Microstructure and Properties of TiB$_2$-TiC-SiC Ternary Phase Ceramics Produced by High-Gravity Field Activated SHS of Ti-Si-B$_4$C Powders

Chuanzeng Pan, Jing Zhang, Kai Han and Yujun Yin

Army Engineering University, 97 Heping west road, Shijiazhuang, 050003, China
E-mail: zhjj116@163.com

Abstract. TiB$_2$-TiC-SiC ternary phase ceramics have been prepared by high-gravity activated combustion synthesis using (Ti-Si-B$_4$C) mixing powders. XRD, FESEM and FETEM results show that the ceramic matrix was mainly composed of TiB$_2$, TiC and β-SiC. Uniformly-distributed TiB$_2$ platelets formed the skeleton of ceramics, and irregular TiC and β-SiC solids were embedded between TiB$_2$ platelets. The relative density, Vickers hardness and fracture toughness of the ternary phase ceramics were measured with values of 97.9 %, 22.2 GPa and 10.1 MPa·m$^{0.5}$. The high-fraction randomly-orientated TiB$_2$ platelets were found to induce continuous crack deflection, and consumed more energy from the crack tip, thereby enhanced the strength and toughness of TiB$_2$-TiC-SiC ceramics.

1. Introduction

As the advanced materials in engineering ceramics, TiB$_2$-TiC is recognized as candidates for advanced engineering applications due to their excellent combination of mechanical and electrical properties as well as their good corrosion at high temperatures [1]. However, the poor oxidation resistance of TiB$_2$-TiC and moderate fracture toughness restrict its wide applications. Fortunately, the shortcomings can be overcome through the recombination of TiB$_2$-TiC and SiC. It has been confirmed that the oxidation resistance of TiB$_2$-TiC can be improved by the addition of SiC. The use of these materials in composites offers the advantage of enhanced fracture toughness [2], especially in the case of TiB$_2$-TiC-SiC. Moreover, TiB$_2$-TiC-SiC ceramics also exhibit a higher hardness and chemical stability at high temperatures, and are identified as a good alternative for wear resistant applications as cutting tools in comparison to conventional cermets based on WC and TiC. It had been found that TiB$_2$-TiC-SiC ceramics show improved tribological behavior and suffer the smallest wear under similar conditions in comparison to TiB$_2$, TiC and SiC monolithic materials [3].

However, it is difficult to fabricate dense TiB$_2$-TiC-SiC composites by the traditional processing route of mixing commercial TiB$_2$, TiC and SiC powders and subsequent solid state sintering. Near fully-dense TiB$_2$-TiC-SiC ceramics were fabricated using TiB$_2$, TiC and SiC mixed powders through hot pressing at 2100°C for 2h under 40 MPa in Ar atmosphere [1]. In order to reduce high pressure and holding times, reactive hot pressing has been adopted as an effective way to fabricate the TiB$_2$-TiC-SiC composites [4, 5]. Zhang G et al synthesized TiB$_2$-(Ti, W)C-SiC using TiH$_2$, Si, B$_4$C and W as raw materials at 2000°C under 30 MPa for 60 min in an Ar atmosphere. Zhao G et al [5] fabricated TiB$_2$-TiC-SiC via reactive hot pressing process using Ti, Si and B$_4$C 1700°C under 32MPa in vacuum for 45min. However, these reaction processings still have some flaws such as as-produced samples with small size. SHS or combustion synthesis which is based on highly exothermic reactions is used to synthesize many ceramic materials including TiB$_2$-TiC. SHS process had been employed to synthesize in-situ TiC-TiB$_2$-hBN-SiC Ceramic composite powders starting from a compacted TiO$_2$-B$_4$C-TiC-Mg-
Si$_3$N$_4$-C powder blend [6]. However, the SHS products are usually porous and therefore have to be compacted or sintered to produce bulk components suitable for engineering applications. SHS densification process which is conducted under the application of pressure has been verified possible to achieve synthesis and densification simultaneously. This process has been used to consolidate TiB$_2$-TiC composites in a number of studies [2]. However, there are very less reports on preparation of the dense TiB$_2$-TiC-SiC composites using SHS and its derivatives.

Recently, a relatively new method, high-gravity field activated combustion synthesis [7], has been used to fabricate TiB$_2$-TiC based materials using B$_4$C and Ti powders with solidified microstructure. In this study, the high exothermicity of the reaction (B$_4$C+Ti) were exploited to carry a second low exothermic reaction (Si+C) for the production of SiC in a self-propagation regime to prepare bulk TiB$_2$-TiC-SiC ternary ceramics through the high-gravity field activated SHS.

2. Experimental

The green reactants used in the experimental were Ti powder (purity >99%, mean particle size<34 μm), B$_4$C powder (purity >97%, mean particle size3.5 μm) and Si powder (purity >99%, mean particle size<34 μm).The molar ratio (Ti:B$_4$C:Si) of 5:2:1 was chosen in the composition shown in reaction (1).

$$5Ti + 2B_4C + Si \rightarrow 4TiB_2 + TiC + SiC$$ (1)

The stoichiometric reactants were mixed with stainless steel balls for 6h, and then filled into graphite crucibles at constant pressure. Finally, the graphite crucibles were inserted into two combustion chambers at the end of the rotating arms of a centrifugal machine. The combustion systems were ignited by the W coil (ignition voltage 220 V, ignition current 4 A) after the centrifugal machine had provide high-gravity acceleration of 2000 g (1 g = 9.8 m·s$^{-2}$). As the combustion chambers were cooled to ambient temperature, the centrifugal machine was stopped and the crucibles were taken out of the combustion chambers. Finally, a series of ceramic discs with 100 mm in diameter and 20 mm in thickness were obtained in succession after the samples were taken out of the crucibles.

Relative density was evaluated using Archimedes method. Theoretical density was calculated assuming a rule of mixtures. The crystalline phases were determined by Rigaku D/max 2550PC X-ray diffractometry (XRD). The microstructures of samples were observed by Ultra-55 field emission scanning electron microscopy (FESEM) and Tecnai F30 field emission transmission electron microscope (FETEM). The phases were also characterized by means of EDAX using Link ISIS-300 energy dispersive spectrometer (EDS). Vickers hardness and fracture toughness was determined by using a Vickers indentor with a load of 196 N.

3. Results and discussion

XRD pattern showed that the reaction products was mainly composed of TiB$_2$, TiC and β-SiC phases, as shown in Figure 1. It was easily noted that no other phases such as compounds of Ti-B or Ti-Si and elementary substance Ti or Si were detected. Almost full conversion of reactants into products was achieved corresponding to reaction (1), which verified the high-gravity field activated SHS is an effect route for preparing TiB$_2$-TiC-SiC. The reaction products are identical to those reported by Zhang G [6] who prepared a platelet reinforced ceramic composite of TiB$_2$-TiC-SiCusing TiH$_2$, Si and B$_4$C as raw materials by reactive hot-pressing at 2000°C under 30 MPa for 60 min in an argon atmosphere. In the previous work [6], the direct reaction of (Ti+B$_4$C) to product TiB$_2$-TiC composite was highly exothermic (ΔH°=-686kJ/mol), and was capable of generating temperatures exceeding the pseudo-eutectic temperature in the TiB$_2$-TiC system of 2620°C. In this study, the high exothermicity of the reaction (2) for the synthesis of TiB$_2$-TiC was exploited to carry a second low exothermic reaction (3) for the production of SiC in a self-propagation regime. The overall reaction (1) exhibited sufficient exothermicity to self-sustain till reaction completion. The process yielded high pure products with tailored composition suitable for the fabrication of TiB$_2$-TiC-SiC composites.

$$5Ti + 2B_4C \rightarrow 4TiB_2 + TiC + C$$ (2)

$$Si + C \rightarrow SiC$$ (3)
Microstructural morphologies of polished surfaces of synthesized products were shown in Figure 2. Three components of TiB$_2$, TiC and SiC in the materials could be clearly distinguished, where the randomly orientated, the dark grey areas were fine TiB$_2$, the light grey areas were TiC, and the dark areas were $\beta$-SiC phases. Further microstructural analysis was carried out by FETEM as shown in Figure 3. These distribution patterns showed the typical feature of solidification microstructure, where most of TiB$_2$ grains possessed regular platelet morphologies with straight edges, but some were with irregular shape and curved edges. However, TiC and SiC grains had no special morphology with their shape completely defined by the surrounding TiB$_2$ platelet grains. In addition, comparing with the interface of TiB$_2$/SiC and TiB$_2$/TiC in the composites fabricated by the other results [1, 3, 4], the interface in these composite was more cleaner and free from any interfacial phase.

It was measured that the relative density, Vickers hardness, and fracture toughness of TiC-TiB$_2$-SiC composites are 97.9\%, 22.2GPa and 10.1MPa·m$^{0.5}$, respectively. FESEM fracture morphologies of TiB$_2$-TiC-SiC ceramic were showed in Figure 5. The fracture presented intergranular fracture of TiB$_2$ platelets and transgranular fracture of TiC and SiC solids, and the grooves of TiB$_2$ platelets were clearly remained at the fracture section even if they were pulled out. As the crack met TiB$_2$ platelets, it had to propagate along the debonded interface around TiB$_2$ platelets due to the mismatch in thermal expansion coefficient between TiB$_2$/SiC and TiB$_2$/SiC interfaces. The high-fraction randomly-orientated TiB$_2$ platelets were homogeneously distributed in the matrix, which induced continuous crack deflection, and consumed more energy from the crack tip. The driving force for further extension could be reduced effectively, thereby enhancing the toughness of TiB$_2$-TiC-SiC composites.
4. Conclusions
TiB$_2$-TiC-SiC ternary ceramics have been successfully prepared by high-gravity activated combustion synthesis (2000 g) using 5Ti/2B$_2$C/1Si powder mixtures. The composites with tailored composition were only composed of TiB$_2$, TiC and β-SiC, and full conversion of reactants into products was achieved. The skeleton of matrix was mainly formed by high-fraction uniformly-distributed TiB$_2$ platelets and meanwhile irregular TiC and β-SiC solids were distributed along TiB$_2$ platelets. The high relative density, Vickers hardness and fracture toughness of the ternary phase ceramics were gained with values of 97.9 %, 22.2 GPa and 10.1 MPa·m$^{0.5}$. Toughening mechanisms of crack deflection and crack bridging by high-fraction randomly-orientated TiB$_2$ platelets were found, which enhanced effectively the strength and toughness of TiB$_2$-TiC-SiC composites.

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6. References
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