General paper

PROCESSING AND MECHANICAL PROPERTIES OF $\text{Si}_3\text{N}_4/\text{SiC}$ NANOCOMPOSITES USING Si NITRIDED Si_3N_4 POWDER

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Abstract: The pressureless sintering was investigated to fabricate dense $\text{Si}_3\text{N}_4/\text{SiC}$ nanocomposites from commercially available Si nitrided Si_3N_4 powder. $\text{MgAl}_2\text{O}_4 + \text{ZrO}_2$ (totally 10 and 15 wt%) or $\text{Y}_2\text{O}_3 + \text{Al}_2\text{O}_3$ (totally 10.5 and 14 wt%) and 5–30 vol% SiC were used as sintering additives and second phase dispersions, respectively. With increasing SiC content, the density of the composite containing less amount of sintering additives decreased linearly, while the large amount of sintering additives decreased gradually the density or kept it constant. The composites with higher SiC content presented a relatively smaller Si_3N_4 grain size, because the Si_3N_4 grain growth was inhibited by SiC particles that pinned the grain boundary movement. While decrease in strength was observed for the composites with less amount of sintering additives, an improvement of the strength was found for the composites with high amount of sintering additives. The strength change of the composites was consistent with their densification behavior and microstructural observation. Composite with 20 vol% SiC exhibited high strength up to 1 GPa. With increasing SiC content, hardness increased but toughness decreased. It is concluded that the results of this study provide an economic way to fabricate the $\text{Si}_3\text{N}_4/\text{SiC}$ nanocomposite with high performance.

Key words: *Silicon nitride, Silicon carbide, Nanocomposite, Densification, Mechanical properties*

1. INTRODUCTION

The dispersion of nano-sized SiC particles into Si_3N_4 can lead to a significant improvement of mechanical properties [1, 2]. For the fabrication of this material, many kinds of starting powder were used such as mixtures of high purity fine Si_3N_4 and nano-sized SiC powder [3, 4], mixed powders fabricated by vapor phase pyrolytic reaction [5] or fine amorphous Si-C-N powders fabricated by polymer pyrolysis [6]. Strength of 1200 to 1500 MPa was reached using these kinds of powders. However, the above-mentioned powders are relatively expensive and require a hot-pressing (1800–1850°C) process to obtain dense composites. For the industrial application of this kind of material, relatively lower cost starting powder and fabrication process are preferable if the high mechanical properties can be achieved. Among the commercially available powders, $\alpha\text{-Si}_3\text{N}_4$ powder prepared by nitridation of Si is much cheaper than that by imide ($\text{Si}(\text{NH})_2$) decomposition. On the fabricating process of Si_3N_4 ceramics, the pressureless sintering is the simplest and industrially most applicable.

Kenney *et al.* [7] studied the fabrication processes of $\text{Si}_3\text{N}_4/\text{SiC}$ nanocomposite from a commercially available low cost Si_3N_4 powder, but showed no improvement of strength by the addition of SiC, which is explained by a decrease in density. Akimune *et al.* [8] also studied the $\text{Si}_3\text{N}_4/\text{SiC}$ composite from the silicon nitrided powder. In pressureless sintering, the flexural strength was decreased for the composite with 10 vol% SiC addition. The results from these studies can not be comparable with that from the powder by imide decomposition, which is expensive due to the high purity. Further improvement of strength is needed.

In the present study, $\text{Si}_3\text{N}_4/\text{SiC}$ nanocomposite was fabricated by pressureless sintering a kind of commercially available Si nitrided Si_3N_4 powder with relatively low purity and cost using $\text{MgAl}_2\text{O}_4 + \text{ZrO}_2$ and $\text{Y}_2\text{O}_3 + \text{Al}_2\text{O}_3$ as the sintering additive. Low sintering temperatures (1700–1750°C) were used to simplify the sintering process. Their density, microstructure and mechanical properties were evaluated. The influence of nano-sized SiC particles on the microstructure and then mechanical properties of the composites were investigated.

2. EXPERIMENTAL PROCEDURES

Commercially available $\alpha\text{-Si}_3\text{N}_4$ powder (SN-9S, Electrical & Chemical Industries, Tokyo, Japan) fabricated by Si nitridation was used as the matrix phase, and $\beta\text{-SiC}$ powder (Ibiden Co. Ltd., Ogaki, Japan, Particle size: 80 nm) was used as reinforcement phase. Two kinds of oxides such as $\text{MgAl}_2\text{O}_4 + \text{ZrO}_2$ and $\text{Y}_2\text{O}_3 + \text{Al}_2\text{O}_3$ were used as the sintering additive. Different amounts of the sintering additives were used such as: (a) 5 wt% $\text{MgAl}_2\text{O}_4 + 5$ wt% ZrO_2 , (totally 10 wt%) (b) 7.5 wt% $\text{MgAl}_2\text{O}_4 + 7.5$ wt% ZrO_2 , (totally 15 wt%) (c) 7.5 wt% $\text{Y}_2\text{O}_3 + 3$ wt% Al_2O_3 , (totally 10.5 wt%) (d) 10 wt% $\text{Y}_2\text{O}_3 + 4$ wt% Al_2O_3 (totally 14 wt%). The $\alpha\text{-Si}_3\text{N}_4$ powder was mixed together with appropriate amounts (0–30 vol%) of $\beta\text{-SiC}$ and sintering additive powders in a plastic bottle to make a homogeneous powder mixture. The mixture was wet-milled in ethanol for 24 h using high purity Si_3N_4 grinding media. The powder slurry was dried in air, followed by dry milling for 4 h. The dried powder mixture was sieved to a particle size smaller than 500 μm . The resultant powder mixture was uniaxially pressed at 30 MPa before being cold isostatically pressed at 200

MPa. The green compacts were placed in a Si_3N_4 crucible and sintered in a graphite resistance furnace at 1700°C and 1750°C for 4 - 8 h at a nitrogen pressure of 0.6 MPa.

Density measurements were carried out in high purity toluene by Archimedes' method. The specimens were machined to make test bars with a size of 40×4×3 mm (JIS R1601) to measure the flexural strength. The tensile surface was ground and polished to a surface finish of 0.3 μm and the transverse surfaces were ground on an 800 grit diamond wheel. The tensile edges were beveled to reduce the effect of edge cracks. The specimens were loaded to failure in a three-point bend mode (span of 30 mm) on a mechanical testing machine (Autograph AG-10TC, Shimadzu, Kyoto, Japan) at a cross-head speed of 0.5 mm/min. The strength was evaluated from the fracture load recorded. Indentations were made with a Vickers diamond pyramid on the polished surface with a peak load of 196 N by Vickers indenter (AVK-C2, Akashi Co. Ltd., Japan). Hardness was calculated from the indentation

diagonal and contact load. Fracture toughness was calculated from measurement of the crack length by using the equation given by Niihara [9].

Microstructure and fracture surfaces of the composites were evaluated by scanning electron microscopy (SEM, Model S-5000, Hitachi, Japan). Transmission electron microscopy (TEM) specimens were prepared by mechanical-thinning and ion-milling techniques. High-resolution TEM (Model H-8100T, Hitachi, Japan) was used to study the microstructure and characteristics of crystalline grains and the Si_3N_4 - Si_3N_4 and Si_3N_4 -SiC interface.

3. RESULTS AND DISCUSSION

3.1 Densification

Figure 1 shows the relative density (percentage of theoretical density, th.d.%) achieved by different sintering conditions as a function of SiC content for $\text{Si}_3\text{N}_4/\text{SiC}$ composites containing different amount of sintering addi-

Fig. 1 Relative density versus content of SiC for $\text{Si}_3\text{N}_4/\text{SiC}$ composites with sintering additives: (a) 5 wt% MgAl_2O_4 + 5 wt% ZrO_2 , (b) 7.5 wt% MgAl_2O_4 + 7.5 wt% ZrO_2 , (c) 7.5 wt% Y_2O_3 + 3 wt% Al_2O_3 , (d) 10 wt% Y_2O_3 + 4 wt% Al_2O_3 .

tives as depicted in the experimental procedures. Figure 1 (a) and (b) shows that the relative density of the composite decreased with the SiC particle contents for two different amounts of $\text{MgAl}_2\text{O}_4 + \text{ZrO}_2$ (10 and 15 wt%). The relative density of the composite with 15 wt% of sintering additives (Fig. 1 (b)) is higher than that with 10 wt% (Fig. 1 (a)). High sintering temperature and long time induced high relative density. For the composites containing 10 wt% of sintering additives, the density decreased linearly with the SiC content. Similarly, for the composites containing 15 wt% of sintering additives, the density decreased gradually with the SiC content. Under the condition of $1750^\circ\text{C}/8\text{h}$, the composite with 20 vol% SiC keeps a density as high as 96.5% which is a little lower than that with no SiC addition.

In the case of $\text{Y}_2\text{O}_3 + \text{Al}_2\text{O}_3$ additives, the densities decreased linearly with the SiC addition for 10.5 wt% additives (Fig. 1 (c)), while the densities did not change with the SiC addition for the 14 wt% additives (Fig. 1 (d)). Large amount of sintering additives promotes the

densification process especially for the sintering conditions of low temperatures as 1750°C in this study.

The change of density with the SiC and sintering additive content can be explained as a reciprocal effect by SiC particles and sintering additives that the SiC particles constrain the densification of composites while the sintering additives promote it. The decreased densification by the SiC addition can be caused by the fact that the grain boundary movement was obstructed by the SiC particles with pinning effect. On the other hand, the increased densification by the sintering additives can be explained by the fact that the glass phase among the grains can enhance the boundary diffusion and volume diffusion. For the pressureless sintering of nanocomposites at low temperature, a relatively high content of sintering additives was preferable to achieve high density.

3.2 Microstructure

SEM observations were made to investigate the distribution of SiC particles and the effect of SiC ad-

Fig. 2 SEM fracture surface of $\text{Si}_3\text{N}_4/\text{SiC}$ composites containing 7.5 wt% $\text{MgAl}_2\text{O}_4 + 7.5$ wt% ZrO_2 as the sintering additives. The samples were sintered at $1750^\circ\text{C}/8\text{h}$. The grain size of $\beta\text{-Si}_3\text{N}_4$ decreases with SiC content. (a) Monolithic Si_3N_4 ; (b) Si_3N_4 -20 vol% SiC.

Fig. 3 TEM micrograph of $\text{Si}_3\text{N}_4/\text{SiC}$ composite containing 7.5 wt% $\text{MgAl}_2\text{O}_4 + 7.5$ wt% ZrO_2 as the sintering additives. Sintering condition: $1750^\circ\text{C}/8\text{h}$. (a) SiC particle dispersion in Si_3N_4 matrix; (b) Si_3N_4 -SiC interface.

Fig. 4 Flexural strength versus SiC content for $\text{Si}_3\text{N}_4/\text{SiC}$ composites with additives: (a) 5 wt% MgAl_2O_4 + 5 wt% ZrO_2 , (b) 7.5 wt% MgAl_2O_4 + 7.5 wt% ZrO_2 , (c) 7.5 wt% Y_2O_3 + 3 wt% Al_2O_3 , (d) 10 wt% Y_2O_3 + 4 wt% Al_2O_3 .

ditions on the Si_3N_4 matrix grain morphology. Figure 2 (a) and (b) show SEM micrographs of fracture surfaces of the monolithic Si_3N_4 and composites containing 20 vol% SiC particles, respectively. From this figure, it can be seen that the addition of SiC gave a great influence on the grain morphology of matrix. Large addition of SiC resulted in a refinement of Si_3N_4 matrix. It is believed that SiC particles limited the Si_3N_4 grain growth by pinning and prohibiting the grain boundary movement [10, 11]. In addition, it was observed that amount of porosity increased with increasing SiC content, which further restricted the grain boundary migration [12].

Figure 3 shows TEM micrograph of $\text{Si}_3\text{N}_4/\text{SiC}$ composite containing 7.5 wt% MgAl_2O_4 + 7.5 wt% ZrO_2 sintered at $1750^\circ\text{C}/8\text{h}$. From Fig. 3(a), it was shown that the SiC particles were uniformly distributed in the matrix and located inside or between the Si_3N_4 grains. Figure 3 (b) shows the $\text{Si}_3\text{N}_4/\text{SiC}$ interface and indicated that the interface did not contain amorphous

phase and the SiC crystal was in direct contact with Si_3N_4 crystal.

3.3 Mechanical Properties

Figure 4 shows the flexural strength of $\text{Si}_3\text{N}_4/\text{SiC}$ composites as a function of SiC volume fraction processed by various sintering conditions. In the case of MgAl_2O_4 + ZrO_2 additives, the strength of the monolithic Si_3N_4 with 10 wt% sintering additives (Fig. 4 (a)) is higher than that with 15 wt% (Fig. 4 (b)). Corresponding to the change of the relative density, the high sintering temperature and long sintering time resulted in a relatively higher flexural strength. For the composites containing 10 wt% sintering additives (Fig. 4 (a)), the strength did not change very much with increasing SiC additions for SiC contents less than 10 vol%. For that containing 15 wt% sintering additives (Fig. 4 (b)), the strength increased with increasing SiC additions for SiC contents less than 20 vol% ($1750^\circ\text{C}/8\text{h}$,

1750°C/4h) or less than 10 vol% (1700°C/8h). Further increase in SiC content resulted in a monotonic decrease in strength for the two kinds of sintering additive contents.

In the case of $Y_2O_3 + Al_2O_3$ additives, the strength decreased monotonically with the SiC contents for the 10.5 wt% of additives (Fig. 4 (c)), while the strength increased with the SiC content for the 14 wt% sintering additives (Fig. 4 (d)) that no decrease can be seen even for the 30 vol% SiC addition. From Fig. 4 (d), it can be seen that the sintering times (4 h and 8 h) have almost no influences on the strength of composites.

The change of the strength of the composites is consistent with the densification behavior (Fig. 1) and microstructural observation (Fig. 2). It is well known that the mechanical properties are closely related with the relative density [13], grain size [11], and properties of glass phase [14]. Since low amount of sintering additives is beneficial to the strength, the strength of monolithic Si_3N_4 with 10 wt% additives is higher than that with 15 wt% additives. As the density decreased with increasing SiC content for the composites with 10 wt% additives, the strength did not increase with SiC content. On the other hand, as the density of the composites with 15 wt% additives decreased gradually with the SiC content, the improvement of strength can be observed. The increase of strength is due to the refinement of matrix. The decrease in strength for the composite with high SiC content is mainly resulted from the low density. As shown in Fig. 4 (b), on the sintering condition of 1750°C/8h, even though the density of the Si_3N_4 /20vol%SiC was a little lower than that of the monolithic Si_3N_4 , a high strength over 1 GPa was reached.

In the case of $Y_2O_3 + Al_2O_3$ additives, the decreased strength with SiC addition is a result of the decreased density for 10.5 wt% additives (Fig. 4 (c)), and the increased strength in Fig. 4 (d) is also considered as a result of refinement of Si_3N_4 matrix and no decrease in density. However, although the strength increased with the SiC contents, the strength is not higher than that of the composites using $MgAl_2O_4 + ZrO_2$ as the sintering additives. The strength over 1 GPa was not obtained. The difference in the strength for the composites with different kinds of sintering additives is thought to come from the difference in the properties of grain boundary phase.

The changes of hardness and fracture toughness with the SiC additions are shown in Fig. 5 for the composites with 7.5 wt% $MgAl_2O_4 + 7.5$ wt% ZrO_2 of the sintering additives. The tendencies of the hardness and fracture toughness were contradictory, as the SiC dispersions improve the hardness but decrease the fracture toughness. Further increase in SiC content (>10 vol%) also resulted in a decrease in the hardness because of the decreasing density. With increasing the sintering temperature, the fracture toughness is improved. This means that the fracture toughness is related with the grain morphology of Si_3N_4 . The decreasing in toughness with the increasing SiC content can be explained by the refinement of Si_3N_4 matrix.

Fig. 5 Hardness and fracture toughness versus content of SiC for Si_3N_4 /SiC composites with 7.5 wt% $MgAl_2O_4 + 7.5$ wt% ZrO_2 as the sintering additives sintered at 1750°C/8h and 1700°C/8h.

4. CONCLUSION

In the present work, the Si_3N_4 /SiC nanocomposite with high performance was successfully fabricated by pressureless sintering the low cost Si nitrided Si_3N_4 powder. The main results obtained in the present work are as follows:

(1) The higher density of the composites was obtained by adding larger amount of sintering additives. The relative density decreased with increasing SiC content, but it is improved by higher sintering temperature or longer sintering period.

(2) The addition of SiC gave a great influence on the grain morphology of the matrix. Large addition of SiC resulted in a refinement of the Si_3N_4 matrix. SiC particles were uniformly dispersed into the Si_3N_4 matrix and directly bonded with the Si_3N_4 .

(3) The mechanical properties of the composites were directly related with the relative density and the microstructure. There is no increase in strength with SiC addition for the composites with lower amount of additives as 10 wt% ($MgAl_2O_4 + ZrO_2$) and 10.5 wt% ($Y_2O_3 + Al_2O_3$), which is caused by the low density. An enhancement of strength by the SiC addition can be seen for the composites with 15 wt% ($MgAl_2O_4 + ZrO_2$) sintering additives, although a slight decrease of density existed. Strength reached above 1 GPa by 20 vol% SiC addition, which resulted from the refinement of Si_3N_4 grain morphology. As a constant density was achieved for the composites with 14 wt% ($Y_2O_3 + Al_2O_3$) additives, a linear enhancement of strength by the SiC addition can be seen, but no high strength (higher than 1 GPa) was obtained.

(4) With increasing SiC content, the hardness increased, but the toughness decreased. High sintering temperature can simultaneously improve the hardness and toughness as a result of high density and Si_3N_4 grain growth.

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