

Pressureless densification of ZrB_2 –SiC composites with vanadium carbide

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Adding a small amount of vanadium carbide as sintering aids, nearly fully dense ZrB_2 –SiC composites were obtained by pressureless sintering methods at 2000–2100 °C. Thermodynamic calculations and experimental results proved that VC is better at removing the surface oxide impurities of ZrB_2 than WC, and played a very important role during the densification process. The mechanical properties of the sintered ceramics were also reported.

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In view of the development of hypersonic aerospace vehicles and advanced reusable atmospheric re-entry vehicles, it is very important to develop ultrahigh-temperature ceramics (UHTCs) which can be used in high heat flux and low oxygen pressure atmosphere [1,2].

Among the family of UHTCs materials, zirconium diboride has been shown to have a better combination of properties, such as low density, high melting point and high thermal conductivity, as a result has been studied since the 1960s [1–3]. Because the addition of silicon carbide can improve the oxidation resistance and mechanical properties of ZrB_2 ceramics, it has been considered as the baseline material of UHTCs, and much work has been carried out on the ZrB_2 –SiC system [1–5].

Unlike other sintering methods [1,3,7] pressureless sintering method allows the fabrication of components to near-net shape and thereby avoids expensive and time-consuming diamond machining [4–6,8,12]. However, due to the covalent character of the bonding and the surface oxides in borides, it is necessary to add sintering aids to obtain high-density ZrB_2 -based ceramics via the pressureless sintering method. The sintering aids can be divided into three groups: (i) C, B_4C , WC or their mixtures, which can react with ZrO_2 impurities on the surface of raw ZrB_2 particles [4,6]; (ii) MoSi_2 , Mo and

other refractory metals, which can form a liquid phase at high temperatures and enhance densification [5,8]; and (iii) ZrH_2 and HfH_2 or other metal hydrides, the mechanism of densification and mechanical properties of which have not been reported [9].

Owing to its high melting point and excellent mechanical properties, vanadium carbide is usually added to WC–Co to inhibit grain growth during sintering [10]. In addition, since the cation field strength of V is higher than that of Zr, the addition of V can be effective in promoting the phase separation of the borosilicate glass formed on the surface of the ZrB_2 –SiC ceramics during the oxidation process and improve its oxide resistance [11]. Accordingly, in this work the densification of ZrB_2 –SiC composite by using a small amount of vanadium carbide as a sintering aid was investigated. The aim of the study was to understand the effects of vanadium carbide and its content on the densification, mechanical properties and microstructural features of ZrB_2 –SiC-based ceramics.

Commercially available ZrB_2 (particle size 1.4 μm), VC (particle size 2.3 μm) and SiC (particle size 0.45 μm) powders were used as the starting powders. In the present study, 0, 1, 3 and 5 vol.% VC were added to a starting mixture of 80 vol.% ZrB_2 –20 vol.% SiC. The corresponding samples were designated as ZS, ZSV1, ZSV3 and ZSV5 for simplicity. The powder mixtures were milled for 8 h in acetone using silicon nitride

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balls as the milling medium. Subsequently, the slurries were dried in a rotary evaporator at 70 °C and then sieved through a 200-mesh. The as-sieved powders were uniaxially pressed at a pressure of 30 MPa for 60 s. Cold isostatic pressing with an applied pressure of 300 MPa for 180 s was subsequently conducted. Sintering was carried out in a graphite element furnace at temperature ranging from 1900 to 2200 °C in vacuum (below 1800 °C) or in an argon atmosphere (above 1800 °C) for 1–2 h. During sintering, an isothermal hold at 1600 °C was used for the recovery of the vacuum (~5 Pa). The final densities were measured by the Archimedes method.

The change of crystalline phase compositions of the samples before and after sintering was identified by X-ray diffraction using Cu K α radiation. The microstructures were observed by scanning electronic microscopy with energy-dispersive spectroscopy (EDS) on the polished surfaces. Vickers hardness was measured by Vickers indentation using a load of 5 kg and a dwell time of 10 s, and fracture toughness was calculated by Antis's equation. Flexural strength was measured by the three-point bending method at a cross-head speed of 0.2 mm min⁻¹ on specimens with dimensions of 2 mm × 1.5 mm × 25 mm. The tensile surface was polished and chamfered according to the ASTM Standard Method C-1161. Young's modulus was obtained from the slope of the flexural curve at the initial linear domain.

Figure 1a shows the relative density of the samples as a function of the addition amount of vanadium carbide at 2000 °C for 2 h, and Figure 1b shows a comparison of the densification between ZS and the ZSV5 specimen at different temperatures. After cold isostatic pressing, the relative green density of the samples was about 65%. When maintaining the sintering temperature at 2000 °C for 2 h, obvious shrinkages occurred for ZSV (the density increased from 65% to 98%) and ZS (from 65% to 78.1%). To sum up, when the temperature and the content of VC increased, the relative density of the samples increased accordingly. However, a turning point is evident as shown in Figure 1a: when the addition of VC was 1 vol.% (sample ZV1), its density was slightly lower compared with ZS. On the other hand, when ZSV5 was sintered at 2100 or 2200 °C for 2 h, its bulk density was a little higher than its theoretical density calculated by the rule of mixture.

The XRD patterns of ZS and ZSV5 sintered at 2200 °C for 2 h are presented in Figure 2. Due to the

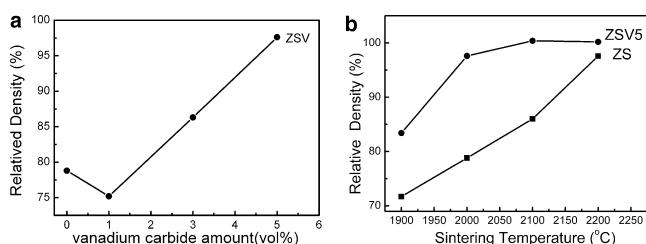


Figure 1. Relative density measured for the pressureless sintered ZrB₂-SiC-based composites: (a) The relative density of ZSV as a function of vanadium carbide amount and (b) the relative densities of ZS and ZSV5 as a function of different sintering temperature.

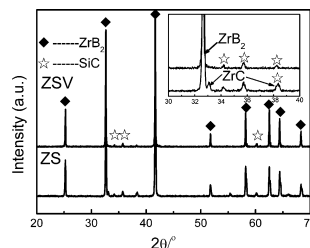


Figure 2. XRD patterns of ZS and ZSV5 samples sintered at 2200 °C for 2 h. The inset image shows enlarged curves for 2θ between 30 and 40° showing that the peak of Zr(B,C) disappeared and the intensity of the SiC in ZSV5 became weaker compared with the ZS results.

raw material of ZrB₂ (which contains small amounts of ZrC) and the carbon contamination derived from the graphite crucible and heater, a small ZrC peak appeared in the ZS (see the inset curve shown in Fig. 2). However, the same thing did not happen in the ZSV5, which used the same raw material of ZrB₂ and was sintered under the same conditions. There was no VC peak for the as-sintered ZSV5 sample, which is similar to the ZrB₂-WC system [6] but different from Chamberlain's result [6], in ZSV5, the peak of ZrB₂ at 32.6° did not shift markedly compared with ZS, indicating that the solid solution of V in ZrB₂ was very limited. Comparing ZSV5 with ZS, the peak of SiC in ZSV5 was a little weaker than that in ZS, indicating a part of the SiC was consumed in the ZSV5 sample via some reactions. The true content of SiC in the as-sintered ZSV5 was calculated by the *K*-value method using the XRD results: after sintering at 2200 °C for 2 h, the content of SiC in ZSV5 reduced from 20 to 18 vol.%. The calculated true theoretical density of ZSV5 with the decreased SiC content was 5.58 g cm⁻³. This means the relative densities of ZSV5 sintered at 2100 and 2200 °C for 2 h were 99.2 and 99.1%, respectively.

Typical microstructural features of ZS and ZSV5 observed by SEM are shown in Figure 3. From 3a and

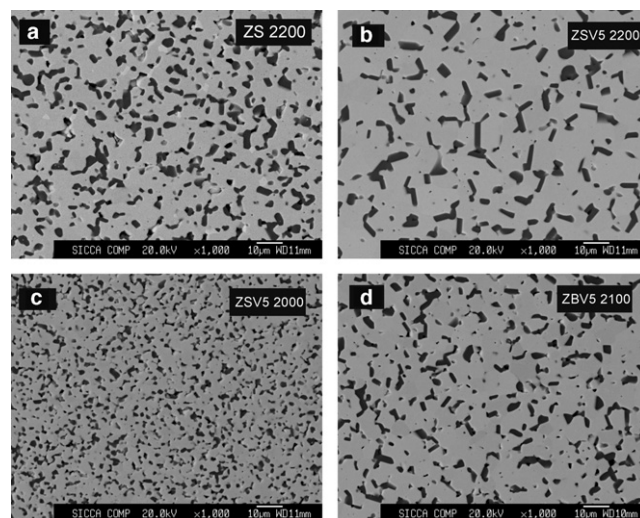
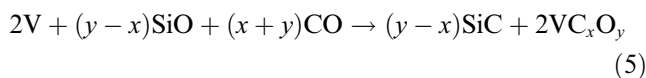
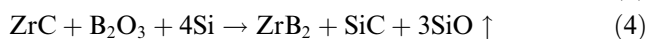
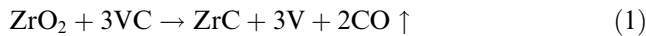


Figure 3. Microstructures of the ZrB₂-SiC based composites sintered at different temperatures for 2 h with and without the addition of VC: (a) ZS sintered at 2200 °C, (b) ZSV5 sintered at 2200 °C, (c) ZSV5 sintered at 2000 °C, and (d) ZSV5 sintered at 2100 °C.

the EDS analysis of ZS which was not shown, as well as ZrB_2 and SiC , a bright phase was also detected that contained Zr, C and B. Combining this with the XRD results shown in Figure 2, it can be concluded that there is some boron dissolved in the ZrC phase. As mentioned above, no Zr(B,C) or VC phases existed in ZSV5. This implies that the addition of VC not only improved the densification process, but also affected the phase composition and inhibited the formation of a Zr(B,C) phase. Generally, the oxide layer containing ZrO_2 and B_2O_3 covered on ZrB_2 particles has been shown to inhibit the densification of the ceramics. B_2O_3 can be removed from the surface of ZrB_2 at high temperature due to its high vapor pressure, and ZrO_2 must be removed by other chemical reactions [4,12]. Through thermodynamic calculation, one possible mechanism for the removal of ZrO_2 and the subsequent acceleration of the densification process of ZrB_2 by the addition of VC are shown in the following reactions:



The standard Gibbs free energies of reactions (1)–(4) as a function of temperature are shown in Figure 4a and b. Considering the very low pressure in the furnace chamber, the real Gibbs free energies of reactions 1 and 4 (below 1800 °C, P_{CO} or P_{SiO} close to 5 Pa) as a function of temperature were also calculated and were designated 1' and 4', respectively. From Figure 4, it is evident that the above reactions can take place at elevated temperatures.

For example, the Gibbs free energy of reaction 1 is

$$\Delta G_T^0 = 987.2 - 0.38T + RT \ln P_{\text{CO}}^2 \quad (6)$$

In the standard state, reaction (1) cannot take place below 2300 °C, but when the P_{CO} is 5 Pa, the reaction can occur at as low as 1828 K. In order to confirm the chemical reaction (1), which was predicted by thermodynamics, a powder mixture with a molar ratio $\text{ZrO}_2:\text{B}_2\text{O}_3:\text{VC} = 1:1:3$ was dry pressed into pellets and then sintered at 1650 and 2000 °C at 5 Pa for 1 h. The XRD patterns of the as-sintered samples are shown in Figure 5a. It can be seen that after a 1 h isothermal hold

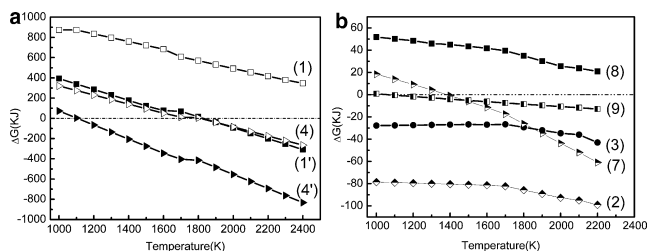


Figure 4. The Gibbs free energy of reaction as a function of temperature for reactions (1)–(5) and (6)–(8) in the standard state, and the real Gibbs free energy of reactions (1) and (4) (below 1800 °C, P_{CO} or P_{SiO} close to 5 Pa) as a function of temperature, indicated as 1' and 4' respectively.

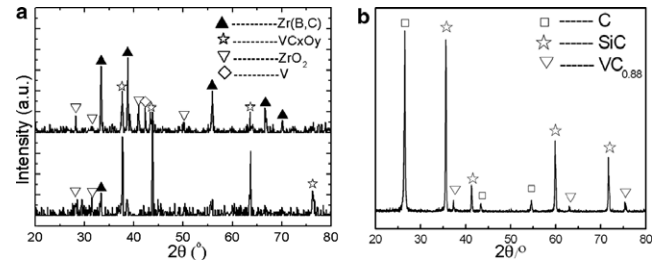


Figure 5. XRD patterns for (a) powder mixtures (molar ratio $\text{ZrO}_2:\text{B}_2\text{O}_3:\text{VC} = 1:1:3$) after heat treatment at 1650 and 2000 °C for 1 h and (b) the collected powders in the graphite crucible for sample sintering of ZSV5.

at 1650 °C, the main phases were VC_xO_y and a solid solution of Zr(B,C) , and no VC or V_2C peak was detected. When the temperature was elevated to 2000 °C, the peak intensity for VC_xO_y decreased while that for Zr(B,C) increased and V was also detected, implying that VC_xO_y was not very stable and decomposed to V, CO or other VO_x gas at higher temperature. These results were also confirmed by thermodynamics. In Zhang et al.'s work [4] on the reaction between WC and ZrO_2 , WC changed into W_2C , which remained in the samples up to as high as 2100 °C, so WC has a relatively poor ability to reduce ZrO_2 . The present work demonstrates that VC is different from WC and could be more efficient at oxygen removal.

Vanadium, formed by reaction (1), would further react with SiC via reaction (2) or (3). The Gibbs free energy of both reactions (2) and (3) was negative at temperatures higher than 300 K. The Gibbs free energy of reaction (2) was slightly lower than that of reaction (3), implying that reaction (2) was thermodynamically more likely to occur, and V_2C would be remaining as a final phase. The as-formed V_2C would also react with ZrO_2 to complete the circulation. Very recently, V_2C phase was reported to exist in the central part of the joint bond when Co–V alloy was joined with SiC at 1573 K [13], indicating that the reaction between V and SiC as shown in reaction (2) is possible.

It should be mentioned that a similar result could occur in the W–SiC system (as reaction (6)), though no experiments have been done to prove this. However, in Zhang et al.'s work [4], when using B_4C and WC as sintering aids to prepare ZrB_2 –SiC composites, the presence of a glassy phase at grain boundaries was proved in the as-prepared samples sintered at 2100 °C for 3 h. This glassy phase disappeared when adding a small amount of C to the mixture after sintering at 1950 °C for 2 h. Zhang et al. did not describe how the glassy phase formed, but we think that the reaction forming liquid Si probably had some effect. When adding additional C, the liquid Si would react with C to reduce the glassy phase



In the Mo–SiC system, this type of phenomenon would not happen. By thermodynamic calculation, the reaction of Mo with SiC (as reactions (8) and (9)) would be inclined to form MoSi_2 , not MoC, no liquid silicon but carbon would be formed, and this carbon would

react further with ZrB_2 . This may be the reason why the solid solutions containing both Mo and Zr(B,C) existed in Yan et al.'s work [5]. The formation of Zr(B,C) might be from the C formed by reaction (9). The standard Gibbs free energies of reactions (7)–(9) as a function of temperature below 2200 K have been shown in Figure 4b



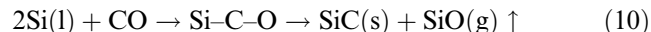
Though the above hypothesis is based only on thermodynamic considerations, it is interesting enough to be the subject of future work.

Liquid silicon formed by reaction (2) or (3) would react further with ZrC and B_2O_3 , as shown in reaction (4). Due to the release of $\text{SiO}(\text{g})$, the content of SiC in ZBV5 was slightly lower than that in ZS, which was in accordance with the true density, micrographs and XRD results. Subsequently, $\text{SiO}(\text{g})$ would react with V and CO as per reaction (5) to form VC_xO_y and SiC.

One possible reason why vanadium could not be detected by EDS is that, like other vanadium oxides, when the temperature is elevated, VC_xO_y would decompose to $\text{VO}_x(\text{g})$, which would be drawn out of the furnace. In order to confirm this reasoning, the collected powder deposited in the graphite crucible for sample sintering of ZSV5 was analyzed by XRD. The detected crystalline phases were mainly graphite (which came from the crucible paper), SiC and $\text{VC}_{0.88}$ (see Fig. 5b), which is in accordance with the above hypothesis.

The backscattered images of the ZSV5 samples sintered at different temperatures are shown in Figure 3. SEM observations confirmed that the ceramics reached nearly full density, with only a very small amount of pores being observed. From these pictures, SiC grains (dark one) were homogeneously distributed in the ZrB_2 matrix. When the sintering temperature increased, the morphology of the SiC grains changed from equiaxed to whisker-like or platelet-like. Considering that the starting particle size of ZrB_2 was 1.4 μm and that of SiC was 0.45 μm , according to the percolation theory and Zhang's results [4], the critical volume percentage of the SiC phase required to form an interconnected three-dimensional network can be calculated as 29.8 vol.%. Below the critical volume, the SiC particles in the matrix remained isolated and the morphology of the SiC grains should have remained equiaxed; above the critical volume, the SiC particles tended to form an interconnected network and had a higher driving force for developing a whisker-like morphology.

In the present work, the content of SiC (18 vol.%) was far below the critical volume (29.8 vol.%), the SiC grains still became whisker-like or platelet-like, so the result cannot be explained by the percolation theory. From reaction (2) or (3), liquid silicon was formed during sintering. It may further react with $\text{CO}(\text{g})$ or other oxide impurities in the samples to form Si–C–O alloys, then SiC would be recrystallized out via reaction (10), followed the VLS mechanism



The as-sintered ZSV ceramics had a Vickers hardness (Hv5) of 15.4 ± 0.6 (GPa), which is clearly lower than the data for pressureless sintered specimens with B_4C and C additives [4,12]. Benefiting from the absence of carbon, whisker-like or platelet-like SiC and large grains of ZrB_2 , the fracture toughness of ZSV5 was 4.93 ± 0.8 $\text{MPa m}^{1/2}$, which was higher than the reported values [4,12]. The large grains of the obtained samples may also improve the thermal conductivity and erosive resistance. The three-point bending strength was 511 ± 70 MPa and the Young's modulus was 454 ± 9 (GPa) which were comparable with the results in the literature.

In summary, fully dense ZrB_2 –SiC-based composites were sintered by pressureless sintering at 2000–2100 °C using a small amount (≤ 5 vol.%) of vanadium carbide as a sintering aid. Thermodynamic calculations and experimental results proved that vanadium carbide could react with the ZrO_2 covering the surface of ZrB_2 particles and could accelerate the densification of ZrB_2 –SiC. The obtained ZrB_2 –SiC-based ceramics had comprehensively comparable mechanical properties with the results reported in the literature for pressureless sintered materials with different additives.

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- [1] W.G. Fahrenholtz, G.E. Hilmas, I.G. Talmy, J.A. Zaykowski, J. Am. Ceram. Soc. 90 (2007) 1347.
- [2] K. Upadhyaya, J.M. Yang, W.P. Hoffman, Am. Ceram. Soc. Bull. 58 (1997) 51.
- [3] G.J. Zhang, Z.Y. Deng, N. Kondo, J.F. Yang, T. Ohji, J. Am. Ceram. Soc. 83 (2000) 2330.
- [4] Shi C. Zhang, Greg E. Hilmas, William G. Fahrenholtz, J. Am. Ceram. Soc. 91 (2008) 26.
- [5] Yongjie Yan, Zhengren Huang, Shaoming Dong, Dongliang Jiang, J. Am. Ceram. Soc. 89 (2006) 3589.
- [6] Adam L. Chamberlain, William G. Fahrenholtz, Gregory E. Hilmas, J. Am. Ceram. Soc. 89 (2006) 450.
- [7] Adam L. Chamberlain, William G. Fahrenholtz, Gregory E. Hilmas, Donald T. Ellerby, J. Am. Ceram. Soc. 87 (2004) 1170.
- [8] Laura Silvestroni Diletta Sciti, Scripta Mater. 57 (2007) 165.
- [9] China Patent. 01143480.5, 2003.
- [10] K. Choi, N.M. Hwang, D.Y. Kim, Powder Metall. 43 (2000) 169.
- [11] M. Gasch, D. Ellerby, E. Irby, S. Beckman, M. Gusman, S. Johnson, J. Mater. Sci. 39 (2004) 5925.
- [12] S.C. Zhang, G.E. Hilmas, W.G. Fahrenholtz, J. Am. Ceram. Soc. 89 (2006) 544.
- [13] Hua-Ping Xiong, Bo Chen, Yan-Sheng Kang, Wei Mao, Akira Kawasaki, Hiroshi Okamura, Ryuzo Watanabe, Scripta Mater. 56 (2007) 173.