# Synthesis and Microstructure of Zirconium Diboride Formed from Polymeric Precursor Pyrolysis

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Zirconium diboride was synthesized by pyrolysis of a novel polymeric precursor. Phase compositions and microstructures of the formed ceramic were characterized. It was found that a precursor with B/Zr molar ratio of 2 can completely transform into zirconium diboride by heating in an inert atmosphere with temperatures above 1500°C. However, the initial formation temperature of zirconium diboride was as low as 1300°C whereas zirconium oxide was also produced from the precursor at 1100°C, the mixture was finally transformed into pure zirconium diboride at the elevated temperature. Zirconium diboride particles, dispersed relatively uniformly with characteristic dimension less than 100 nm, were found to be formed following a liquid phase reaction mechanism.

### I. Introduction

U LTRA-HIGH temperature ceramics (UHTCs) such as borides, carbides, and nitrides of the early transition metals are attractive candidates for extreme environments which require oxidation resistance at temperature above 2000°C, due to their unusually high melting points, high hardness, and good oxidation resistance.<sup>1–3</sup> Zirconium diboride (ZrB<sub>2</sub>), a member of UHTCs, exhibits a unique combination of chemical stability, high thermal and electrical conductivities which makes it suitable for the extreme thermal and chemical environments associated with hypersonic flight, rocket propulsion, and atmospheric re-entry.<sup>4–6</sup> Interest in UHTCs, especially introducing UHTCs into continuous fiber-reinforced ceramic matrix composites (CMCs), which generally acquire polymeric ceramic precursors for a densification process has increased significantly in the past few years.<sup>2,4</sup>

It is well known that there are two kinds of ablation mechanisms including mechanical denudation and chemical erosion (oxidation) which determine ablation performances of CMCs. During the ablation process, mechanical denudation refers to the denudations of the surfaces of materials under high pressure and shearing forces of ablative gases. And chemical erosion mainly means the oxidation and gasification of carbon and forming oxide with low melting points ( $B_2O_3$ , etc). Introducing Zr $B_2$  into CMCs such as carbon fiber-reinforced silicon carbide (C/SiC) composites can effectively depress the oxidation reaction during the ablation pro-

cess by means of forming boron oxide and zirconium dioxide simultaneously to make up for the defects of materials and inhibit further oxidation damage.<sup>7</sup> It has been shown that, C/SiC composites can withstand exposure to an oxidizing environment between 1100°C and 1650°C for aerospace applications since SiC matrix has an inherent limit due to the transition from the passive to active oxidation that occurs below 1700°C.<sup>8</sup> Although pure ZrB<sub>2</sub> actively oxidizes above 1200°C due to intensive volatilization of B<sub>2</sub>O<sub>3</sub>, adding ZrB<sub>2</sub> into C/SiC composites provides more efficient oxidation resistance due to the formation of borosilicate glass on exposed surfaces above 900°C, formation of silica-enriched glass between 1100°C and 1700°C, and formation of zirconia-containing scales for temperatures higher than 1800°C.<sup>9–11</sup> The development of ZrB<sub>2</sub> with improved properties using low-cost processes is essential to increase the performance and to reduce the cost of hypersonic aerospace vehicles. ZrB<sub>2</sub> can be prepared by several techniques. Chen et al.<sup>12,13</sup> prepared nanocrystalline  $TiB_2$  and  $ZrB_2$  by the benzene-thermal reaction at 400°C and 700°C, respectively. Corral et al.<sup>1</sup> improved the ablation resistance of carbon-carbon composites at high temperature using B<sub>4</sub>C and ZrB<sub>2</sub> particles synthesized by the reaction of  $ZrCl_4$ , NaBH<sub>4</sub>, and 1,2-dimethoxyethane and heat treatment. Jensen *et al.*<sup>15</sup> obtained TiB<sub>2</sub>, ZrB<sub>2</sub>, and HfB<sub>2</sub> thin films by chemical vapor deposition (CVD) of the binary tetrahydroborates Ti(BH<sub>4</sub>)<sub>4</sub>, Zr(BH<sub>4</sub>)<sub>4</sub>, and Hf(BH<sub>4</sub>)<sub>4</sub>, respectively. Berthon *et al.*<sup>16</sup> used a mixture of ZrCl<sub>4</sub>, BCl<sub>3</sub>, and H<sub>2</sub> to synthesize ZrB<sub>2</sub> by CVD technique. Yan *et al.*<sup>17</sup> synthesized ZrB<sub>2</sub> powders using hybrid precursors of zirconium oxychloride, boric acid, and phenolic resin as sources of zirconia, boron oxide, and carbon, respectively. However, fewer studies were conducted on the synthesis of metal borides by polymeric solution processing.

Using polymeric precursor pyrolysis routes has been drawing significant attention in the past few years as an alternative method for preparing ceramics and more importantly for CMCs by polymer impregnation and pyrolysis (PIP). One of the most important reasons for this is the potential for reductions in manufacturing costs and relatively simple equipment requirements. A new and multistep method for preparing  $ZrB_2$  by polymeric precursor pyrolysis route is reported herein where the phase compositions and microstructures were characterized. Moreover, the heat treatment process for precursors was studied and a hypothesized formation mechanism of  $ZrB_2$  is also presented.

## **II. Experimental Procedure**

The starting Zr-containing precursors and B-containing precursors were both synthesized and patented in our laboratory.<sup>18</sup> The Zr-containing precursor was  $[(C_4H_8O)Zr(acac)_2]n$ with molecular weight about 64870 and a softening point of

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 Table I.
 Component Contents (wt%) of the Zr-Containing and B-Containing Precursors

Component	Zr (%)	O (%)	N (%)	C (%)	B (%)	H (%)
Zr-containing precursor	29.82	26.40	-	37.90	-	5.88
B-containing precursor	-	_	34.41	29.89	27.25	8.45

170°C. The B-containing material was 2, 4, 6-tri-methylamino borazine with the chemical formula  $(NHCH_3)_3B_3N_3H_3$ and molecular weight ~600. The component contents of these precursors are shown in Table I. Then  $ZrB_2$  polymeric precursor solution were prepared by dissolving Zr-containing polymeric precursor and B-containing precursor into dimethylbenzene, and the solvent was removed by the reduced pressure distillation technology at 80°C. Therefore,  $ZrB_2$  precursors with various B/Zr molar ratios, namely 1, 2, 4, 6, and 8, were prepared. The subsequent heat treatment was performed at a heating rate of 2°C/min to the desired temperature of 1500°C and then held for 2 h in a MoSi<sub>2</sub> furnace under flowing argon atmosphere.

A standard X-ray diffractometer (XRD; D/max-rb, Rigaku Corporation, Tokyo, Japan) with CuKa radiation was used to determine phase compositions and crystalline state of the products after heat treatment. On-line Fourier transform infrared spectroscopy (FTIR; Bruker Tensor 27, Bruker, Ettlingen, Germany) detection was performed over the range from 4000 to 400  $\text{cm}^{-1}$  from the outlet of the tube furnace during heating process with a rate of 10°C/min in nitrogen atmosphere, using the ZrB<sub>2</sub> precursor powders prepared using grinding method to analyze the pyrolysis process. Yields of solids were calculated as a ratio of the mass of products after heat treatment to the mass of precursors at 1500°C, and the components were determined by chemical elemental analysis. Specifically, the content of boron was determined by alkali-based titration and the relative standard deviation was less than 5%. The content of zirconium was tested using a gravimetric method with a relative standard deviation less than 1%. To determine the contents of oxygen and nitrogen, inert gas pulse infrared thermal conductivity method was used (QB-QT-33-1997). The content of carbon was determined by high-frequency combustion infrared method (ASTM E 1941-2004) while that of hydrogen was tested using an inert gas pulse infrared method (ASTM E 1447-2009). Microscopic structures of ZrB<sub>2</sub> were investigated using a scanning electron microscope (SEM; Quanta 200 FEG, FEI, Eindhoven, the Netherlands).

## III. Results and Discussion

The XRD analysis of the  $ZrB_2$  polymeric precursors after heat treatment at 1500°C with various B/Zr molar ratios are shown in Fig. 1, which shows that there were several prod-



**Fig. 1.** XRD patterns of samples produced by precursors with various B/Zr molar ratios: (a) 1; (b) 2; (c) 4; (d) 6; and (e) 8.

ucts transformed from the precursors with various B/Zr molar ratios. Specifically, the diffraction peaks match well with the data for hexagonal  $ZrB_2$  reported by the JCPDS (card No. 01-089-3826) when B/Zr molar ratio was 2, which indicates an excellent finding that the precursor could be completely transformed into  $ZrB_2$ . According to XRD patterns, the precursor with B/Zr ratio of 1 may transform into  $ZrB_2$ ,  $ZrO_2$ , and ZrN during heat treatment. Meanwhile, as B/Zr molar ratio increased, there was also a small quantity of cubic ZrC produced other than  $ZrB_2$  with a ratio of 4. ZrC mixed with a bit of  $ZrO_2$  and C was obtained with the ratio of 6 and more ZrC,  $ZrO_2$ , and C were obtained as the ratio reached 8.

To understand transformation mechanism, FTIR was performed on the ZrB<sub>2</sub> precursor. According to FTIR spectra shown in Fig. 2, the peaks at about 2930 cm<sup>-1</sup> were assigned to be C–H stretching whereas the humps at 1720 and 1610 cm<sup>-1</sup> were due to stretching and bending of C=O bond, respectively.<sup>19</sup> The humps observed at 1070 and 960 cm<sup>-1</sup> were believed to be due to C–N and N–H stretching, respectively. A set of two bands appeared at 2340 and 660 cm<sup>-1</sup>, which could be attributed to antisymmetric and symmetric stretching vibration of O=C=O, respectively. Therefore, it could be deduced that gaseous products such as CH<sub>4</sub>, CO<sub>2</sub>, and NH<sub>3</sub> were produced and the CO<sub>2</sub> generating rate went up gradually with increasing temperature.

To characterize the generative process of  $ZrB_2$ , the phase compositions and crystalline state of the products after heat treatment at various temperatures were characterized using XRD analysis. Figure 3 shows XRD patterns of pyrolysized products of  $ZrB_2$  polymeric precursor heat treated at various temperatures. After heat treatment at 1100°C, tetragonal zirconia (t-ZrO<sub>2</sub>) was detected.  $B_2O_3$  and carbon were not detected, implying that these phases were present in amorphous form or in minute amount. Initial formation of  $ZrB_2$ was observed at 1300°C, while monoclinic zirconia (m-ZrO<sub>2</sub>)



Fig. 2. FTIR spectra of the  $ZrB_2$  precursors at various temperatures: (a) 120°C; (b) 220°C; (c) 400°C; and (d) 900°C.



Fig. 3. XRD patterns for the  $ZrB_2$  polymeric precursors that were heat treated at various temperatures: (a) 1100°C; (b) 1300°C; and (c) 1500°C.

Table II.Component Contents (wt%) of the SynthesizedZrB2 Powders at 1500°C

Component	Zr (%)	B (%)	N (%)	C (%)	O (%)	Н (%
ZrB <sub>2</sub> powders	79.04	18.39	0.37	0.78	0.91	< 0.1

was produced and t-ZrO<sub>2</sub> was detected as well. Whereas the precursor was heat treated at 1500°C, zirconia phases disappeared and transformed into ZrB<sub>2</sub> completely. Therefore, it could be deduced that zirconia was an intermediate product which reacted with B<sub>2</sub>O<sub>3</sub> at 1500°C to form ZrB<sub>2</sub> completely. According to the chemical thermodynamics of the system, methane is a very stable phase. Excess carbon must be gasified by the excess of hydrogen in the system. The following reactions occurred:



Fig. 4. SEM photos of  $ZrB_2$  transformed from the precursor: (a) low magnification, (b) large magnification, and EDS spectrum of  $ZrB_2$  (c).

$$ZrO_2(s) + B_2O_3(l) + 5C(s) \rightarrow ZrB_2 + 5CO(g)$$
(1)

$$C(s) + 4H \rightarrow CH_4(g)$$
 (2)

From the elemental analysis of the precursors (Table I), the theoretical yield of  $ZrB_2$  should be 30.1% when the B/Zr ratio of the precursor was 2. During heat-treatment process, a great deal of gases including CO and CH<sub>4</sub> were produced and escaped away. As a result, the yield of  $ZrB_2$  powders was measured to be 31.9%. Within the limits of experimental error, the calculated result coincides with the experimental result. Further chemical elemental analysis was characterized on the synthesized  $ZrB_2$  powders. The component contents are shown in Table II. It could be found that the final powders consist of Zr, B, and a little amount of O, N, C, and H. The B/Zr molar ratio is about 1.97, which indicates that the synthesized  $ZrB_2$  powders have a high purity.

Microstructures of the formed ceramic are shown in Figs. 4(a) and (b). As shown in Fig. 4(c), only Zr and B are detected using EDS analysis, indicating that the precursor has almost entirely been transformed into ZrB<sub>2</sub>. This result agrees well with that of XRD analysis and chemical elemental analysis. According to the SEM micrographs, a multitude of ZrB<sub>2</sub> particles were formed and dispersed relatively uniformly, with the sizes of a majority of  $ZrB_2$  particles being on the order of 50-100 nm, which is hypothesized to be the consequence of the homogeneous nucleation and crystal growth of ZrB<sub>2</sub>. The large magnification micrograph shows that the  $ZrB_2$  particles tended to be spherical and aggregated. There are a host of spherical droplet ZrB<sub>2</sub> particles whose grain sizes are diverse around the large ZrB<sub>2</sub> aggregate, which indicates that the formation of  $ZrB_2$  particles was via the liquid phase reaction mechnism.<sup>20</sup> At higher temperatures, the spherical droplet ZrB<sub>2</sub> particles thus formed are ready to proceed by liquid diffusion and have the tendency of aggregating together to form large particles.

#### IV. Conclusions

In summary, ZrB<sub>2</sub> polymeric precursors were prepared using [(C<sub>4</sub>H<sub>8</sub>O)Zr(acac)<sub>2</sub>]n and (NHCH<sub>3</sub>)<sub>3</sub>B<sub>3</sub>N<sub>3</sub>H<sub>3</sub>, and the precursor with a B/Zr molar ratio of 2 can be completely transformed into hexagonal ZrB2 during heat treatment at 1500°C in argon for 2 h. ZrC, ZrO<sub>2</sub>, and even C could be obtained if molar ratios of B/Zr are increased larger than this value. Keeping a constant B/Zr molar ratio of 2 and decreasing the temperature as low as 1100°C, t-ZrO<sub>2</sub> was formed from the precursor, while large amounts of ZrB<sub>2</sub> with a little m-ZrO<sub>2</sub> were formed at increased temperatures up to 1300°C. The precursor could only transform into pure ZrB<sub>2</sub> at temperatures above 1500°C, with the formed diboride particles dispersed uniformly and sizes around 50-100 nm. It was also assumed that the formation of ZrB<sub>2</sub> particles was via the liquid phase reaction mechanism with an aggregation phenomenon occurring during pyrolysis.

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