Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 953–957

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Microstructure and mechanical properties of ZrB_2–SiC porous ceramic by camphene-based freeze casting

Jiancong Du*, Xinghong Zhang, Changqing Hong, Wenbo Han

Center for Composite Materials and Structure, Harbin Institute of Technology, Harbin 150001, PR China

Received 4 June 2012; received in revised form 4 July 2012; accepted 4 July 2012
Available online 20 July 2012

Abstract

Camphene-based freeze casting technique was adopted to fabricate ZrB_2–SiC porous ceramic with 3-dimensional (3D) pore network. ZrB_2–SiC/camphene slurries (initial solid loading: 20 vol%, 25 vol% and 30 vol%) were prepared for freeze casting. Regardless of initial solid loading, the fabricated sample had dense/porous dual microstructure. The thickness of dense layer was about 200–300 μm. The microstructures of ZrB_2–SiC porous ceramics were significantly influenced by the initial solid loading, which determines the pore size, porosity and mechanical properties of the final products.

Keywords: Ceramic; Aerospace material; Microstructure; Mechanical properties

1. Introduction

Because of the excellent combination of mechanical and physicochemical properties, ZrB_2–SiC ultra-high temperature ceramics (UHTCs) have attracted great interests in recent years. ZrB_2–SiC ultra-high temperature ceramics (UHTCs) are the leading candidates as potential materials for high temperature structural applications [1–5]. However, high density and low thermal shock resistance are disadvantages of UHTCs for applications. Porous structure can reduce the density and improve the thermal shock resistance by metal infiltration. In recent years, several methods have been developed to fabricate porous ceramics.

More recently, Deville developed the freeze-casting techniques of a ceramic/camphene slurry [6] to fabricate porous ceramics. During freeze casting, the ceramic/camphene slurry is solidified to obtain 3-dimensional (3D) crystal network and ceramic walls. After demolding, camphene sublimates and develops a network pore structure as a replica. Because freeze casting is a physical procedure, the technique can be applicable to any ceramic particles. The method has been adopted to fabricate ultra-high porosity alumina and zirconia ceramics [7,8]. Nevertheless, up to date, there are few papers devoted to the study on ZrB_2–SiC ultra-high temperature ceramics (UHTCs) by camphene-based freeze casting.

In this work, we investigated the procedure of the camphene-based freeze casting. The fabricated samples were characterized by evaluating the development of the structure and the mechanical properties.

2. Experimental

Commercially available raw materials were used to fabricate the porous ceramics in this work. ZrB_2 (the Northwest Institute for Non-Ferrous Metal Research, China, 1 μm, purity > 99.4%, with a trace of MgO, Al_2O_3 and CaO) and SiC powder (2 μm, Weifang Kaihua Micro-powder Co., Ltd., China) was used as the ceramic framework. Camphene ($C_{10}H_{16}$, Guangzhou Huangpu Chemical Factory, Guangzhou, China) was used as a freezing vehicle. An amine derivative of a fatty acid condensation polymer (963, Beijing Huadong Polymer Co., Ltd., Beijing, China) was used as dispersant and binder.

ZrB_2–SiC/camphene slurries containing 3 wt% of 963 (initial solid loading: 20 vol%, 25 vol%, 30 vol%) were prepared by ball-milling at 50 °C for 12 h. The prepared

---

*Corresponding author. Tel./fax: +86 451 86402382.
E-mail address: infegil@163.com (J. Du).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.07.012

warm slurry had excellent flow ability for casting, regardless of initial solid loading. The prepared warm slurry was poured into graphite molds in cool environment (about 5 °C) to produce a sample with 50 mm in diameter and 15 mm in height. After casting, the slurry quickly started to solidify. The solidification was completed within about 30 min. The green body was carefully removed from the mold, which had two pre-cuts for easy demolding. We placed the green samples in ambient atmosphere to sublime the frozen camphene for 72 h, and then placed the samples into oven at 35 °C for 72 h to make sure that the frozen camphene sublimates completely. After freeze drying, the green samples were sintered at 1950 °C for 2 h in Ar atmosphere.

The bulk density and porosity of fabricated sample was calculated by measuring its dimension and weight. Microstructure of the sintered sample was observed with scanning electron microscopy (SEM; FEI Sirion, Philips, Holland). Specimens (4 mm × 4 mm × 5 mm) were tested (Instron-5569, UK) to determine the unidirectional compressive strength. At least, six specimens were tested for each test condition.

3. Results and discussion

3.1. Microstructure

After sintering, the fabricated samples with dual-phase porous structure had a good shape without macroscopic defects, such as cracking or distortion. This excellent shape tolerance was as a result of the presence of the highly concentrated ZrB_2–SiC powder walls formed during the freeze-casting process [8].

Regardless of initial solid loading, there was a relatively dense layer on surface of the sample. The thickness of the dense layer was about 200–300 μm, as shown in Fig. 1(a)–(c). The dense layer connected with inner porous structure smoothly, without defects. As shown in Fig. 1(d)–(f), it should be noted that the relative density of the dense layer decreased, as the initial solid loading decreased from 30 vol% to 20 vol%. The formation mechanism of the dense layers in different parts of the fabricated sample is different.

The formation of the dense layer on the top surface is attributed to two evaporation stages that occurred during

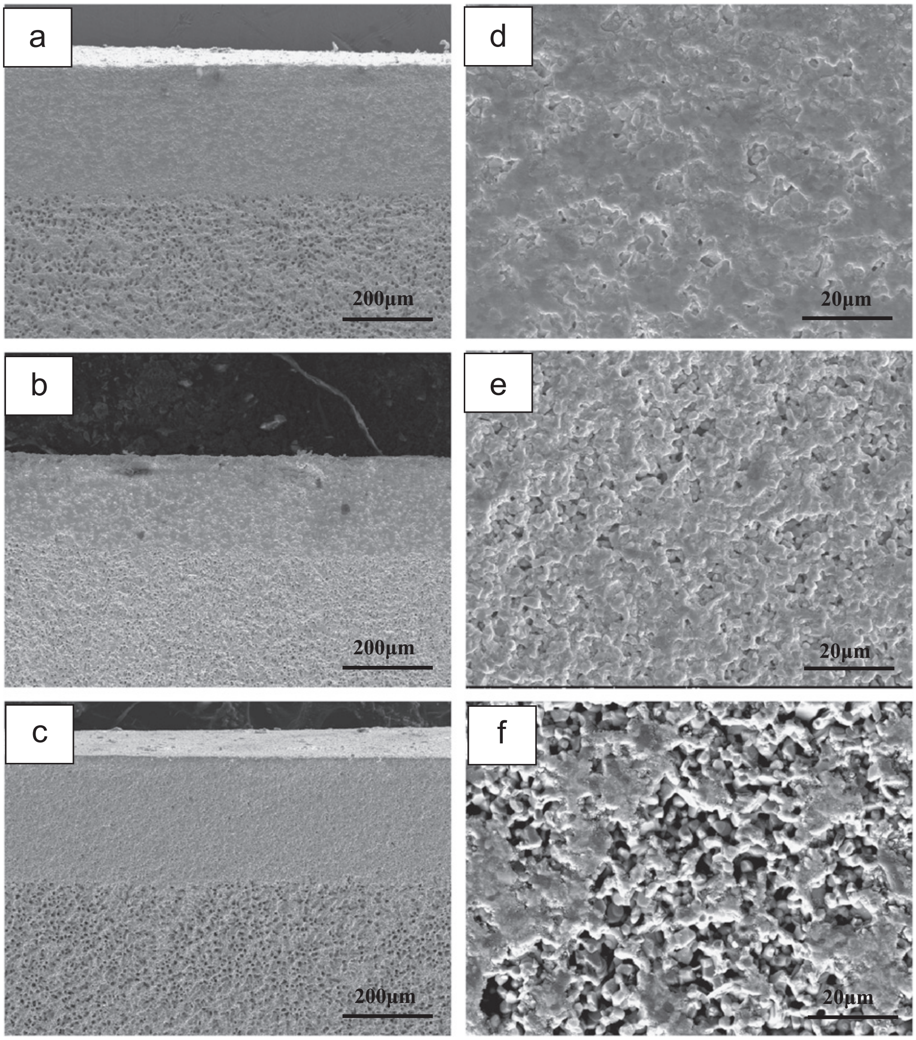

Fig. 1. SEM graphs of the dense surface layer: (a), (d) 30 vol% solid loading; (b), (e) 25 vol% solid loading and (c), (f) 20 vol% solid loading.

freeze casting [9]. During solidification, the top surface of the green body was exposed to air. In the first stage, because of the evaporation of the molten camphene near the sample surface, the rate of weight loss had a rapid increase. The second stage is sublimation, and meanwhile, the rate of evaporation is decreased and remains relatively constant. In this work, because of relatively high-vapor pressure (2×10^3 Pa at 55 °C), the camphene near the top surface could evaporate readily until solidification was completed, resulting in the increase of density on the surface.

Different to the top surface, the dense layer on the button surface of the fabricated sample was formed due to the phenomenon that solid–liquid interface moves quickly to capture ceramic particles. Meanwhile, the solute segregated from camphene crystals gathered in front of the solidified layer. When the solute concentration was higher than a critical value, the flat interface was destroyed [10]. As the moving rate of the interface decreased, the morphology of camphene crystal changed and particle capture changed into particle transpiration. As a result, over-layer was formed.

With further solidification, camphene crystal grew into dendrites, and ceramic particles were repelled to gather between the dendrite arms or neighboring dendrites. Such solidification behavior results in the unique structure of concentrated ceramic powder walls, surrounding a 3-dimensionally (3D) interconnected camphene network, regardless of initial solid loading. The 3D porous structure is the replica of solidified camphene network, which has been sublimated in green body. In this paper, the frozen direction was from the aluminum button to the top of the green body. The typical micrographs perpendicular to the frozen direction of the fabricated ZrB_2–SiC composites after sintering at 1950 °C for 2 h are shown in Fig. 2. The sintered samples had preserved their unique porous structures with completely 3-dimensional (3D) interconnected pore channels with diameters of several tens of micrometers, and the pore sizes were uniform. As shown in Fig. 2, it should be noted that the ceramic walls possessed relatively high density because of the rather high solid content before sintering.

The microstructures of ZrB_2–SiC porous ceramics were significantly influenced by the initial solid loading sintered

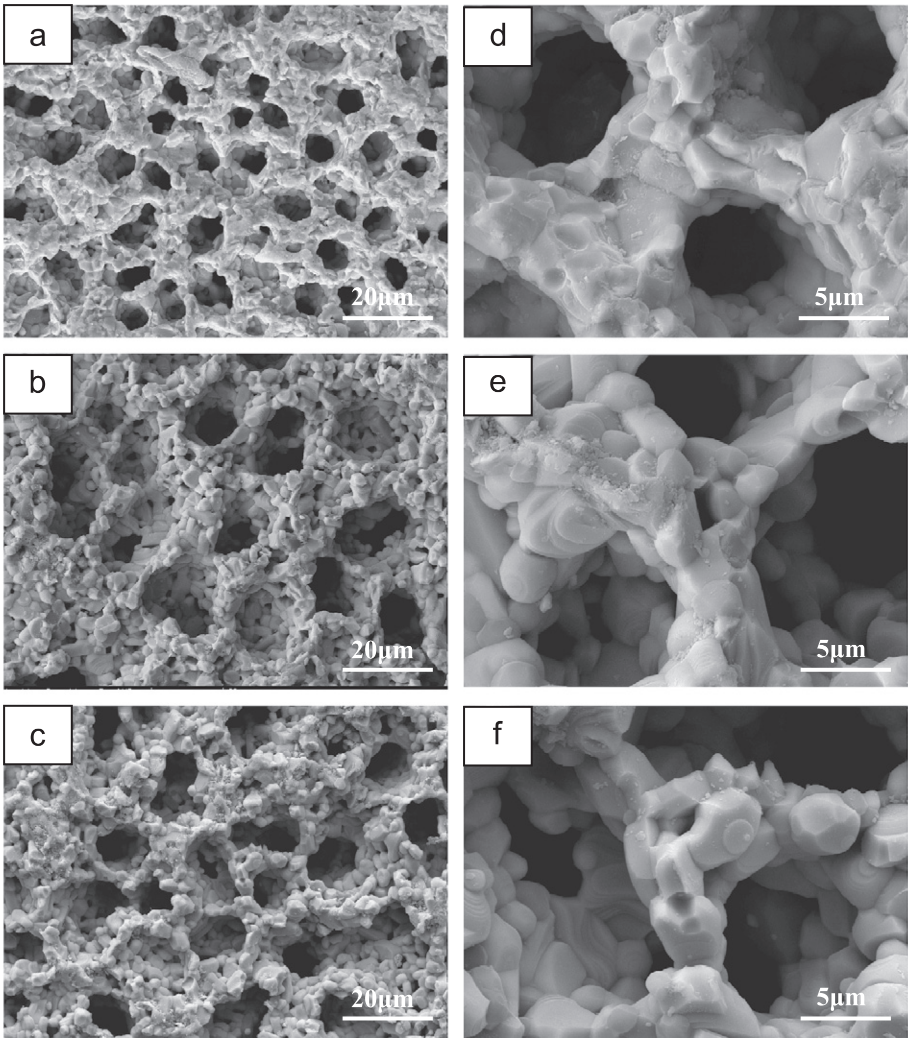

Fig. 2. SEM graphs of the porous microstructure: (a), (d) 30 vol% solid loading; (b), (e) 25 vol% solid loading and (c), (f) 20 vol% solid loading.

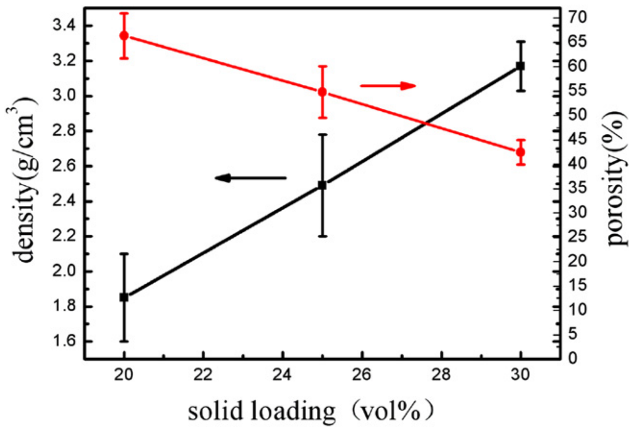

Fig. 3. Measured density and porosity of the fabricated samples sintered at 1950 °C for 2 h as a function of the initial solid loading.

at a given temperature, which determines the pore size, porosity and mechanical properties of the final products. Fig. 2(a)–(c) shows the microstructures of ZrB_2–SiC porous ceramics after sintering at 1950 °C for 2 h with the initial solid loading varying from 20 vol% to 30 vol%. Regardless of initial solid loading, the 3D interconnected network microstructure has been fabricated by camphene-based freeze casting. It should be noted that as the initial ZrB_2–SiC content employed in the slurry was increased from 20 to 30 vol%, the pore size was remarkably decreased. It is clear that lower solid loading results in higher porosity and larger pore sizes, while the sintered ZrB_2–SiC ceramic walls became thinner, as shown in Fig. 2(d)–(f).

3.2. *Mechanical properties*

The bulk density and porosity of sintered samples were calculated by measuring its dimension and weight. The results are shown in Fig. 3. Regardless of initial solid loading, the density was much less than the theoretical density of fully dense ZrB_2–20 vol% SiC ceramic (5.51 g/cm^3). With the initial solid loading increasing from 20 vol% to 30 vol%, the density varied from 1.8 g/cm^3 to 3.2 g/cm^3. As the initial ZrB_2–SiC content employed in the slurry was increased from 20 to 30 vol%, the porosity was remarkably decreased from 66% to 42%. The relationship between the porosity (P) and initial solid loading (φ_i) can be expressed as follows:

$$P = 114 - 2.4\varphi_i \tag{1}$$

From this equation, no pores would be expected to be formed for an initial solid loading of 47 vol%. This result indicates that the final porosity can easily be tuned by adjusting the initial solid loading used in the ZrB_2–SiC ceramic/camphene slurry.

Generally, the strength of the ceramic wall (or strut), and the surface flaws on the strut affects the compressive strength of a porous ceramic strongly [11]. Compressive strength tests were conducted to evaluate the mechanical properties of the fabricated samples, and the results are shown in Fig. 4. As the initial solid loading was decreased from 30 to 20 vol%, the compressive strength remarkably decreased from 364 MPa to 173 MPa. The decrease of the mechanical properties was owing to the porous microstructure. However, The strength of the porous ceramic fabricated by freeze casting is much higher than those prepared by other methods (> 100 μm), as a result of not only the full densification of the ZrB_2–SiC ceramic walls, but also the smaller pore size (several tens of microns).

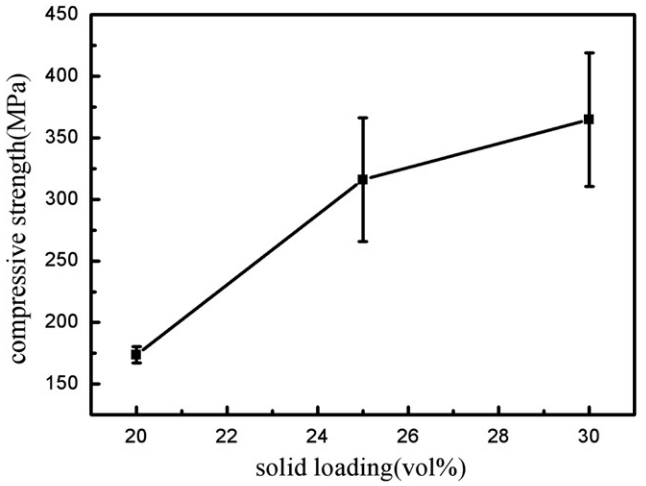

Fig. 4. Compressive strengths of the samples as a function of the initial solid loading.

4. Conclusion

In this paper, the freeze-casting technique was adopted to fabricate ZrB_2–SiC porous ceramic. The initial solid loading employed in the slurry were 20 vol%, 25 vol% and 30 vol%. After sintering at 1950 °C for 2 h in Ar atmosphere, the fabricated sample had dense/porous dual microstructure. There was a relatively dense layer on the surface of the fabricated sample. The evaporation of camphene and the different growth rates of camphene crystals lead to the formation of dense surface layer. The sintered sample had preserved completely 3-dimensional (3D) network porous structure with diameters of several tens of micrometers. The compressive strength of the fabricated sample was 364 MPa when the initial solid loading was 30 vol%.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (no. 50972029).

References

[1] A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, D.T. Ellerby, High strength zirconium diboride-based ceramics, Journal of the American Ceramic Society 87 (6) (2004) 1170–1172.

[2] S.R. Levine, E.J. Opila, M.C. Halbig, J.D. Kiser, M. Singh, J.A. Salem, Evaluation of ultra-high temperature ceramics for aeropropulsion use, Journal of the European Ceramic Society 22 (14–15) (2002) 2757–2767.

[3] X.H. Zhang, L. Xu, S.Y. Du, J.C. Han, P. Hu, W.B. Han, Fabrication and mechanical properties of ZrB_2–SiCw ceramic matrix composite, Materials Letters 62 (2008) 1058–1060.

[4] B.K. Jang, Microstructure of nano SiC dispersed Al_2O_3–ZrO_2 composites, Materials Chemistry and Physics 93 (2005) 337–341.

[5] S.Q. Guo, J.M. Yang, H. Tanaka, Y. Kagawa, Effect of thermal exposure on strength of ZrB_2-based composites with nano-sized SiC particles, Composites Science and Technology 68 (2008) 3033–3040.

[6] S. Deville, Freeze-casting of porous ceramics: a review of current achievements and issues, Advanced Engineering Materials 10 (10) (2008) 155–156.

[7] Y.H. Koh, J.H. Song, Freezing dilute ceramic/camphene slurry for ultra-high porosity ceramics with completely interconnected pore networks, Journal of the American Ceramic Society 89 (2006) 3089–3093.

[8] C.Q. Hong, X.H. Zhang, J.C. Han, Ultra-high-porosity zirconia ceramics fabricated by novel room-temperature freeze-casting, Scripta Materialia 60 (2009) 563–566.

[9] Y.H. Koh, I.K. Jun, J.J. Sun, H.E. Kim, In situ fabrication of a dense/porous bi-layered ceramic composite using freeze casting of a ceramic/camphene slurry, Journal of the American Ceramic Society 89 (2006) 763–766.

[10] S. Deville, E. Saiz, A.P. Tomsia, Freeze casting of hydroxyapatite scaffolds for bone tissue engineering, Biomaterials 27 (2006) 5480–5489.

[11] B.H. Yoon, W.Y. Choi, H.E. Kim, J.H. Kim, Y.H. Koh, Aligned porous alumina ceramics with high compressive strengths for bone tissue engineering, Scripta Materialia 58 (2008) 537–540.