



# IN-SITU REACTION SYNTHESIS AND MECHANICAL PROPERTIES OF ULTRA HIGH TEMPERATURE CERAMICS

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## Abstract

ZrB<sub>2</sub>-SiC ultra high temperature ceramics were prepared by a mixture of zirconium, silicon, and B<sub>4</sub>C with various molar ratios via in-situ reactive hot pressing at temperature (1900 °C) for 60min under 30 MPa in vacuum. Experimental analysis revealed that the ZrB<sub>2</sub>-SiC composite through in-situ reaction synthesis exhibited higher flexural strength and fracture toughness. The sinterability and densification properties of ZrB<sub>2</sub>-based UHTCs increased as the amount of Si increased, however many large ZrB<sub>2</sub> agglomerates formed when the amount of synthesized SiC in the product reached 25vol%, which led to decrease the mechanical property. Moreover the SEM result indicates that the distributions of the in situ formed ZrB<sub>2</sub>, SiC, and ZrC phases in the composite are not homogenous.

## 1 Introduction

Future reentry space vehicles will need better maneuverability to improve safety and performance. Vehicles with sharp leading edges, as opposed to the blunt nose and leading edges on the current space shuttle can provide improved lift-to-drag and thus improved maneuverability [1-5].

ZrB<sub>2</sub> and HfB<sub>2</sub> composites containing SiC are known to have good thermal shock and configurational stability at elevated temperatures. These are promising ultra-high temperature ceramics (UHTCs) for use on the sharp leading edges of next generation space vehicles [6, 7]. Sharp leading edges on these vehicles will need to withstand repeated exposures to temperatures greater than 2200°C in oxidizing environments have good thermal shock and ablation resistance and withstand the mechanical

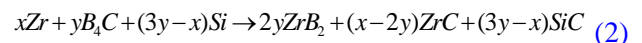
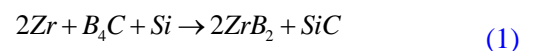
stress of launch and reentry. The potential for ZrB<sub>2</sub> (HfB<sub>2</sub>)-SiC composites to meet the requirements of hypersonic flight depends on controlling processing techniques [8-10].

For most of the reported studies, ceramic composites have been fabricated simply by hot pressing from commercially available powders. Reactive hot pressing (RHP) is an alternative route. It can produce materials with novel and controlled microstructures, with high chemical compatibility of the in situ formed individual phases, and phase distribution uniformity

This presentation will focus on understanding processing method to optimize the material properties of ZrB<sub>2</sub>-SiC composites for the application in ultra high temperature environment. The correlation between *in situ* reaction processing techniques, microstructure and mechanical properties will be investigated.

## 2 Experimental procedure

For zirconium boride-containing UHTCs, a high-strength ZrB<sub>2</sub>-SiC composite can be prepared by reactive hot pressing processing from a mixture of Zr, Si and B<sub>4</sub>C according to reaction(1) as following:



The existence of ZrC to ZrB<sub>2</sub>-SiC to form a ternary composite of ZrB<sub>2</sub>-SiC-ZrC can tailor the microstructure and properties of ZrB<sub>2</sub>-SiC, especially the superior resistance to fracture and strength at a high temperature. In this work, a composite in the ZrB<sub>2</sub>-SiC-ZrC system was prepared by reactive hot pressing, using Zr, Si and B<sub>4</sub>C as starting powders.

When  $x = 2$  and  $y = 1$ , reaction (2) reduces to reaction (1). In the present work, we took different variation value based on calculations for maintaining

the volume content of SiC at 10%, 15%, 20%, 25%. The calculated volumetric composition is shown in Table.1. The reactions are thermodynamically favorable and exothermic. In this communication, the samples were produced under relatively mild conditions (1900°C), and the detailed preparing process is shown in Fig.1.

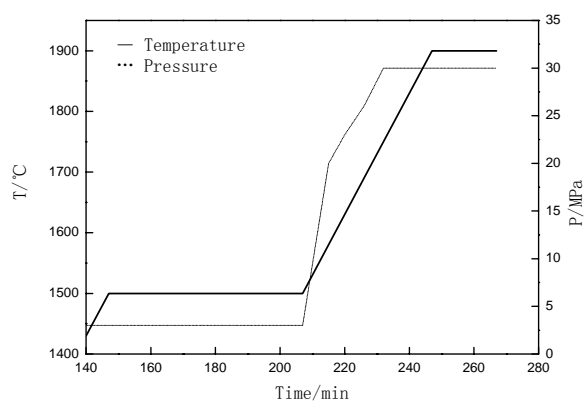


Fig.1 Curve of sintering temperature (T) and pressure (P) versus sintering time during in-situ reaction

The microstructure of ZrB<sub>2</sub>-SiC composite was studied by scanning electron microscopy (SEM). Crystal-phase identification of the synthesized sample was determined by X-ray diffractometry (XRD) with Ni filtered CuK $\alpha$  radiation (0.1542 nm). Flexural strengths were measured with three-point bending tests (sample size = 30×3×4 mm and span = 20mm) at a crosshead speed of 0.5 mm/min. Load-displacement curves were recorded by attaching strain gauges to the specimen tensile surface. Fracture toughness was evaluated using single-edge notched bend (SENB) beams (2×4×20 mm, notch depth and radius of 2 mm and 0.2 mm, respectively) with a span of 16 mm and a crosshead speed of 0.05 mm/min. The bulk density was measured using the Archimedes method.

Table.1 Volume percentage of each phase in the samples

Sample	Volume content Of crystalline phase		
	ZrB <sub>2</sub>	ZrC	SiC
ZrB <sub>2</sub> -10vol%SiC	72.07	17.93	10
ZrB <sub>2</sub> -15vol%SiC	72.97	12.03	15
ZrB <sub>2</sub> -20vol%SiC	73.86	6.14	20
ZrB <sub>2</sub> -25vol%SiC	74.76	0.24	25

### 3 Results and discussion

#### 3.1 XRD

According to the XRD patterns of the reactive hot-pressed ZrB<sub>2</sub>-20vol%SiC composite at 1900°C and 1600°C as shown in Fig.1.

There are no other phases occur, and the phases present in the composites agree with those predicted from reactions (1) and (2). This observation means that either ZrB<sub>2</sub>-SiC-ZrC can be produced by in situ reaction.

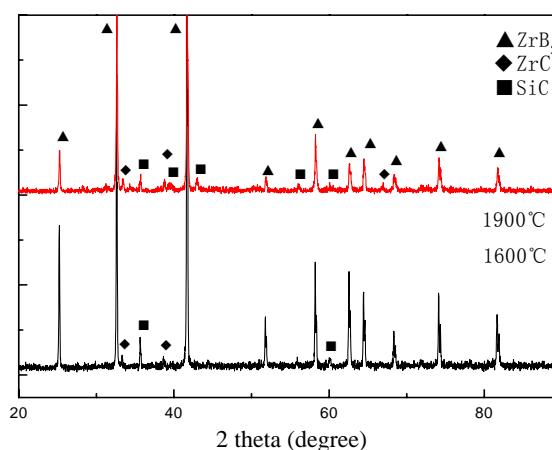
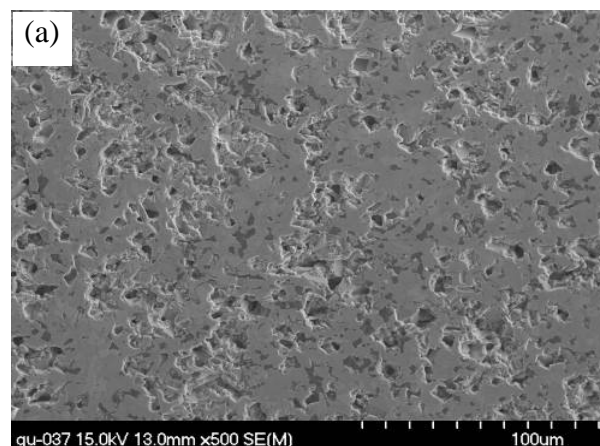


Fig.2 X-ray diffractometry patterns of the reactive hot-pressed ZrB<sub>2</sub>-20vol%SiC composite at 1900°C and 1600°C.

#### 3.2 Base microstructure

The microstructure of ZrB<sub>2</sub>-SiC-ZrC composite with different SiC content is shown in Fig.2 (a)-(d). This picture indicates that the distributions of the in situ formed ZrB<sub>2</sub>, SiC, and ZrC phases in the composite are homogenous when the Si content is low.

The particle size of SiC and ZrC is similar and generally small, about 1~3  $\mu$ m, whereas that of ZrB<sub>2</sub> is large, which is about 4~10  $\mu$ m. SiC and ZrC grains are mainly located at the ZrB<sub>2</sub> grain boundaries. However the ZrB<sub>2</sub> particles were agglomerated and not homogenous when the SiC content exceeds 20% (shown in Fig.2(d)).



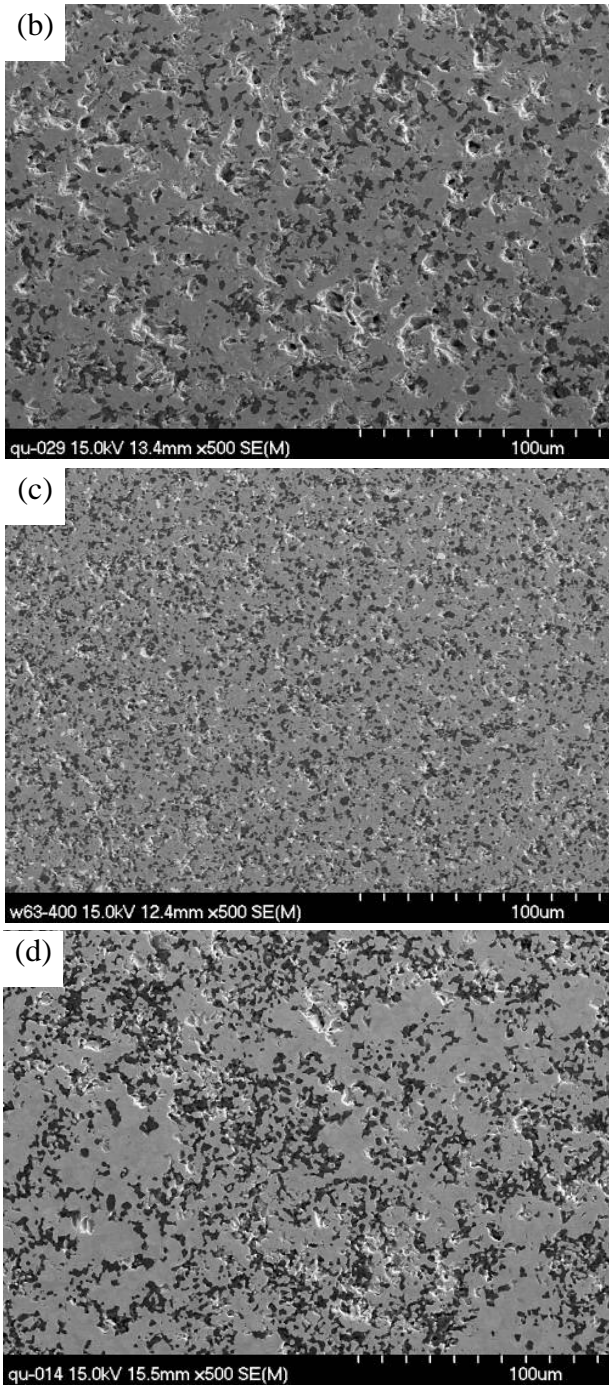


Fig.3 SEM of polished surfaces of the in situ reactive hot-pressed composite with the different SiC content. The gray phase is  $ZrB_2$ , the dark phase is SiC, and the white phase is ZrC.  
(a)10vol%;(b)15vol%;(c)20vol%;(d)25vol%

The possible reasons for this are attributed to the fact that the SiC phase is formed from ZrC. It is assumed that B and C atoms from  $B_4C$  diffuse faster than Zr and Si. Moreover, Si has a lower reactivity than Zr, so the  $ZrB_2$  and ZrC phase formed before

any Si compounds [11, 12]. Especially at higher temperatures, SiC formed *in situ* as a result of the reaction between Si,  $ZrC$ , and the residual  $B_4C$ . Therefore the regions rich in SiC are poor in ZrC.

From Fig. 4, it can be seen that the  $ZrB_2$  grains surrounded by SiC are finer than those not surrounded by SiC. On the other hand, the existence of ZrC seems to promote the growth of the  $ZrB_2$  platelets, and this should have improved the fracture toughness of the composite.

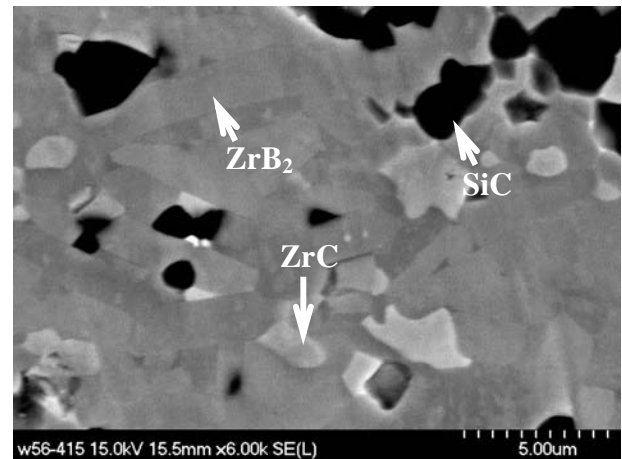


Fig. 4. SEM images of a polished surface of the reactive hot-pressed composite. The gray phase is  $ZrB_2$ , the dark phase is SiC, and the white phase is ZrC.

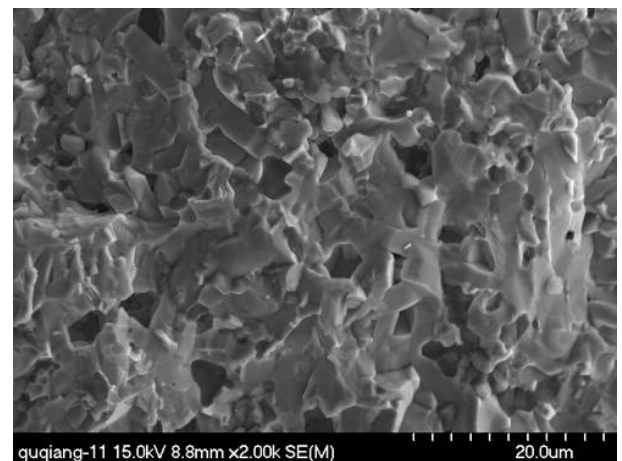


Fig.5 Fracture morphology of  $ZrB_2$ -20SiC composite

The general configuration of the microstructure (shown in Fig.5) presents regularly faceted and plateleted  $ZrB_2$  grains and intergranular SiC and ZrC particulates. The fracture mode is chiefly intergranular even if, in correspondence with the largest grains, intragranular events seem to prevail.

The debonding of  $ZrB_2/ZrB_2$  and  $ZrB_2/SiC$  interfaces is also observed.

### 3.3 Mechanical properties

The measured relative density is over 100% in  $ZrB_2-20SiC$  and  $ZrB_2-25SiC$  samples and reaches 90.9% and 96.8% for  $ZrB_2-10SiC$  and  $ZrB_2-15SiC$  composite respectively. The relative density of the  $ZrB_2-SiC-ZrC$  composite was higher than that of the  $ZrC$ -free composite. This indicates that the presence of  $ZrC$  improves the densification of the material, even though the reactants of the four systems are similar.

The flexural strength and fracture toughness of the prepared composites are listed in the Table 2. The mechanical properties of  $ZrB_2-20vol\%SiC$  is obviously higher than the others due to the finer columnar  $ZrB_2$  grains and the homogeneous distribution of  $SiC$  and  $ZrC$  particulates. The cracks will propagate through intergranular rather than intragranular and consume more energy before fracture, and the columnar  $ZrB_2$  grains also have a bridging effect between grains. All the factors above can improve the flexural strength and fracture toughness effectively. The fracture toughness is higher than the most literature reported due to the higher sintering temperature and good densification characterization of the sintered product. The flexural strength and fracture toughness of  $ZrB_2-10\%SiC$  and  $ZrB_2-15vol\% SiC$  are relative lower, which is relevant to the existing pores retained in the products. For  $ZrB_2-25vol\% SiC$  composite, many large  $ZrB_2$  agglomerates and thus inhomogeneous  $SiC$  particles may lead to the intragranular cracks which will deteriorate the mechanical properties.

Table.2 Mechanical properties of the in situ synthesized  $ZrB_2-SiC-ZrC$  composite

property	Flexual strength (Mpa)	Fracture toughness (MPa·m <sup>1/2</sup> )
ZrB <sub>2</sub> -10vol%SiC	405.5±65	4.19±0.07
ZrB <sub>2</sub> -15vol%SiC	338.5±25	3.95±0.43
ZrB <sub>2</sub> -20vol%SiC	645.8±35	5.66±0.40
ZrB <sub>2</sub> -25vol%SiC	384.5±75	4.41±0.60

- \* 1-  $ZrB_2-20vol\%SiC$ ;  
 2-  $ZrB_2-20vol\%SiC$ ;  
 3 -  $ZrB_2+20vol\%SiC+4vol\%Si_3N_4$ ;  
 4 -  $ZrB_2+15vol\%SiC+4.5vol\%ZrN$ ;  
 5 -  $ZrB_2+20vol\%SiC+6.14vol\%ZrC$

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### References

- [1] Levine SR., Opila EJ, and Salem JA. "Evaluation of Ultra-high Temperature Ceramics for Aeropropulsion Use". J.Euro.Ceram.Soc, Vol.22, pp 2757-67, 2002
- [2] ZHANG GJ., OHJI T. "In Situ Reaction Synthesis of Silicon Carbide-Boron Nitride Composites". J. Amer. Ceram. Soc, Vol.48, No.7, pp 1475-1479, 2001
- [3] Monteverde F., Guicciardi S, and Bellosi A. "Advances in Microstructure and Mechanical Properties of Zirconium Diboride Based Ceramics". Mater.Sci.Eng.A, Vol.A346, pp 310-319, 2003
- [4] Monteverde F., Bellosi A. "Development and characterization of metal-diboride-based composites toughened with ultra-fine SiC particulates". Solid State Sciences, Vol.7, pp 622-630, 2005
- [5] Hodulak L, Blauel JG, Siegele D. and Urich B. "Thermal shock experiments on cracked cladded plates". Nuclear Engineering and Design. Vol.188, pp 139~147, 1999
- [6] Chamberlain A, Fahrenholtz W, Hilmas G. and Ellerby D. "Oxidation of  $ZrB_2-SiC$  Ceramics Under Atmospheric and Reentry Conditions". Refractories Applications Transactions, Vol.7, pp 2-8, 2005.
- [7] Monteverde F, Bellosi A. "Effect of the addition of silicon nitride on sintering behaviour and microstructure of zirconium diboride". Scripta Materialia . Vol.46, pp 223~228, 2002
- [8] Tsuchida T, Yamamoto S. "Mechanical activation assisted self-propagating high-temperature synthesis of  $ZrC$  and  $ZrB_2$  in air from  $Zr/B/C$  powder mixtures". Journal of the European Ceramic Society Vol.24, pp 45-51, 2004
- [9] Gasch M, Ellerby D, Irby E, Beckman S. and Gusman M. "Processing, Properties and Arc Jet Oxidation of Hafnium Diboride/silicon Carbide Ultra High Temperature Ceramics". Journal of Materials Science. Vol.39, pp 5925-5937, 2004
- [10] Opeka MM, Talmy IG. and Zaykoski JA. "Oxidation-based Materials Selection for 2000 °C Hypersonic Aerosurfaces: theoretical Considerations and Historical Experience". Journal of Materials Science. Vol.39, pp 5887-5904, 2004
- [11] Zhang GJ, Deng ZY. and Kondo N. "Reactive hot pressing of  $ZrB_2-SiC$  composites". J.Am. Ceram. Soc, Vol.83, pp 2330-2334, 2000
- [12] Fahrenholtz WG. "Reactive processing in Ceramic-based systems". Int.J.Appl. Ceram. Technol. Vol. 3, pp 1-12, 2006