Microstructures and Mechanical Properties of Si_3N_4 -SiC Composites Prepared by Combustion Synthesis and HIP Sintering

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The microstructures and mechanical properties of Si_3N_4 -SiC composites containing 8 to 46 vol% SiC, which were prepared from combustion synthesis and HIP sintering without additives, were studied and compared with those of Si_3N_4 prepared from conventional methods. Transmission electron microscopic observation revealed the existence of some small SiC particles within the Si_3N_4 matrix grains. The fracture toughness of the Si_3N_4 -SiC composite was independent of SiC content, probably because the SiC grains were smaller than the critical size for effective toughening and the formation of elongated Si_3N_4 grains was not promoted by the SiC dispersions. But SiC additions modified the high-temperature strength of the Si_3N_4 -SiC composites and increased the microhardness at all temperatures.

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I. Introduction

Reinforcement of Si_3N_4 by SiC began nearly two decades ago when Lange¹⁾ hot-pressed mixtures of Si_3N_4 and SiC powders. Since then, SiC second phase of different sizes and morphologies have been introduced to strengthen Si_3N_4 matrix by different methods^{1,2,3)}. Recently, we successfully produced Si_3N_4 -SiC composite powders by combustion synthesis and conducted a preliminary survey on the sintering behaviors and mechanical properties⁴⁾. In this investigation, we examined the microstructures of the Si_3N_4 -SiC composites and their influence on the mechanical properties, and compare them with conventional ones.

II. Material and Experimental

The Si_3N_4 -SiC composite powders, containing a wide range of compositions from 8 to 46 vol% SiC (which corresponds to $3\text{Si}_3\text{N}_4 + \text{SiC}$ and $\text{Si}_3\text{N}_4 + 3\text{SiC}$ in nominal composition), were synthesized by a simultaneous reaction of metal Si powders

with N_2 and C in 10 MPa N_2 gas by simply changing the Si/C ratios in the reactant mixtures. The heat released from Si nitridation promoted the formation of SiC. A detailed description of the formation mechanism is presented elsewhere⁵⁾. The synthesized Si_3N_4 -SiC powders were composed mainly of α - Si_3N_4 , β - Si_3N_4 and β -SiC, and free from unreacted Si or C. As shown in Photo 1, the powders after pulverization using ball-milling with Si_3N_4 balls consisted of fine grains. The average particle sizes and specific surface areas of these powders were in the range of 0.6 to $0.8\mu\text{m}$ and 5 to $8\text{m}^2/\text{g}$, respectively.

The Si_3N_4 -SiC powders were HIP sintered without additives to study the intrinsic property of these powders using the glass encapsulation method. The sintering condition was 1950°C for 1h at 170MPa Ar gas pressure. Fracture toughness was measured by IM method⁶⁾ with a 5kg x 10s loading condition at room temperature. Microstructures of the sintered bodies were observed using both transmission electron microscopy

(TEM) and scanning electron microscopy (SEM).

III. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the Si_3N_4 -SiC composites after sintering. The composites were mainly composed of β - Si_3N_4 and β -SiC. As shown in the XRD chart, the amount of SiC increased with the SiC content indicated in nominal composition. A small amount of $\text{Si}_2\text{N}_2\text{O}$ phase, apparently due to oxygen impurity existing in the Si powder, appeared after sintering. The relative densities of the Si_3N_4 -SiC composites decreased with SiC content, but reached over 99.5% for all the compositions when the influence of $\text{Si}_2\text{N}_2\text{O}$ was taken into consideration, as shown in Fig.2.

The composites consisted of fine grains smaller than $1\mu\text{m}$ with low aspect ratio. The microstructure of $\text{Si}_3\text{N}_4+3\text{SiC}$ composite is shown in Photo 2. Similar to the Si_3N_4 -SiC nanocomposites prepared from amorphous Si-C-N precursor powder⁷⁾, some small SiC grains were included in the Si_3N_4 matrix grains, while the larger ones remained at the grain boundaries. Photo 3 shows some SiC inclusions in a Si_3N_4 grain at higher magnification.

Figure 2 shows the dependence of fracture toughness on SiC content. The fracture toughness values of two HIP sintered monolithic Si_3N_4 ceramics, which were prepared from combustion synthesized powder⁸⁾ and from commercial Si_3N_4 powder⁹⁾, are also plotted for comparison. The fracture toughness of a monolithic Si_3N_4 from commercial Si_3N_4 powder HIP sintered by the same condition but with Y_2O_3 and Al_2O_3 as sintering aids, is also indicated. The fracture toughness of Si_3N_4 prepared from combustion was $4\text{MPa}\cdot\text{m}^{1/2}$. This value is $\sim 30\%$ higher than the fracture toughness of Si_3N_4 sintered without additives using commercial Si_3N_4 powders⁹⁾. For

Photo 1 Scanning electron micrographs of pulverized Si_3N_4 -SiC powders.

Fig.1 X-ray diffraction patterns of Si_3N_4 -SiC composites.

Photo 2 Transmission electron micrograph of $\text{Si}_3\text{N}_4+3\text{SiC}$ composite.

the commercial Si_3N_4 powders, the fracture mode was entirely transgranular, whereas intergranular fracture is dominant in the Si_3N_4 prepared from combustion synthesis. The difference in fracture toughness seems to reflect the different fracture modes.

The propagation of a crack introduced by Vickers indentation on the $\text{Si}_3\text{N}_4\text{-SiC}$ ceramic is shown in Photo 4. The crack propagated along grain boundaries not only between Si_3N_4 grains, but also between Si_3N_4 and SiC grains. Although the intergranular fracture provides the primary condition for many toughening mechanisms to come into effect, the fracture toughness in the present systems was almost independent of SiC content. Lange¹⁾ reported that among SiC dispersions of 5, 9, and 32 μm , only the largest one affected to increase the fracture toughness of a MgO-fluxed Si_3N_4 . Similar to this result, Greskovich and Palm¹⁰⁾ used very fine SiC particle of 0.25 μm to streng-

Photo 3 Transmission electron micrograph of $\text{Si}_3\text{N}_4+3\text{SiC}$ composite.

Photo 4 Transmission electron micrograph of crack propagation path for $\text{Si}_3\text{N}_4+3\text{SiC}$ composite.

Fig. 2 Variation of fracture toughness with SiC content.

then Si_3N_4 but found almost no improvement. On the other hand, Niihara et al.⁷⁾ fabricated Si_3N_4 -SiC nanocomposites by hot-pressing the mixtures of amorphous Si-C-N precursor powder with various C/N ratios and sintering additives. They observed a remarkable increase of fracture toughness with a maximum value of $6.7\text{MPa}\cdot\text{m}^{1/2}$ at 25 vol% SiC and attributed this increase to the formation of uniformly elongated Si_3N_4 grains where the nano-size SiC particles act as nuclei for the solution-diffusion-precipitation process. The above results show that SiC particles of large size and/or an adequate sintering aid is necessary for improving the fracture toughness of Si_3N_4 ceramics. On the base of the above argument, and SEM and TEM observations, the independence of fracture toughness on SiC content revealed in the present systems is explained as follows: (1) the SiC grains, being smaller than $1\mu\text{m}$ as seen from Photo 1, were smaller than the effective particle size to enhance fracture toughness effectively, and (2) a proper sintering aid was absent to promote formation of elongated Si_3N_4 grains. This hypothesis is also supported by the result that the fracture toughness of the Si_3N_4 prepared from conventional method and the same HIPing condition but with 6wt% Y_2O_3 +2wt% Al_2O_3 as additive exhibits a very high fracture toughness of $7\text{MPa}\cdot\text{m}^{1/2}$.

The temperature dependence of fracture strength (conducted by 4 point-bending with the cross-head-speed of 0.5mm/min) for different compositions is shown in Fig.3. The results of monolithic Si_3N_4 ⁸⁾ from combustion synthesis and high-purity Si_3N_4 with 5wt% SiO_2 addition¹¹⁾ were also plotted for comparison. It is noticed that degradation of strength is apparent at above 1200°C for the ceramics prepared from combustion synthesis. Since the conventional high-purity Si_3N_4 with 5wt% SiO_2 exhib-

Fig.3 Temperature dependence of fracture strength.

Fig.4 Temperature dependence of Vickers hardness.

ited no degradation at corresponding temperatures, the degradation can only be attributed to the difference in the composition of the intergranular glass phase. However, the degradation of strength at 1400°C was somehow reduced with SiC at high SiC contents, similar to previous studies^{1,7)}. These results indicate that the strength degradation at high temperatures is most strongly controlled by the composition of the intergranular glass phase, and can be modified by the SiC dispersions. The temperature dependence of Vickers microhardness of the Si_3N_4 -SiC composites is shown in Fig.4. The microhardness was also improved by SiC dispersions at room temperature and elevated temperatures.

IV. Conclusions

Si_3N_4 -SiC composites containing 8 to 46vol% SiC, which were prepared by combustion synthesis and densified by HIP without additives, were examined in terms of microstructure and mechanical properties. The following results were obtained:

- (1) Large SiC particles remained at the grain boundaries, while some finer ones were confined within the matrix Si_3N_4 grains.
- (2) Fracture toughness was not improved by SiC, probably because the SiC particles were too small in size to induce effective toughening, and were not effective in promoting growth of elongated Si_3N_4 grains.
- (3) Microhardness increased with SiC at all temperatures. The degradation of strength at 1400°C was improved at high SiC contents.

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