

## Hot pressed ZrB<sub>2</sub>–SiC–C ultra high temperature ceramics with polycarbosilane as a precursor

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### Abstract

ZrB<sub>2</sub>–SiC–C ultra high temperature ceramics (UHTCs) have been produced by hot pressing pyrolyzed mixtures of ZrB<sub>2</sub> and polycarbosilane (PCS). Samples with SiC contents of 0%, 5% and 16% in volume derived from PCS were prepared. The phase composition, microstructure and mechanical properties were characterized for composites hot pressed at 2073 K for 60 min under the pressure of 20 MPa in an argon atmosphere. Analysis showed that the addition of PCS improved the relative density from 78% (without PCS addition) to ~ 100% (with 16% SiC derived from PCS addition). Hardness and fracture toughness of the composite were also improved.

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**Keywords:** Zirconium diboride; Polycarbosilane; Densification; Hot pressing; Ultra high temperature ceramics

### 1. Introduction

MB<sub>2</sub> (where M=Hf, Zr, Ti) based composites, including ZrB<sub>2</sub>/SiC, HfB<sub>2</sub>/SiC and ZrB<sub>2</sub>/SiC/C, are materials of choice for ultra high temperature structural applications, primarily in the aerospace area. The addition of SiC not only enhances the strength and toughness, but also improves the oxidation resistance. The addition of C also improves the thermal shock resistance, but at the cost of hardness, strength and oxidation resistance [1]. Usually, these composites are fabricated by hot pressing at above 2123 K and under high pressures. Using sintering additives such as Ni and Ta may lower the sintering temperature, but these additives also decrease strength, especially at high temperature [2].

In recent years, the mechanical properties of the ZrB<sub>2</sub>-based UHTCs have been greatly improved by reducing grain size and minimizing impurities [3,4]. On the other hand, reactive processing has also been applied to prepare densified boride-containing composites at relatively mild temperatures from 2073 K to 2273 K [5–8]. However, reactive processing can only produce a limited range of composition.

Using the polymeric precursor as the source of SiC and C is an accepted way to improve the sintering behavior. Polycarbosilane (PCS) has been widely used as a polymer precursor for preparing SiC fibers, fiber-reinforced composites and nano-structured ceramics [9]. In this work, PCS was used to coat ZrB<sub>2</sub>

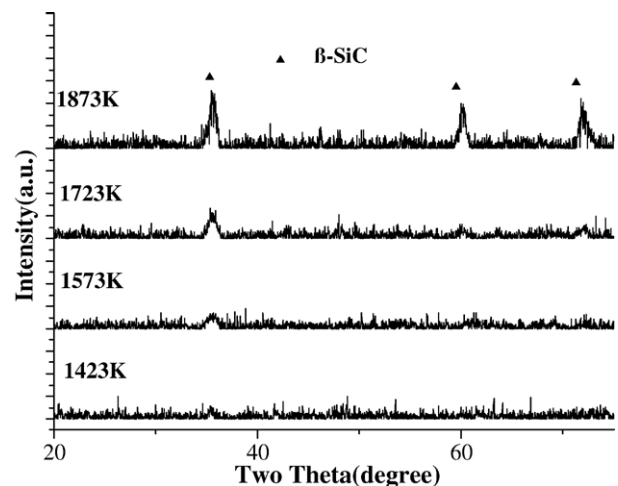


Fig. 1. XRD patterns of PCS pyrolyzed at different temperatures.

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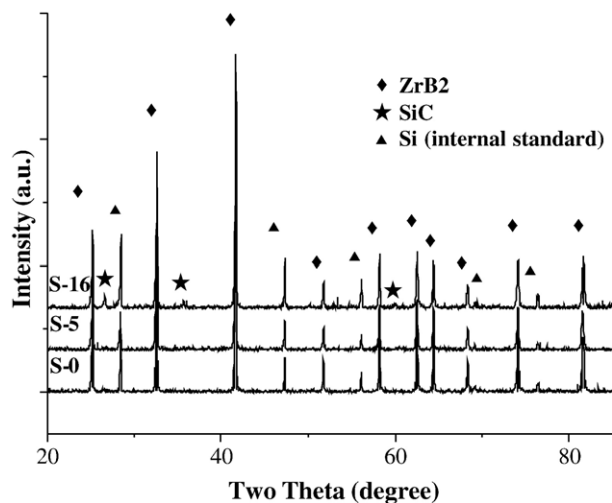


Fig. 2. XRD patterns of S-0, S-5, S-16 after hot pressing at 2073 K. Peaks for Si are from the internal standard used for XRD analysis.

powder, which was then pyrolyzed to form SiC and C in-situ. Not only did this enhance densification, but it also affected the composite properties.

## 2. Experimental procedure

The raw powders used in this work were  $ZrB_2$  (purity 97%, particle size 5–10  $\mu m$ , Kojundo Chemical Laboratory Co. Ltd, Saitama, Japan) and PCS ( $(SiH(CH_3)-CH_2-)_n$ , average molecule weight  $\sim 1250$ , National University of Defense Technology, Changsha, China). The PCS proportion was set according to the desired SiC contents, which were 0%, 5% and 16% in volume. The products were labeled as S-0, S-5 and S-16, respectively.  $ZrB_2$  powder was added into gasoline containing dissolved PCS.

The mixture was ball milled for 24 h. After being dried, the mixed powder was pyrolyzed in a tube furnace in a flowing Ar atmosphere. The heating program was as follows: from room temperature to 423 K in 30 min, held at 423 K for 60 min, from 423 K to 1073 K in 210 min, held at 1073 K for 90 min, and finally cooled to room temperature at a rate of about 3 K/min. The obtained powders were pulverized to  $-200$  mesh and then hot pressed at 2073 K in Ar for 60 min under a pressure of 20 MPa. The estimated cooling rate from the hot pressing temperature to room temperature was about 20 K/min. The density of the product was measured using the Archimedes' method. Hardness and toughness were tested by indentation after polishing the surface [10]. The phase composition was determined by X-ray diffraction (XRD). The microstructure was observed by scanning electron microscopy (SEM).

## 3. Result and discussion

### 3.1. Pyrolysis and phase composition

PCS is a preceramic polymer with a Si–C backbone. When heated in an inert atmosphere, PCS gradually cross-links and forms some low molecular weight species, which results in weight loss. In this work, the product pyrolyzed at 1073 K was amorphous, the mass yield was about 58% and the C/Si ratio was near 1.6. When the temperature was increased to above 1273 K, the amorphous product converted to  $\beta$ -SiC plus amorphous carbon with a volume ratio of about 4:1 [11].

Fig. 1 shows the XRD patterns of pyrolyzed PCS after heat treatment for 60 min at different temperatures. As the temperature increased, the peak height increased and the peak width decreased, which showed that the  $\beta$ -SiC particles coarsened and crystallized. No diffraction peak was observed for the amorphous carbon or other carbon-rich phases.

The XRD patterns for materials that were hot pressed at 2073 K are shown in Fig. 2. It could be seen that all of the strong peaks were from

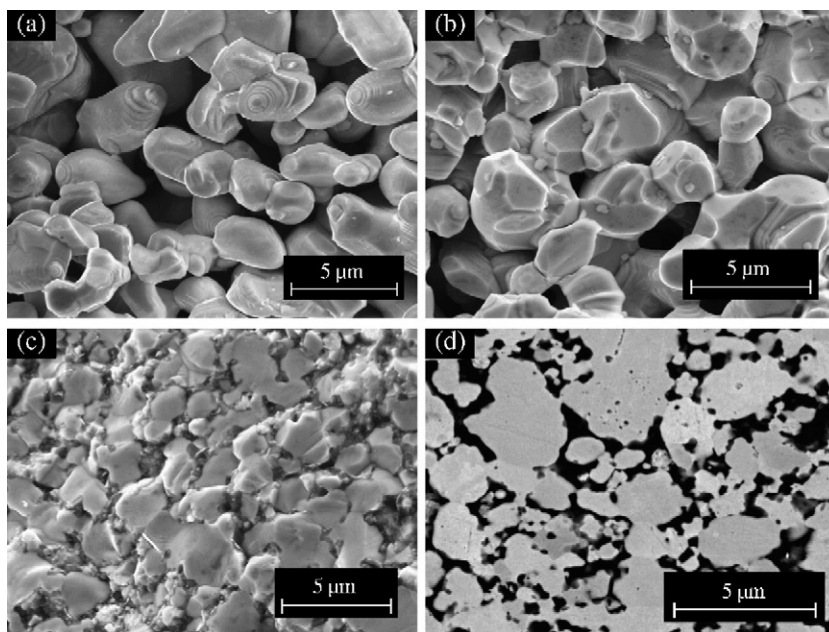


Fig. 3. SEM micrographs of (a) the starting powder of  $ZrB_2$ , (b) a fracture surface of sample S-0, (c) a fracture surface of sample S-16 and (d) a polished surface of sample S-16.

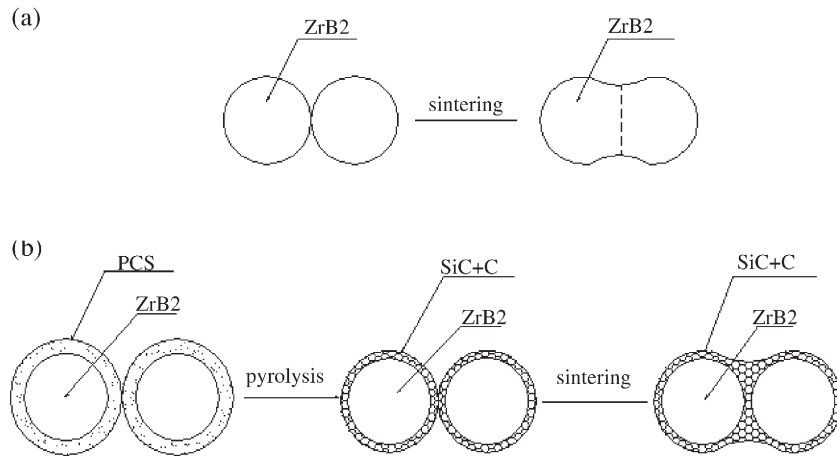


Fig. 4. Microstructure development schematics for (a) pure  $ZrB_2$  sample S-0 and (b) samples with PCS.

$ZrB_2$  and only very weak peaks for  $\beta$ -SiC appeared in S-16. The reason for this should be the low contents of the formed SiC and C as well as their poor crystallinity. The Si peaks were from the internal standard for calibrating peak position.

### 3.2. Microstructure and properties

Fig. 3 shows the morphology of the raw  $ZrB_2$  powder and samples S-0 and S-16. As shown in the micrographs, sample S-0 was highly porous with a relative density of 78%. The  $ZrB_2$  grains were bonded to each other to form porous networks. With the addition of PCS, the densification process was much improved. Sample S-5 had a relative density of 90%, and sample S-16 was fully dense. The  $ZrB_2$  matrix grains were evenly separated by the pyrolyzed SiC and C. It can be concluded that as PCS content increased, composites with full densification and homogeneous microstructure could be obtained.

In sample S-0, little grain growth occurred compared to the raw  $ZrB_2$  powder. In sample S-16, the SiC and C, which had very fine particle sizes, were homogeneously dispersed in the  $ZrB_2$  matrix. The particle size of the  $ZrB_2$  was similar to that of the starting powder. It appears that the newly-formed fine SiC and C were highly active, which not only improved the densification process but also hindered grain growth.

Based on the microstructure, a microstructure development schematic was proposed, as shown in Fig. 4. In the case of  $ZrB_2$  without the addition of PCS, grain distortion, rearrangement, and surface diffusion under the applied pressure of 20 MPa allowed the  $ZrB_2$  particles to form a network structure. When PCS was added, it was evenly coated on the  $ZrB_2$  particles as it was dried from the solvent. In the pyrolysis process, the PCS converted to a coating of SiC + C on the surface of the  $ZrB_2$  particles. The SiC + C coating had a fine particle size resulting in a high activity that bonded the  $ZrB_2$  particles together and filled the spaces between the matrix particles to form a dense structure. The active C could also possibly react with and remove the oxide layer on the  $ZrB_2$  particles and improve the sinterability of the  $ZrB_2$  particles themselves [12].

The hardness and toughness of the dense S-16 specimen were measured in this work. The hardness was 16.2 GPa and the fracture toughness was  $3.4 \text{ MPa m}^{1/2}$ . The values were lower than the reported results of  $ZrB_2$ -SiC composites (reported hardness was about 21 GPa and the toughness was  $4\text{--}4.5 \text{ MPa m}^{1/2}$  for specimens with 10–20 vol.% SiC). On the other hand, the hardness of a material with the addition of weak second phases, such as carbon/graphite, h-BN and pores generally

decreased [13–16]. Accordingly, the reduction in the hardness of the current composite could be attributed to the existence of soft amorphous C, even though the volume content was only about 4%.

### 4. Summary

$ZrB_2$ -SiC-C composites were produced by hot pressing  $ZrB_2$  powders that were coated with PCS. The pyrolyzed PCS was amorphous at temperatures below 1073 K, but it crystallized and converted to  $\beta$ -SiC and amorphous C when the temperature was increased to 1273 K or above. With the addition of PCS, the densification behavior was markedly improved. The relative density of the sample without PCS was only 78% after hot pressing at 2073 K. However the sample with the 16 vol.% SiC derived from PCS addition (S-16) was fully dense under the same conditions. The PCS derived SiC and C were homogeneously distributed in the  $ZrB_2$  matrix. These findings showed that the incorporation of PCS reduced the densification temperature. It was suggested that the reason for the low hardness and fracture toughness for the fully dense sample might be the existence of C (volume content about 4%) derived from the PCS.

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