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Effects of amorphous silica coatings on the sintering behaviours of SiC whisker-reinforced Al_2O_3 composites

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In this study, pressureless sintering of silicon carbide whisker (SiC_w)-reinforced alumina composites was investigated. SiC whiskers or Al_2O_3 powders were coated with amorphous silica, and sintering behaviour was analysed according to the powder characteristics of the composite. It was found that amorphous silica coatings improved densification as compared with uncoated powders, because the viscous flow allows the release of any tensile stress due to differential shrinkage between the matrix and the silicon carbide whiskers. Mullite occurred when amorphous silica coatings reacted with alumina at ~1500 °C, which resisted the viscous sintering of the amorphous silica coatings.

1. Introduction

SiC-whisker-reinforced composites (SiC_w–RC) are promising candidate materials with better mechanical properties for specific environments. They have been studied extensively in recent years [1–21].

It is well known that the presence of rigid inclusions can significantly reduce the densification rate of a sinterable matrix [22–24]. Several explanations have been offered for this phenomenon, including (i) tensile stresses resulting from the presence of inclusions in the matrix that resist the sintering stress [25–27] and (ii) increases in the transport path length for diffusion during the sintering stage [28–31].

This phenomenon becomes especially obvious when a higher inclusion-volume fraction is involved, because rigid networks may be developed in the composite which resist deformation under the sintering stress [32, 33]. Because of these adverse effects on densification, SiC_w–RC is generally prepared by hot pressing. Other recent studies [14–17] have demonstrated that suspension-processing techniques can also be used to prepare green compacts for SiC whisker-reinforced-α-Al_2O_3 with high green density; thus the length of the transport path and the resistance to the tensile stress in the matrix can be decreased.

Moreover, transient-viscous sintering (TVS) has been proposed as a possible fabrication technique in mullite composites. Achieving densified mullites is known to be difficult. Powder compacts prepared by alumina particles which were previously coated with amorphous silica can be sintered to almost full density at relatively low temperatures by TVS methods [34].

In this study, the characteristics and sintering behaviour of SiC_w-reinforced alumina composites were investigated. They were fabricated with composite powders, which were either uncoated or coated with amorphous silica.

2. Experimental procedure

2.1. Starting materials and processing

Commercially available SiC whisker (SCW-1, Tateho Chemical Industries, Hyogo-Ken, Japan), α-Al_2O_3 powders (AKP-50, Sumitomo Chemical Company, Ltd, Tokyo, Japan), and silicon tetraethoxide (TEOS; T-5083, Ferak Laboratory Chemicals, Berlin, Germany) were used as the starting materials. The as-received SiC whisker was treated with 5% HF solution for 10 h to remove impurities on the whisker surface and to improve the dispersability of the whisker in suspensions. The HF-treated whiskers were then cleaned with deionized water, and the agglomorated portions removed by gravity sedimentation. They were then dispersed ultrasonically in an aqueous solution, pH = 10.5. The suspensions were filtered with filter paper washed with deionized water, and dried at 80 °C.

SiC_w/Al_2O_3 composites were fabricated using SiC whiskers or alumina powders. The SiC whisker and α-Al_2O_3 were each separately coated with amorphous silica derived by hydrolysis of TEOS in a NH_4OH (Art-Nr.00140, Ferak Laboratory Chemicals, Berlin, Germany) solution, pH = 12.6, designated as Sc and Ac (Fig. 1). The molar ratio of NH_4OH:TEOS:C_2H_5OH was 30:1:20. The silica-coated alumina powders (sample Ac) were prepared at a ratio of ~76 alumina/~24 silica (wt %). The silica-coated SiC whisker (sample Sc) were prepared at ~87 SiC whisker/~13 silica (wt %). Fig. 2 shows transmission electron micrographs (TEM) of the silica-coated Al_2O_3 particles and the SiC_w.

Green compacts were formed by slip-casting techniques. At first, to obtain a well-dispersed suspension, the solids in the aqueous systems used were tested by measuring their Zeta potential (Zeta Meter ZM-80, Zeter Meter Inc., New York, USA). Five samples were

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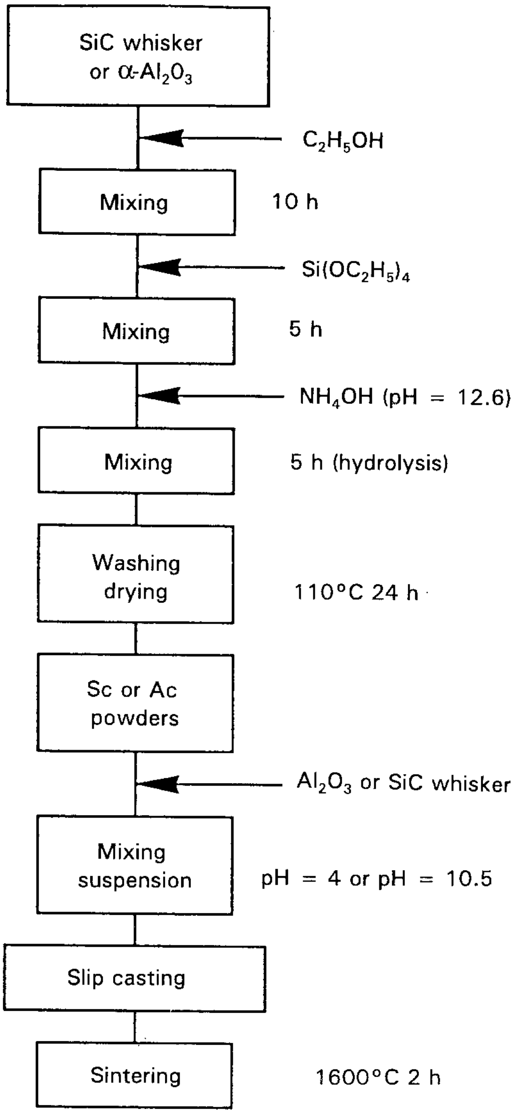

Figure 1 Processing flow for alumina composites.

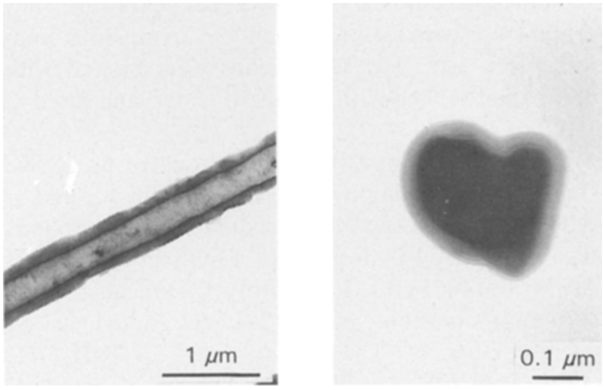

Figure 2 TEM micrographs of SiC whisker and α-alumina particle that have been coated with amorphous silica.

prepared, being dispersed at pH 4 and 10.5. The 'pure' alumina (designated as sample A), SiC_w/Al_2O_3 composites (sample SA), and silica-coated SiC_w/Al_2O_3 composite (sample ScA) were at pH = 4. The silica-coated Al_2O_3 (sample Ac) and the SiC_w/silica-coated Al_2O_3 composite (sample SAc) were at pH = 10.5. Solid concentration of the suspensions was about 30 vol %. The green compacts were dried and pressureless sintered in Ar atmosphere at 1600 °C (heating rate: 5 °C min^{-1}) for 2 h.

2.2. Characterization

The bulk density of sintered bodies was determined by Archimedes methods, and the relative density was calculated based on the densities of Al_2O_3 (3.987 g cm^{-3}), SiC_w (3.215 g cm^{-3}) and SiO_2 (cristobalite, 2.334 g cm^{-3}) assuming a rule of mixtures. Microstructural examination was completed by scanning electron microscopy (SEM) (Jeol JSM-35F) and transmission electron microscopy (TEM) (Hitachi H700-H). Mineral-phase analysis was completed by X-ray diffraction (XRD) (Rigaku, D/MAX IIB), using CuK_α radiation. The sintering shrinkage was detected by high-temperature dilatometer (SETARAM, DHT 2050KN). Differential thermogravimetric analysis (DTA) (SETARAM, HTC1800K) was performed on powder samples at 10 °C min^{-1} heating rates in Ar to investigate phase transformations occurring in silica-coated alumina powders.

3. Results and discussion

3.1. Dispersion and slip casting

Table I shows that the densities for the green compacts and the sintered ceramics of alumina composites vary with the starting materials used. The green density ranged from 62 to 64% theoretical density and the 'pure' alumina (sample A) eventually had the highest value. However, alumina powders coated with silica would have similar green density to those samples mixed with SiC_w, being only 62.1% theoretical density.

To obtain a homogeneously dispersed suspension for slip casting, water-solid systems were prepared by adjusting the aqueous pH through Zeta potential measurements. The relationships between the pH values and the Zeta potentials for the four powders are shown in Fig. 3. In terms of dispersion, a homogeneous mixture of S/A or S/Ac systems (Table I) should not be a problem because pH = 4 or pH = 10.5 would provide a higher positive or negative Zeta potential environment for the mixtures. This is demonstrated by the four pH–Zeta potential curves (Fig. 3). The curves of whiskers and powders that have been silica-coated (samples Sc and Ac) would shift to the negative Zeta potential side (left), compared with the curves of S and A, and would show similar characteristics. It appears

TABLE I Green and sintered relative densities for alumina composites

Sample	Starting material	Green density (%)	Sintered density (%)
A	Al_2O_3	63.6	97.2
SA	SiC_w/Al_2O_3	62.4	68.1
ScA	coated SiC_w/Al_2O_3	62.5	84.7
Ac	coated Al_2O_3	62.1	96.0
SAc	SiC_w/coated Al_2O_3	61.9	92.2

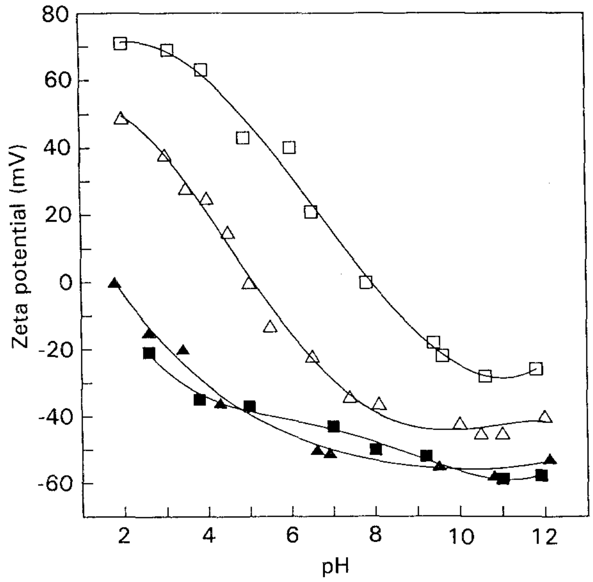

Figure 3 Plots of zeta potential against pH for SiC whisker (△), silica-coated SiC whisker (▲), α-alumina (□) and silica-coated alumina (■).

that the surface properties of both whiskers and powders were affected by the silica coating (Fig. 2). Thus a pH value of 4 was employed to disperse the composite mixtures of samples SA and ScA. However, a homogeneously mixed suspension made of Sc and A (sample ScA) can also be obtained at $pH = 4$, although the alumina powders and the whisker may behave differently at the same pH value. This is because at $pH = 4$ the surface charge of the alumina materials, A, is positive, while the whisker, Sc, is negative. The opposite surface–charge phenomenon was expected to provide a sufficient force for the two to attract each other. Powders of α-Al_2O_3-coated Sc were formed (Fig. 4), which behave like sample A. Consequently, a well-dispersed suspension of samples Sc and A was obtained at $pH = 4$. This is shown by the high green density (sample ScA in Table I).

3.2. Sintering behaviour

Green compacts were pressureless sintered at 1600 °C in Ar atmosphere for 2 h. Table I lists the densities for the sintered composites. It is found that sample A had the highest density, of 97.2% theoretical density. When 20 vol % of uncoated SiC whisker was added, the density reduced to only 68.1% theoretical density (sample SA). However, it is noted that whiskers or powders coated with amorphous silica will promote the sinterability and increase the densities in different ways. For example, the addition of the same amount of inclusion of SiC whisker which has been coated with amorphous silica, could increase the theoretical density to 84.7% (sample ScA), while sample SAc had a theoretical density of 92.2%. This result was different from that of sample SA and could be explained by high-temperature dilatometry curves (Fig. 5).

Fig. 5 shows that the sintering shrinkage of samples A and SA started from 1100 °C. However, SA samples stopped shrinkage at 1200 °C, even when brought to a higher sintering temperature. This result could be explained by the tensile stress that occurred in the alumina matrix due to the presence of SiCw, which presumably inhibited the sintering shrinkage [25–27]. The shrinkage of sample ScA also began at 1100 °C, and terminated at 1200 °C, and then restarted again at 1300 °C and terminated at 1500 °C, forming a two-stage shrinkage phenomena. Shrinkage at the 1100–1200 °C stage was possibly similar to that of sample SA, resulting from the sintering shrinkage of α-Al_2O_3; the shrinkage at 1300–1500 °C resulted from the viscous flow [34] of the silica coatings, which started to shrink at > 1300 °C. The viscous flow

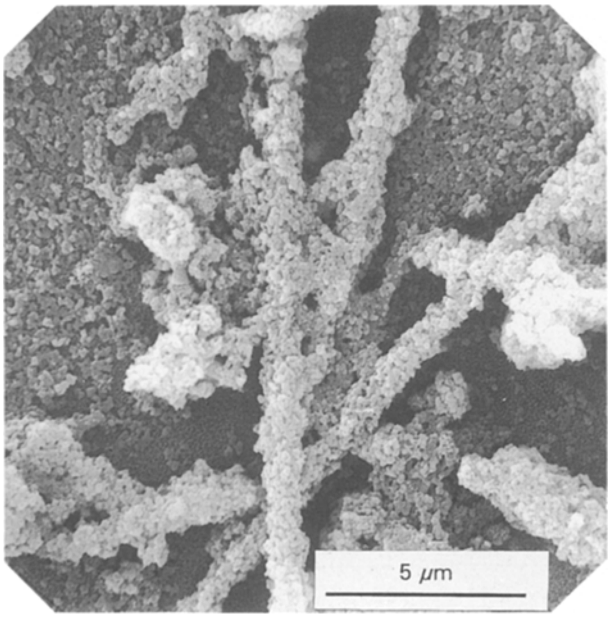

Figure 4 SEM micrographs of sample ScA powders. The silica-coated SiC whiskers have been adsorbed by α-alumina particles.

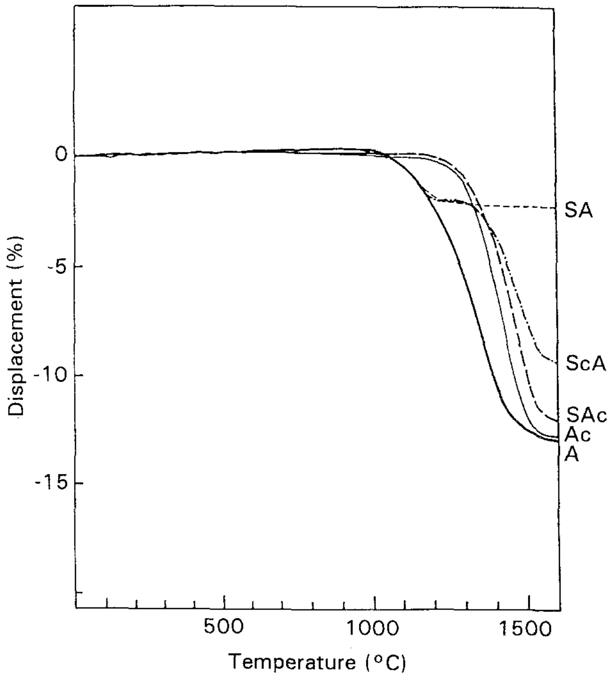

Figure 5 Axial shrinkage of the green compacts against temperature for samples A, SA, ScA, Ac and SAc, sintered at 5 °C min^{-1}.

appears to have acted as a lubricant between the SiC whiskers and the alumina matrix, thus releasing the tensile stress that would be present in the alumina matrix due to the addition of SiC_w. It should be noted that before the viscous flow occurred, pores were formed at ~ 1200–1300 °C because of the differential shrinkage between the alumina matrix and the SiC whiskers. These pores resulted in an increase in the length of the transport path for diffusion [28–31]. When the sintering temperature rose and the viscous flow occurred, part of the larger pores could not be removed, and a theoretical density of 84.7% was attained for sample ScA.

Sintering shrinkage for sample Ac began at 1300 °C. As the shrinkage of alumina had been retarded by the presence of silica coatings on the alumina particle surface, shrinkage was delayed until 1300 °C when the viscous flow of SiO_2 occurred. The shrinkage of sample SAc originating from the viscous flow of silica was similar to that of sample Ac. The effect of the SiC whisker inclusion on the densification rate was found to be negligible.

3.3. Effects of mullite formation

When the temperature increased to above 1500 °C, the amorphous silica reacted with alumina particles to form mullite, and the shrinkage for samples ScA, Ac, and SAc ceased. Mineral phases occurring in the samples studied at temperatures of 1300, 1400 and 1500 °C revealed that SiC_w and α-Al_2O_3 remained unchanged, while the coated amorphous silica independently experienced a series of phase transformations, as reported elsewhere [34], existing as amorphous (< 1300 °C), cristobalite (~ 1400–1500 °C), and finally reacted with Al_2O_3 at 1500 °C to form mullite.

Fig. 6 demonstrates the typical XRD patterns of the samples studied. For comparison, phase transformation for the amorphous silica is also listed (Fig. 6a). It is found that when the temperature was below 1300 °C, the silica-coated alumina particles (sample Ac) existed as the α-alumina phase only, and the silica was amorphous. The cristobalite phase appeared when the temperature rose above 1400 °C. Then mullite, which eventually was formed by reaction of silica (cristobalite) and Al_2O_3, was evident at

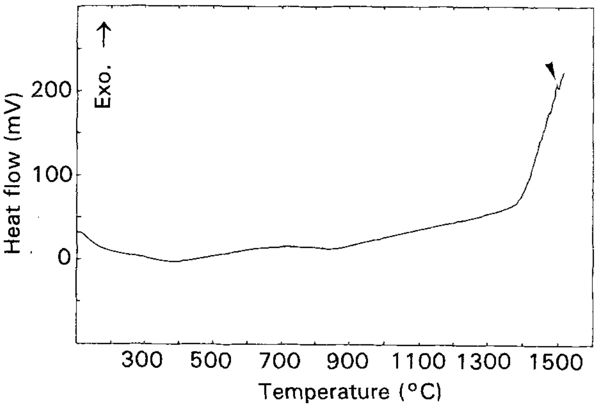

Figure 7 DTA curve of silica-coated alumina (sample Ac), the formation temperature of mullite indicated by the arrow.

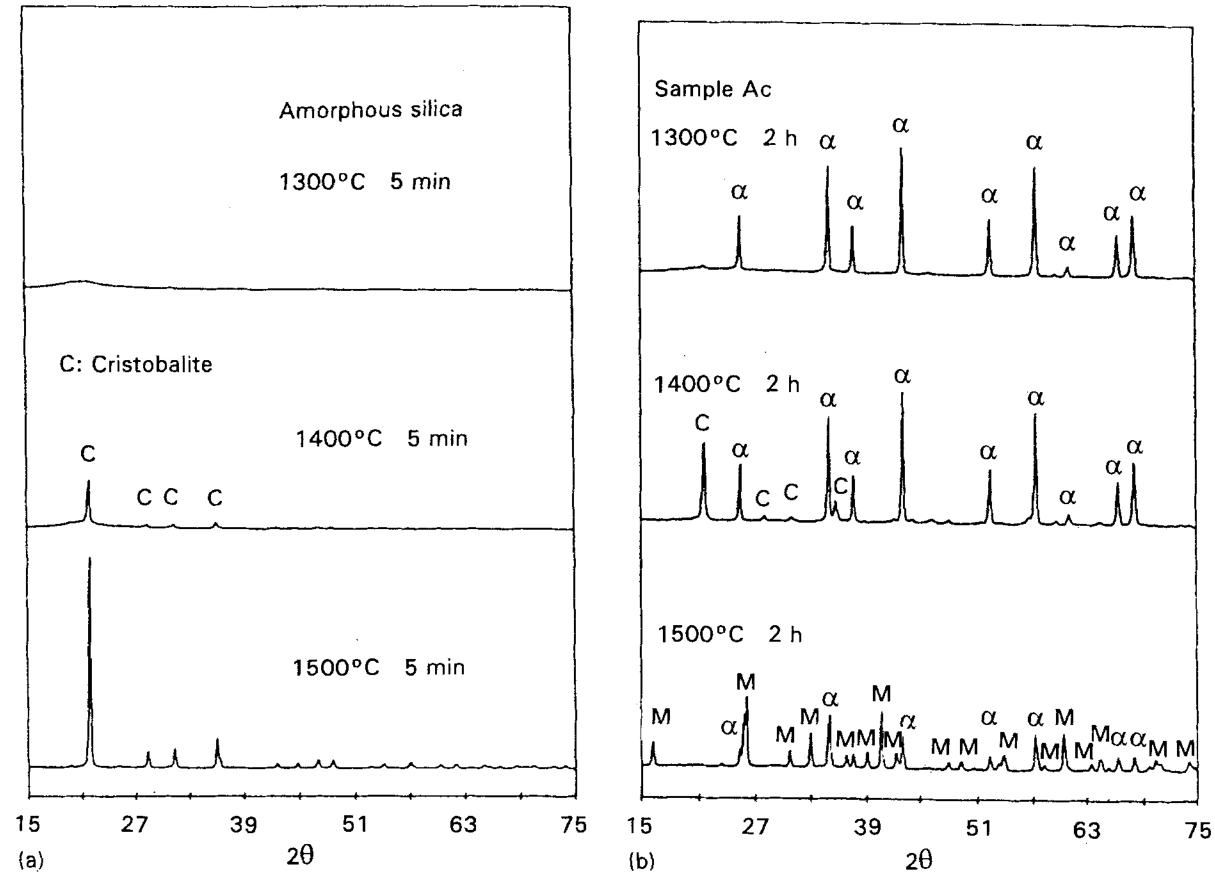

Figure 6 XRD patterns for (a) amorphous silica powders and (b) sintered body of sample Ac. α, α-Al_2O_3; C, cristobalite; M, mullite.

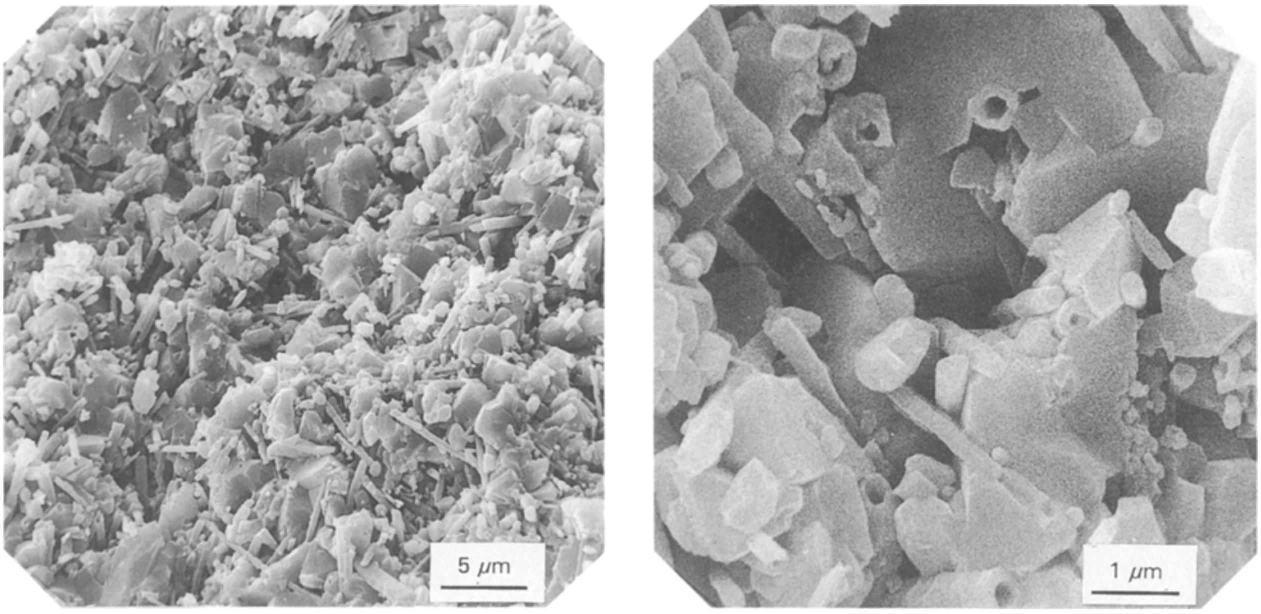

Figure 8 SEM micrographs of fracture surface for sintered body. The silica-coated SiC whisker/alumina (sample ScA) was sintered at 1600 °C for 2 h. The tubes were the outer-layer coatings of SiC whisker which pulled out.

1500 °C. The formation of the mullite phase can also be observed by DTA (Fig. 7). An exothermic peak for sample Ac was found at $T \sim 1500\,^{\circ}C$. This result differed from the thermal behaviour of Al_2O_3–SiO_2 gels in previous research [35, 36] which reacted to mullite at 1200–1300 °C. As a coarser scale of the Al_2O_3 particles delayed the mullitization until 1500 °C, the viscous flow is capable of enhancing the densification rate at temperatures ranging from 1300–1500 °C. It is possible that the appearance of mullite may change the viscosity of viscous flow, which may provide sufficient lubrication for the silica-coated powders to shrink at 1300–1500 °C. Once the mullite was formed, the viscosity increased quickly, and the densification rate for these samples decreased.

SEM examination found that the tube-like, pull-out structures at the fractured surface of sample ScA (Fig. 8) can be attributed to the formation of mullite outlayers on the SiC_w.

4. Conclusions

The characterization and sintering behaviour of SiC-whisker-reinforced alumina composites by composite powders with or without amorphous silica coatings have been examined using XRD and high-temperature dilatometry analysis. On the basis of the results obtained in this study, a number of conclusions can be drawn.

1. At pH = 12.6 hydrolysis condition, either the SiC whisker or the alumina particles could be coated homogeneously by amorphous silica.
2. The high-temperature dilatometry curve has shown that the viscous flow of amorphous silica occurred at 1300 °C, and the alumina matrix shrank at 1100 °C. The shrinkage of sample SA was only 2.1% because the SiC whisker resisted the shrinkage. The shrinkage could be increased by using SiC whiskers coated with amorphous silica. However, the sinterability of the alumina matrix could not cooperate with the viscous flow if alumina particles were uncoated, and its density only increased to 84.7% theoretical density. When alumina particles were coated, the viscous sintering became effective, and a theoretical density of 92.2% was obtained.
3. The amorphous silica phase transformed to the cristobalite phase at 1400–1500 °C, and reacted with the alumina matrix to form mullite at ~ 1500 °C. This reaction resisted viscous sintering of silica.

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