

## Fabrication of SiC Reinforced ZrO<sub>2</sub> Composites via Polymeric Precursor Route

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### 1. Introduction

Zirconium dioxide (ZrO<sub>2</sub>) is one of the potential candidates for use as a matrix for inert matrix fuels (IMF) due to its low neutron absorption cross section, chemical stability, and the compatibility with water. Irradiation and chemical stability testes performed on yttria stabilized zirconia (YSZ) and calcium stabilized zirconia (CSZ) have shown that they have a good irradiation and chemical stability [1,2]. Despite the good irradiation and chemical stability, its low thermal conductivity is considered the main disadvantage of YSZ. Core loading with the YSZ IMF pellets experienced about a 100 K higher center line temperature than the limit specified for UO<sub>2</sub> [3].

Efforts to improve the thermal conductivity of ZrO<sub>2</sub> include adding a high thermal conductivity material as demonstrated in dual phase MgO-ZrO<sub>2</sub> and rock like oxide fuel concepts with a high volume fraction of the reinforcement materials [4,5]. A more effective method to improve the thermal conductivity is having a connected microstructure of the reinforcement materials. For example, two different types of BeO structures were used to improve the thermal conductivity of UO<sub>2</sub>; a connected microstructure and dispersed particles. The thermal conductivity measured at 1100°C was higher than that of UO<sub>2</sub> by 25% for the continuous type and about 10% for the dispersed particles, respectively [6]. Due to the toxicity of Be, BeO was replaced by SiC for a reinforcement material in UO<sub>2</sub>; because of its low neutron absorption cross section, high thermal conductivity, good chemical and irradiation stability [7]. It is reported that the thermal conductivity of UO<sub>2</sub> was improved by 62 % with only 10 vol. of the SiC whiskers [8]. A. Ortona et al. fabricated ZrB<sub>2</sub>-SiC composites with SiC phase surrounding the grains of ZrB<sub>2</sub> matrix through a polymeric precursor route by using Si and phenol [9]. S. Li et al. measured the thermal conductivity of Al composites reinforced with a continuous phase SiC and SiC particles and found that the difference in the thermal conductivity measured at room temperature was about 70.2 W/m·K [10]. To the best of authors' knowledge, no study has been performed about the fabrication of the connected SiC microstructure to improve the thermophysical properties of oxides.

Ceramics due to their high melting point require a high sintering temperature. For example, the sintering SiC at temperature below 2000°C is very difficult

without sintering aids [11]. The sintering temperature can be reduced by using a polymeric precursor for SiC formation. However, the decomposition of polymeric precursors producing a non-stoichiometric SiC and excess carbon cannot be avoided [12]. Therefore, in addition to the polymeric precursors, Si is commonly added to react with the excess carbon to form SiC and to facilitate the densification of the sintered composites by melting [13].

In this study SiC-ZrO<sub>2</sub> composites was fabricated by applying a polymeric precursor route at temperatures up to 1500°C. The phase composition, the microstructure, and the elemental composition of the sintered pellets were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive x-ray analysis (EDS), respectively. The effects of sintering temperature and Si addition to the sintered pellets were investigated. The thermal conductivity of the interconnected SiC-ZrO<sub>2</sub> composites was estimated by using analytical models.

### 2. Methods

Si powder (325 mesh, 99% purity, Sigma Aldrich), SMP-730 (1 g/cm<sup>3</sup>, Starfire USA), and ZrO<sub>2</sub> powder (5 μm, Sigma Aldrich) were used as starting materials. SMP-730 is a polycarbosilane polymeric precursor with ceramics yield of 65-67 wt.% [14]. The chemical composition of the polymer driven ceramics was analyzed and the Si to carbon ratio was measured [13]. It was experimentally found that Si/C ratio from the decomposition of SMP-730 in an Ar atmosphere at 1400°C was about 0.475. Based on the chemical analysis of the polymer driven ceramics from the decomposition of SMP-730, the amount of Si needed was calculated and the volume fraction of SiC was set to 20 %.

In order to fabricate the interconnected SiC-ZrO<sub>2</sub> composites, ZrO<sub>2</sub> powder was compacted by a uni-axial press under a pressure of 167 MPa, sieved, and self-mixed without balls for more than 6 hours. Then, SMP-730 were added and the mixing continued for more than 6 hours. The corresponding amount of Si was added and the mixing continued for further 6 hours. Then, the mixed powder was poured in a 13 mm graphite die sprayed with BN to prevent the reaction between ZrO<sub>2</sub> and the graphite die. After that, the green pellets were slightly pressed and placed in an alumina crucible and inserted into a tube furnace. The sintering was

performed under an Ar gas flow at temperature of 1450 and 1500°C for 2 hours with a heating rate of 10°C/min.

### 3. Results

Fig. 1 shows the XRD patterns for SiC-ZrO<sub>2</sub> composites sintered at 1450°C and 1500°C. At 1450°C sintering temperature only ZrO<sub>2</sub> diffraction peaks were detected indicating that the sintering temperature was not enough for the fabrication of the SiC (Fig.1 a). At 1500°C sintering temperature, in addition to ZrO<sub>2</sub> diffraction peaks, SiC diffraction peaks were detected only in the pellets containing Si powder, and ZrC diffraction peaks were detected in the pellets without the Si addition.

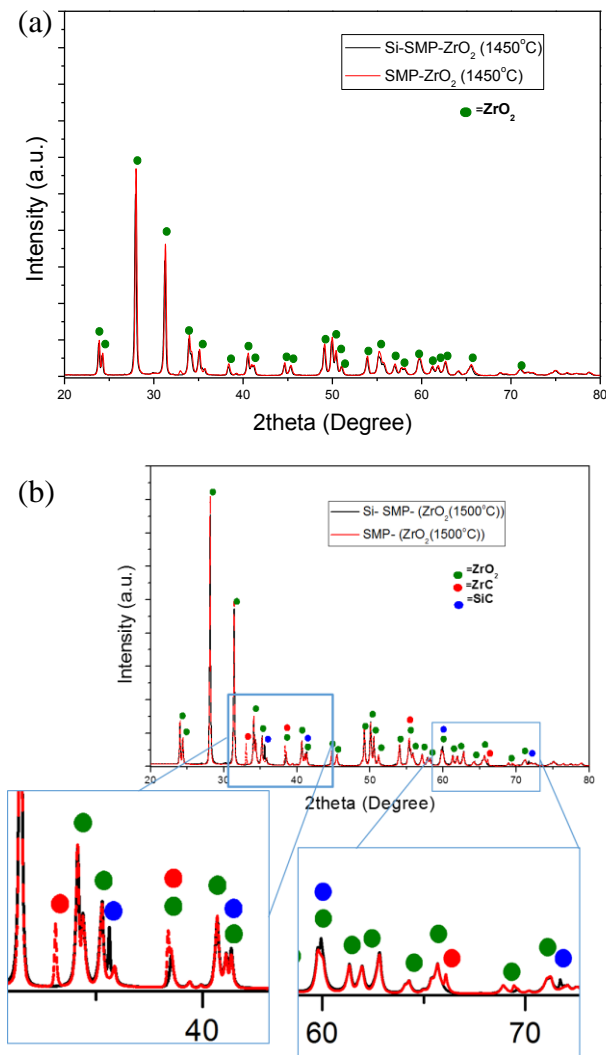


Fig. 1. XRD analysis of SiC-ZrO<sub>2</sub> composites sintering at (a) 1450°C and (b) 1500°C.

The microstructure and EDS results of the second phase of the SiC-ZrO<sub>2</sub> composites sintered at 1500°C with and without Si addition are shown in Fig. 2 and Fig. 3, respectively. As can be seen from Fig. 2 and Fig. 3, connected microstructure was not formed and the porosity was mainly in the second phase. The second

phase was mainly composed of Si and C with atomic ratio of about 1 indicating that amorphous SiC phase was formed as result of the decomposition of SMP-730 at 1500°C.

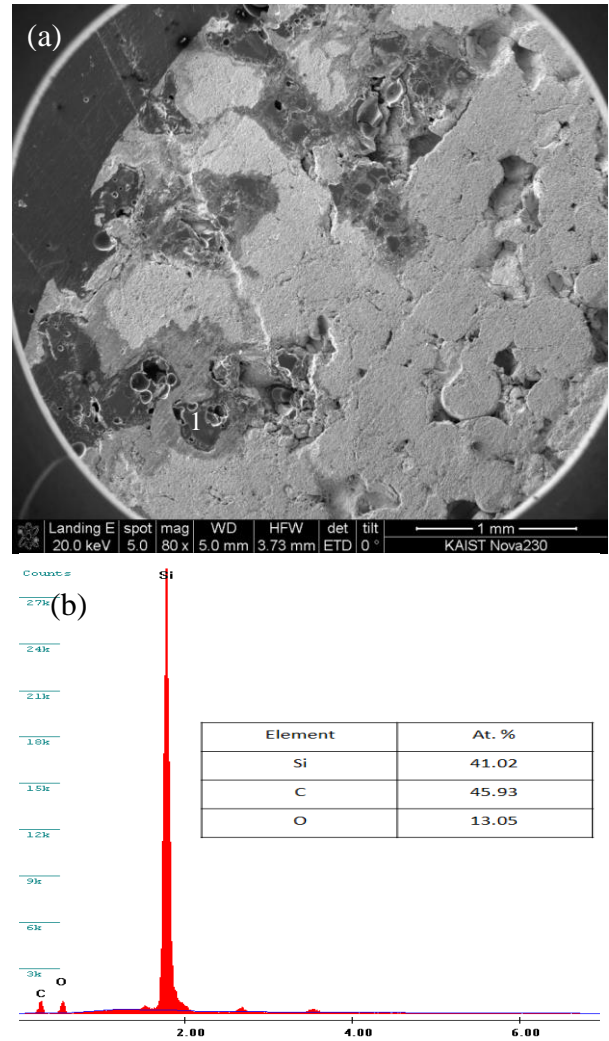


Fig. 2. The microstructure (a) and the EDS analysis of point 1 (b) of the pellets sintered at 1500°C without Si addition.

The relative density of SiC-ZrO<sub>2</sub> composites considering 20 vol. % of the SiC phase with and without the addition of Si was about 96 and 85 % respectively. The low densification of the composites and porous microstructure was formed because the consolidation pressure was not applied during the sintering and the evolution of the gas from the decomposition of the polymeric precursor [15]. The absence of the SiC diffraction peaks of the pellets sintered without the addition of the Si could be attributed to formation of amorphous SiC phase from the pyrolysis of SMP-730 at 1450°C or 1500°C. The detection of SiC in the pellets sintered at 1500°C with the Si addition could be attributed to the solid-liquid reaction between excess carbon from the decomposition of SMP-730 and the molten Si [16].

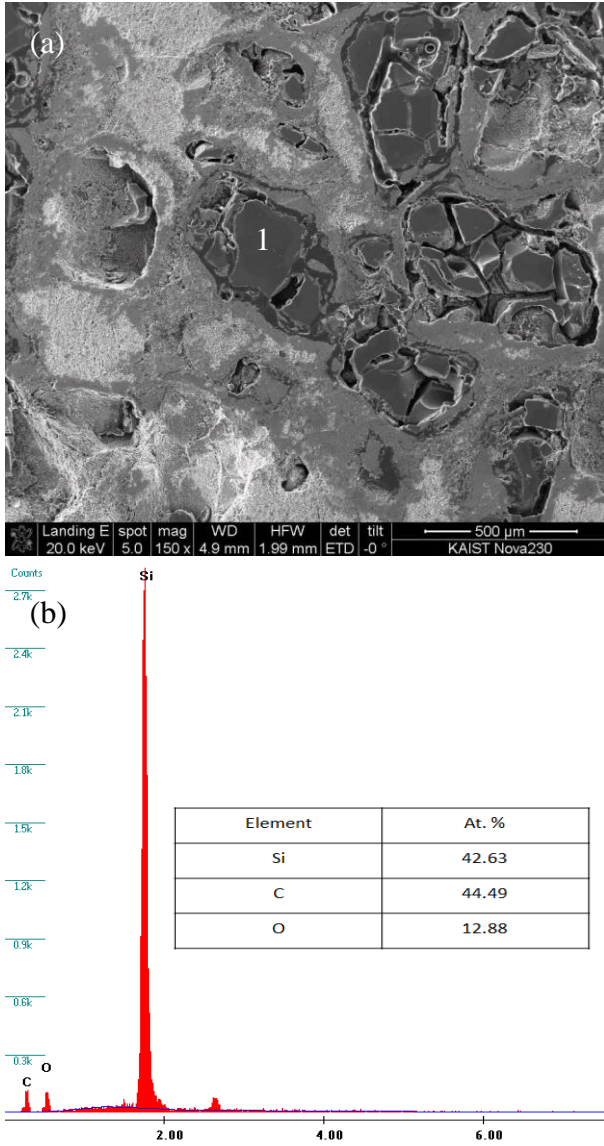


Fig. 3. The microstructure (a) and the EDS analysis of point 1(b) of the pellets sintered at 1500°C with Si addition.

E. Bouillon et al. studied the mechanism of the pyrolysis of the polycarbosilane polymeric precursor into SiC based ceramic materials. They found that the pyrolysis mechanism of polycarbosilane involves three main steps: (1) for  $550 < T < 800^{\circ}\text{C}$ , the transition from the organic to metallic materials with breaking most of the Si-H and C-H and the formation of amorphous SiC, SiO<sub>2</sub>, and silicon oxycarbide. (2) For  $800 < T < 1000^{\circ}\text{C}$ , nucleation of SiC surrounded with aromatic carbon layer. (3) For  $800 < T < 1600^{\circ}\text{C}$ , a SiC coarsening consuming the residual amorphous phases and evolution of SiO and CO [17]. J. Yin et al. analyzed the properties of SMP-730 and found that a major part of the polymer driven ceramics were in the amorphous state even after pyrolysis at 1500°C [12].

Several models have been proposed to predict the thermal conductivity for composites. The Maxwell's model is the basis for many of them. The Maxwell's model depends on the thermal conductivity of the matrix, thermal conductivity of the particles, and the volume fraction of the particles, and it predicts the thermal conductivity with a good accuracy for spherical, non-interacting particles with low volume fraction (less than 10%) (Equation 1) [18]. The percolation model predicts the thermal conductivity with sufficient accuracy for foam reinforced composites which resembles the microstructure of the interconnected SiC-ZrO<sub>2</sub> composites. Calmidi and Mahajan proposed a percolation model with a hexagonal unit cell structure with square intersections to predict the thermal conductivity of high porosity metallic and reticulated vitreous carbon foam [19]. The effective thermal conductivity is expressed by equation 4. Where  $K_r$ ,  $K_m$  and  $K$  is the thermal conductivity of the reinforcement, the matrix and the composite respectively,  $V_r$  is the volume fraction of the reinforcement,  $P$  is the porosity,  $r$  is the aspect ratio ( $t/b$ ),  $(b/L)$  is the dimensionless parameter of the length ratio,  $t$  is half thickness of the foam skeleton,  $b$  is the length of the square intersections, and  $L$  is the half length of the of the hexagonal unit cell.

$$K = K_m \frac{(2 - 2V_r)K_m + (1 + 2V_r)K_r}{(2 + V_r)K_m + (1 - V_r)K_r} \quad (1)$$

(2)

$$K = \left( \left( \frac{2}{\sqrt{3}} \right) \left( \frac{r \left( \frac{b}{L} \right)}{K_m + \left( 1 + \frac{b}{L} \right) \frac{(K_r - K_m)}{3}} + \frac{(1-r) \left( \frac{b}{L} \right)}{K_m + \frac{2}{3} \left( \frac{b}{L} \right) (K_r - K_m)} + \frac{\frac{\sqrt{3}}{2} - \frac{b}{L}}{K_m + \frac{4r}{3\sqrt{3}} \left( \frac{b}{L} \right) (K_r - K_m)} \right) \right)^{-1}$$

$$\frac{b}{L} = \frac{-r + \sqrt{r^2 + \frac{2}{\sqrt{3}} (1-P) \left( 2 - r \left( 1 + \frac{4}{\sqrt{3}} \right) \right)}}{\frac{2}{3} \left( 2 - r \left( 1 + \frac{4}{\sqrt{3}} \right) \right)}$$

Table 1 shows the referenced thermal conductivity in W/m·K of  $\beta$ -SiC [20] and ZrO<sub>2</sub> powders at different temperatures. The thermal conductivities of SiC (10 vol. %)-ZrO<sub>2</sub> composites predicted by the Maxwell's model and the Calmidi and Mahajan's model at 25, 500, 800, and 1100°C are shown in Fig. 4. As can be seen from the figure, the Calmidi and Mahajan's model predicted a higher thermal conductivity of the SiC-ZrO<sub>2</sub> composites since it considers the interconnectivity of the reinforcement. Whereas, the Maxwell model's considers the volume fraction of homogenously non-interacting dispersed particles. The thermal conductivity of SiC-ZrO<sub>2</sub> composites at 1100°C was about 48 % and 28 % higher than the thermal conductivity of the pure ZrO<sub>2</sub> for the interconnected phase and the dispersed particles phase, respectively.

Table 1: Thermal conductivity of  $\beta$ -SiC [20] and ZrO<sub>2</sub> powders at different temperature in W/m·K.

Temperature (°C)	SiC [20]	ZrO <sub>2</sub>
25	150	7.5
500	100	3.9
800	80	3.3
1100	60	2.9

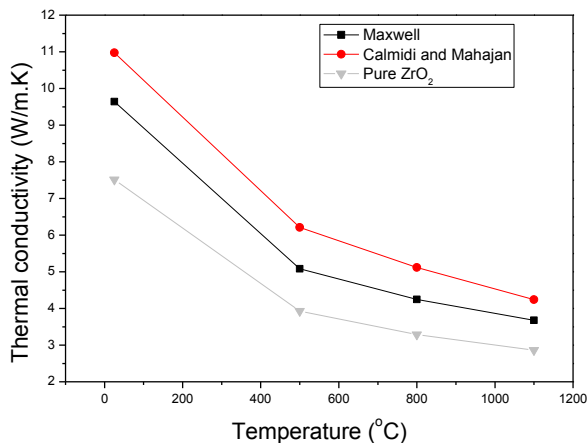


Fig. 4. The thermal conductivities of SiC (10 vol.%) - ZrO<sub>2</sub> composites predicted by the Maxwell's model and the Calmidi and Mahajan's model at different temperatures.

### 3. Conclusions

SiC-ZrO<sub>2</sub> composites were fabricated through a polymeric precursor route at 1450°C and 1500°C and the effects of the Si addition and sintering temperature were studied. The XRD analysis showed that SiC phase was not detected in the samples sintered at 1450°C and SiC diffraction peaks were only detected in the samples sintered at 1500°C with the addition of Si. The formation of SiC could be attributed to the solid-liquid reaction between the Si and excess carbon from the decomposition of SMP-730.

In the microstructure of the sintered samples. A connected microstructure was not formed and the

porosity was mainly in the SiC phase due to the low sintering temperature and the evolution of gases from the decomposition of the polymeric precursor. In addition, a second phase with SiC composition was observed in the microstructure in all the sintered samples. This indicates that as a result of the decomposition of the SMP-730 at temperatures less than or equal to 1500°C, amorphous SiC was formed.

This study suggests that a higher compaction pressure followed by an intermediate decomposition temperature of the polymeric precursor and a higher sintering temperature are needed in order to fabricate interconnected SiC-ZrO<sub>2</sub> composites.

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