Fabrication and properties of ZrC–ZrB<sub>2</sub>–SiC composites by spark plasma sintering

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Ternary composites of ZrC–ZrB<sub>2</sub>–SiC were successfully synthesized via spark plasma sintering at 1600, 1700 and 1800°C for 5 min under a pressure of 40 MPa with ZrB<sub>2</sub>, ZrC and SiC powder as the raw materials, respectively. The microstructures, phase composition and mechanical properties were studied by scanning electron microscopy, X-ray diffraction and three-point bending test, respectively. The relative density, apparent porosity and flexural strength of the ZrC–ZrB<sub>2</sub>–SiC composite were 93.1%, 0.89% and 383.15 ± 13.56 MPa at 1800°C, which showed the preferable mechanical property and denser microstructure than these properties of 88.0%, 1.68%, 369.77 ± 12.73 MPa at 1600°C and 90.1%, 1.20%, 379.71 ± 12.44 MPa at 1700°C. The comparison showed 1800°C was the best sintering temperature that the ternary composites owned the best microstructures, phase composition and mechanical properties in this experiment.

Key-words: ZrC–ZrB<sub>2</sub>–SiC, Spark plasma sintering, Mechanical properties, Phase composition, Microstructures

1. Introduction

Zirconium boride and Zirconium carbide are very useful Ultra High Temperature Ceramics (UHTC) which are widely used in the domain of aviation because of their extremely high melting point (>3000°C), excellent thermal stability, chemical inertness against molten metals and low electrical resistivity.1)–5) Superior oxidation resistance, perfect densification behavior, and excellent thermal shock resistance make Silicon carbide to be one of the most widely used inorganic materials for making applicable composites with ZrB<sub>2</sub>.6) A complex oxide is regarded as the protective film on the surface to provide improved high-temperature resistance and reduce oxygen permeability in the composites. Moreover, Silicon carbide has a smaller coefficient of expansion which make it possess a better thermal shock resistance than Zirconium boride and Zirconium carbide.7) In addition, ZrC is one kind of ceramic to reinforce the composites system to fabricate available materials. Recent studies have shown that ternary composites of ZrC–ZrB<sub>2</sub>–SiC have superior combination property than do the corresponding ZrB<sub>2</sub>–SiC composites under arc-jet environment that has drawn the horizon of numerous researchers.1) All above contents make ternary composites of ZrC–ZrB<sub>2</sub>–SiC attractive for people’s exploration and reveal that do an in-depth investigation of ternary composites of ZrC–ZrB<sub>2</sub>–SiC is becoming a very necessary job.

At present, Ultra High Temperature Ceramics were fabricated by pressureless sintering (PLS), reactive sintering (RS), hot-press sintering (HPS) and spark plasma sintering (SPS). Spark plasma sintering (SPS) was a booming and progressive technique with the development of sintering technology. Combining to plasma activated sintering, hot-press sintering and resistance heating, SPS made it possible to acquire a swift heating rate, cooling speed and short sintering time.8) On the other side, sintering atmosphere and external pressure can be commanded at discretion.

According to the investigate of Ma et al.,9) ZrB<sub>2</sub>–SiC and ZrC–SiC composites were fabricated by spark plasma sintering at 1800°C for 5 min under a pressure of 40 MPa. The relative density, an apparent porosity, and the bending strength of ZrC–SiC composites were 89.7%, 1.20%, and 257 MPa, respectively. While ZrB<sub>2</sub>–SiC composites showed the better properties by 97.9%, 1.08%, and 310 MPa. Most of the research about Ultra High Temperature Ceramics were focus on two-phase composites such as ZrC–SiC and ZrB<sub>2</sub>–SiC. Few studies have looked at the sintering of ternary ZrC–ZrB<sub>2</sub>–SiC composites specially sintered by SPS. Based on the previous research, many advantages like high relative density and diminutive apparent porosity of ZrC–SiC and ZrB<sub>2</sub>–SiC two-phase composites can be attached by SPS have been proved. SiC was added into ZrB<sub>2</sub>–SiC composites to constitute a new system with the crystal size down to the nanoscale of ZrC–ZrB<sub>2</sub>–SiC composites then processed by high-energy ball-milling was very rare.

Many researches showed ZrC–ZrB<sub>2</sub>–SiC composites with different compositions consolidated by spark plasma sintering had a more refinement microscopic structure and better mechanical property than ZrC–SiC and ZrB<sub>2</sub>–SiC.1)–15) In this experiment, bending resistance, density and porosity were measured by three point bending test and Archimedes Method, respectively.

2. Experimental procedure

ZrB<sub>2</sub> powder (<10 μm, >90 wt % pure, Dandong Chemical Co. Ltd., Dandong, China) or ZrC powder (Kaier Nanometer Technology Development Co. Ltd., Hefei, China) and SiC (99.9 wt % pure, Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) were distributed of 74:10:16 of volume ratio in the present study, respectively. Experimental procedure for fabrication of ZrC–ZrB<sub>2</sub>–SiC composites was shown in Fig. 1.

The 3-D mixing of materials were milled in ball mill (TENCAN powder Co. Ltd., Shanghai, China) for 24 h with 150 r/min with...
ethyl alcohol as the milling medium. The powder to ball weight ratio was 1:10. In order to reduce the contamination of the starting powder during the milling process, a minor average size of about 8 mm of zirconium oxide balls were used. After milling for 24 h, the slurry was generated. Then make the slurry dried at 80°C for 24 h in vacuum. Polyvinyl alcohol (PVA) was added in the mixture powders to obtain the homogenous mixture powders to mold during the drying process. The composites were dried and milled in order to be sieved through a metallic sieve with 100 mesh screen size. The homogeneous mixture powders of ZrC–ZrB2–SiC composite were put into graphite die with compaction after finishing the above work and sintered in spark plasma sintering furnace (Chen Hua Electric Furnace Corp Ltd., Shanghai, China) at 1600, 1700, and 1800°C under a pressure of 40 MPa for 5 min, respectively. The sintered composites samples were ground and polished by SiC powder and cut into three pieces of strip specimens with a size of 3 mm × 4 mm × 35 mm by EC-400 slicer. The chamfering and span were 0.3 and 30 mm, respectively.

The bending strength of the specimens were measured by electronic universal testing machine (CMT5105 100 KN, China) with a crosshead speed of 0.5 mm/min. The density and porosity were identified based on the Archimedean principle with distilled water as medium. The theoretical density of the corresponding composites were calculated through rule of mixture. X-ray diffraction (XRD) with Cu Ka radiation was used to verify the phase composition of the composites by SPS. The microstructure of the composites were studied by Scanning Electron Microscope (SEM, FEI QUANTA FEG250, USA).

3. Results and discussion

The samples were fabricated by the volume ratio of 74:10:16 of ZrC–ZrB2–SiC powders prepared at 1600, 1700 and 1800°C. The X-ray diffraction patterns of the ZrC–ZrB2–SiC composite materials consolidated by SPS are presented in Fig. 2. When sintered at 1600 and 1700°C, the peaks of ZrC, ZrB2 and SiC phase can be detected. In addition, few oxides such as SiO2, B2O3, ZrO2 were presented as other peaks in the X-ray diffraction patterns (XRD) with Cu Ka radiation was used to verify the phase composition of the composites by SPS. The microstructure of the composites were studied by Scanning Electron Microscope (SEM, FEI QUANTA FEG250, USA).

occurred because of the lower sintering temperature at 1600 and 1700°C. Fewer oxides were fabricated at 1800°C that proved 1800°C was the best sintering temperature in this experiment.

The Scanning Electron Microscope (SEM) images of polished surfaces of ZrC–ZrB2–SiC at 1600, 1700 and 1800°C were shown in Fig. 3. As the SEM images of polished surfaces shown, there were the least pores in Fig. 3(c) while Fig. 3(a) contains the most pores. What was more, substantial pores are present in the composites as shown in Fig. 3(a), indicating the composite is not sintered completely. It can be inferred sintering character of the powders were improved at 1700°C with less pores in Fig. 3(b) than that in Fig. 3(a). The pores on the surface were less and homogeneous at 1800°C that can be seen in Fig. 3(c). This sample was the best one with such excellent polished surface among the obtained ones contrasted with the further two, some conclusions can be inferred that properties of the powder improving with the increase of sintering temperature during the design sintering temperature range in this experimental.

The pores were presented larger in Fig. 4(a) than that in Figs. 4(b) and 4(c), which illustrated the process of elimination stomata proceeded incompletely at 1600°C. The relative density of ZrC–ZrB2–SiC composites at 1700°C what showed in Fig. 4(b) was higher than Fig. 4(a) showed due to big pores can be seen scarcely. Compared with the SEM images of Figs. 4(a)–4(c) showed the least pores, the highest density and the most tightly adhesion of the grain structure. The relative density and apparent porosity of these three samples which sintered at 1600, 1700 and 1800°C for 5 min under a pressure of 40 MPa were calculated to be 88.0% and 1.68%, 90.1% and 1.20%, 93.1% and 0.89% by Archimedes Method, respectively. The higher sintering point leaded to a better sintering character during the range of the design sintering temperature that can be reflected based on these conclusions.
The flexural strength of these three samples with the sintering temperature of 1600, 1700 and 1800°C were calculated by three-point bending test out as results of \(369.77 \pm 12.73\) MPa, \(379.71 \pm 12.44\) MPa and \(383.15 \pm 13.56\) MPa, respectively. While the flexural strength changed in keeping with the increase of sintering temperature. A large amount of pores were observed in Fig. 3(a). It was the reason that this composite had the lowest flexural strength at 1600°C compared with those at 1700 and 1800°C. The conclusions were directly illustrated in Fig. 2. SiO\(_2\), B\(_2\)O\(_3\), ZrO\(_2\) were existed as impurity phases in XRD diffraction patterns at 1600 and 1700°C. These impurity phases had a negative effect on the mechanical properties of composites. Compared with the XRD patterns between at 1600 and 1700°C, all peaks were higher resulting in the preferable crystallinity at 1700°C. Therefore, a larger flexural strength at 1700°C was obtained than 1600°C. While only B\(_2\)O\(_3\), ZrO\(_2\) were present in XRD diffraction patterns at 1800°C. Thus, the composites with less impurity phases had the best mechanical properties with the flexural strength of \(383.15 \pm 13.56\) MPa. This shown that the variation trend was in accordance with the change trend of fracture and polished surfaces. Thereby, what made the change of the flexural strength with structural factor have been proved from the characteristic of microstructure.

The sample which was sintered at 1800°C for 5 min under a pressure of 40 MPa with ZrB\(_2\), ZrC and SiC powder as the raw materials. Sintering point at 1800°C have been confirmed to be the best temperature by the analysis of XRD and SEM among the experiment. The phase compositions, the mechanical properties, and the microstructures were investigated in the form of comparison. The ZrC–ZrB\(_2–\)SiC composite have a prodigious consistency of 93.1%, a wonderful apparent porosity of 0.89% and a great bending stress of \(383.15 \pm 13.56\) MPa at 1800°C that were proved as the best sintering temperature in the present study.

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4. Conclusions

The ZrC–ZrB\(_2–\)SiC composites were successfully consolidated via SPS at a relatively low temperature (1600, 1700, 1800°C) for 5 min under a pressure of 40 MPa with ZrB\(_2\), ZrC and SiC powder as the raw materials. Sintering point at 1800°C have been confirmed to be the best temperature by the analysis of XRD and SEM among the experiment. The phase compositions, the mechanical properties, and the microstructures were investigated in the form of comparison. The ZrC–ZrB\(_2–\)SiC composite have a prodigious consistency of 93.1%, a wonderful apparent porosity of 0.89% and a great bending stress of \(383.15 \pm 13.56\) MPa at 1800°C that were proved as the best sintering temperature in the present study.

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