Effects of SiO₂ formed on SiC filler particulates on the thermal and mechanical properties of a SiC/Si-C-N composite

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SiO₂ surface layer of SiC filler particles decreased thermal stability and creep resistance of particulate-reinforced Si-C-N-based ceramic composites made by precursor-impregnation and pyrolysis (PIP) method due to the decomposition of SiO₂ at and above 1350°C. The oxide layer could be removed by a pre-treatment of SiC particle compact at 1750°C in Ar before precursor impregnation. The composites fabricated with pre-treated SiC compact show clear improvements in thermal stability and creep resistance.

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1. Introduction

Precursor-derived ceramics have excellent high temperature stability in air and inert atmosphere up to 1500 and 2000°C, respectively.^{1,2)} Consequently, ceramic matrix composites (CMC) fabricated by precursor-impregnation and pyrolysis (PIP) method have been intensively investigated for high temperature application.^{3,4)} The room and high temperature strength of SiC or Si₃N₄ particulate-filled composites made by PIP method has been reported to be often inferior to those of composites without filler.⁵⁾ There have been also publications, however, showing contradicting results.⁶⁾ The reason for the inconsistency is not yet clear.

One of the possible reasons for the property variation would be SiO₂ layer which typically presents at the surface of SiC or Si₃N₄ filler. Because the mechanical property and thermal stability of SiO₂ is inferior to those of SiC and Si₃N₄, the SiO₂ layer may deteriorate the properties of CMC.⁷⁾ The present investigation reports on the effect of SiO₂ layer on the thermal deterioration of a CMC composed of SiC filler and precursor-derived Si-C-N matrix (here after termed SiC_{filler}/Si-C-N_{matrix}).

2. Experimental procedures

SiC_{filler}/Si-C-N_{matrix} CMC were fabricated by the impregnation of compacted SiC powder (A-10, H. C. Starck, d₅₀: 0.51 μm) with a liquid precursor and its pyrolysis at elevated temperature. The SiC powder was compacted and heat treated in Ar at 1300, 1400, 1650 or 1750°C for 2 h in order to reduce the amount of SiO₂ at the particle surface. The oxygen content of the pellets heat treated that way was analysed by hot gas extraction (TC436DR, Leco) and transmission electron microscopy (TEM, JEM 4000EX, Jeol).⁸⁾ Based on these results, SiC pellets were heat treated in Ar at 1750°C for 2 h (termed 1750-CMC). For a comparison, the pristine SiC powder was used for the CMC fabrication. In that case, the pellets were dried at 350°C for 6 h in vacuum (termed 350-CMC) to prevent the reaction of the precursor with residual humidity of the SiC particles. Then, both types of pellets were impregnated with a commercial liquid

Si-C-N precursor (VL20, KION), which were subsequently cross-linked at 430°C for 6 h and pyrolyzed at 1350°C in flowing Ar for 2 h (heating rate: 5°C/min). The process was repeated up to six times.⁹⁾ The microstructure and chemical composition of the CMC were analyzed by scanning electron microscopy (SEM, Stereoscan 200, Oxford) and energy dispersive spectroscopy (EDS, Phoenix, EDAX), respectively.

For mechanical testing the specimens were cut into disks (diameter: 10 mm, thickness: ~300 μm) and were polished up to 1 μm finish. Parts of the polished specimens were heated in Ar at 1400°C for 2 h. Then, strength of the CMC before and after the heating was measured by the “ball on three balls” method.¹⁰⁾ Young’s modulus and Poisson’s ratio of the specimens, which are required to calculate the strength, were determined by a resonance frequency and damping analyzer (RFDA system 23, IMCE). Hardness was measured by the Vickers indentation method (Micromet, Buehler).¹¹⁾ For creep testing, the specimens were machined into bars of 2 × 2 × 8 mm³, and were compressively loaded along the long axis with 100 MPa at 1350°C for 60 h in air (Amsler DSM 6101).

3. Results and discussion

Table 1 shows the oxygen content of the SiC filler particles before and after heat treatments in Ar at different temperatures. The oxygen content decreased with the increase of the treatment temperature up to 1750°C. The decomposition of the oxide surface layer on SiC can occur by the reactions between SiO₂, SiC and carbon.¹²⁾ Carbon could be supplied from the graphite furnace.

Figure 1(a) clearly shows an amorphous layer at the surface of a SiC particle. Although the thickness of this layer was not uniform in the starting SiC powder and varied within the range of 2.5–9 nm, the amorphous surface layer was nearly completely removed after the heat treatment at 1750°C (Fig. 1(b)). There-

Table 1. Oxygen content of SiC filler after the heat treatment at different temperatures (Ar atmosphere, 2 h, heating rate: 5°C/min)

Raw powder	1300°C	1400°C	1650°C	1750°C
0.9	0.7	0.4	0.1	0.06

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Fig. 1. TEM image of SiC particles (a) before and (b) after the heat treatment at 1750°C in Ar for 2 h.

Fig. 2. Formation of whisker on the surface of the 350-CMC. (a) Morphology and (b) EDS data of the surface of the 350- and 1750-CMC and the whisker.

fore, the heat treatment temperature of the SiC compact before the impregnation of the precursor was selected as 1750°C to ensure the removal of SiO₂.

Figure 2 shows the effect of the surface SiO₂ layer of SiC filler on the morphology of the CMC after the first impregnation/pyrolysis cycle at 1350°C in Ar. A white coating containing SiO₂ and SiC whiskers were formed on the CMC made with the dried SiC compact (350-CMC, Figs. 2(a), (b)). In contrast, the coating and whiskers were not observed when using the SiC compact that was heat treated at 1750°C (1750-CMC, Fig. 2(b)). The formation of SiC whisker was attributed to gas–gas or gas–solid reactions between SiO, CO and carbon.¹³⁾ SiO₂ coating which was deposited at the surface of the 350-CMC (confirmed by EDS analysis, Fig. 2(b)) was most probably formed by the reaction between SiO gas and oxygen. SiO and Oxygen gas may be supplied from the decomposed SiO₂ and contaminant in Ar atmosphere, respectively.

Table 2 summarized the strength and hardness of both types of specimens before and after heating at 1400°C for 2 h in Ar. The relative density of the 1750-CMC was higher than that of the 350-CMC. The viscosity of polymer precursors may increase rapidly when oxygen is incorporated.¹⁴⁾ During infiltration, the precursor might react with –OH groups remaining at the surface of the 350-CMC, thus the infiltration of the liquid precursor was presumably suppressed. In contrast, the –OH groups of the 1750-CMC were mostly removed during the intensive heating at 1750°C. The different relative density of the CMC affected the as-fabricated 1750-CMC had higher strength and hardness than the 350-CMC.¹⁵⁾ The 350-CMC revealed both inter- and transgranular fracture (**Fig. 3(a)**), while a dominant transgranular fracture occurred in the 1750-CMC samples (**Fig. 3(b)**). Figures 3(a) and (c) show that the grain size of the SiC filler in

Fig. 3. Fractured surface of (a) 350-CMC, room temperature (A: filler, B: matrix), (b) 1750-CMC, room temperature, (c) after the plasma etching of the 1750-CMC, room temperature, (d) 350-CMC, after heating at 1400°C and (e) 1750-CMC, after heating at 1400°C.

Fig. 4. Compressive creep behavior of CMC at 1350°C with 100 MPa in air (●: 350-CMC, ▲: 1750-CMC).

both types of the CMC was similar. The results indicate that the SiO₂ layer on SiC filler also affected the fracture behavior of the CMC at room temperature.

The fracture surface of both types of the CMC after the heating at 1400°C show the detrimental effect of SiO₂. SiC particles were pulled out during fracture due to the weak bonding between the filler and the matrix in the 350-CMC samples (Fig. 3(d)). In contrast, the fracture behavior of the 1750-CMC was not much affected by the heating at 1400°C (Fig. 3(e)).

The decrease of the strength and hardness of the 350-CMC after the heating at 1400°C (Table 2) can be understood in terms of the weakening of bonding between the filler particles and the matrix by the decomposition of SiO₂ interlayer, because the bonding state between matrix and filler particles strongly affects the particle reinforcement in CMC.¹⁶⁾ Decomposition of Si-C-N did not strongly deteriorate the mechanical properties of the CMC at 1400°C, which was evident from the substantial improvement of mechanical properties after the heating of the 1750-CMC (Table 2). The strength of the 1750-CMC became so high that the applied force to break the samples exceeded the capacity of the load cell in use (20 N). Therefore the value could not be measured exactly with the experimental set up. The results clearly indicated that thermal stability of the CMC was substantially improved by removing SiO₂ from the SiC particles before the impregnation of precursor into the SiC compact.

The creep behavior of the CMC was also affected by the surface SiO₂ of SiC particles (Fig. 4). With the 1750-CMC there was almost no additional strain up to 60 h after the initial strain of some 0.18%. In contrast, the creep strain of the 350-CMC sample increased continuously up to 0.37%.

Various reasons can be considered to explain the excellent creep resistance of the 1750-CMC. The intrinsic oxygen content of the 350-CMC was higher than that of the 1750-CMC (Table 1). During creep testing in air, the formation of SiO₂ within the 350-CMC was also believed to be more intensive than the case of the 1750-CMC because of its high porosity. SiO₂ might induce the densification of the composites under pressure

because the creep resistance of SiO₂ is much lower than that of SiC.¹⁷⁾ In addition, the mass transfer through the oxide layer might be promoted due to the high diffusivity of the oxide compared to the non-oxide ceramics.¹⁸⁾ The deterioration of bonding between the filler and the matrix is also believed to induce the low creep resistance of the 350-CMC.

4. Conclusions

The weakening of the bonding between the filler and the matrix by the decomposition of the SiO₂ interlayer is considered as the main reason for the deterioration of a SiC_{filler}/Si-C-N_{matrix} CMC at high temperature. The results clearly show that if the surface SiO₂ of silicon-based ceramic filler particles is removed prior to the impregnation of liquid precursor in the PIP process, the creep resistance and high temperature stability of the resultant composites can be substantially improved.

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