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# Sintering Phenomena and Thermodynamic Analysis in the SiC Whisker-Reinforced Mullite Matrix Ceramic Composites During RF Plasma Sintering

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Mullite ceramics can be sintered by rf plasma sintering to densities as high as 97% compared to the theoretical density of the mullite, while SiC whisker-reinforced mullite matrix ceramic composites were not sintered by plasma sintering Decomposition of mullite occurs in a superficial regions at the outside surface of the specimen by volatilization of SiO at elevated temperature by plasma. SiC whiskers were destroyed, and the matrix was converted to alumina from SiC-whisker reinforced mullite matrix ceramic composites during the plasma sintering. Accelerated volatilization from the SiC whisker in the mullite prevents sintering. The volatile species are mainly SiC and CO gas species. The effects of plasma on mullite and SiC-whisker reinforced mullite matrix composites are interpreted by thermodynamic simulation of the volatile species in the plasma environment. The thermodynamic results show that the decomposition will not occur during hot pressing.

***Key words :*** Ceramic composites, Plasma sintering, Silicon earbide, Mullite decomposition

## I. Introduction

Engineering ceramics are considered for a variety of high temperature applications because of their high temperature capabilities such as strength, wear resistance, and chemical durability. The study of the ceramic matrix composites has been expanding to increase their toughness, which may extend their applications.[1,2] Laminated composites may be designed to produce functionally gradient materials for application such as heat exchanger tubes, high temperature bearings, etc.[3] Ceramics in the $Al_2O_3$-$SiO_2$ system are promising in high temperature applications because of their high melting point, stability, and corrosion resistance. Therefore, alumina or mullite composites are attractive for both electrical and structural applications. SiC whisker-reinfored mullite composites may be used for material design requirements,[3] and SiC whisker-reinforced mullite or alumina matrix composites show improved toughness over monolithic ceramics.[4]

The common method for the fabrication of CMC's (Ceramic matrix composites) is that impregnated fiber is passed through the matrix slurry, formed to the desired geometry, and then densified by hot pressing. It is known that SiC whisker-reinforced mullite matrix composite is hard to sinter because of covalent bonding of SiC and the rigid frame-work of the SiC whiskers prevent densification of the sinterable materials.[5-7] However, hot pressing is limited to small-scale use because of its low productivity and expensive maintenance.[8] Densification using microwave and plasma energy may be considered as densification techniques for these composites since these techniques can accomplish faster sintering in an ionized plasma environment. Plasma sintering has been investigated for ceramics such as alumina, silicon carbide, magnesia, and zirconia.[9-14] The densification of the SiC whisker reinforced mullite composites using a plasma source is considered to overcome the size and economic limits of the conventional hot press sintering method.

This paper addresses the sintering phenomena for the mullite and SiC whisker-reinforced mullite ceramic matrix composites, and compares them to conventional sintering by thermodynamic simulation.

## II. Experimented Procedure

Plasma sintering was performed in a water cooled fused silica unit as shown in Fig. 1. The plasma zone was generated Ar gas with a flow rate of 10 $cm^3$/sec at standard state. Power was supplied by a Lepel rf generator with 8 MHz and 8 KV and a three turn induction coil. Tape-cast mullite and 10 vol % SiC whisker-reinforced mullite matrix composites were cut from tape-cast laminated tubes (O.D. 45 mm, I.D. 35 mm, length 75 mm).[15] The specimens were heated in air at a rate of 2°C/min, and held 10-15 hrs at 600°C to eliminate organic binders used during tape casting, and then extented heating was

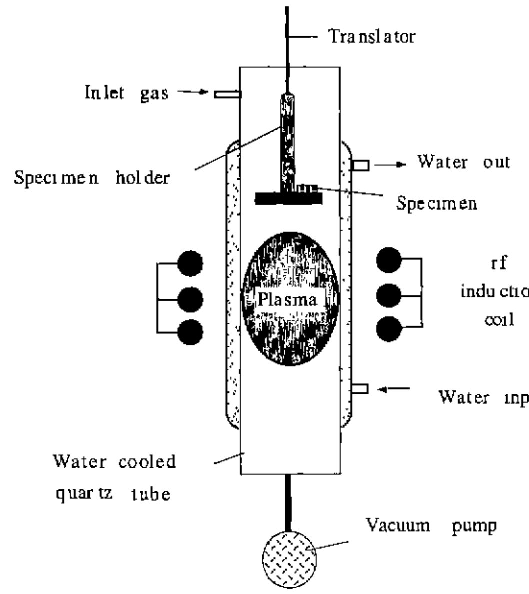


**Fig. 1.** Plasma sintering unit by Ar gas.

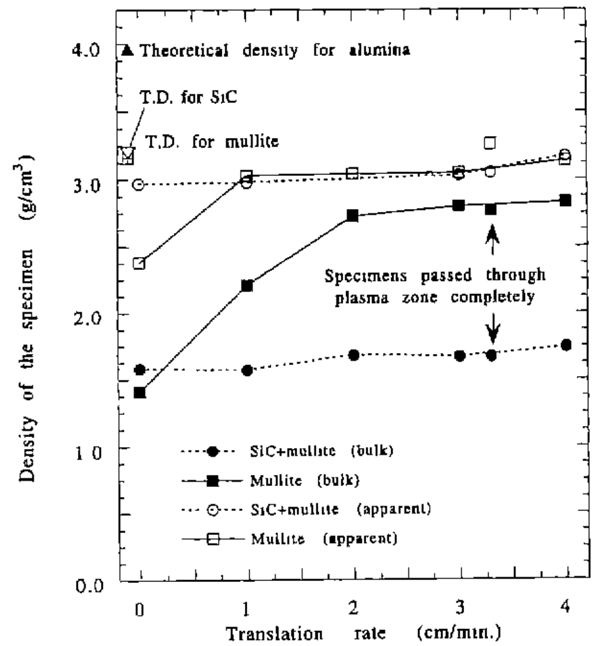


**Fig. 2.** Density changes for the mullite and SiC-whisker reinforced mullite ceramic composites after plasma sintering.

used up to 900°C to assure complete elimination of carbon. After binder burn out, the specimen was put into a water-cooled quartz tube, the system was evacuated to a pressure of 200 millitorr, and the plasma was ignited by controlled generator. After the plasma was stabilized, the sample with alumina tube was translated into the plasma formed near the rf induction coil. The translation rate was 1 to 4 cm/min, and the duration time of the exposure was within three minutes.

After plasma sintering, specimens were characterized by density measurement and Scanning Electron Microscopy with Energy Dispersive Spectroscopy analysis (EDS) and X-ray diffraction (XRD). Thermodynamic simulation was used to interpretate the reaction during plasma sintering in comparison to conventional hot pressing.

## III. Results and Discussions

### *1. Density*

Figure 2 shows the density changes of the specimens after plasma sintering. Because of the geometry of the plasma unit, the specimens which were translated at rates of less than 3 cm/min did not translate far enough into the plasma zone to completely sinter. The diagram shows that densification is essentially complete for samples translated 2 cm/min. or higher, even if they were not fully translated through the plasma zone.

In the diagram, filled symbols represent bulk densities, and open symbols represent solid densities which are not influenced by the open porosity of the specimens. Figure 2 indicates that the mullite specimens were densified close to their theoretical density.

However, SiC whisker-reinforced mullite matrix CMCs did not density and remained with as-received CMC (1.6 g/cm$^3$ after binder burn-out) in bulk density. The solid density of the CMC increases slightly with translation rate and has higher density than the theoretical density of mullite after complete translation. This diagram indicates that mullite can be densified by plasma, while SiC whisker reinforced composite is not densified.

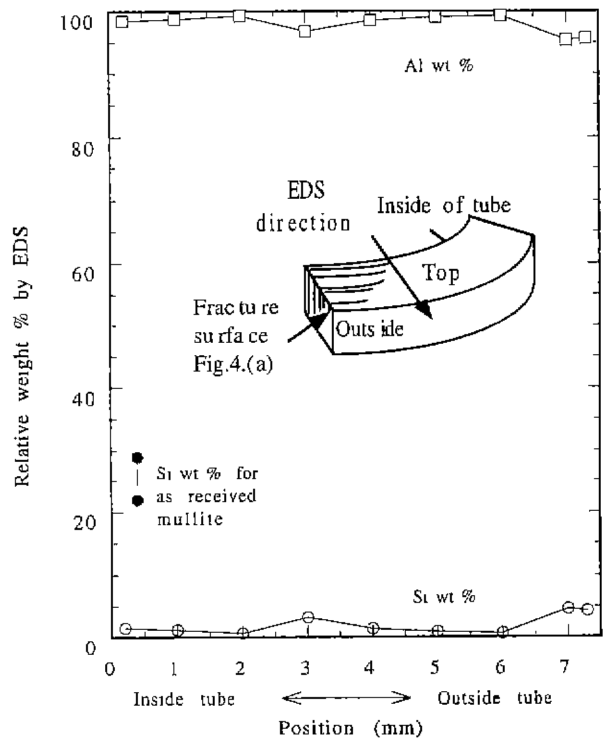


**Fig. 3.** Relative composition variation at the surface of the mullite specimen after plasma sintering.

### 2. *Plasma sintering of mullite*

Figure 3 shows EDS results from the surface of the mullite specimen which was passed through the plasma zone completely. The Si wt% from the surface of the specimen was much lower compared to the as-received materials and too low to be consistent with stoichiometry mullite. The microstructure from this specimen shows sintered structures through the transverse fracture surface as shown in Fig. 4(a). Fig. 4(b) shows the XRD pattern for this sample, which was ground from the bulk into powder. The XRD result shows that the bulk of the sample was identified as mullite with small amount of alumina. This indicates that plasma sintering of mullite ceramics completes the sintering with a small amount of decomposition on the surface of the specimen. The sintered solid-phase density of mullite was consistent with mullite but inconsistent with alumina as shown in Fig. 2.

Thermal decomposition of mullite at high temperature (1760°C at 1 atm, 1350°C at 50 torr) has been reported.[17,18] Possible decomposition of mullite in the plasma may occur by

$$Al_6O_{13}Si_2(s) = 2SiO(g) + O_2(g) + 3Al_2O_3(s) \qquad (1)$$

This decomposition only occurs in the superficial surface area of the mullite ceramics, and has no effect on the materials in the interior.

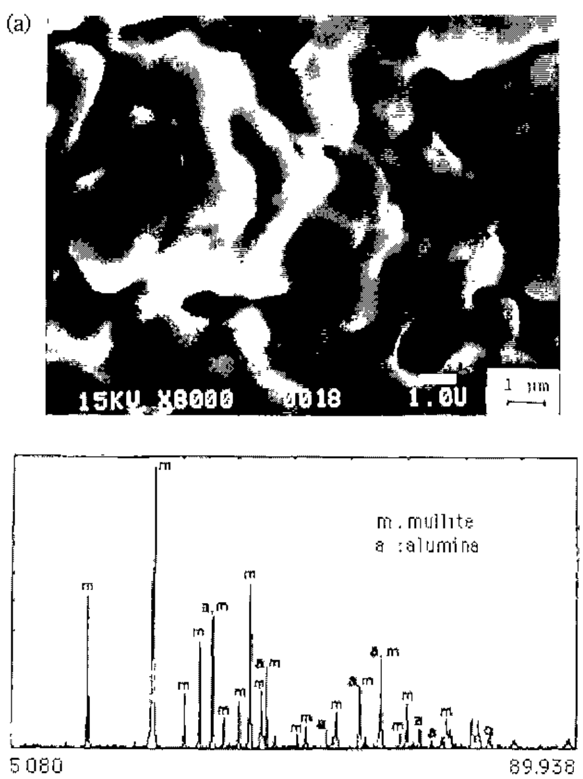


**Fig. 4.** (a) SEM micrograph observed from transverse fracture surface of the mullite after plasma sintering, (b) XRD pattern of the mullite specimen, which is ground into powder from the bulk specimen.

### 3. *Plasma sinteing of SiC whisker-reinforced mullite matrix ceramic composites*

The EDS analysis on the outside surface of the plasma sintered SiC whisker-reinforced mullite composite is shown in Fig. 5(a). The direction of the arrow in Fig. 5(a) shows the examined direction for EDS analysis. Only Al was detected except for the top side of the specimen

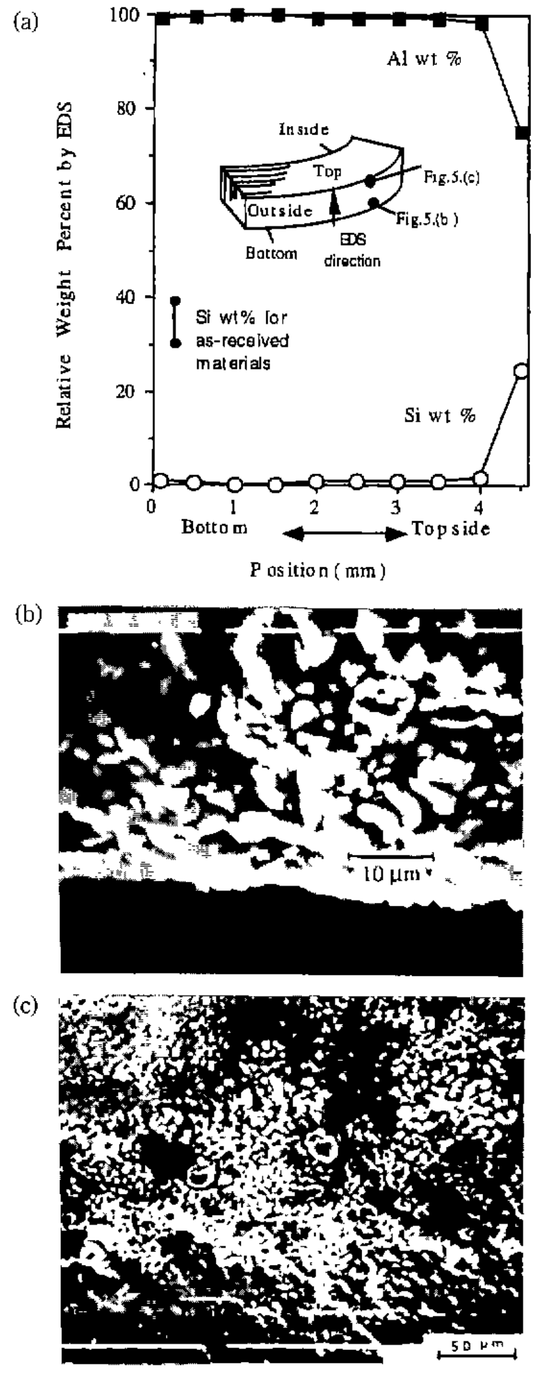


**Fig. 5.** (a) Relative composition changes at the outer surface of the sintered SiC-whisker reinforced mullite matrix composite passed through the plasma completely in Fig. 2, (b) The microstructure observed from the bottom side of the sample illustrated in (a), (c) Microstructure observed from the top side of the specimen illustrated in (a).

which was the last part of the sample to pass though the plasma during the plasma sintering. The microstructure of this sample shows a sintered structure, as shown in Fig. 5(b), at the bottom of side of the sample. However, near the top surface, which passed through the plasma last, it shows some deposits as shown in Fig. 5(c). This may indicate that there is an evaporation from SiC whisher-reinforced composites, and these evaporated species are redeposited on the top side of the outside surface. Figure 6(a) shows EDS analysis performed at the fracture surface of the composite specimen, which passed through the plasma zone completely as shown in Fig. 2. EDS shows that Si wt% on the outside is lower than the center of the fracture surface. The microstructure of the outside of the fracture surface illustrated in Fig. 6(b) shows sintered structure only within 10 μm of the surface, where no SiC whiskers were found. The microstructure at the center of the fracture surface, illustrated in Fig. 6(c), is the same as that of as-received structures with SiC whiskers visible

The reaction of the SiC with mullite at elevated temperature has been reported.[18-22] The possible decomposition of the SiC whisker-reinforced mullite composites in the plasma may occur by

$$Al_6O_{13}Si_2(s) + SiC(s) = CO(g) + 3SiO(g) + 3Al_2O_3(s) \qquad (2)$$

The reaction between mullite and SiC whisker was accelerated with the very short time within 3 minutes in the plasma. This results differ from the conventional sintering reaction which could be related to plasma characteristics.

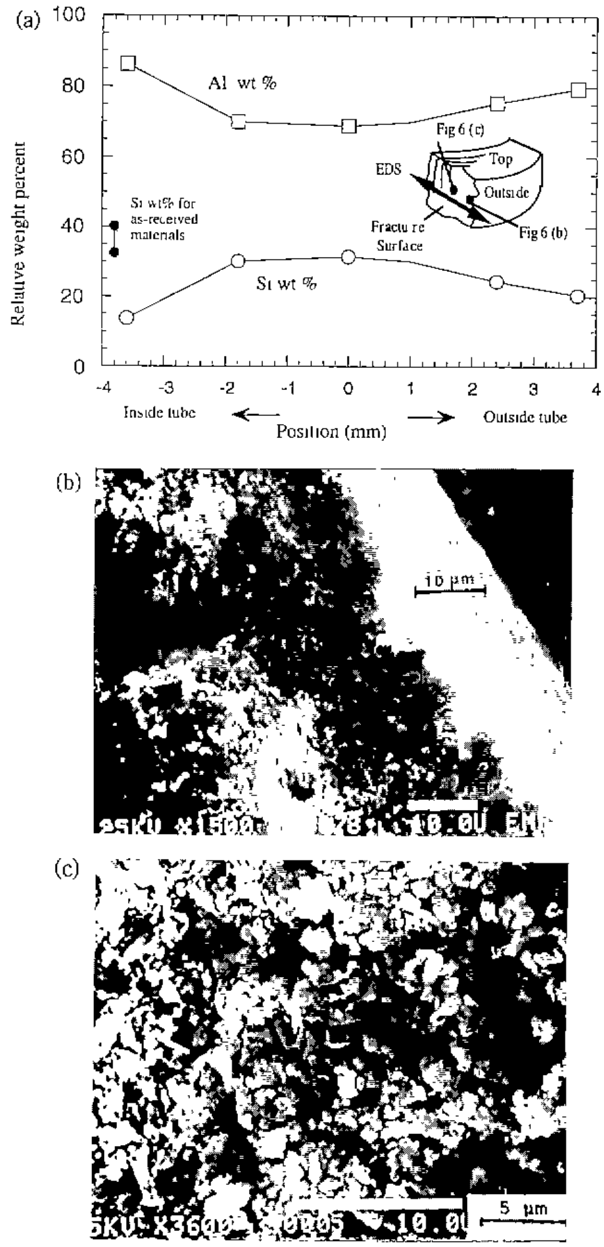


**Fig. 6.** (a) EDS analysis from the fracture surface of the SiC-whisker reinforced mullite matrix composite, which passed through the plasma zone completely, (b) Microstructures from the outside of the fracture surface of the SiC whisker-reinforced mullite matrix composite in (a), (c) The microstructure from the center of the specimen illustrated in Fig. 6(a).

### 4. *Themodynamic simulation*

There is a thermodynamic driving force for the decomposition reaction when the total pressure of the decomposition products exceeds the total pressure in the plasma system, 500 millitorr. The SOLGASMIX computer program[23] allows one to predict the decomposition of mullite and SiC and to compare conventional hot pressing sintering and plasma sintering for the SiC whisker reinforced mullite composites. This program calculates the amount of species present at the state with the lowest Gibbs free energy. For the simulation the STEPSOL program, modified for PC, was used.[24] The program can simulate input species and reactants defined by user.

Figure 7 shows the simulated result for the mullite plasma sintering at the temperature range from 1400 K to 3000 K at a total pressure of 500 millitorr. Figure 7(a) shows the condensed phases, while Fig. 7(b) shows the gas species in the system. The mullite is predicted to decompose into $Al_2O_3$ at 2300 K as shown in Fig. 7(a). In the temperature range where the decomposition occurs, most of the volatile species are SiO(g) and oxygen gas species, which become significant in comparison to the total pressure in the system. At higher temperatures, aluminum and atomic oxygen are formed because of alumina decomposition. This simulation confirms that decomposition of mullite occurs in the plasma by Eq. (1).

Figure 8 is the thermodynamic simulation results for the mullite with added 10 mole % SiC under the same conditions as in Fig. 7. Partial mullite decomposition occurs, and SiC drops to zero at 1500-1600 K, while alumina rises. At 2300 K, the remaining mullite decomposes into alumina similar to the behavior shown in Fig. 7(a). As shown in Fig. 8(b), SiO(g) and CO(g) rise sharply between 1400 K to 1600 K, while above 2300 K the oxygen content increases and CO(g) falls. The simulation in Fig. 8 indicates that decomposition of SiC whisker-reinforced mullite composite occurs by Eq. (2).

Figure 9 shows calculated results for the mullite with added 10 volume % SiC under the same conditions as in Figs. 7 and 8. The mullite and SiC start to decompose at 1400 K, and more mullite decomposition occurs than in the 10 mole % SiC case in Fig. 8. Most of the volatile species are SiO(g) and CO(g) at the decomposition temperature range, which shows the same trend with 10 mole% SiC in mullite as shown in Fig. 8. More gas phase CO is formed because more SiC is in the system. When more SiC is added, more decomposition occurs as shown in Figs. 8 and 9.

The series of simulations make it possible to explain the sintering of mullite and decomposition from SiC

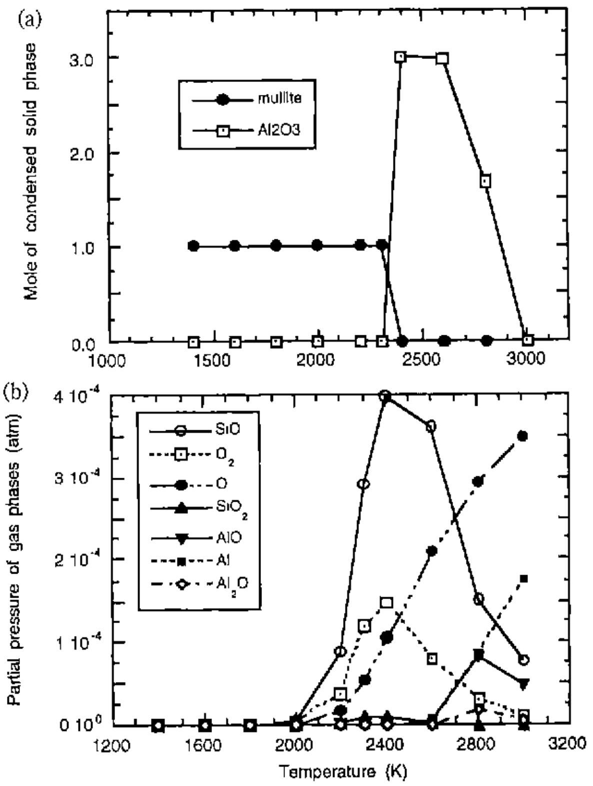


**Fig. 7.** Simulated equilibrium states for the mullite at the temperature range from 1400 K to 3000 K at a total pressure of 500 milli torr in Ar plasma: (a) decomposition of condensed phase (mullite) at 2300 K, (b) Volatile gas species formed with reaction of mullite.

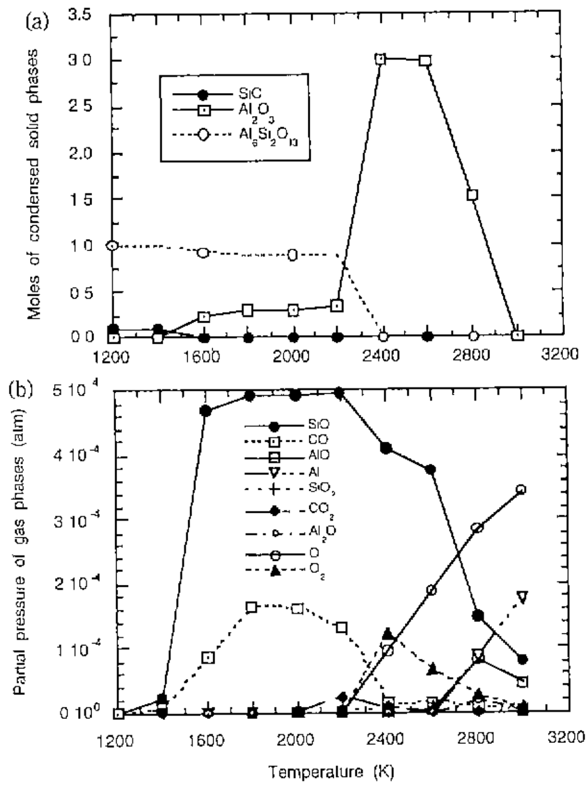


**Fig. 8.** Simulated equilibrium states for the 10 mole% SiC whisker-reinforced mullite matrix composite at the temperature range from 1200 K to 3000 K at a total pressure of 500 milli torr in Ar plasma: (a) decomposition of condensed phase (mullite and SiC) starts at 1400 K, (b) Volatile gas species formed with reaction of SiC reinforced mullite matrix composite.

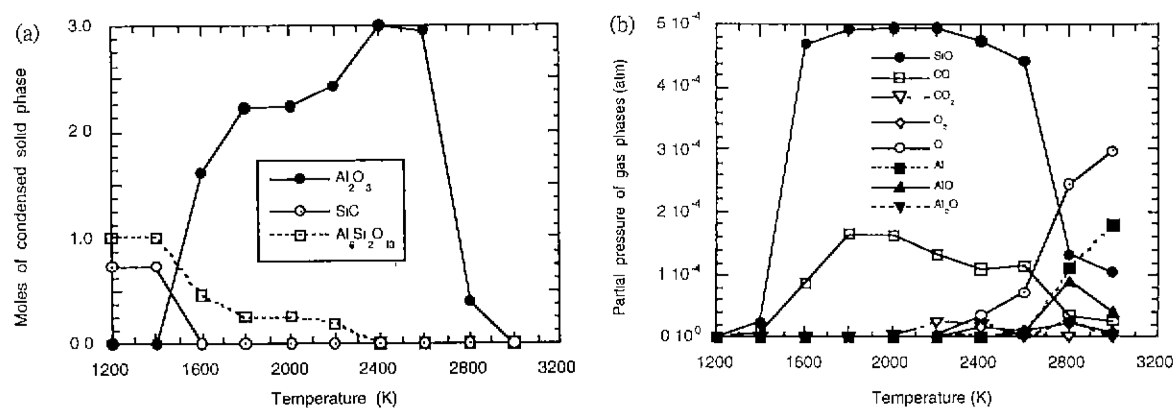


**Fig. 9.** Simulated equilibrium states for the 10 volume% SiC whisker-reinforced mullite matrix composite at the temperature range from 1200 K to 3000 K at a total pressure of 500 milli torr in Ar plasma: (a) decomposition of condensed phase (mullite and SiC) starts at 1400 K, (b) Volatile gas species formed with reaction of SiC reinforced mullite matrix composite.

whisker-reinforced mullite matrix composites in the plasma environments. For mullite, endothermic decomposition of mullite occurs by Eq. (1) forming SiO(g), $O_2$(g), and $Al_2O_3$(s). Simulated equilibrium pressure of gas phases for the mullite system exceeds the plasma chamber pressure at 2300 to 2400 K which implies that the temperature would be high enough to sinter the mullite samples before decomposition begins during the plasma sintering. In other words, because the decomposition temperature is above the melting point of mullite, there is no significant hindrance for mullite sintering in the plasma environment. For SiC whisker-reinforced mullite matrix composites, endothermic decomposition of SiC in mullite occurs by Eq. (2) forming SiO(g) and CO(g) at 1500 to 1600 K. The decomposition temperature for SiC whisker-reinforced mullite composite is too low to permit the densification of the sample in the plasma. Input heat by the plasm is contributed to the SiC volatilization not to the sintering of the sample. Therefore, composite samples do not reach high enough temperature for the rapid sintering, but they consume the input energy to the decomposition reaction by Eq. (2).

### 5. *Pressure effect*

The successful densification of SiC-reinforced ceramic matrix composites by hot pressing can be explained by the effect of pressre on the reaction, Eq. (2). Plasma sintering is usually performed at low pressure, however conventional sintering is at atmospheric pressure and hot pressing is at elevated pressure. Pressure was considered for simulation as 500 millitorr for the plasma environment, 1 atm for the atmospheric sintering, and 250 atm for typical hot pressing.

Figure 10 shows the effect of pressure on the mullite densification. As shown in Fig. 10, the plasma environment lowers the decomposition temperature about 200 K compared to higher-pressure environments. There is little difference between the two high pressure environments.

Figure 11 shows the simulated pressure effect of the mullite decomposition containing 10 mole % and 10 volume % SiC. The diagram shows moles of mullite phase with respect to temperatures with different sintering atmosphere. As shown in Fig. 11, in the plasma environment, decomposition occurs at 1400 and 1600 K for the composites containing 10 mole % and 10 volume % SiC respectively. More decomposition of mullite occurs when more SiC is added. The decomposition temperature rises to 2000 K at 1 atm for both composites containing 10 mole % and 10 volume % SiC. When the pressure was raised to 250 atm for the hot pressing condition, the decomposition temperature was raised to 2200 K for composites containing 10 mole % SiC. Figures 10 and 11 show lower decomposition temperatures for SiC-reinforced mullite composite than that for mullite alone in the plasma environment, while SiC has little effect in

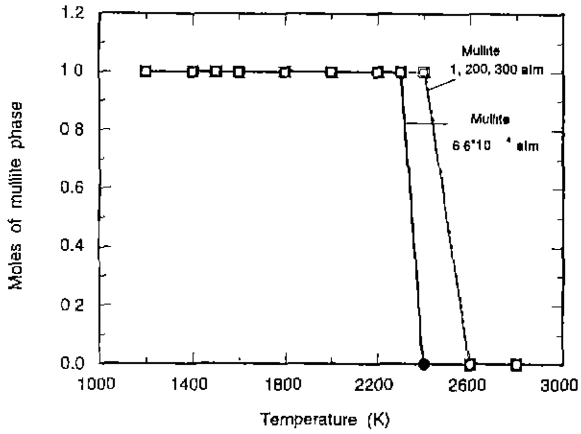


**Fig. 10.** Pressure effects on the decomposition of mullite

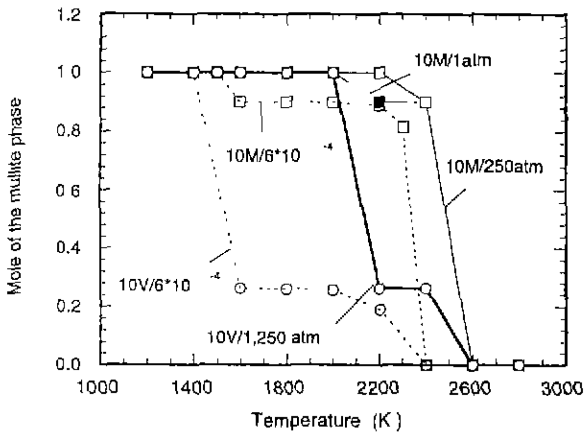


**Fig. 11.** Pressure effects on the decomposition reaction (Eq. 2) in SiC-reinforced (10 mole% and 10 volume%) mullite matrix composite $6.6*10^{-4}$ atm (plasma), 1 atm (conventional atmospheric sintering), and 250 atm (hot pressing).

**Table 1.** Enthalpy Changes of the Decomposition Reaction from Mullite and Mullite with Added SiC

| Equation | Temperature (K) | $\delta H_f^o$ (KJ/mole) |
|---|---|---|
| 1 | 2300 | 1531.0 |
| | 2400 | 1527.1 |
| 2 | 1500 | 1405.4 |
| | 1600 | 1394.4 |

the hot pressing enviroment. Therefore, SiC acts as a reducing agent in the system and increases the rate of decomposition of the mullite composite. Second the decomposition temperature for hot pressing is sufficiently high to produce densification of the SiC reinforced mullite composite, therefore, Eq. (2) cannot hinder the sintering in hot pressing or conventional sintering at atmospheric pressure because densification is completed before decomposition of SiC whisker reinforced mullite matrix ceramic composite occur.

In the plasma environment, the significance of the hindrance of the densification of SiC mullite composite over conventional sintering is that the evaporation of SiC in the mullite is an endothermic reaction, as shown in Table 1. The input heat is contributed by the plasma to the SiC volatilization, not to the sintering of the whole composites.

## IV. Conclusions

It is feasible to plasma sinter mullite ceramics, while it is not feasible to plasma sinter SiC whisker reinforced mullite matrix ceramic composites because the decomposition temperature of the reaction between the mullite and SiC is lower in the composites. The decomposition reaction produces alumina and SiO(g) for mullite. Alumina, SiO(g), and CO(g) were produced for SiC reinforced mullite composite. Energy input by the plasma can sinter the mullite ceramic while thermally decomposing the exterior surface of the samples, while endothermic decomposition in SiC-reinforced mullite composite consumes the input energy before the composite sample reaches the temperature for sintering. SiC-reinforced mullite composites cannot be sintered by rapid plasma sintering but can be sintered by the hot pressing technique because the higher pressure raises the decomposition reaction up to temperatures of 2200 to 2400 K.

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