TiB₂-TiC-SiC composites prepared through high-gravity field activated SHS

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Abstract. TiB₂-TiC-SiC composites were prepared by high-gravity activated SHS using (Ti+B₂C+Si) mixing powders. XRD, FESEM and FETEM results showed that the matrix of composites was mainly composed of TiB₂, TiC and β-SiC. Uniformly-distributed TiB₂ platelets formed the skeleton of composites, and irregular TiC and β-SiC solids were embedded between TiB₂ matrix. It is supposed that TiB₂ phases firstly precipitate prior to TiC from the molten reactive product in high-gravity field due to higher concentration of boron atom, and SiC solids solidify at final solidification stage and feed the TiB₂ platelet skeleton, which effectively reduce the porosity and promote the relative density of composites.

1. Introduction
TiB₂, TiC and SiC ceramic materials are all recognized as candidates for advanced engineering applications due to their excellent combination of mechanical and electrical properties as well as their good corrosion and oxidation resistance at high temperatures [1]. However, these monolithic materials possess a low fracture toughness, which hinders their application. The use of these materials in composites offers the advantage of enhanced fracture toughness [2], especially in the case of TiB₂-TiC-SiC, which has been shown the improved fracture toughness [1]. Moreover, TiB₂-TiC-SiC composites also exhibited a higher hardness and chemical stability at high temperatures, and were identified as a good alternative for wear resistant applications as cutting tools in comparison to conventional cerments based on WC and TiC [3].

However, due to the extremely high melting points, high degree of covalent bonding and low self-diffusion coefficients of the constituents, the processing of TiB₂, TiC and SiC into dense composites through traditional sintering routes by mixing powders of the pre-prepared components requires high temperatures or high pressure for long holding times. Near fully-dense TiB₂-TiC-SiC composites were fabricated using TiB₂, TiC and SiC mixed powders through hot pressing at 2100°C for 2h under 40MPa in Ar atmosphere [1]. Moreover, the use of the reactive hot-pressing also for in-situ processing of TiB₂-TiC-SiC composites had been made using TiH₂, Si and B₂C as raw materials at 2000°C for 60min under 30MPa in Ar atmosphere [4]. SHS which is based on highly exothermic reactions is used to synthesize many ceramic materials including TiB₂-TiC-SiC. SHS process had been employed to synthesize in-situ TiC-TiB₂-hBN-SiC ceramic composite powders starting from a compacted TiO₂-
B_{4}C-TiC-Mg_{3}Si_{4}N_{4}-C powder blend [5]. 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 SHS [6], 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 for the production of SiC in a self-propagation regime to prepare solidified TiB_{2}-TiC-SiC composites through the high-gravity field activated combustion synthesis.

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 size 3.5 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).

\[
5\text{Ti}+2\text{B}_{4}\text{C}+\text{Si} \rightarrow 4\text{TiB}_{2}+\text{TiC}+\text{SiC}
\]

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. No other phases such as compounds of Ti-B or Ti-Si and elementary substance Ti or Si were detected.

![Figure 1. XRD patterns of the SHSed products](image)

It is easily concluded that almost full conversion of reactants into products is achieved corresponding to reaction (1), which verifies 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[4], who
prepares a platelet reinforced ceramic composite of TiB₂-TiC-SiC using TiH₂, Si and B₂C as raw materials by reactive hot-pressing at 2000°C under 30MPa for 60min in argon atmosphere. The direct reaction of (Ti+B₂C) to product TiB₂-TiC composite is highly exothermic (ΔH°=−686kJ/mol) [6], and is capable of generating temperatures exceeding the pseudo-eutectic temperature in the TiB₂-TiC system of 2620°C. In this study, the high exothermicity of the reaction (2) for the synthesis of TiB₂-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 completion. The process yielded high pure products with tailored composition suitable for the fabrication of TiB₂-TiC-SiC composites.

\[
5\text{Ti} + 2\text{B}_2\text{C} \rightarrow 4\text{TiB}_2 + \text{TiC} + \text{C} \quad (2)
\]

\[
\text{Si} + \text{C} \rightarrow \text{SiC} \quad (3)
\]

Microstructural morphologies of polished surfaces of synthesized products is shown in Figure 2. Three components of TiB₂, TiC and SiC in the materials could be clearly distinguished, where the randomly orientated, the dark grey areas are fine TiB₂, the light grey areas are TiC, and the dark areas are β-SiC phases. Further microstructural analysis was carried out by FETEM as shown in Figure 3. These distribution patterns shows the typical feature of solidification microstructure, where most of TiB₂ grains possess regular platelet morphologies with straight edges, but some are with irregular shape and curved edges. However, TiC and SiC grains have no special morphology with their shape completely defined by the surrounding TiB₂ platelet grains. In addition, comparing with the interface of TiB₂/SiC and TiB₂/TiC in the composites fabricated by the, the interface in these composite is more cleaner and free from any interfacial phase.

Comparing with many other fabrication process, hot pressing or pressureless sintering process [4,5], high-gravity field activated SHS affords the advantage that the resultant microstructures are not dependent upon the particle size or shape of the starting materials, but rather related to the solidification conditions. According to our previous study [6], the high-gravity field consolidated mass and heat transportation between the products and the unreacted powders, accelerated the deposition of liquid products, and strengthened energy accumulation of the unreacted powders. Therefore, in the present study, after ignition by the W coil, burning rate and energy releasing rate of combustion reaction (2) was improved in the high-gravity field to form Ti-B-C mixed liquids. Then the lower-melting-point Si powder (1414 °C) dissolved into Ti-C-B mixed liquids forming Ti-Si-C-B mixed melt.

In terms of TiB₂-TiC composites [2] prepared through the reactive sintering or high energy ball milling of (Ti+B₂C) mixed powders, TiC phase is usually prior to precipitate due to the fact that the diffusivity of carbon is significantly greater than that of boron. However, TiB₂ in the present study is supposed to take a lead in precipitating from the microstructural evidence of sufficiently grown TiB₂ platelets and irregular TiC and SiC solids. The reason for this observation is likely to be due to the kinetic factors such as formation of high-temperature Ti-Si-C-B mixed melt and high concentration of boron compared to carbon in mixed melt. Provided taking no account of lower-melting-point SiC, according to TiB₂-TiC phase diagram [2], TiB₂ content in this study is higher than that of the eutectic composition. Therefore TiB₂ is prior to precipitate thermodynamically out of the saturated Ti-Si-C-B mixed melt in the cooling and solidification process, and grows into platelet crystals due to their anisotropy crystallographic characteristic. Subsequently, TiC nucleates and precipitates following the continuous precipitation of TiB₂ crystals. However, TiC is characterized by a NaCl-type crystal structure, presents the isotropy in crystal growth, and distributes along TiB₂ platelets. Eventually, residual Si-C melt is forced to inject into the skeleton of TiB₂ platelets due to the effect of high-gravity field.

High-gravity field is thought to effectively reduce the cavity resulting from solidification shrinkage, as shown in Figure 4. The well-defined interface in TiB₂-TiC-SiC has no defects and combine closely, which is supposed to play a key role to promote mechanical properties of TiB₂-TiC-SiC composites. The relative density of TiB₂-TiC-SiC composites was measured 98.9 % which was compared with result reported by Zhang G [3]. As discussed above, Ti-Si-C-B full liquid and high-gravity field greatly...
promoted the densification process. SiC solidified at final solidification stage and fed the TiB₂ platelet skeleton as shown in Figure 3, which effectively reduced the porosity of composite in high gravity field and promote the relative density.

4. conclusions
TiB₂-TiC-SiC composites have been successfully prepared by high-gravity activated combustion synthesis (2000 g) using 5Ti/2B₄C/1Si powder mixtures. The composites with tailored composition are only composed of TiB₂, TiC and β-SiC, and full conversion of reactants into products is achieved. The skeleton of matrix is mainly formed by high-fraction uniformly-distributed TiB₂ platelets, and meanwhile irregular TiC and β-SiC solids distribute along TiB₂ platelets. It is supposed that TiB₂ phases firstly precipitate prior to TiC from the molten reactive product of Ti-Si-C-B in high-gravity field due to higher concentration of boron atom according to TiB₂-TiC phase diagram, and SiC solids solidify at final solidification stage and feed the TiB₂ platelet skeleton, which effectively reduce the porosity and promote densification of composites. The high relative density of the ternary phase ceramics is gained with values of 98.9 %.

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