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Processing and Mechanical Properties of Laminated Composites of Mullite/Woven Fabrics of Si–Ti–C–O Fibers

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Abstract

A sol–gel-processed mullite powder and Si–Ti–C–O fiber woven fabrics were formed into laminated composites by filtration or doctor blade method using aqueous mullite suspensions containing polyacrylic ammonium (PAA) and methyl cellulose (MC) at pH 8·5. The laminate green composites with 6 and 10 vol% fabrics were hot-pressed to near full density at 1500–1650°C for 1 h under a pressure of 39 MPa in a N_2 atmosphere. However, the composites with 20 and 30 vol% fabrics resulted in delaminated porous ones after hot-pressing due to the exfoliation of filament yarn in woven fabrics. A linear relation of stress–displacement in fracture behavior of monolithic mullite changed to a non-linear relation in the composites with 10–30 vol% of Si–Ti–C–O fabrics and hot-pressed at 1650°C. Addition of Si–Ti–C–O fabrics decreased the four point flexural strength of monolithic mullite (328 MPa) to 292 MPa at 6 vol%, 271 MPa at 10 vol% and 59–78 MPa at 20–30 vol% of fabrics whereas the fracture toughness by the single edge precracked beam (SEPB) method increased from 1.6 MPa $m^{0.5}$ for the monolithic mullite to 4·7 MPa $m^{0.5}$ for the composites with 10 vol% of Si–Ti–C–O fabrics. Enhancement of the mechanical properties can be interpreted by the partial decomposition of Si–Ti–C–O fibers during hot-pressing at 1500–1650°C, which caused the diffusion of C and Ti elements of fibers to the interfaces between the fibers and mullite matrix. The diffusion of Al from mullite matrix into fibers was also observed. The change of composition, microstructure and strength at the interfaces would increase debonding or pull-out effect of fibers.

1 Introduction

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is a candidate oxide for high temperature structural applications because of a high melting point, a low thermal expansion coefficient, good thermal shock fracture resistance, a low true density and high creep resistance. For increase of mechanical reliability of mullite ceramics with a low fracture toughness (1–2 MPa $m^{0.5}$), some papers reported the increase of fracture toughness by addition of SiC whiskers, long carbon or Si–Ti–C–O fibers to mullite matrix.[1–5] Especially, the long fiber-reinforced mullite matrix composites are attractive materials because this type of composites show usually high fracture toughness and non-linear fracture behaviour of stress–displacement curves, along with remarkably high fracture energy. A typical mullite composite reinforced by 35 vol% of uniaxial carbon fiber showed significantly high strength above 800 MPa and high fracture toughness reaching 29 MPa $m^{0.5}$ at 1200°C.[3] The most important factor in the processing of fiber-reinforced composites would be the control of strength of interface between fiber and matrix. An adequate interface strength that is not too strong or too weak can lead to the excellent mechanical properties of composite materials.[6–8] The objective of this research was to study the processing, mechanical properties, and microstructure of the laminated mullite/woven fabric composites with high fracture toughness and high strength. In this study, mullite green sheets formed by doctor blade of aqueous mullite suspensions and woven fabrics of Si–Ti–C–O long fibers were laminated to sinter by hot-pressing at 1500–1650°C. The Si–Ti–C–O long fibers show

high tensile strength (3.2 GPa), high oxidation resistance, and good wettability to oxide ceramics.[9]

2 Experimental Procedure

2.1 Starting materials and colloidal processing

A sol–gel-processed mullite powder (Fig. 1(a)) was mixed with aqueous solutions to form thick green sheets or to pour into the spaces separated with the woven fabrics of Si–Ti–C–O fibers. The mullite powder used was supplied from Chichibu Cement Co., Ltd, Japan. It has the following properties: particle size distribution: 0·1–1·5 μm, specific surface area: 3·2 m^2/g (equivalent diameter of spherical particle: 0·59 μm), chemical composition: 71·80 mass% Al_2O_3, 28·05 mass% SiO_2, 0·10 mass% TiO_2, and 0·01 mass% Na_2O. The Si–Ti–C–O woven fabrics of 270 μm thick (Ube Industries, Ltd, Yamaguchi, Japan), were made of long fibers with an average diameter of 8·5 μm (Fig. 1(b)), and a chemical composition of 50·4 mass% Si, 29·7 mass% C, 17·9 mass% O, and 2·0 mass% Ti. The surface characteristics of the mullite and crushed Si–Ti–C–O fibers in dilute aqueous suspensions (0·02 mass%) were studied by measuring the electrophoretic mobility. The pH of each suspension was adjusted using 0·01N HCl and 0·01N NH_4OH solutions. Electrosterically stabilized mullite suspensions of 40 vol% solid at pH 8·5 were prepared by adding 0·75 mass% of polyacrylic ammonium (PAA, $(HCOONH_4CH_2)n$, average molecular weight: 10000) and 2·0 mass% of methyl cellulose (MC) against the weight of mullite to give flexibility and strength for handling of thick films formed. The suspensions were stirred for 24 h and ultrasonic vibration at 20 kHz was applied for an additional 5 min to disperse particle agglomerates. Air bubbles in the suspensions were eliminated in a bell jar connected to a vacuum pump. These suspensions were formed into thick films by doctor blade of a blade clearance of 500 μm at a transfer rate of 15 cm/min of polyethylene carrier tape (DP-100, Tsugawa Seiki Seisakusho, Tokyo, Japan). In the preparation of composite with 6 vol% fabrics, the mullite suspensions of 52 vol% solid containing 0·75 mass% of PAA at pH 8·5–8·8 were poured into the rectangular spaces separated at 2·7 mm intervals of four Si–Ti–C–O fabric sheets (thickness, 270 μm, 38 mm long and 25 mm wide) which were set on a gypsum mold.

2.2 Hot-pressing and measurement of mechanical properties

Before hot-pressing in a N_2 atmosphere, a set of 5–7 layers of a mullite sheet (thickness, 200–250 μm) and one layer of Si–Ti–C–O fabric sheet, (thickness, 270 μm, 38 mm long and 25 mm wide) were alternately laminated to 10–12 mm in thickness. The green laminated composites of 6–30 vol% Si–Ti–C–O fabrics were pressed with a carbon die under a pressure of 39 MPa at room temperature and heated to 1500 or 1650°C at the rate of 10°C/min, and sintered for 1 h in a N_2 atmosphere (FVH-5 type, Fuji Denpa Kogyo Co., Osaka, Japan). The densities of hot-pressed composites were measured in distilled water by the Archimedes method. A hot-pressed sample was cut into five test specimens 38 mm long, 3–4 mm wide and 4–7·5 mm thick, parallel to the hot-pressing direction.

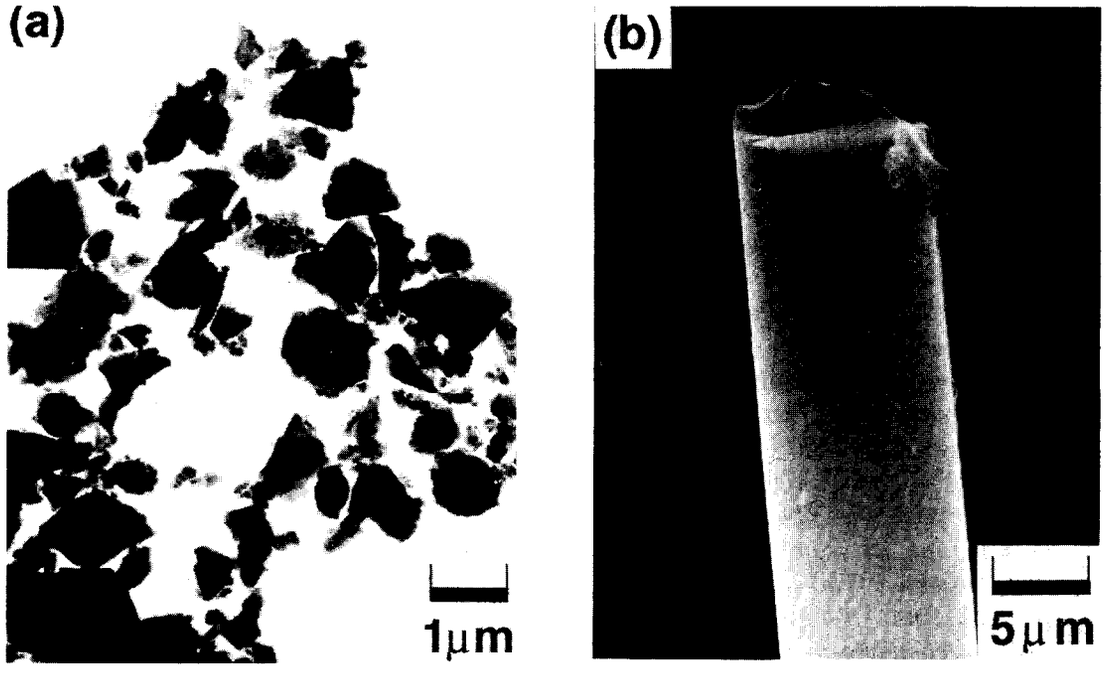

Fig. 1. Photographs of: (a) sol–gel-processed mullite powder and (b) Si–Ti–C–O long fiber.

The flexural strength of test specimens parallel to the hot-pressing direction was measured at room temperature by the four-point flexural method over spans of 30 mm (lower span) and 10 mm (upper span) at a crosshead speed of 0·5 mm/min. The test specimens were prepared by grinding with a No. 400 diamond wheel and finished with No. 2000 abrasive paper. The average strength was calculated from the data for 3–4 specimens. The fracture toughness was evaluated by single edge precracked beam (SEPB) method. The strengths of the flexural specimens, precracked by a Vickers indenter (model MVF-K, Akashi Seisakusho Co., Tokyo, Japan) of 98 N to induce microcracks, were measured by three-point loading over a span of 30 mm at a crosshead speed of 0·5 mm/min, and then calculated to fracture toughness.[10] Data for 3–4 test specimens were used to calculate the average fracture toughness. Microstructures of the composites were observed by scanning electron microscopy with energy dispersive X-ray spectroscopy (EDX: S-5000 Type, Hitachi Co., Tokyo, Japan) and analytical transmission electron microscopy (TEM: EM430, Philips Co., Eindhoven, Netherlands).

3 Results and Discussion

3.1 Forming of laminated composites

As shown in Fig. 2, the isoelectric points for the suspensions of the mullite particles and crushed Si–Ti–C–O fibers were pH 4·9 and 3·5, respectively. The electrophoretic mobility of both of the negatively charged powders reached the maximum values of –4 – –5 μm s^{-1} V^{-1} cm in the pH range of 8–10. The above result suggests that: (1) the mullite particles are to be dispersed due to the strong electric repulsion at high pH and (2) strong repulsive interaction is also formed between the negatively charged mullite particles and Si–Ti–C–O fibers at high pH. Thus, the mullite suspensions in this experiment were adjusted at pH 8·5 to enhance the dispersion state of mullite powder. In the doctor blade method, 2·0 mass% of MC and 0·75 mass% of PAA against the weight of mullite were added to the suspensions to give an apparent viscosity of 45·1 Pa s at a shear rate of 3·83 s^{-1}. For the preparation of laminated composites with 6 vol% fabrics by filtration of the mullite suspension in the space separated with Si–Ti–C–O fabrics, 0·75 mass% of PAA was added to the concentrated mullite suspensions of 52 vol% solid at pH 8·5–8·8.[5] This electrosterically stabilized mullite suspensions behaved as a Newtonian flow and the viscosity was 122 mPa s. The green compacts obtained from this suspension was 63% of the theoretical density (TD).[11]

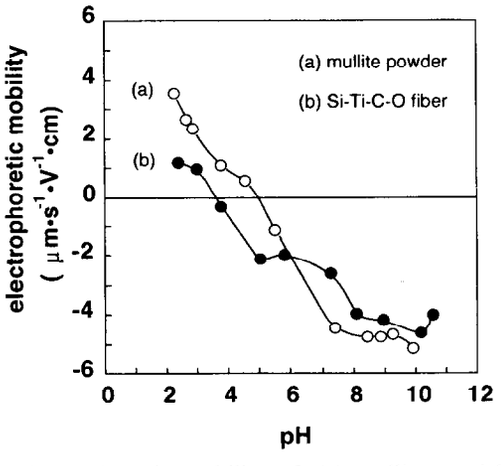

Fig. 2. Electrophoretic mobility of: (a) mullite particles and (b) Si–Ti–C–O fibers in aqueous suspensions.

3.2 Hot-pressing and mechanical properties of laminated composites

The monolithic mullite and mullite/Si–Ti–C–O fiber fabric (6 and 10 vol%) composites were densified to near full densities (99·7–99·9% TD) at 1500 to 1650°C for 1 h by hot-pressing under a pressure of 39 MPa. However, the composites with 20 and 30 vol% fabrics resulted in delaminated porous bodies and the filament yarns in the woven fabrics exfoliated. The density of the composites with 30 vol% fabrics was 64% TD. Since the Si–Ti–C–O fabrics introduce a high porosity, the increase of fabrics content may cause the insufficient packing of mullite particles in the open spaces of fabrics. The above phenomenon indicates a limit of fiber loading in this type of laminated composites.

Figure 3 shows the stress–displacement curves

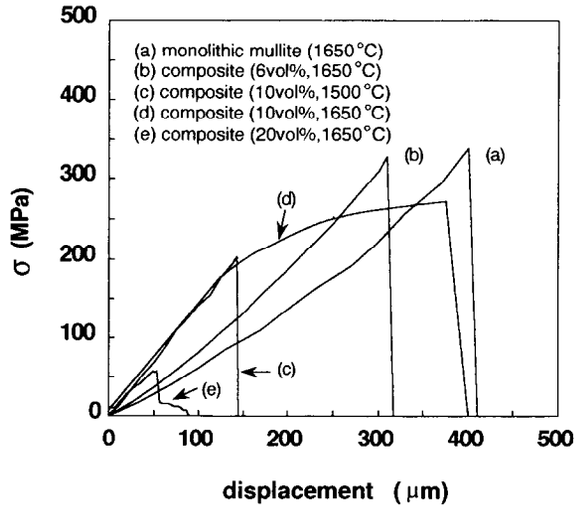

Fig. 3. Stress–displacement curves at room temperature for: (a) monolithic mullite hot-pressed at 1650°C; (b) mullite/Si–Ti–C–O fabrics composites with 6 vol% fabrics hot-pressed at 1650°C; (c) composites with 10 vol% fabrics hot-pressed at 1500°C; (d) composites with 10 vol% fabrics hot-pressed at 1650°C and (e) composites with 20 vol% fabrics hot-pressed at 1650°C.

for monolithic mullite and mullite/Si–Ti–C–O fabric composites. The fracture behavior of composites was affected by two factors, i.e. hot-pressing temperature and Si–Ti–C–O fabrics content. The stress–displacement curve of the composites with 10 vol% fabrics hot-pressed at 1500°C was similar to that of mullite hot-pressed at 1650°C. This result suggests that the inserted fabrics behaved like a part of mullite matrix and they fractured in the clear absence of pseudoplastic behavior. Increase in the hot-pressing temperature of the composites with 10 vol% fabrics to 1650°C caused a non-linear fracture behavior with a high fracture energy as seen in Fig. 3(d). This effect of hot-pressing temperature may be corresponding to decrease in strength of interface between the mullite matrix and Si–Ti–C–O fabrics. Increase in the Si–Ti–C–O fabric content from 6 to 10 vol% in the composites hot-pressed at 1650°C was effective to achieve the non-linear fracture behavior and to increase fracture energy as shown in Fig. 3. On the other hand, the delaminated porous composites with 20–30 vol% fabrics showed a non-linear fracture behavior with a low fracture strength. It is also noted that the composites with 10 vol% fabrics hot-pressed at 1650°C and precracked by a Vickers indenter of 98 N showed a clear non-linear fracture behavior as shown in Fig. 4, indicating a high damage tolerance. However, the precracked composite with 6 vol% fabrics fractured with a linear relation of stress–displacement.

Figure 5 summarizes the mechanical properties of mullite/Si–Ti–C–O fabric composites hot-pressed at 1650°C. Increase of the Si–Ti–C–O fabric content caused a slight decrease of flexural strength up to 10 vol% fabrics but gave a drastic decrease at 20 and 30 vol% fabrics. The fracture toughness that was calculated at the highest stress

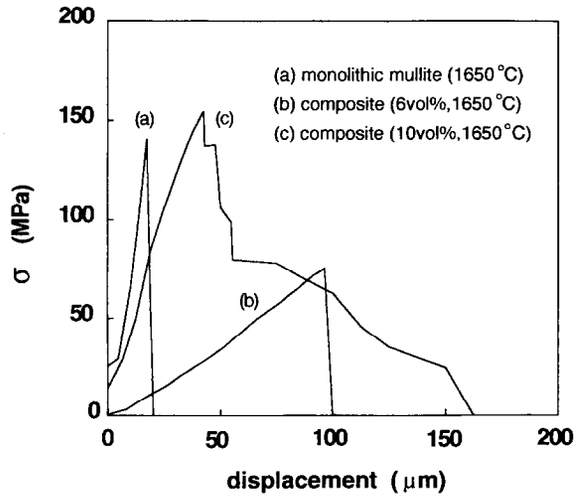

Fig. 4. Stress–displacement curves for: (a) monolithic mullite; (b) composites with 6 vol% fabrics and (c) composites with 10 vol% fabrics, precracked by a Vickers indenter of 98 N.

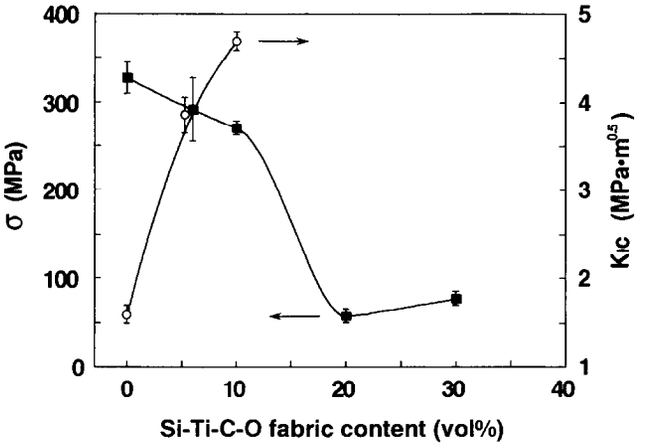

Fig. 5. Dependence of flexural strength and fracture toughness on Si–Ti–C–O fabric content for composites hot-pressed at 1650°C.

of samples with precracks in SEPB method, increased from 1·6 MPa $m^{0.5}$ for monolithic mullite to 4·7 MPa $m^{0.5}$ for the composite with 10 vol% fabrics. That is, it was possible to increase fracture toughness of the laminated composites significantly with a comparable strength to monolithic mullite.

Figures 6 and 7 show the SEM photographs

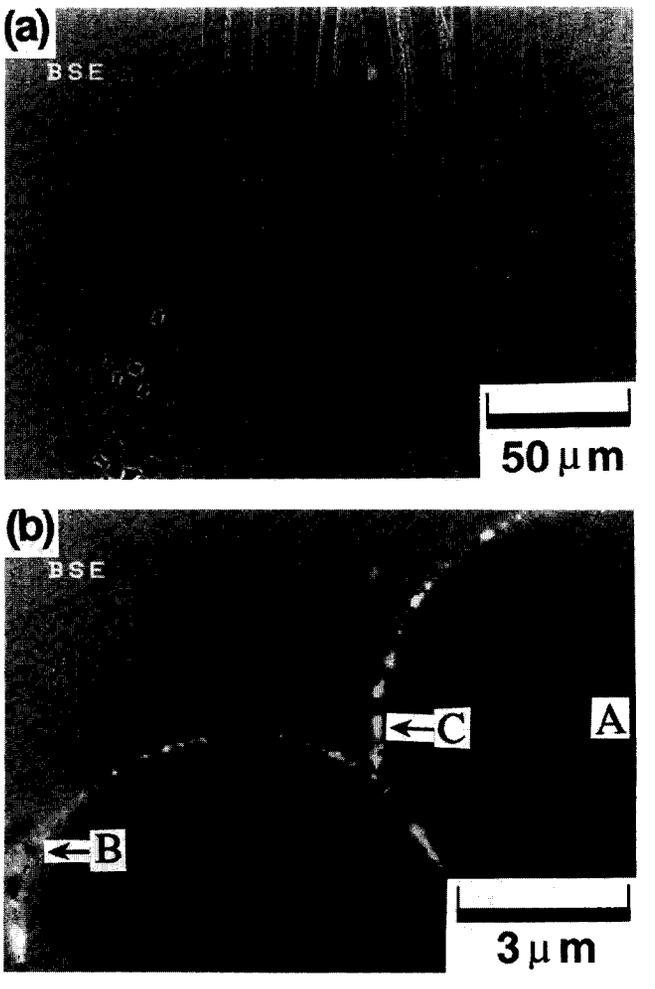

Fig. 6. SEM photographs of composites with 10 vol% fabrics hot-pressed at 1650°C.

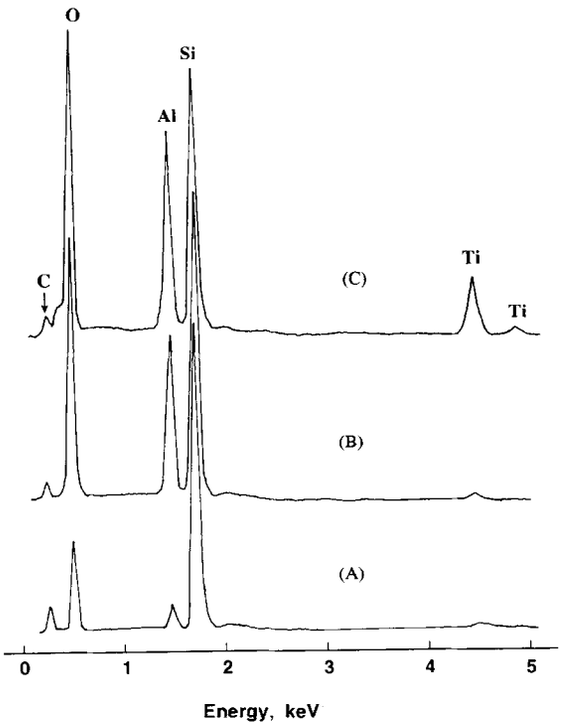

Fig. 7. EDX analysis of Si–Ti–C–O fiber (point A) and interface (points B and C).

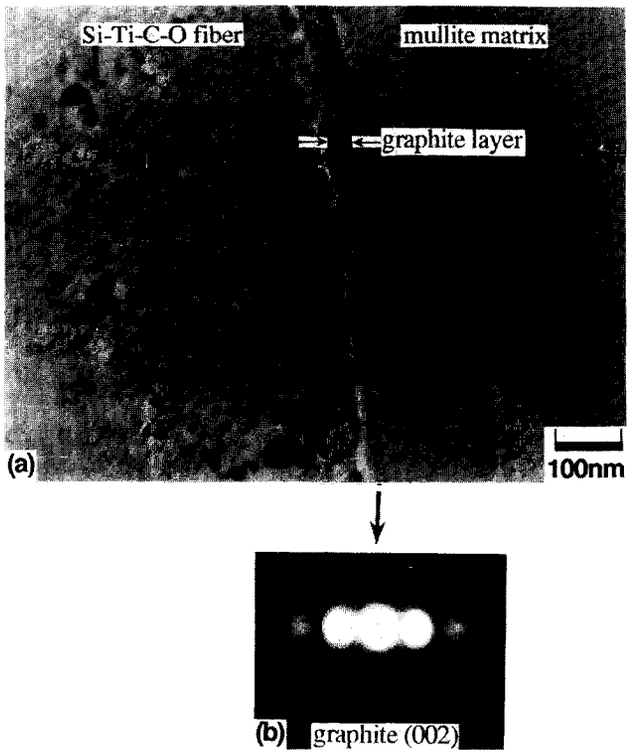

Fig. 8. TEM photograph (a) and selected area electron diffraction pattern (b) at the interface between Si–Ti C O fiber and mullite matrix of composites hot-pressed at 1650°C.

and corresponding EDX spectra of the composites with 10 vol% fabrics hot-pressed at 1650°C. Pore-free microstructure was observed in the mullite matrix of the composites. A few pores remained in the spaces surrounded by the Si–Ti–C–O fibers (Fig. 6(a)). The interface between the mullite matrix and Si–Ti–C–O fibers contained a light colored precipitate (Fig. 6(b)). The EDX analysis for Si–Ti–C–O fibers and the interface indicates that: (1) the inside of Si–Ti–C–O fibers contained the elements of Si, C, O and Al; (2) the chemical composition of the interface without precipitate was more enriched in Al and O than that of the center of Si–Ti–C–O fiber and (3) the light color precipitate in the interface contained a relatively high concentration of Ti in addition to the elements of Si, Al, O and C. The above results suggest that Ti in fibers diffused into interfaces and Al in mullite diffused into fibers during hot-pressing. Similar EDX spectra were measured in the composites with 10 vol% fabrics hot-pressed at 1500°C but the interfaces were enriched in C than the inside of fibers. These results can be explained by the thermal decomposition of Si–Ti–C–O fibers in the mullite matrix above 1500°C.[12] In the observation of the interfaces of the mullite/Si–Ti–C–O fabric (6 vol%) composites hot-pressed at 1650°C by transmission electron microscopy (Fig. 8), the following phenomena were shown: (1) formation of thin graphite layer (30–50 nm) at interface and (2) formation of fine SiC particles (< 50 nm) in the Si–Ti–C–O fiber. The basal planes of graphite were parallel to the interface. The observation of graphite layer was also reported by Sato *et al.*[4] in the interfaces of the composites of mullite/cho ɔped Si–Ti–C–O fiber hot-pressed at 1650°C. In espect to the thermal stability of Si–Ti–C–O fibe , Yamamura *et al.*[13,14] reported that: (1) the oxygen content of Si–Ti–C–O fibers hot-pressed in Ar atmosphere decreases above 1500°C and reaches below 1 mass% at 1800–2100°C and (2) the atomic ratio of C/(Si + Ti) decreases from 1·5 to 1·0. Decomposition of Si–Ti–C–O fiber to form SiC–TiC fiber, therefore, releases excess carbon at the interfaces of the composites above 1500°C. The graphite layer formed would reduce the interface strength and enhance the debonding or pull-out effect of Si–Ti–C–O fibers. The precipitate enriched with Ti and the compositional gradient of Al element at the interfaces may also contribute to the improvement of mechanical properties.

Figure 9 shows a transmission electron micrograph of the mullite grains in the composites hot-pressed at 1650°C. The mullite matrix consisted of granular-shaped grains of 0·8–1·1 μm in size. Since the granular shape of mullite grains is correlated to little existence of glassy phase in the grain boundaries,[15,16] it may be expected to show high possibility of mechanical strength at high temperatures.

Fig. 9. TEM photograph showing granular-shaped mullite grains in the matrix of composites hot-pressed at 1650°C.

4 Conclusions

Laminated green compacts of mullite/Si–Ti–C–O fiber fabrics (6–30 vol%) were formed by the doctor blade method or filtration of aqueous mullite suspensions (40–52 vol% solid) containing 0·75 mass% of polyacrylic ammonium and 2·0 mass% of methyl cellulose against the weight of mullite at pH 8·5. These green compacts with 6–10 vol% fabrics were densified to nearly full density (>99% of theoretical density) by hot-pressing under a pressure of 39 MPa in a N_2 atmosphere at 1500–1650°C. Increase of the fabric content to 20 or 30 vol%, however, resulted in a delaminated porous composite. The fracture toughness of monolithic mullite hot-pressed at 1650°C (1.6 MPa $m^{0.5}$) was enhanced to 4·7 MPa $m^{0.5}$ in the composites with 10 vol% Si–Ti–C–O fabrics which showed a non-linear fracture behavior at room temperature. The strength of monolithic mullite (328 MPa) at room temperature decreased slightly with addition of Si–Ti–C–O fabrics to 292 MPa at 6 vol% and to 271 MPa at 10 vol% of fabrics. The composites with 20–30 vol% fabrics showed a non-linear fracture behavior but their strengths were significantly lower (59–78 MPa) compared to the strength of monolithic mullite. The improvement of mechanical properties in the mullite/Si–Ti–C–O fabric composites was interpreted by the thermal decomposition of Si–Ti–C–O fibers above 1500°C, which caused the diffusion of C and Ti from the fibers to the interfaces between Si–Ti–C–O fibers and mullite matrix of granular-shaped grains (~1μm). The diffusion of Al from mullite matrix to fiber was also observed. These change of composition, microstructure, and strength of the interface would enhance the debonding or pull-out effect of Si–Ti–C–O fibers in the composites.

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