Effect of Y_2O_3 addition on the properties of mullite bonded porous SiC ceramics prepared by an infiltration technique

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Mullite bonded porous SiC ceramics were synthesized by infiltrating a powder compact of SiC and Y_2O_3 with a liquid precursor of mullite which on subsequent heat treatment at 1300-1500 °C produced mullite bonded porous SiC ceramics. The effect of Y_2O_3 content and sintering temperature on phase composition, microstructure, oxidation degree of SiC, flexural strength, porosity and pore size distribution were studied. Due to enhance oxidation and well developed neck formation by the addition of Y_2O_3 a high strength 49 MPa was achieved for the porous mullite bonded SiC ceramics with porosity 28 vol %.

Keywords: Silicon carbide; Infiltration; Y_2O_3 ; Mechanical property; Mullite.

Efecto de la adición de Y_2O_3 sobre las propiedades de materiales porosos de SiC-Mullita preparados mediante infiltración

Se han sintetizado materiales porosos de SiC-Mullita mediante la infiltración de polvo prensado de SiC y Y_2O_3 con un precursor líquido de mullita, el cual con un tratamiento térmico posterior a 1300-1500 °C da lugar a los materiales porosos de SiC-Mullita. Se estudió el efecto del contenido de Y_2O_3 y la temperatura de sinterización en la constitución mineralógica, en la microestructura, en el grado de oxidación del SiC, la resistencia a la flexión, la porosidad total y su distribución de tamaño. Debido a la oxidación y a la mejora en la formación de los cuellos por la adición de Y_2O_3 , se alcanzan altos valores de resistencia, 49 MPa, para estos materiales porosos de SiC-Mullita con porosidad 28 % en volumen.

Palabras clave: carburo de silicio, infiltración, Y_2O_3 , propiedad mecánica; mullita.

1. INTRODUCTION

Porous SiC ceramics possesses many advantageous properties such as high strength, high thermal conductivity, low thermal expansion coefficient, excellent thermal shock resistance, very good oxidation and corrosion resistance, low density and so on which make them suitable for several industrial applications (1-6). However sintering of SiC at moderate temperatures is difficult because of the high extent of covalence of the C-Si bond (7). To achieve porous SiC ceramics at low temperatures different secondary phases of oxide and non-oxide are used. They include silica, mullite, cordierite, silicon nitride, etc. (8-18). Among these bond phases mullite possesses a high melting point, low oxygen diffusion coefficient and matching thermal expansion coefficient with SiC. Therefore mullite bonded SiC ceramics could exhibit high temperature strength, better oxidation resistance and thermal shock resistance properties. Several methods of synthesis of mullite bonded porous SiC ceramics were reported. Majority of these investigations have dealt

with an in-situ reaction bonding process (10-16). The effect of addition of Y_2O_3 , alkaline earth metal oxides with the starting materials on the properties of the reaction bonded porous SiC ceramics are also discussed by several authors (15,16). Recently we have fabricated mullite bonded porous SiC ceramics by infiltrating a SiC porous compact with a liquid precursor of mullite followed by sintering at 1300–1500 °C in air (19,20).

The objective of the present work is to investigate the effect of Y_2O_3 addition on the formation of mullite bonded porous SiC ceramics (MBSC) where the bond phase (mullite) is incorporated into porous SiC compact by infiltration technique. Comparison of the materials property (porosity, pore size distribution, density), mechanical strength, phase composition and microstructure of porous mullite bonded SiC ceramics with or without Y_2O_3 addition have been studied. The effects of Y_2O_3 content and sintering temperatures on the properties of porous SiC ceramics have also been investigated.

2. EXPERIMENTAL

A Commercial α -SiC powder (Grindwell Norton, India; SiC 98.20 %, free carbon 0.25 %, SiO_2 0.50 %, Fe_2O_3 0.04 % w/w; $d_{10}=9.48 \mu m$, $d_{50}=22.48 \mu m$, $d_{90}=43.11 \mu m$), Y_2O_3 (Sigma-Aldrich, St. Louis, United States, 99.9 % purity) were used in this study. The powders of SiC and 0-5 wt % Y_2O_3 were mixed with 10 % solution of polyvinyl alcohol binder (Loba Chemie, India, 10 wt % PVA in water) and pressed in a hydraulic press to produce rectangular green bars ($50 \times 20 \times 16 \text{ mm}^3$). The bars were dried and subsequently fired in air at $1100^\circ C$ for 4 h for formation oxide bonds between the touching particles and thereby eliminating the possibility of formation of surface cracks prior to any precursor infiltration. The porous bars were evacuated and further infiltrated with a liquid precursor of mullite. The precursor of mullite was prepared by mixing stoichiometric amount of tetraethyl ortho silicate (TEOS) (Acros Organics, Pittsburgh, USA, 98 % purity) in ethanol to a solution of aluminium nitrate nonahydrate (ANN) (Merck Specialist Pvt. Ltd., India, 95 % purity) in ethanol under suitable condition following the method described earlier (19). The infiltrated samples were dried at $100^\circ C$ for 18 h to remove the solvent and the process was repeated five times. Finally the infiltrated or without infiltrated samples were sintered in air at 1300 – $1500^\circ C$ for 4 h in an electrically heated ceramic tube furnace (Model No.-TE-3499-2, M/s Therelek Engineers (P) Ltd., Bangalore, India). The weight and dimensions of fired samples were measured, density was determined by Archimedes method, open porosity by boiling water method and pore size distribution was determined by Hg-intrusion porosimetry (Model 60, Poremaster, Quantachrome Instruments Inc., Florida, USA). The oxidation degree of SiC (%) was estimated by measuring the weight changes of the samples before and after sintering (21). The average of the five readings was reported for the material and mechanical properties data. Phase identification was done by X-ray diffractometry technique (XRD, PW 1710, Philips, Holland, with $Cu K\alpha$ radiation, $\lambda=1.5406 \text{ \AA}$). Microstructural examination was done using scanning electron microscopy (SEM, Model SE-440, Leo-Cambridge, Cambridge, UK). For mechanical property evaluation the specimens were sliced to produce rectangular pieces of cross section of $4.75 \times 3.25 \text{ mm}^2$. They were ground and polished up to $10 \mu m$ finish and tensile surfaces were chamfered. The room temperature flexural strength was determined in a three-point mode (with a span of 40 mm, speed of 0.5 m/min) in an Instron Universal Testing machine (Model 1123, Instron, Canton, MA, USA). The deflection was monitored through LVDT with a resolution of 0.05 % of full scale and from the load – deflection data Young's modulus was determined using standard software (Instron Bluehill-2, UK).

3. RESULTS AND DISCUSSION

After firing at $1100^\circ C$, the bars referred as pre-formed precursor SiC samples were found to be strong with no sign of corner breakage and surface cracks. The characteristics of pre-formed precursor SiC samples are summarized in Table I. Weights of all samples were measured before and after sintering to estimate the oxidation degree of SiC (%). Pre-formed precursor SiC samples exhibited mass gain due to oxidation of SiC particles, which lead to formation of strong necks between the contacting particles making the bars strong and the problem of surface cracking during infiltration was removed. Oxidation bonding and neck formation between the touching SiC particles at $1100^\circ C$ were also reported other authors (9,15).

Figure 1. Variation of density and porosity as a function of sintering temperature.

Figure 2. XRD pattern of porous MBSC ceramics prepared at $1500^\circ C$.

TABLE I: CHARACTERISTICS OF THE PRESSED AND PREFORMED PRECURSOR SiC SAMPLES

Y_2O_3 content (wt%)	Bulk density of pressed bar ($kg m^{-3}$) $\times 10^3$	Materials properties of preformed precursor SiC samples			
		% wt gain	% SiC oxidation degree	Density($kg m^{-3}$) $\times 10^3$	Porosity (vol.%)
0	1.72	2.48	5.02	1.75	44
3	1.82	2.51	5.14	1.85	42
5	1.84	2.56	5.34	1.88	41

Figure 3. Effect of sintering temperature on oxidation degree of SiC (%).

Figure 5. Effect of variation of Y₂O₃ concentration on pore size distribution profile of MBSC ceramics prepared at 1300 °C.

Figure 4. SEM micrograph of porous MBSC ceramics (a) with 3 wt % Y₂O₃ addition sintered at 1300 °C (b) with 3 wt % Y₂O₃ addition sintered at 1500 °C (formation of needle like mullite crystals is indicated by arrow) (c) with 5 wt % Y₂O₃ addition sintered at 1300 °C (d) with 5 wt % Y₂O₃ addition sintered at 1500 °C (formation of cracks are shown by arrows).

The heat treated porous bars were evacuated and further infiltrated with a liquid precursor of mullite. Weights of the samples were taken after each infiltration to assess the infiltration weight gain and finally to calculate amount of mullite. The MBSC ceramics exhibited negligible dimensional changes ($\leq 1.0\%$) after sintering at 1300-1500 °C. The dependence of density and porosity as a function of sintering temperature and Y₂O₃ content are shown in Fig. 1. Density was found to increase with increase in sintering temperature and Y₂O₃ addition and reverse trend was observed for porosity.

Figure 2 showed the XRD patterns of the MBSC ceramics prepared without and with 3-5 wt % Y₂O₃ addition. SiC, mullite and cristobalite were detected as the major crystalline phases. The peak intensity of cristobalite was found to increase with addition of Y₂O₃. She et al. (22) observed that during sintering a powder mixture of alumina, quartz and

Figure 6. Effects of sintering temperature on flexural strength (open symbol) and Young's modulus (closed symbol) of MBSC ceramics with and without Y₂O₃ addition.

yttria in certain ratio above 1100 °C some Y₂SiO₅ were formed. As the temperature was further increased to 1150 °C, Y₂SiO₅ reacted with quartz to form Y₂Si₂O₇. In our case also these type of reaction resulted the formation of yttrium silicate, which is proved by the presence of additional peak in XRD analysis for yttria added MBSC ceramics.

The oxidation degree of SiC (%) of the sintered ceramic samples is presented in Fig. 3. In the present study, the oxidation degree of SiC (%) at 1100 °C was independent of Y₂O₃ concentration, but above this temperature the oxidation degree of SiC (%) increases with increase of Y₂O₃ concentration.

In presence of mullite, Y₂O₃ addition leads to the formation of lower viscosity of Y-Al-Si-O glass phase (22) which improved the diffusion rate of oxygen in it and accelerated the oxidation of SiC. With increase in sintering temperature oxygen diffusion through surface silica layer of SiC becomes faster hence oxidation of SiC increased. As a

result SiC oxidation degree (%) of MBSC ceramics prepared without and with yttria addition increases from 14 to 26 and 22 to 44 % respectively, when the temperature increases from 1300 to 1500 °C.

Typical microstructures of porous MBSC ceramics are shown in Fig. 4. During microstructure examination of the sintered ceramics SiC particles were seen to be bonded by well developed necks (Fig. 4(a)). Needle like mullite crystals were seen to be present in the bonds formed between the SiC particles (Fig. 4 (b)). With increasing amount of yttria and sintering temperature small pores were seen to be filled up and diameters of large pores were decreased due to formation of more glassy phase as shown in Fig. 4(c). For the samples containing 5 wt % yttria sintered at 1500 °C, surface cracks were seen to developed (Fig. 4(d)) which may be due to the mismatch of thermal expansion coefficient of SiC and glassy phase which might cause the failure of the individual struts.

The typical pore size distribution pattern of samples sintered at 1300 °C is presented in Fig. 5. The average pore size of the sintered ceramics was found to be 7.8, 6.4 and 5.8 μm respectively for the samples containing 0, 3 and 5 wt % Y_2O_3 . The decrease of pore size with increase of yttria contents were also observed from microstructure. Formation of glassy phase have partly covered the pores hence the pore size was reduced.

The variation of flexural strength and Young's modulus of porous MBSC ceramics with variation of Y_2O_3 content is plotted against sintering temperature in Fig. 6. It was found that both the addition of Y_2O_3 and increase of sintering temperature improved the strength up to certain extent and then decreased. Addition of Y_2O_3 promoted the oxidation of SiC hence increased the formation of cristobalite and the glassy phase which closed the porosity, combination of which strengthen the bonding of SiC particles as a consequence the strength is improved. However flexural strength increased with Y_2O_3 content, and then decreased with 5 wt % Y_2O_3 . Both the increase of Y_2O_3 content and sintering temperature caused the formation of excessive Y-Al-Si-O and silica glass at high sintering temperature and resulted surface cracks and reduced the strength. The maximum flexural strength of 49 MPa was achieved with porosity 28 vol. % for 3 wt % Y_2O_3 added samples sintered at 1500 °C. The increase of flexural strength of MBSC ceramics with addition Y_2O_3 or alkaline earth metal oxides were also reported in literature (15,16). Choi *et al.* (16) reported flexural strength of 44 MPa at 46 % porosity for MBSC ceramics with addition of SrO. Ding *et al.* (15) reported the maximum strength 27.5 MPa with open porosity of 44.4 % for reaction bonded porous ceramics prepared at 1450 °C using 1.5 wt. % Y_2O_3 . They also reported strength of 24.0 MPa with open porosity of 43.4 % for reaction bonded porous ceramics prepared at 1550 °C without Y_2O_3 addition (10). The flexural strength of MBSC with no additives in the literature were 9.8 MPa at 50 % porosity, (12) 24 MPa at 43 % porosity, 39 MPa at 36 % porosity and 45.49 MPa at 29.54 % porosity (11,13). The particle sizes of SiC used in the literature were 0.5-20 μm , which is smaller or comparable with the present work. Furthermore the sintering temperature 1300-1500 °C and compaction pressure (26 MPa) used in this study were lower than reported sintering temperature (1450-1550 °C) and compaction pressure (30-90 MPa), in the literature. The higher strength in the present MBSC ceramics were attributed due to

the combined effect of sintering temperature, Y_2O_3 addition and incorporation of bond phase by infiltration assisted technique.

4. CONCLUSION

Mullite bonded porous SiC ceramics were synthesized by an infiltration based processing consisting of intrusion of monophasic mullite precursor sol into a porous compact of SiC with Y_2O_3 addition followed by sintering at 1300-1500 °C in air. In addition to SiC, mullite and cristobalite phases, $Y_2Si_2O_7$ were also detected for Y_2O_3 added samples. The oxidation degree of SiC (%) of MBSC ceramics prepared without and with yttria addition increases from 14 to 26 and 22 to 44 % respectively with increase of temperature from 1300 to 1500 °C. The final ceramics was found to have porous network formed by the interconnected void spaces. SiC particles were seen to be bonded by well developed necks of cristobalite and needle shaped mullite crystals. The increase of density and decrease of porosity in the final ceramics were observed with increase of Y_2O_3 content. However, the flexural strength of the MBSC ceramics first increased than decreased with the Y_2O_3 contents. The average pore diameter decreased from 7.8 to 5.8 μm with increase in Y_2O_3 contents. The maximum flexural strength of 49 MPa was achieved at a porosity 28 vol. % for 3 wt % Y_2O_3 added samples sintered at 1500 °C.

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