributed to oxygen uptake during the milling and/or handling procedures. A trace quantity of ZrH_2 was detected only for the sample annealed at 800°C. At 900°C or above, the peaks corresponding to the ZrH_2 phase are non-existent, as a result of its decomposition. However, neither excess Zrnor excess B was detected by XRD. Note that the absence of peaks for B phase is a result of amorphous boron powder used. The absence of peaks for Zr phase suggests that Zr was not an intermediate phase during the reaction of ZrH_2 with B to form ZrB_2 investigated in this study.

The samples annealed at 900°C or below exhibited a broad, weak diffraction peak corresponding to ZrB2 phase (Fig. 3). Increasing the annealing temperature resulted in the appearance of narrow and strong diffraction peaks of ZrB_2 phase, which indicates an increase in the crystallite size and concentration with increased temperature. The average crystallite size of ZrB2 was calculated by Scherrer's formula [Eq. (2)] using (101) and (100) reflections. The lattice parameters and crystallite size of ZrB₂ powders prepared by high-energy milling and subsequent annealing are summarized in Table I. It was found that the average crystallite size of the synthesized ZrB_2 powder increased with increase of annealing temperature. In addition, annealing at 900°C resulted in very similar crystallite size for the samples milled for 5 and 10 h. After annealing at 1100°C, however, the crystallite size was larger for the 10 h-milled sample than for the 5 h-milled sample. Thus, an increase in milling time promoted coarsening of grains during the subsequent annealing at higher temperature. Furthermore, the lattice parameters of the ZrB₂ samples milled for 10 h and annealed at 1100°C or above are nearly identical to those of the pure hexagonal ZrB₂ phase (a = 3.168 Å, c = 3.530 Å).

(2) Morphology of ZrB_2 Powder

Morphologies of the ZrB₂ powder, prepared by mechanochemical processing and annealing, were observed under FE-SEM, as shown in Fig. 4. It was found that the ZrB₂ powders had a spherical shape and a broad size distribution, with particle sizes in the range of 50-300 nm. Comparing these micrographs with the results determined by XRD (Table I) revealed that the size distributions of ZrB₂ particles determined by XRD and FE-SEM were marked differently. This suggests that the particles of ZrB₂ powder were not single crystals but polycrystals with nano-sized grains with a tendency to agglomerate. Interestingly, the particles size of the sample milled for 10 h was similar to and/or slightly larger than that of the sample milled for 5 h. Similar observations were previously reported for ZrB₂ and/or TiB₂ powders prepared by a mechanochemical treatment of the borothermic reduction of titania and zirconia.²¹

 Table I.
 Lattice Parameters and Crystallite Size of the ZrB2 Powders Prepared by Mechanochemical Processing of ZrH2-B

 Mixture and Subsequent Annealing

Powders	Mixture time (h)	Processing conditions (°C/60 min/Ar)	Heating rate (°C/min)	Lattice parameters (Å)		
				а	с	Crystallite size (nm)
ZHB51	5	900	10	3.171	3.524	14.32
ZHB52	5	1100	10	3.169	3.523	18.63
ZHB11	10	800	10	3.179	3.523	12.49
ZHB12	10	900	10	3.173	3.568	14.42
ZHB13	10	1000	10	3.175	3.517	16.93
ZHB14	10	1100	10	3.167	3.527	20.42
ZHB15	10	1200	10	3.166	3.530	24.87



Fig. 4. Typical FE-SEM images of the powders prepared by ball milling for (a, b) 5 h and (c-f) 10 h and annealing from 900°C to 1200°C.



Fig. 5. Typical TEM images of the powders prepared by ball milling for 10 h and annealing from 900°C to 1200°C.



Fig. 6. High-magnification TEM images of the powders prepared by ball milling for 10 h and annealing from 900°C to 1200°C.

Figure 5 shows TEM images of the ZrB_2 powders prepared by ball milling for 10 h and annealing between 900°C and 1200°C. Here, TEM showed that the particles of ZrB_2 were spherically shaped and were the submicrometer agglomerates consisting of nano-sized grains. Under high magnification (Fig. 6), it is clearly revealed that the sizes of the nano-sized ZrB_2 crystallites were in the range 5–20 nm at 900°C, 10– 25 nm at 1000°C, 10–30 nm at 1100°C, and 20–40 nm at 1200°C, showing a narrow size distribution. An increase in the annealing temperature increased the crystallite size. The average crystallite sizes estimated from TEM micrographs are consistent with those determined by XRD.

IV. Summary

Nanocrystalline ZrB_2 powder was successfully prepared by mechanochemical processing of a ZrH_2 -B mixture and subse-

quent annealing from 800°C to 1200°C. At 800°C, the ZrH_{2} -B mixture was converted into ZrB_2 . However, a trace quantity of unreacted ZrH_2 was detected. At 900°C or above, the ZrH_2 -B mixture was completely converted into ZrB_2 without the presence of any residual ZrH_2 . The particles of the resulting ZrB_2 powder consisted of agglomerates of submicrometer particles with an annealing temperature-dependent crystallite size between 5 and 40 nm. An increase in annealing temperature led to an increase of crystallite size.

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