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Preparation and Microstructure of Porous ZrB_2 Ceramics Using Reactive Spark Plasma Sintering Method

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Abstract: Zirconium oxide (ZrO_2) and boron carbide (B_4C) were added to ZrB_2 raw powders to prepare ZrB_2 porous ceramics by reactive spark plasma sintering (RSPS). The reactions between ZrO_2 and B_4C which produce ZrB_2 and gas (such as CO and B_2O_3) result in pore formation. X-Ray Diffraction results indicated that the products phase was ZrB_2 and the reaction was completed after the RSPS process. The porosity could be controlled by changing the ratio of synthesized ZrB_2 to raw ZrB_2 powders. The porosity of porous ceramics with 20 wt% and 40 wt% synthsized ZrB_2 are 0.185 and 0.222, respectivly. And dense ZrB_2-SiC ceramic with a porosity of 0.057 was prepared under the same conditions for comparison. The pores were homogeneously distributed within the microstructure of the porous ceramics. The results indicate a promising method for preparing porous ZrB_2-based ceramics.

Key words: zirconium diboride; porous ceramic; reactive spark plasma sintering

1 Introduction

Ceramics based on the transition metal borides, nitrides, and carbides have extremely high melting points (>2 500 ℃) and are referred to as ultra-high temperature ceramics[1-4]. UHTCs are good choices for several extreme applications: thermal protection materials on hypersonic aerospace vehicles or reusable atmospheric re-entry vehicles, specific components for propulsion, furnace elements, refractory crucibles, *etc*[5-7]. Within the family of transition metal ultra-high temperature ceramics, diborides such as ZrB_2 and HfB_2 have unique combinations of mechanical and physical properties, including high melting points (>3 000 ℃), high thermal and electrical conductivities, chemical inertness against molten metals, and great thermal shock resistance[1-3, 8, 9].

However, the use of single-phase materials was not sufficient for high temperature structural applications. ZrB_2 resists oxidation at temperatures up to 1 000-1 300 ℃[10]. Thus, many additives such as Nb, V, C, disilicides and SiC were evaluated to improve the resistance to oxidation. Of these additives, SiC seemed to be particularly valuable and 20 vol% was judged optimal for hypersonic vehicles by the US Air Force [5]. The oxidation resistance of ZrB_2-SiC is improved, to at least 1 600 ℃, by compositional modifications which promote immiscibility in the glass component of the scale[11,12].

In the applications, the thermal conductivity, the temperature difference and strength between the outside surface and the inside surface of the ZrB_2-based ceramic layer will determine the success or failure of the thermal protection system (TPS)[13]. However, the addition of SiC increases the thermal conductivities of ZrB_2-based ceramics. Thermal conductivity value of single-crystal ZrB_2 is 140 $W\cdot m^{-1}\cdot K^{-1}$ in the basal direction and 100 $W\cdot m^{-1}\cdot K^{-1}$ along the *c*-axis. Thermal conductivity values for SiC range from 125 $W\cdot m^{-1}\cdot K^{-1}$ for sintered SiC to 490 $W\cdot m^{-1}\cdot K^{-1}$ for 6H single-crystal SiC. Thermal conductivity of ZrB_2-SiC is expected to be similar to or greater than polycrystalline ZrB_2[14]. The high thermal conductivity, which leads to

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low temperature difference between the outside surface and the inside surface of the thermal protection system, reduces the heat-insulating property of the TPS.

According to reported literature, porosity has the greatest effect on the thermal diffusivity and thermal conductivity. In comparison with the ZrB_2-SiC ceramics, the diffusivities of the porous samples are very small. Based on these results, the ceramics designed with low porosity may present low thermal conductivity and good thermal shock resistance[10,15]. Based on these results, a porous ZrB_2 layer between outside ZrB_2-SiC dense ceramic and inside part is expected to improve the heat-insulating property of the TPS.

In this article, ZrB_2 porous ceramic material was prepared by reactive spark plasma sintering (RSPS). Partial sintering, the most straightforward processing route for the preparation of porous ceramics, was used to prepare porous ceramics. ZrO_2 and B_4C were added to raw ZrB_2 powders to produce higher porosity, and the gas escape (such as CO and B_2O_3) resulted in higher porosity[2,16-18]. Dense ZrB_2SiC ceramic was prepared by SPS for comparison. The relative density and microstructure of the products were investigated to determine the effect of ZrO_2 and B_4C content on the porosity, grain size, and pores size of porous ZrB_2 ceramics and ZrB_2-SiC ceramics.

2 Experimental

The raw materials used in the present study were as follows: commercial monolithic ZrO_2 (monolithic ZrO_2, no stabilizers, particle size about 0.1 μm, Jiaozuo Weina Co., Ltd, Henan, China), B_4C (particle size <10 μm, Alfa Aesar Co., Ltd.), ZrB_2 (particle size about 3 μm, Alfa Aesar Co., Ltd.), and SiC (particle size 5.5 μm, Shandong Weifang Huamei Co., Ltd, Shandong, China). During reactive sintering processing, the final ZrB_2 in ZrB_2 porous ceramics consisted of two parts, one part was from the commercial ZrB_2 and the other was from the chemical reaction between ZrO_2 and B_4C according to Reaction (1). The ratio of synthesized ZrB_2 to starting materials was changed according to Table I. The powder mixtures of ZrO_2, B_4C (with the mole ratio of 7:5 according to Reaction (1)) and ZrB_2 were ground using alcohol as the solvent in agate mortar, followed by rotating evaporation to remove the solvent.

$$7ZrO_2 + 5B_4C \rightarrow 7ZrB_2 + 3B_2O_3\ (l) + 5CO\ (g) \quad (1)$$

After evaporation, the obtained mixtures were sintered to ZrB_2-SiC porous ceramics in graphite die under vacuum (about 10 Pa) by SPS (Model SPS-1 050, Sojitz Machinery Corporation, Japan). The sintering temperature was 1 800 ℃ at a heating rate of 100 ℃ per minute from 600-1 200 ℃ and 50 ℃ per minute from 1 200-1 700 ℃, and a hold time of 3 min at 1 700 ℃ and 1 800 ℃, as seen in Fig.1. The processing conditions consisted of three stages:

(1) Stage 1: The powders were heated from room temperature to 600 ℃ at a rate of 300 ℃/min, and then to 1 200 ℃ at 100 ℃/min.

(2) Stage 2: The temperature was increased to 1 700 ℃ at 50 ℃/min and held for 3 minutes.

(3) Stage 3: The temperature was increased to 1 850 ℃ and held for 3 minutes (see Fig.1).

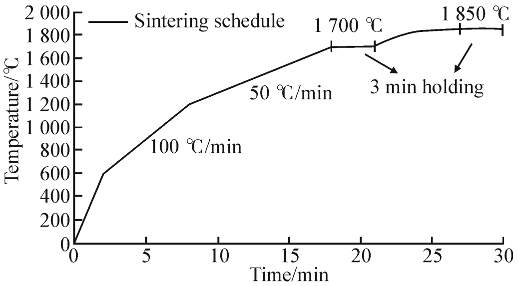

Fig.1 The spark plasma sintering processing used in this paper

A pressure of about 2 MPa was applied during the whole sintering process. Changes in the vacuum level of the chamber and shrinkage of the powder were monitored and recorded during the sintering.

The mixtures of ZrB_2 and SiC were sintered using the same temperature conditions and 30 MPa pressure

Table 1 Batch of ZrB_2-SiC ceramics

Composition	Designation	ZrB_2/wt%		SiC/wt%
		ZrB_2 from raw powder	Syntheized ZrB_2 from reaction[a]	
ZrB_2-11.5%SiC	$Z_{89}Z_0S_{11}$	88.5	0	11.5
ZrB_2	$Z_{80}Z_{20}$	80.0	20.0	0
ZrB_2	$Z_{60}Z_{40}$	60.0	40.0	0

[a] $7\ ZrO_2 + 5\ B_4C \rightarrow 7\ ZrB_2 + 3\ B_2O_3\ (l) + 5\ CO\ (g)$

(The content of ZrB_2 from starting powder and synthesized ZrB_2 from reaction was changed in order to control the porosities of the final products) to dense ZrB_2-SiC composite for comparison.

The phase analysis of the products was carried out using X-ray diffraction (XRD, Model Ultima III, Rigaku, Japan). Archimedes' method and the rule of mixtures were used to determine the actual and theoretical densities, respectively, based on a theoretical density of 6.085 g/cm^3 for ZrB_2 and 3.16 g/cm^3 for SiC. The microstructure was observed using a scanning electron microscope (SEM, Model 4300N, Hitachi, Japan).

3 Results and discussion

The ZrB_2 are consisted of two parts: one is from the ZrB_2 starting material, the other is synthesized ZrB_2 from the chemical reaction between ZrO_2 and B_4C, shown in Table I. The relative density and microstructure of ZrB_2 porous ceramics were controlled by changing the content of synthesized ZrB_2 in ZrB_2 porous ceramics. The content of ZrB_2 from starting powder and synthesized ZrB_2 was changed in order to control the porosity of the final products. The $Z_{80}Z_{20}$, and $Z_{60}Z_{40}$ mixtures were reactively sintered at 1 800 ℃ and held for 3 min at 1 700 ℃ and 1 800 ℃, respectively. The resultant XRD patterns are shown in Fig.2. According to the XRD results, both ZrB_2 and SiC phases were detected in $Z_{89}Z_0S_{11}$, and ZrB_2 phase was found in $Z_{80}Z_{20}$, and $Z_{60}Z_{40}$ products. It is obvious that the reduction between oxide and B_4C was completed after the RSPS process.

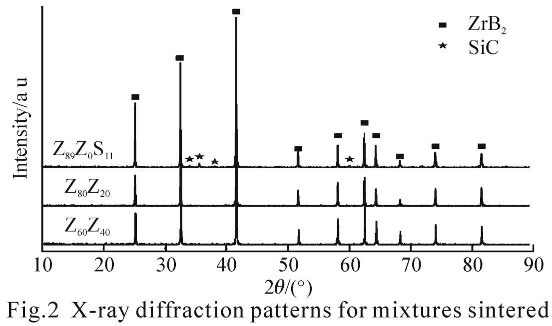

Fig.2 X-ray diffraction patterns for mixtures sintered in vacuum by SPS

ZrB_2 porous ceramics were synthesized by the spark plasma sintering-reactive synthesis (SPS-RS) technique using ZrO_2 and B_4C. According to the former work, the reaction between ZrO_2 and B_4C is strongly endothermic, and is only thermodynamically favorable (*i e*, ΔG^{θ} is negative) above 1 265 ℃. Based on reaction favorability, the heat absorbed, and the product (B_2O_3) evaporation, temperature of 1 600 ℃ and a 10 minutes holding were employed to synthesize diborides[19-21]. In this paper, a temperature of 1 700 ℃ and a 3 minutes holding were used to complete the reaction.

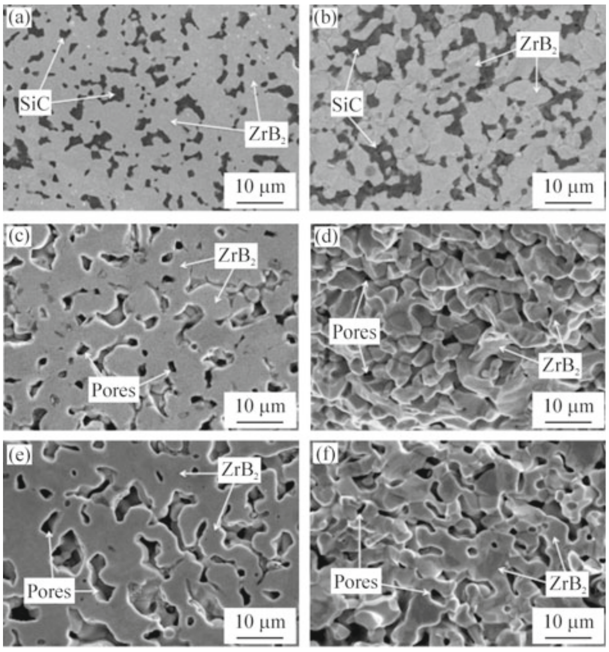

Fig.3 Scanning electron and back-scattered electron images of ZrB_2 based porous ceramics prepared by RSPS: (a)-(b) polished and fracture surface of $Z_{89}Z_0S_{11}$; (c)-(d) polished and fracture surface of $Z_{80}Z_{20}$; (e)-(f) polished and fracture surface of $Z_{60}Z_{40}$

The microstructure was also observed to explain the reaction process and Fig.3 shows the microstructure of ZrB_2-SiC porous ceramics synthesized at 1 700 ℃ for 3 minutes holding and sintered at 1 800 ℃ for 3 minutes holding, respectively. The gray phase and black particles in Figs.3 (a) and (b) are ZrB_2 and SiC, respectively. SiC particles with particle size of mainly 1-3 μm are well distributed with the ZrB_2 matrix. The density of $Z_{89}Z_0S_{11}$ is 5.19 g/cm^3, which is 94.3% of the theoretical density.

The processing route for the preparation of porous ceramic in this paper is the partial sintering of initial powder and powder mixtures which undergo solid state reaction that leads to the pore formation. In $Z_{80}Z_{20}$ and $Z_{60}Z_{40}$ samples, 20 wt% and 40 wt% ZrB_2 was synthesized by the reaction between ZrO_2 and B_4C, and the byproducts gas (CO) and volatile phase (B_2O_3) were produced[2,22]. As expected, the microstructure changed with the increase in the content of synthesized ZrB_2, shown in Figs.(c)-(f). The pores size and volume increased as the content of synthesized ZrB_2 increased, comparing $Z_{80}Z_{20}$ (Fig.(c)) with $Z_{60}Z_{40}$ (Fig.(e)). The relative densities of $Z_{80}Z_{20}$ and $Z_{60}Z_{40}$ are 81.5% and 77.8%, respectively.

4 Conclusions

Zirconium oxide (ZrO_2) and boron carbide (B_4C) were added to ZrB_2 raw powders to prepare ZrB_2 porous ceramics by reactive spark plasma sintering (RSPS), and the gas escape (such as CO and B_2O_3) resulted in higher porosity. X-Ray Diffraction results showed that the reduction reaction was completed after the RSPS process. The porosity could be controlled by changing the ratio of synthesized ZrB_2. The porosity of porous ceramics with 20 wt% and 40 wt% synthsized ZrB_2 is 0.185 and 0.222, respectivly, and dense ZrB_2SiC with a prosity of 0.057 was prepared for comparison. This work showed how RSPS method could give high pure porous ZrB_2 ceramics in just one step without the assistence of additives or further treatment.

References

[1] S Guo. Densification of ZrB_2-based Composites and Their Mechanical and Physical Properties: A Review[J]. *J. Euro. Ceram. Soc*., 2009, 29(6): 995-1 011

[2] W G Fahrenholtz, Hilmas G E, Talmy I G, *et al.* Refractory Diborides of Zirconium and Hafnium[J]. *J. Am. Ceram. Soc*., 2007, 90(5): 1 347-1 364

[3] K Upadhya, Yang J, Hoffmann W. Materials for Ultrahigh Temperature Structural Applications[J]. *Am. Ceram. Soc. Bull.*, 1997, 76(12): 51-56

[4] D Chen, Zhao Y, Li G, *et al.* Mechanism and Kinetic Model of In-Situ TiB_2/7055Al Nanocomposites Synthesized under High Intensity Ultrasonic Field[J]. *J. Wuhan Univ. Technol.-Mater. Sci. Ed.*, 2011, 26(5): 920-925

[5] J F Justin, Jankowiak A. Ultra High Temperature Ceramics: Densification, Properties and Thermal Stability[J]. *Onera J. Aerospace Lab.*, 2011, 3: 1-11

[6] J Li, Yu Z, Wang H, *et al.* Microstructure and Mechanical Properties of an *In Situ* Synthesized TiB and TiC Reinforced Titanium Matrix Composite Coating [J]. *J. Wuhan Univ. Technol.-Mater. Sci. Ed.*, 2012, 27(1): 1-8

[7] J Zhang, Tang W, Fu Z, *et al.* Fabrication of homogenous dispersion TiB_2-Al_2O_3 Composites [J]. *J. Wuhan Univ. Technol.-Mater. Sci. Ed.,* 2011, 26(4): 681-683

[8] X Zhang, Wang Z, Sun X, *et al.* Effect of Graphite Flake on the Mechanical Properties of Hot Pressed ZrB_2-SiC Ceramics[J]. *Mater. Lett.*, 2008, 62(28): 4 360-4 362

[9] C Mroz. Zirconium Diboride[J]. *Am. Ceram. Soc. Bull.*, 1994, 73(6): 141-142

[10] R Loehman, Corral E, Dumm H P, *et al. Ultra High Temperature Ceramics for Hypersonic Vehicle Applications*[R]. Sandia report: SAND 2006-2925, Albuquerque, NM, 2006

[11] M M Opeka, Talmy I G, Zaykoski J A. Oxidation-Based Materials Selection for 2 000 ℃ Hypersonic Aerosurfaces Theoretical Considerations and Historical Experience[J]. *J. Mater. Sci*., 2004, 39: 5 887-5 904

[12] Z Wang, Hong C, Zhang X, *et al.* Microstructure and Thermal Shock Behavior of ZrB_2-SiC-Graphite Composite[J]. *Mater. Chem. Phys*., 2009, 113(1): 338-341

[13] E Wuchina, Opila E, Opeka M, *et al. UHTCs: Ultra-High Temperature Ceramic Materials for Extreme Environment Applications*[C]. Electrochem. Soc.-Interface, 2007

[14] J W Zimmermann, Hilmas G E, Fahrenholtz W G, *et al.* Thermophysical Properties of ZrB_2 and ZrB_2-SiC Ceramics[J]. *J. Am. Ceram. Soc.*, 2008, 91(5): 1 405-1 411

[15] Y Chen, Vandeperre L J, Stearn R J. The Effect of Porosity in Thermal Shock[J]. *J. Mater. Sci*., 2008, 43: 4 099-4 106

[16] H Zhang, Yan Y, Huang Z, *et al.* Pressureless Sintering of ZrB_2-SiC Ceramics:The Effect of B_4C Content[J]. *Scr. Mater.*, 2009, 60(7): 559-562

[17] W G Fahrenholtz, Hilmas G E, Zhang S C, *et al.* Pressureless Sintering of Zirconium Diboride: Particle Size and Additive Effects[J]. *J. Am. Ceram. Soc*., 2008, 91(5): 1 398-1 404

[18] H Zhao, He Y, Jin Z. Preparation of Zirconium Boride Powder[J]. *J. Am. Ceram. Soc*., 1995, 78(9): 2 534-2 536

[19] H Yuan, Li J, Shen Q, *et al. In Situ* Synthesis and Sintering of ZrB_2 Porous Ceramics by the Spark Plasma Sintering-Reactive Synthesis (SPS−RS) Method[J]. *Inter. J. Ref. Metal. Hard Mater*., 2012, 34: 3-7

[20] H Yuan, Li J, Shen Q, *et al.* Preparation and Thermal Conductivity Characterization of ZrB_2 Porous Ceramics Fabricated by Spark Plasma Sintering[J]. *Inter. J. Ref. Metal. Hard Mater*., 2013, 36: 225-231

[21] H Yuan, Li J, Shen Q, *et al.* Preparation and Microstructure of Laminated ZrB_2-SiC Ceramics with Porous ZrB_2 Interlayers[J]. *J. Phys.: Conf. Ser.*, 2013, 419: 012001

[22] S C Zhang, Hilmas G E, Fahrenholtz W G. Pressureless Densification of Zirconium Diboride with Boron Carbide Additions[J]. *J. Am. Ceram. Soc*., 2006, 89(5): 1 544-1 550