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Hot Isostatic Pressing of SiC/Si_3N_4 Composite with Rare Earth Oxide Additions

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Abstract: SiC/Si_3N_4 composites with rare earth oxide additions have been prepared by glass encapsulated hot isostatic pressing at 1850°C and 200 MPa pressure. Mechanical properties and microstructures of the sintered samples have been studied. It is shown that different molar ratios of La_2O_3 to Y_2O_3 and the total amount of La_2O_3 and Y_2O_3 additions can affect the mechanical properties significantly. With 3 wt% La_2O_3 + Y_2O_3 additions, lower La_2O_3/Y_2O_3 molar ratio exhibits higher bending strength and median fracture toughness, but relatively lower Vickers hardness. For addition of 6 wt% La_2O_3 + Y_2O_3, the higher bending strength, Vickers hardness and fracture toughness correspond to a certain La_2O_3/Y_2O_3 molar ratio of 1·5, 1·0 and 0·5, respectively. SEM observation shows that the SiC matrix composite with fine grain size and homogeneous microstructure can be obtained.

1 INTRODUCTION

Silicon carbide (SiC) and silicon nitride (Si_3N_4) are important structural materials for high temperature applications because of their excellent mechanical properties.[1–3] Incorporating a second phase to the matrix is a very attractive design concept to improve the mechanical properties of the composite.[4,5] However, due to the high degree of covalent bonding and low self diffusivity of SiC and Si_3N_4, densification of the monolithic ceramics and their composite is difficult. Many works have been done to achieve fully densified samples through the addition of metal oxide as sintering aid.[6–10] The additives are effective to promote densification controlled by the mechanism of liquid phase sintering at elevated temperature. But the problems for this process are that the liquid phase can exist in grain boundaries so that it can deteriorate the high temperature properties. To strengthen the grain boundary structure of SiC, Si_3N_4 and their composites, many efforts have been devoted to decreasing the amount of sintering aids or using rare earth oxide additives.[11,12] Meanwhile, hot isostatic pressing is also an effective sintering technique for preparing fully densified ceramics by using less or no sintering additives.[13,14]

In this study, the mechanical properties of HIPed SiC–25 vol% Si_3N_4 composite containing La_2O_3 and Y_2O_3 additives have been determined. The effects of rare earth oxide additions on densification process and microstructure development, and the relationship between microstructural features and mechanical properties are discussed.

2 EXPERIMENTAL PROCEDURE

The starting materials used in this experiment were α-SiC (FCP-15), α-Si_3N_4 (UBE-SN10), La_2O_3 (99·95% pure) and Y_2O_3 (99·95% pure). The average particle sizes of SiC and Si_3N_4 were 0·6 and 0·7 μm, respectively. The SiC–25 vol% Si_3N_4 powders and the additives were mixed with ethanol in a polyethylene ball mill for 24 h. The additions of La_2O_3 and Y_2O_3 were 3 and 6 wt%, and the La_2O_3/Y_2O_3 molar ratio was changed from 0·5 to 2·0. The powder mixture was uniaxially pressed and cold isostatically pressed. Powder compacts were subsequently dewaxed, glass encapsulated, and then HIPed at 1850°C under 200 MPa pressure. The HIPed samples were machined into

4 mm*3 mm*36 mm bars for measuring three point bending strength carried out in 1195 Instron testing machine. The span length and the cross head speed were 30 mm and 0·5 mm/min, respectively. Bulk density of the sintered specimens was measured by the Archimedes method. Hardness and fracture toughness were estimated through Vickers indentation experiments in a Akashi (AVK-A) test machine. During the experiment, the indentation load was 10 kg (98N), and the loading time, 15 s.

X-ray diffraction was used to determine the phase composition after HIPing. Microstructures were observed by scanning electron microscopy (SEM) on fracture surfaces of the bending test specimens.

3 RESULTS AND DISCUSSION

3.1 Microstructures

Figure 1 (A) to (D) shows the X-ray diffraction for SiC–25 vol% Si_3N_4 composite containing 3 wt% Y_2O_3 and La_2O_3 as sintering additives. As the

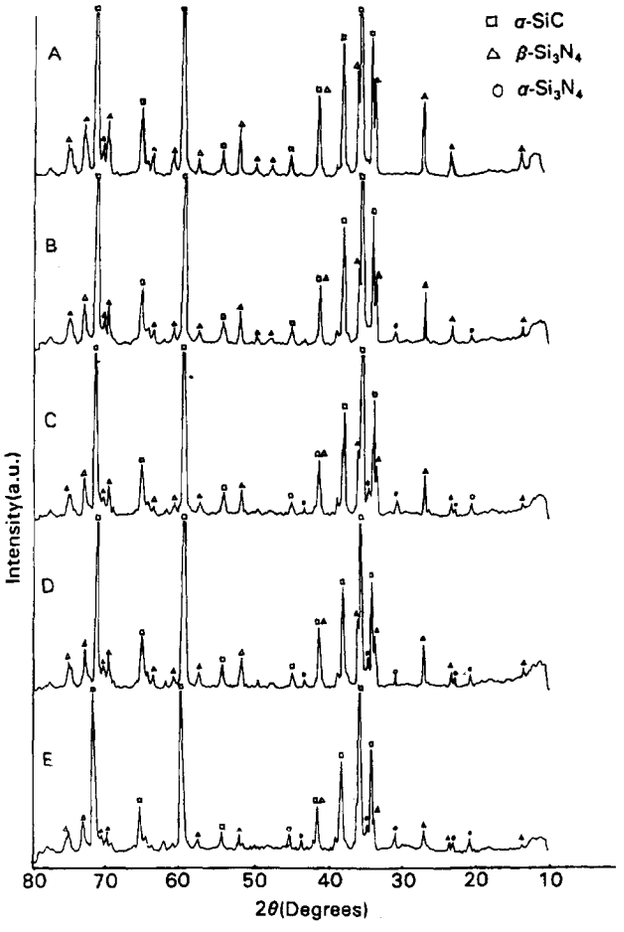

Fig. 1. X-ray diffraction patterns of SiC–25 vol% Si_3N_4 with (A) La_2O_3/Y_2O_3 = 0·5, La_2O_3 + Y_2O_3 = 3 wt%, (B) La_2O_3/Y_2O_3 = 1·0, La_2O_3 + Y_2O_3 = 3 wt%, (C) La_2O_3/Y_2O_3 = 1·5, La_2O_3 + Y_2O_3 = 3 wt%, (D) La_2O_3/Y_2O_3 = 2·0, La_2O_3 + Y_2O_3 = 3 wt%, (E) La_2O_3/Y_2O_3 = 1·5, La_2O_3 + Y_2O_3 = 6 wt%.

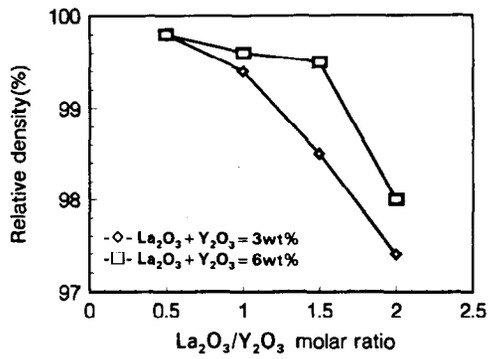

Fig. 2. Relative density as a function of La_2O_3/Y_2O_3 molar ratio.

La_2O_3/Y_2O_3 molar ratio changed from 0·5 to 2·0, the α-Si_3N_4 appeared in the sintered samples, and X-ray intensity of β-Si_3N_4 decreased while that of α-Si_3N_4 increased. Addition of 3 and 6 wt% La_2O_3 + Y_2O_3 at La_2O_3/Y_2O_3 = 1·5 exhibits the same trend of variation, as shown in Fig. 1(C) and (E). These changes indicate that the transformation of α-Si_3N_4 to β-Si_3N_4 was inhibited by increasing La_2O_3 addition. Figure 2 shows the relationship between relative density and La_2O_3/Y_2O_3 molar ratio. When the amount of Y_2O_3 addition is larger, the relative density is higher. Meanwhile, 6 wt% La_2O_3 + Y_2O_3 additions give the higher density of the sintered samples. These results suggest that Y_2O_3 is effective to promote the densification of the composite.

Figure 3 gives the SEM micrographs of fracture surface of the composite with 3 wt% La_2O_3 + Y_2O_3 additions. It is clearly shown that the fine grain size and homogeneous microstructure can be obtained in the present experimental conditions. For 3 wt% La_2O_3 + Y_2O_3 additions, higher Y_2O_3 content such as La_2O_3/Y_2O_3 = 0·5 exhibit the dense compact structure, while the lower Y_2O_3 content such as La_2O_3/Y_2O_3 = 2·0 gives the loose microstructure. This is consistent with the above mentioned results. The fracture patterns obviously show that the fracture path is along the grain boundaries.

3.2 Mechanical properties

Bending strength as a function of La_2O_3/Y_2O_3 molar ratio is shown in Fig. 4. Addition of 3 wt% La_2O_3 + Y_2O_3, maximum bending strength of 810 MPa was reached at the La_2O_3/Y_2O_3 = 0·5. When La_2O_3/Y_2O_3 increased, the bending strength decreased to a lower value of 580 MPa at La_2O_3/Y_2O_3 = 2·0. While adding 6 wt% La_2O_3 + Y_2O_3, no obvious variation of bending strength occurred as the La_2O_3/Y_2O_3 molar ratio changed. Maximum bending strength of 660 MPa was

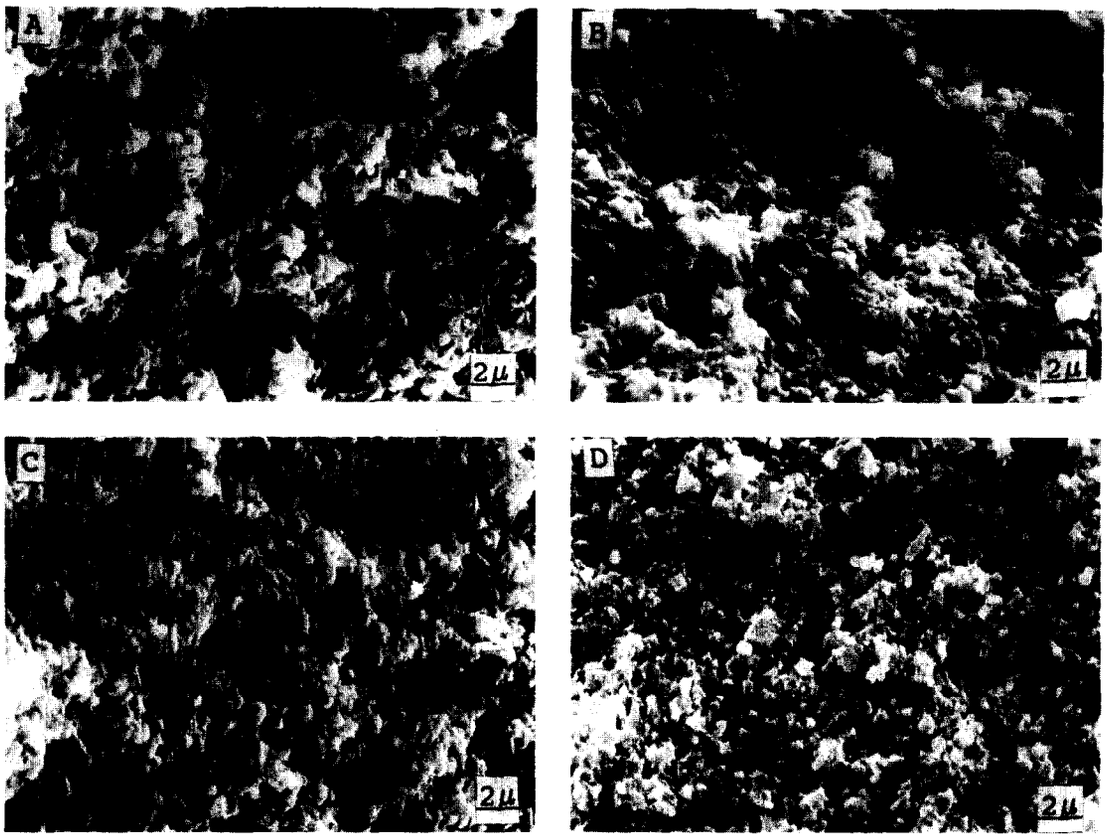

Fig. 3. SEM micrographs showing fracture surface of the composite with 3 wt% $La_2O_3 + Y_2O_3$ additions, (A) $La_2O_3/Y_2O_3 = 0{\cdot}5$, (B) $La_2O_3/Y_2O_3 = 1{\cdot}0$, (C) $La_2O_3/Y_2O_3 = 1{\cdot}5$, (D) $La_2O_3/Y_2O_3 = 2{\cdot}0$.

obtained at $La_2O_3/Y_2O_3 = 1{\cdot}5$. As mentioned in the previous section, the fracture path was along the boundary of fine grains, so that the strength was mainly affected by the bonding strength of the grain boundary phase. When $La_2O_3 + Y_2O_3$ additions were 3 and 6 wt%, the lower densities at $La_2O_3/Y_2O_3 = 2{\cdot}0$ correspond to the weak bonding of grains. At $La_2O_3/Y_2O_3 = 0{\cdot}5$, the higher densities imply that the fine grains bonding together closely, and at this time, the small amount of addition of sintering aids such as $La_2O_3 + Y_2O_3 = 3$ wt% may produce less amorphous phase to strengthen the grain boundaries. Compared with the above case, for 6 wt% of La_2O_3/Y_2O_3 additions, relatively larger amount of amorphous phase may occur at grain boundaries to weaken the bonding strength of grains. In this case, as La_2O_3/Y_2O_3 increased, much La_2O_3 was melted into grain boundaries to form a high viscosity amorphous phase which may strengthen the grains bonding. At $La_2O_3/Y_2O_3 = 1{\cdot}5$, it reaches the highest bending strength value of 660 MPa. When La_2O_3/Y_2O_3 increased to 2, density as mentioned before may become the dominant factor to affect the bending strength.

Figures 5 and 6 show the hardness and indentation fracture toughness of the composite as a function of La_2O_3/Y_2O_3 molar ratio, respectively.

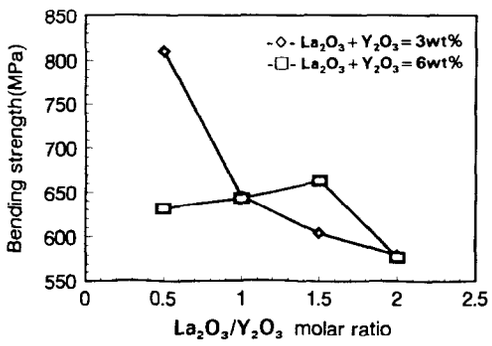

Fig. 4. Bending strength as a function of La_2O_3/Y_2O_3 molar ratio.

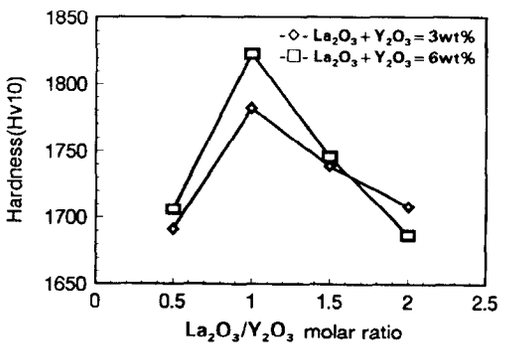

Fig. 5. Vickers hardness as a function of La_2O_3/Y_2O_3 molar ratio.

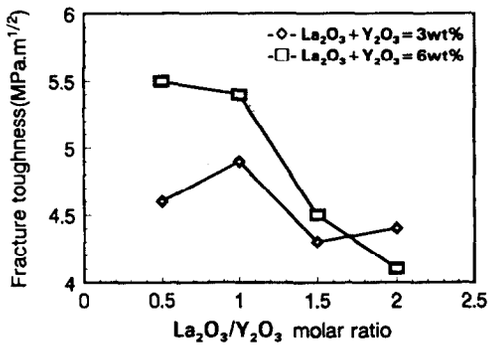

Fig. 6. Fracture toughness as a function of La_2O_3/Y_2O_3 molar ratio.

Grain boundary phase and density are also the dominant factors to affect these two mechanical properties. Ueno and Toibana[11] have shown in their experiment that higher La_2O_3/Y_2O_3 molar ratios exhibit the greater microVickers hardness of hot pressed Si_3N_4 when the apparent relative density of samples is higher. In Fig. 5, at La_2O_3/Y_2O_3 = 2·0, the relatively lower hardness may be caused by the lower density. When La_2O_3/Y_2O_3 = 1·0, and addition of 3 and 6 wt% La_2O_3 + Y_2O_3 occurs, both of the maximum values of hardness were obtained. This is probably due to the crystallization of the compound containing La_2O_3, Y_2O_3 and Si_3N_4.[15,16] But in this experiment, XRD analysis didn't reveal the above mentioned fact partly because of the small amount of La_2O_3 and Y_2O_3 additions.

Indentation fracture toughness was improved by increasing the amount of additions from 3 to 6 wt% at $La_2O_3/Y_2O_3 \leq 1{\cdot}0$. The reason for this might be that the liquid phase containing more Y_2O_3 in grain boundaries led to the weak bonding of grains as mentioned before so that it can produce a higher energy dissipation path. The work of Xu[17] also found a similar result to this, but the toughening mechanism is still not clear. Many complicated factors like the wettability and compatibility of the grain boundary phase containing La_2O_3, Y_2O_3 and Si_3N_4 with the SiC matrix may play an important role in improving the mechanical properties. Further experimental research is still in progress.

4 CONCLUSIONS

(1) Fine grain size and homogeneous microstructure of SiC–25 vol% Si_3N_4 composite with La_2O_3 and Y_2O_3 additions were obtained by glass encapsulated hot isostatic pressing at 1850°C and 200 MPa pressure. Fracture pattern of this composite was typically along the grain boundary.

(2) The density of the composite was increased by decreasing the La_2O_3/Y_2O_3 molar ratio, that is, Y_2O_3 was effective to promote the densification of the composite.

(3) Bending strength reached the maximum value of 810 MPa at La_2O_3 + Y_2O_3 = 3 wt% and La_2O_3/Y_2O_3 = 0·5. The improvement of strength was due to the strengthening of grain boundaries by relatively lower amorphous phase existing in grain boundaries.

(4) Maximum values of hardness (*Hv* 10 1820) and fracture toughness (K_1c 5·5 MPa.m$^{1/2}$) were obtained at La_2O_3/Y_2O_3 = 1·0 and 0·5 with La_2O_3 + Y_2O_3 = 6 wt%, respectively. Composition and the bonding strength of the grain boundary phase may dominate these two mechanical properties. Further explanation still left the scientific challenge for future experimental work.

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