# Synthesis of Plate-Like ZrB<sub>2</sub> Grains

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Plate-like  $ZrB_2$  grains were synthesized at 1550°C by *in situ* solid/liquid reaction using Zr and B powders mixed with transition metal (Mo, Nb, Ti, or W) and Si powder. The preferred growth direction of plate grains was along *a*- or *b*-axis depending on the initial content of transition metal and silicon in the mixtures. The synthesis mechanism of plate-like grain was possibly related to the catalysis of *in situ* formed silicides.

# I. Introduction

WING to the high melting point, high Young's modulus, as well as the good oxidation resistance, transition diboride ZrB<sub>2</sub> has been considered as the candidate material for high-speed aircrafts and re-entry vehicles.1 To date, many articles have been published to describe the synthesis, microstructure, physical and mechanical properties, and ablation behavior of dense ZrB<sub>2</sub>-based composites.<sup>2-8</sup> Especially, ZrB<sub>2</sub> -SiC composites have the promising application as the nose and thermal protective cladding downside the re-entry vehicles. These series of composites possess good oxidation resistance, ablation resistance, and interesting high-temperature strength.9 However, due to the intrinsic brittleness of ceramic composites, their toughness is in a range of 3-6 MPa $\cdot$ m<sup>1/</sup> which is not high enough to show the high reliability during application. Recently, Zou *et al.*<sup>10</sup> confirmed that plate-like ZrB<sub>2</sub> grains could be formed in the dense ZrB<sub>2</sub>-SiC composite with addition of WC. These plate-like grains can deflect the crack path and enhance the fracture surface energy, as well as blunting the crack tip.<sup>2</sup> Therefore, the fracture toughness of composites can be increased. In addition, using the strong magnetic field alignment (SMFA) method, the textured ZrB2 and ZrB2-SiC composite could be well prepared and exhibited the anisotropic physical and mechanical properties along *a*- or *b*- and *c*-axes directions.<sup>11</sup> Most recently, Hu *et al.*<sup>12</sup> used the plate-like Nb<sub>4</sub>AlC<sub>3</sub>, one of MAX phases, to fabricate a composite showing the surprising high flexural strength above 1 GPa and fracture toughness above 18  $MPa \cdot m^{1/2}$ . This result was attributed to the orderly alignment of Nb<sub>4</sub>AlC<sub>3</sub> grains in the final synthesized ceramic. The question is whether we can prepare the plate-like  $ZrB_2$  powder and then tailor the microstructure using the SMFA method to obtain improved physical and mechanical properties. The most important obstacle is how to synthesize the plate-like  $ZrB_2$  grains.

In previous investigation, Wu *et al.*<sup>13</sup> found that the rodlike ZrB<sub>2</sub> grains appeared in the Zr–B–Mo–Si system when sintered above 1550°C. She found that the ZrB<sub>2</sub> grains displayed preferential growth vertical to the *c*-axis, resulting in elongated and rod-like grains dispersed throughout the fabricated ZrB<sub>2</sub>–MoSi<sub>2</sub> composite. In this study, we systemically investigated the effect of Mo and Si content on the fabrication of plate-like ZrB<sub>2</sub> particles. In addition, other kinds of transition metals, such as Nb, Ti, and W, were also confirmed to accelerate the plate-like growth of ZrB<sub>2</sub> grain.

# **II. Experimental Procedure**

Commercial powders of Zr (99%, 45 µm) (Kojundo Chemical Lab. Co., Ltd, Saitama Prefecture, Japan), amorphous B (99%, 1 µm) (ABCR GmbH & Co. KG, Karlsruhe, Germany), Mo (99%, 1.5 µm) (Furuuchi Chemical Co., Ltd, Tsukuba, Japan), and Si (99%, 9.9 µm) (Yamayishi Metal Co. Ltd., Tokyo, Japan) were used to fabricate the ZrB<sub>2</sub> powder. Designed initial element compositions are listed in Table I. The mass of zirconium, boron, silicon, and molybdenum powders was weighed by a balance with an accuracy of 10 mg. The weighed powders were mixed by dry ball milling in a rotary milling mode. The milling media was Si<sub>3</sub>N<sub>4</sub> balls with a diameter of 3 mm. The milling speed was 50 rpm and the milling time was 12 h. After separating the mixture and balls, the mixed powder was put into a graphite crucible and heat-treated in flowing argon at 1550°C for 30 min. The heating rate was 20°C/min. The as-prepared powder was examined by an X-ray diffraction (XRD) analyzer (JDX-3500; JEOL Ltd, Tokyo, Japan) with CuKa radiation and a scanning electron microscope (SEM) (JSM-6500; JEOL Ltd) equipped with an energy dispersive spectroscopy (EDS) system. The formed MoSi<sub>2</sub> probably catalyzed the growth of plate-like ZrB<sub>2</sub> grains, and the optimized composition was sample 5.

To deeply investigate the catalysis behavior of transition metal silicide, several kinds of transition metal powders, such as Mn (99%, 10  $\mu$ m) (Kojundo Chemical Lab. Co., Ltd), Nb (99%, 45  $\mu$ m) (Kojundo Chemical Lab. Co., Ltd), Ni (99%, 0.2  $\mu$ m) (Shoei Shokai Co., Ltd, Tokyo, Japan), Ti (99%, 20  $\mu$ m) (American Elements, Los Angeles, CA), and W

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 Table I.
 Initial Element Compositions for Preparing ZrB2 Grains

Sample no.	Zr (g)	B (g)	Mo (g)	Si (g)	
1	15.25	3.59	0	0	
2	15.25	3.59	0.94	0	
3	15.25	3.59	0.98	0.8	
4	15.25	3.59	1.03	1.8	
5	15.25	3.59	1.10	3.08	
6	15.25	3.59	1.18	4.79	
7	15.25	3.59	0.66	3.08	
8	15.25	3.59	0.22	3.08	
9	15.25	3.59	0	3.08	

(99%, 1  $\mu$ m) (Furuuchi Chemical Co., Ltd) powders, were used to replace Mo. The optimized composition was similar to sample 5.

# III. Results and Discussion

The experimental results showed that without the additive of molybdenum and silicon (sample 1), the synthesized grains agglomerated seriously and was not possible to be separated independently (not shown for brevity). All of the grains were equiaxed. Interestingly, it was found that some powders were ejected and adhered onto the wall of furnace chamber. This phenomenon was due to the high energy of the self-propaga-tion high-temperature synthesis (SHS).<sup>14</sup> The quick reaction between zirconium and boron induced the rapid thermal diffusion and gas generation, resulting in the ejection. In addition, when sintering the sample 6, the plate-like ZrB<sub>2</sub> grains distributed homogeneously in the obtained powder. Figure 1 shows the SEM morphologies of as-obtained ZrB<sub>2</sub> particles. It is seen that all of the grains have the plate-like microstructure. The mean grain size is 4.1 µm wide and 1.0 µm thick. Especially, the hexagonal crystallized grains indicate the growing mode. The surface energy on the (000*l*) planes is higher in comparison with other planes.<sup>10,15</sup> For  $ZrB_2$ , the low activation energy diffusion path is along <210> and <110> directions.<sup>10</sup> Therefore, the ZrB<sub>2</sub> grains grow very well along a- or b-axis. Figure 2(a) shows the layer-by-layer growth of ZrB2 grain. Through this mode, the small grains could coarsen and coalesce. To understand the growing mechanism, the ZrB2 grains were analyzed by EDS and XRD. In EDS analysis, it was confirmed that except the peaks of Zr-L and B-K, the typical peaks of Mo-L and Si-K exist. In addition, the XRD spectrum displays the sharp peaks of main ZrB<sub>2</sub> phase [Fig. 2(b)], indicating the good crystallization. Only a few amount of MoSi2 and β-SiC were formed owing to the reactions between molybdenum and sili-



Fig. 1. Scanning electron microscope (SEM) photograph of synthesized plate-like  $ZrB_2$  grains from the sample 6.





Fig. 2. (a) SEM micrograph of single growing  $ZrB_2$  grain and (b) X-ray diffraction (XRD) pattern of as-obtained  $ZrB_2$  powder.

con, as well as the silicon and graphite. Here, the reducing environment is due to the graphite crucible. In addition, silicon was detected in the powder. It is concluded that the formation of plate-like grain is associated with the existence of molybdenum, silicon, or MoSi<sub>2</sub>. Based on the reference intensity ratio (RIR) method,<sup>16</sup> the estimated weight fraction of ZrB<sub>2</sub> is 91.1%, as shown in Table II.

To clearly distinguish the effects of molybdenum and silicon, a series of mixture powders were prepared and sintered. First, the silicon content was modified as the samples 2-5. It was found that increasing the silicon content, the  $ZrB_2$  grains were prone to become plate-like and only when the initial composition was the sample 5, the plate-like grains could develop well, as shown in Fig. 3(a). Furthermore, by XRD analysis, it was confirmed that silicon could not be found in the sintered sample [Fig. 4(a)]. The weight fraction of  $ZrB_2$  is 95.4%. It is known that the melting point of silicon is 1410° C and the boiling point is 2355°C. As mentioned above, selfpropagation reaction occurred during the sintering process. Although the accurate temperature was unknown during SHS, Fang et al.<sup>17</sup> reported that the highest temperature should be above 2300°C in the SHSed Zr-B system. The calculated adiabatic temperature during SHS was 3051°C, which was much higher than the boiling point of silicon (2355°C).<sup>18</sup> Therefore, the silicon in present sample was possible to evaporate during the SHS process or reacted with Mo to form MoSi<sub>2</sub>. Second, the mixture powders were prepared as the samples 7-9 and heat-treated up to 1550°C. The result indicated that increasing molybdenum content, the morphology of ZrB<sub>2</sub> changed from equiaxed to plate-like. When the initial composition was the sample 7, nearly all of the grains were plate-like. It is concluded that enough additive of silicon and molybdenum is necessary to synthesize the plate-like  $ZrB_2$  powder. In the final sample, as there is no residual

Table II. Calculated Phase Compositions in the Prepared Powders Based on RIR Method

Phase weight fraction (wt%)	ZrB <sub>2</sub>	MoSi <sub>2</sub>	β-SiC	Si	NbSi <sub>2</sub>	ZrC	$ZrSi_2$	WSi <sub>2</sub>
Mo additive (Sample 6)	91.1	4.6	0.7	3.6				
Mo additive (Sample 5)	95.4	3.1	1.5					
Nb additive	94.5		1.5		1.7		2.3	
Ti additive	78.4		3.8			11.7	6.1	
W additive	93.1		1.2				1.2	4.5



**Fig. 3.** SEM photographs of synthesized plate-like  $ZrB_2$  grains with the same sample 5 composition: (a) Mo additive, (b) Nb additive, (c) Ti additive, and (d) W additive. The figures are at different magnifications.



**Fig. 4.** X-ray diffraction (XRD) patterns of  $ZrB_2$  powders synthesized at 1550°C with the same sample 5 composition: (a) Mo additive, (b) Nb additive, (c) Ti additive, and (d) W additive.

silicon or molybdenum, the only factor affecting the growth of  $ZrB_2$  grains is MoSi<sub>2</sub>. That is, the *in situ*-formed MoSi<sub>2</sub> probably imposes the catalysis effect on the growth of  $ZrB_2$ 

grains. This result is in agreement with former studies on the  $ZrB_2$ -MoSi<sub>2</sub> system.<sup>13</sup>

When using Mn, Nb, Ni, Ti, and W to replace Mo, it was confirmed that except Mn and Ni, the addition of Nb, Ti, and W contributed to the growth of plate-like ZrB<sub>2</sub> grains, as shown in Figs. 3(b)-(d). The hexagonal-shaped grains distribute randomly in the powder. Respectively, the mean grain sizes are 2.1, 3.2, and 3.7 µm wide and 0.6, 0.9, and 0.9 µm thick in the Zr-B-Nb-Si, Zr-B-Ti-Si, and Zr-B-W-Si systems. Figures 4(b)-(d) show the XRD spectra of as-fabricated plate-like ZrB2 grains. Apart from β-SiC and ZrSi2 which were observed in all the samples, NbSi2 and WSi2 were, respectively, found in the powders fabricated from Zr-B-Nb-Si and Zr-B-W-Si systems. However, in the powder synthesized from Zr-B-Ti-Si system, the impurities are β-SiC, ZrC, and ZrSi<sub>2</sub>. No TiSi<sub>2</sub> phase could be detected. It has been reported that the reaction between  $TiSi_2$  and  $ZrB_2$  could form  $ZrSi_2$  and  $TiB_2$  at 1650°C.<sup>19</sup> It can be possible that during the heat treatment at 1550°C, all of the TiSi<sub>2</sub> has been completely consumed. The calculated ZrB<sub>2</sub> weight fractions in the obtained powders from Zr-B-Nb-Si, Zr-B-Ti-Si, and Zr-B-W-Si systems are 94.5%, 78.4%, and 93.1%, respectively (Table II). The less ZrB<sub>2</sub> content in the Zr-B-Ti -Si system is probably due to the serious C diffusion based on the formation of ZrC. In addition, in the same system, it is seen that all of the diffraction peaks of ZrB<sub>2</sub> diffract to higher angles indicating possible formation of solid solution. Owing to the smaller atomic radius of Ti (0.147 nm) than that of Zr (0.162 nm), the crystal structure of  $ZrB_2$  contracts a little.<sup>20</sup> All of the formed TiB<sub>2</sub> dissolved into ZrB<sub>2</sub> grains to form (Zr,Ti)B<sub>2</sub> solid solution.

# IV. Conclusions

In summary, the plate-like  $ZrB_2$  grains were successfully fabricated by *in situ* reaction between zirconium and boron with the additive of silicon and transition metal. In present research, Mo, Nb, Ti, and W were confirmed to accelerate the growth of plate-like  $ZrB_2$ . The formed silicides probably catalyzed the preferred growth of  $ZrB_2$  grains along *a*- or *b*-axis by decreasing the surface energy.

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### References

<sup>1</sup>K. Upadhya, J. M. Yang, and W. P. Hoffman, "Materials for Ultrahigh Temperature Structural Applications," *Am. Ceram. Soc. Bull.*, **76**, 51–6 (1997).

<sup>2</sup>L. Silvestroni, D. Sciti, C. Melandri, and S. Guicciardi, "Toughened ZrB<sub>2</sub>-Based Ceramics Through SiC Whisker or SiC Chopped Fiber Additions," *J. Eur. Ceram. Soc.*, **30**, 2155–64 (2010).

<sup>3</sup>X. H. Zhang, P. Hu, J. C. Han, and S. H. Meng, "Ablation Behavior of ZrB<sub>2</sub>–SiC Ultra High Temperature Ceramics Under Simulated Atmospheric Re-Entry Conditions," *Comp. Sci. Technol.*, **68**, 1718–26 (2008).

<sup>4</sup>S. C. Zhang, G. E. Hilmas, and W. G. Fahrenholtz, "Pressureless Sintering of ZrB<sub>2</sub>–SiC Ceramics," *J. Am. Ceram. Soc.*, **91**, 26–32 (2008).
<sup>5</sup>S. Q. Guo, Y. Kagawa, T. Nishimura, and H. Tanaka, "Pressureless Sinter-

<sup>5</sup>S. Q. Guo, Y. Kagawa, T. Nishimura, and H. Tanaka, "Pressureless Sintering and Physical Properties of ZrB<sub>2</sub>-Based Composites with ZrSi<sub>2</sub> Additive," *Scripta Mater.*, **58**, 579–82 (2008).

<sup>6</sup>A. L. Chamberlain, W. G. Fahrenholtz, and G. E. Hilmas, "Pressureless Sintering of Zirconium Diboride," *J. Am. Ceram. Soc.*, **89**, 450–6 (2006). <sup>7</sup>L. Silvestroni and D. Sciti, "Effects of MoSi<sub>2</sub> Additions on the Properties of Hf– And Zr–B<sub>2</sub> Composites Produced by Pressureless Sintering," *Scripta Mater.*, **57**, 165–8 (2007).

<sup>8</sup>D. Sciti, S. Guicciardi, and A. Bellosi, "Properties of A Pressureless-Sintered ZrB<sub>2</sub>-MoSi<sub>2</sub> Ceramic Composite," *J. Am. Ceram. Soc.*, **89**, 2320–2 (2006).

<sup>9</sup>S. Q. Guo, "Densification of ZrB<sub>2</sub>-Based Composites and Their Mechanical and Physical Properties: A Review," *J. Eur. Ceram. Soc.*, **29**, 995–1011 (2009).

<sup>10</sup>J. Zou, S. K. Sun, G. J. Zhang, Y. M. Kan, P. L. Wang, and T. Ohji, "Chemical Reactions, Anisotropic Grain Growth and Sintering Mechanisms of Self-Reinforced ZrB<sub>2</sub>–SiC Doped with WC," *J. Am. Ceram. Soc.*, **94**, 1575– 83 (2011).

<sup>83</sup> (2011). <sup>11</sup>D. W. Ni, G. J. Zhang, Y. M. Kan, and Y. Sakka, "Highly Textured ZrB<sub>2</sub>-Based Ultrahigh Temperature Ceramics via Strong Magnetic Field Alignment," *Scripta Mater.*, **60**, 615–8 (2009). <sup>12</sup>C. F. Hu, Y. Sakka, S. Grasso, T. Nishimura, S. Q. Guo, and H. Tanaka,

<sup>12</sup>C. F. Hu, Y. Sakka, S. Grasso, T. Nishimura, S. Q. Guo, and H. Tanaka, "Shell-Like Nanolayered Nb<sub>4</sub>AlC<sub>3</sub> Ceramic with High Strength and Toughness," *Scripta Mater.*, **64**, 765–8 (2011).

ness," *Scripta Mater.*, **64**, 765–8 (2011). <sup>13</sup>W. W. Wu, Z. Wang, G. J. Zhang, Y. M. Kan, and P. L. Wang, "ZrB<sub>2</sub>– MoSi<sub>2</sub> Composites Toughened by Elongated ZrB<sub>2</sub> Grains via Reactive Hot Pressing," *Scripta Mater.*, **61**, 316–9 (2009).

<sup>14</sup>D. D. Radev and D. Klissurski, "Mechanochemical Synthesis and SHS of Diborides of Titanium and Zirconium," *J. Mater. Synth. Proc.*, **9**, 131–6 (2001).

<sup>15</sup>J. K. Jung, Y. J. Park, N. M. Hwang, and Y. C. Joo, "Tertiary Grain Growth Driven by Surface Energy," *Scripta Mater.*, 45, 267–72 (2001).
 <sup>16</sup>F. H. Chung, "Quantitative Interpretation of X-ray Diffraction Patterns:

<sup>10</sup> F. H. Chung, "Quantitative Interpretation of X-ray Diffraction Patterns: I. Matrix Flushing Method of Quantitative Multicomponent Analysis," *J. Appl. Crystallogr.*, 7, 519–25 (1974). <sup>17</sup>Z. Fang, H. Wang, and Z. Y. Fu, "Preparation of ZrB<sub>2</sub> Ceramics Powder

<sup>17</sup>Z. Fang, H. Wang, and Z. Y. Fu, "Preparation of ZrB<sub>2</sub> Ceramics Powder in Zr-B System by Self Propagating High-Temperature Synthesis," *J. Chin. Ceram. Soc.*, **32**, 1016–8 (2004).

<sup>18</sup>W. W. Ji, Y. P. Song, and J. Yang, "Calculation and Verification of Adiabatic Temperature of Self-Propagating Reaction System Based on the Database of Materials' Thermodynamics," *Bull. Chin. Ceram. Soc.*, **28**, 1300–5 (2009).

<sup>19</sup>J. K. Sonber, T. S. R. C. Murthy, C. Subramanian, S. Kumar, R. K. Fotedar, and A. K. Suri, "Investigations on Synthesis of ZrB<sub>2</sub> and Development of New Composites with HfB<sub>2</sub> and TiSi<sub>2</sub>," *Int. J. Refract. Met. Hard Mater.*, 29, 21-30 (2011).
 <sup>20</sup>C. F. Hu, Y. Sakka, H. Tanaka, T. Nishimura, and S. Grasso, "Synthesis,

<sup>20</sup>C. F. Hu, Y. Sakka, H. Tanaka, T. Nishimura, and S. Grasso, "Synthesis, Microstructure and Mechanical Properties of (Zr,Ti)B<sub>2</sub>-(Zr,Ti)N Composites Prepared by Spark Plasma Sintering," J. Alloys Compd., **494**, 266–70 (2010). □