New Route to Synthesize Ultra-Fine Zirconium Diboride Powders Using Inorganic–Organic Hybrid Precursors

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Ultra-fine zirconium diboride (ZrB₂) powders have been synthesized using inorganic–organic hybrid precursors of zirconium oxychloride (ZrOCl₂ · 8H₂O), boric acid, and phenolic resin as sources of zirconia, boron oxide, and carbon, respectively. The reactions were substantially completed at a relatively low temperature (~1500°C). The synthesized powders had a smaller average crystallite size (<200 nm), a larger specific surface area (~32 m²/g), and a lower oxygen content (<1.0 wt%), which were superior to some commercially available ZrB₂ powders. The thermodynamic change in the ZrO₂–B₂O₃–C system was mainly studied by thermogravimetric and differential thermal analysis. The crystallite size and morphology of the synthesized powders were characterized by transmission electron microscopy and scanning electron microscopy.

I. Introduction

 $Z_{\rm IRCONIUM}$ diboride (ZrB₂) ceramics have a high melting point (3250°C), high hardness (22 GPa), good solid-state phase stability, high thermal and electrical conductivity (9.2 \times 10⁻⁶ Ω/\rm{cm}), and good thermal shock resistance. $^{1-3}$ ZrB₂ is wetted but not attacked by molten metals and it has been used as molten-metal crucibles, Hall–Heroult cell cathodes, and thermowell tubes for steel refining.¹ Also, by addition of SiC and other reinforcements to increase their oxidation resistance, ZrB₂-based ceramics are expected to be a good potential material for ultra-high-temperature applications in the aerospatial industry: hypersonic re-entry vehicles, leading edges, nose caps, rocket nozzle inserts, and air-augmented propulsion system components.

Currently, ZrB_2 powders can be synthesized by various methods such as solid-state reaction, electrochemical, mechanical alloying, and self-propagating high-temperature synthesis.^{7–9} However, a high temperature and a long production period are required, and the synthesized powders have a relatively large crystallite size and poor sinterability. Hence, hot pressing is usually necessary to produce high-density bulk materials. The synthesis of ultra-fine powders has received much attention as it can increase the driving force in the sintering process, improve the microstructure of the sintered body, and enhance the mechanical properties.¹⁰

The sol-gel method is an effective method for low-temperature synthesis of ultra-fine powders because of the formation of amorphous phases and the intimate contact of the reactants. Preiss *et al.*¹¹ used chelated derivatives of zirconium *n*-propoxide and various soluble carbon-yielding compounds to synthesize ZrC fibers, films, and powders. Sacks *et al.*¹² prepared ZrC and HfC powders using zirconium *n*-butoxide and hafnium isopropoxide, and polyhyclric alcohol as the carbon sources. However, very limited studies were conducted on the synthesis of metal borides using solution-phase reactions. Chen *et al.*^{13,14} prepared nanocrystalline TiB₂ and ZrB₂ powders by the benzene-thermal reaction at 400° and 700°C, respectively.

Although ultra-fine ZrB_2 and ZrC powders were successfully synthesized via the sol-gel method using alkoxides and other organic substances as the precursors, there are still several problems such as high cost, toxicity, and the difficulty in determining C/Zr and C/B/Zr molar ratios due to the pyrolyzed carbon yielded by the organic substances. In the present study, we use inorganic precursors $ZrOCl_2 \cdot 8H_2O$ and H_3BO_3 as sources of zirconia and boron oxide, and pyrolyzed carbon from phenolic resin to synthesize ultra-fine ZrB_2 powders. The thermodynamic change process in the ZrO_2 -B₂O₃-C system and the synthesis mechanism were mainly studied.

II. Experimental Procedure

Zirconium oxychloride (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) and boric acid (Shanghai Experiment Reagent Co. Ltd., Shanghai, China), used as the sources of zirconia and boron oxide, were of analytical grade. Phenolic resin (PF-04872, Henan Bond Chemical, Zhengzhou, China) was used as the carbon source, whose char yield was about 50 wt%.

The synthesis of ZrB_2 precursor powders has been described in Fig. 1. Firstly, an inorganic hybrid solution was prepared by dissolving a certain amount of $ZrOCl_2 \cdot 8H_2O$ and H_3BO_3 in ethanol. The molar ratio of zirconium oxychloride, boric acid, and phenolic resin was basically 1:2:10 according to reaction (1), while the amount of boric acid could be changed according to the purity of the synthesized ZrB_2 powders. The pH value of the mixed solution was adjusted to 4 using dilute ammonia under stirring to form a zirconia solution. Phenolic resin was then added to form a binary sol and dilute ammonia was added to promote the gelation process. The gel with some precipitations was then transferred to a tank, ball milled for 24 h with ZrO_2 milling media, and then aged in open air for 4 h. Finally, the binary gel was dried at 80°C for 12 h, grounded, sieved and finally the precursor powders were obtained.

The heat treatment of the precursor powders was carried out in a graphite crucible using a high-temperature graphite resistance furnace (High-Multi 10000, Fujidempa Kogyo Co. Ltd., Saitama, Japan) in the range of the $1100^{\circ}-1400^{\circ}$ C in vacuum at a rate of 10° C/min.

The thermodynamic change process of the precursor powder was measured by differential thermal analysis (TG-DTA, Netzsch STA 449C, Selb, Germany) in an argon atmosphere at a heating rate of 10°C/min. Phase analysis of the sintered composite powders was determined on the basis of X-ray diffraction (XRD) data from a Guinier–Hägg camera (Expectron XDC-1000, Jungner Instrument, Solna, Sweden) with CuKα radiation and S_i as an internal standard. The measurement of

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Fig. 1. Flowchart for synthesis of zirconium diboride precursor powders using inorganic–organic precursors.

X-ray film and refinement of lattice parameters were completed by a computer-linked line scanner system and SCANPI, PIRUM programs. The crystallite size and morphology were characterized by a field emission scanning electron microscope (JSM-6700F, Jeol, Japan) and a field emission transmission electron microscope (JEM 2100F, JEOL, Tokyo, Japan) equipped with selected-area electron diffraction (SAED). The element contents were determined by chemical analysis. The surface areas were characterized by nitrogen adsorption– desorption isotherms obtained with an automatic adsorption instrument (ASAP 2010, Micromeritic, Atlanta, GA) at 77 K.

III. Results and Discussion

Figure 2 shows the TG-DTA curves of the precursor powders. TG analysis shows that a considerable weight loss occurs at about 400°C due to the evaporation of the bonded water and the decomposition of H₃BO₃. The weight loss between 400° and 600°C is thought to be due to the decomposition of phenolic resin. After 1100°C, the weight loss accelerates again and tends to stabilize after 1450°C, which is believed to be the carbo-



Fig. 2. Thermogravimetric and differential thermal analysis curves of the precursor powders.



Fig. 3. X-ray diffraction patterns of the precursor powders at different heat-treatment temperatures from 1200° to 1600° C (1500° C* represents the starting materials with 10 wt% excessive H₃BO₃).

thermal reduction process. The maximal weight loss is about 62.32 wt%.

From the DTA curve, we can see that there is a sharp endothermic peak at about 311.6° C with a considerable weight loss in the TG curve. The exothermic peak at 606.4° C is caused by the crystallization from amorphous zirconia to tetragonal zirconia reported by Bokhimi *et al.*^{15,16}

$$ZrO_2 + B_2O_3 + 5C \rightarrow ZrB_2 + 5CO^{\uparrow}$$
(1)

For reaction (1), the calculated enthalpy change below 1500° C is positive, which shows that the carbothermal reduction process is endothermic. So the endothermic peak that appeared at 1229.6°C indicates the beginning of the ZrB₂ synthesis process. Two weak endothermic peaks are found at 826.7° and 1416.7°C, but the concomitant reactions have not been clearly understood.

XRD patterns of the precursor powders at different heattreatment temperatures for 1 h from 1100° to 1600°C are shown in Fig. 3. The curve marked by 1500°C* indicates that the starting materials used 10 wt% excessive H3BO3. At 1100°C, m-ZrO₂, t-ZrO₂, and B₂O₃ phases are observed and t-ZrO₂ is the dominant phase. The carbon present in the sample remains amorphous. At 1200°C, the intensity of m-ZrO₂ and t-ZrO₂ decreases and the ZrB₂ phase has already appeared. The intensity of ZrC decreases with increasing temperature. XRD patterns at 1500° and 1600°C show no significant change, which indicates that the carbothermal reduction process is complete. In addition, we can see that the ZrC phase is still present at 1500°C, which is believed to be the result of the volatilization of B_2O_3 at high temperatures because of its low melting point. When the starting materials used have 10 wt% excessive H3BO3, only the ZrB_2 phase is observed in the XRD pattern at 1500°C for 1 h.

The lattice parameters, crystallite sizes, and BET surface areas of the synthesized powders at different heat-treatment temperatures are listed in Table I. The average crystallite sizes of ZrB₂ and ZrC are computed by Scherrer's Equation using (101) and (200) reflections, respectively. The lattice parameter of ZrC decreased with increasing temperature and not so obviously of the ZrB₂ phase. The lattice parameter of ZrC at 1300°C is a = 4.678 Å, which is lower than the pure ZrC phase (a = 4.693 Å, PDF#350784), which is caused by the dissolved oxygen in the ZrC lattice.^{12,17,18} The lattice parameters of ZrB₂ at 1500°C are a = 3.168 Å and c = 3.530 Å, which are nearly identical to those of the pure tetragonal ZrB₂ phase (a = 3.168Å, c = 3.530 Å, PDF#340423). The crystallite sizes of both ZrC and ZrB₂ increase with increasing temperature, and the BET surface areas decrease accordingly. It should be noted that the

Table I. Lattice Parameters, Crystallite Sizes, and BET Surface Areas of ZrB₂ and ZrC in the Synthesis of Ultra-Fine ZrB₂ Powders at Different Heat-Treatment Temperatures (T) for 1 h

	Lattice	paramete	ers (Å)	Crystallit	e size (nm)	
<i>T</i> (°C)	ZrC (a)	$ZrB_2(a, c)$		ZrC	ZrB_2	BET $(m^2 \cdot g^{-1})$
1200		3.169	3.532		28.808	
1300	4.678	3.168	3.533	24.310	34.829	215.7 ± 0.5648
1400	4.683	3.169	3.531	30.256	41.864	106.8 ± 0.5443
1500	4.692	3.167	3.529	40.325	43.588	32.35 ± 0.1453
1500*		3.168	3.530		47.562	

The crystallite sizes of the ZrC and ZrB2 phases were calculated using the Scherrer equation, $D_{hkl} = K\lambda/\beta \cos\theta$, where K is a constant whose value is approximately 0.931, λ is the wavelength of X-ray, β is the width of the peak in degrees of 20 at $\frac{1}{2}$ of maximum intensity, and 0 is the Bragg angle.

synthesized ultra-fine powders have large BET surface areas, which is believed to be helpful for further sintering process.

Figure 4 shows the TEM images of the synthesized ZrB_2 powders at 1500°C for 1 h with EDS and SEAD analysis. The crystallite sizes of the synthesized powders mainly distribute over 100-200 nm but exhibit agglomerated particle morphology. There are some floccules under or around the ZrB₂ particles and this is believed to be amorphous carbon. The SEAD pattern shows the diffraction of a certain ZrB₂ particle that is well crystallized. The calculated lattice parameters of ZrB_2 are a = 3.169Å and c = 3.530 Å, which are in accordance with the XRD results. EDS analysis shows the presence of Zr, B, C, and O, and the strong X-ray signals of Zr and B. It indicates that the synthesized ZrB₂ powders at 1500°C/1 h still contain a small amount of oxygen and carbon in the ZrB₂ lattice.

SEM images of the synthesized powders at 1500°C for 1 h are shown in Fig. 5. From the SEM images, the particle sizes of the synthesized ZrB₂ powders also distribute over 100-200 nm with spherical morphology, and several agglomerations appear.

Table II lists the elements content of the synthesized ZrB_2 powders at different heat-treatment temperatures for 1 h. It can be seen that the carbon and oxygen contents decrease with increasing temperature. At 1500°C, the Zr/B molar ratio is about 0.506, which indicates that the synthesized ZrB_2 powders had a



Fig. 4. Transmission electron microscopy image, selected-area electron diffraction image, and EDS analysis of the synthesized powders at 1500°C for 1 h.



Fig. 5. Scanning electron microscopy images of the synthesized ZrB₂ powders at 1500°C for 1 h.

Table II. Element Contents (wt %) of the Synthesized Ultra-Fine Powders at Different Heat-Treatment Temperatures (T) for 1 h

<i>T</i> (°C)	Zr (%)	B (%)	C _{Total} (%)	$C_{Free}\left(\%\right)$	O (%)	Cl (%)	N (%)
1300	60.46	5.79	18.35	7.02	12.97	0.034	<0.1
1400	75.36	13.06	3.56	2.94	5.03	0.028	<0.1
1500*	79.21	18.54	0.34	0.15	0.96	0.023	<0.1

high purity. The oxygen content at 1500°C/1 h is about 0.96 wt%, which is lower than or comparable to the commercially available ZrB₂ powders.

IV. Summary and Conclusions

Ultra-fine ZrB₂ powders have been successfully synthesized at lower temperature ($\sim 1500^{\circ}$ C) using inorganic–organic hybrid precursors. The synthesized powders have small crystallite size (<200 nm) and large BET surfaces (\sim 32 m²/g). The oxygen content of the synthesized powders is below 1.0 wt%. Considerable improvements of this work are the decreased particle size up to 100 nm and the potential superior sinterability due to the large BET surface area. The synthesized powders are expected to be used in the pressureless sintering of ZrB2-based ceramics and this method can be extended to the synthesis of other metal diborides and carbide.

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