

Chemical reactions in mullite matrix SiC whisker reinforced composites in RF plasma

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Decomposition of mullite by volatilization of SiO occurs during elevated temperature exposure to reducing gases. RF induction coupled argon plasma power sources have been used for rapid sintering of a number of ceramics and ceramic matrix composites. During plasma sintering of SiC whisker reinforced mullite matrix composites, whiskers were destroyed and the matrix converted to alumina by accelerated volatilization of silicon containing species. The results of these experiments are interpreted through the use of thermodynamic calculations of SiO pressures in the plasma environment.

1. Introduction

Ceramic matrix composites (CMCs) have superior properties to monolithic engineering ceramics for a number of high temperature applications. In particular, the fracture toughness of ceramic matrix composites is often higher than that of monolithic ceramics. The morphology of the reinforcing phase and the properties of the interface between the reinforcing phase and the matrix can be controlled to optimize the fracture toughness in a given system [1].

Ceramics in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system such as mullite are useful in high temperature oxidizing environments because of their high melting points, thermodynamic stability, and resistance to many corrosion reactions [2]. The toughness and thermal conductivity of mullite are both low, however, so this material is of limited use in applications which involve high stresses or heat flux. SiC and Si_3N_4 whiskers can be synthesized inexpensively and are particularly effective as reinforcements in CMCs because of their morphology [3]. The addition of a carbide reinforcing phase to an oxide matrix ceramic permits the properties of the CMC to be controlled in order to optimize its thermal and mechanical properties [4].

CMCs are fabricated by mixing the phases in the appropriate geometry and then densifying the matrix by sintering or hot pressing. Low pressure sintering of SiC whisker reinforced CMCs with whisker contents greater than 10 vol % has usually been unsuccessful because of the formation of a stiff network of intersecting SiC whiskers which resists densification unless external pressure is applied [5, 6]. As a result, SiC whisker reinforced oxide matrix CMCs are generally densified by hot pressing and the cost and size limitations of this process have limited the application of these materials.

Advanced densification techniques based on microwave or plasma energy may be useful in the fabrication of such composites. Plasma sintering has been

used to produce rapid densification of alumina [7], magnesia [8], Zirconia [9], and silicon carbide [10]. Therefore, it is reasonable to expect that plasma sintering could be used to densify composites of these materials. If successful, plasma sintering could be used to fabricate CMCs in larger sizes than can be produced economically by hot pressing.

The thermal expansion coefficients of SiC and mullite match closely, so the residual stresses which develop during cooling from the processing temperature in SiC reinforced mullite matrix composites are smaller than those in alumina matrix composites. This makes CMCs in the SiC–mullite system easier to fabricate than those in the SiC–alumina system. Unlike alumina, which is thermodynamically stable to very high temperatures, mullite can thermally decompose at elevated temperatures with the evolution of silicon monoxide [11, 12]. Therefore, chemical reactions between the matrix and reinforcing phase are likely to be more important in SiC–mullite composites than in SiC–alumina composites [13]. This paper describes the results of experimental studies on densification of mullite matrix SiC reinforced composites by plasma sintering and the resulting whisker–matrix reactions.

2. Apparatus and procedures

Plasma sintering was performed in argon at a pressure of approximately 67 Pa fed into a water-cooled fused-silica tube. Fig. 1 is a schematic diagram of the plasma sintering apparatus. Power was provided by a Lepel radio frequency (RF) generator with a 30 kVA power capability operating at 8 MHz and 8 kV and using a three-turn induction coil centred around the outside of the fused-silica tube.

Samples of mullite or SiC whisker reinforced mullite were fabricated at the Center for Advanced Materials at the Pennsylvania State University using a slip casting technique and wound around a mandrel to

produce a tube geometry suitable for use in high temperature heat exchangers [14]. In the green state, the materials had sufficient strength for normal handling and could be cut with a band saw. Test coupons with geometries as shown in Fig. 2 were cut from the tubes in the green state. Before plasma sintering, the samples were placed on alumina holders and heat treated in air to burn out binders used in the tape fabrication. The binder burn out procedure consisted of heating at $2^{\circ}\text{C min}^{-1}$ to 600°C and holding for 15 h at 600°C , followed by heating at $1.5^{\circ}\text{C min}^{-1}$ to 900°C before furnace cooling to room temperature. After binder burn out, the samples were fragile and

were not removed from the holders until plasma sintering was complete. The mullite produced in this manner was slightly alumina rich. A scanning electron micrograph of the microstructure of the unsintered material after binder burnout is shown in Fig. 3.

To begin each experiment, the silica tube was purged with Ar and evacuated to approximately 27 Pa. An argon flow of $10\text{ cm}^2\text{ s}^{-1}$ (STP) was started through the tube, and the plasma was ignited by activating the RF coil. The pressure in the system typically rose to approximately 67 Pa after ignition. When the pressure had dropped to 47 Pa, the sample was translated into the plasma zone on a

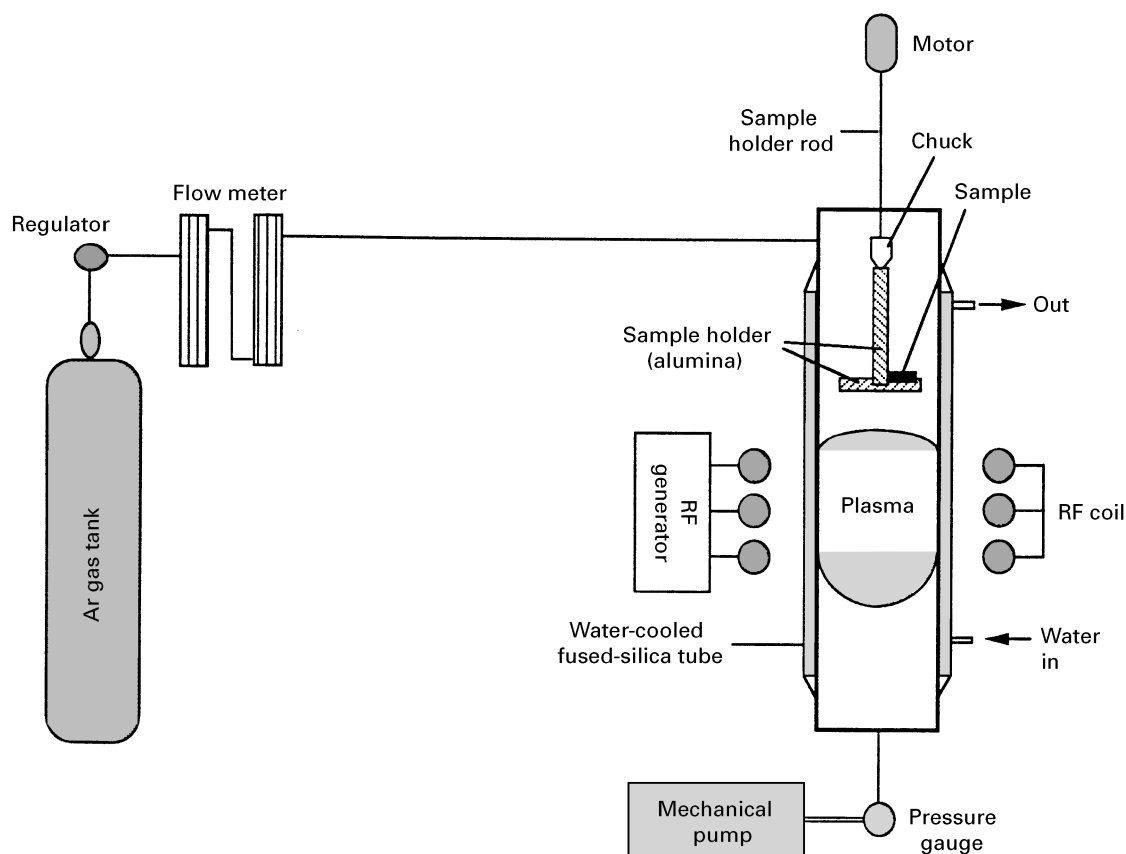


Figure 1 Schematic diagram of plasma sintering apparatus.

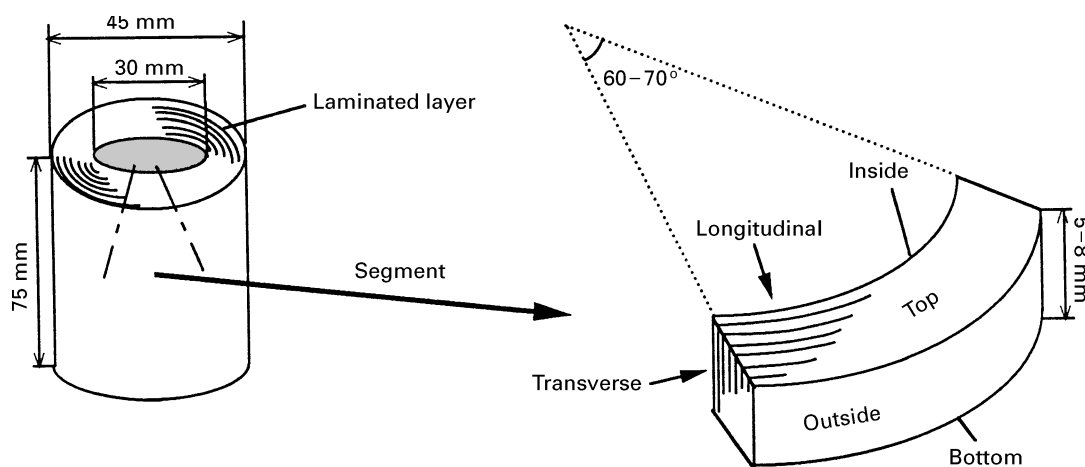


Figure 2 Geometry of test samples for plasma sintering of tape cast SiC whisker reinforced mullite matrix composite tubing.

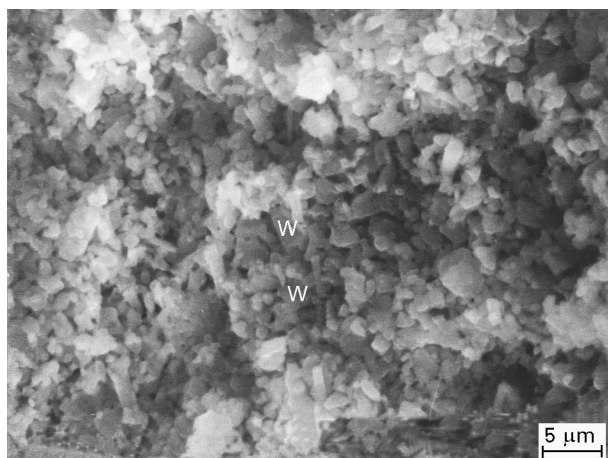


Figure 3 Scanning electron micrograph of microstructure of SiC whisker reinforced mullite matrix composite after binder burnout.

rotating alumina holder as shown in Fig. 1. The pressure in the chamber typically rose to 67 Pa or more again when the sample entered the RF coil. The samples were translated through the reaction tube at a rate of 1 to 4 cm min^{-1} producing an exposure of 3 min for samples which are translated fully through the coil at the lowest rate. The sintered specimens were characterized by measurement of the density and by examination by scanning electron microscopy (SEM), and microchemical analysis by energy dispersive X-ray spectroscopy (EDS).

3. Results and discussion

3.1. Densification

In order to evaluate the capability of the plasma furnace to sinter SiC/mullite composites, a series of experiments were performed in which specimens of mullite and SiC whisker reinforced mullite containing approximately 10% SiC whiskers, were translated into the plasma for 60 s each at increasing translation rates. The bulk densities of the samples after treatment are shown in Fig. 4 as a function of translation velocity. The initial densities of the materials were 1.4 and 1.6 g cm^{-3} , respectively. Because of the geometry of the system, it is likely that the samples translated at 1 cm s^{-1} did not fully enter the RF plasma. All of the mullite specimens translated at higher rates were densified to approximately 90% of the theoretical value, while there was no effect of the treatment on the bulk densities of the SiC whisker reinforced mullite composites. This indicates that while the plasma treatment is suitable for densifying mullite, it is not effective for densifying the SiC whisker/mullite matrix composite.

3.2. Chemical and structural changes during sintering

Samples of mullite and SiC whisker reinforced mullite which had been translated through the plasma at 3 cm min^{-1} were subjected to microstructural and elemental analysis in a scanning electron microscope. The surface of the mullite specimen was porous as

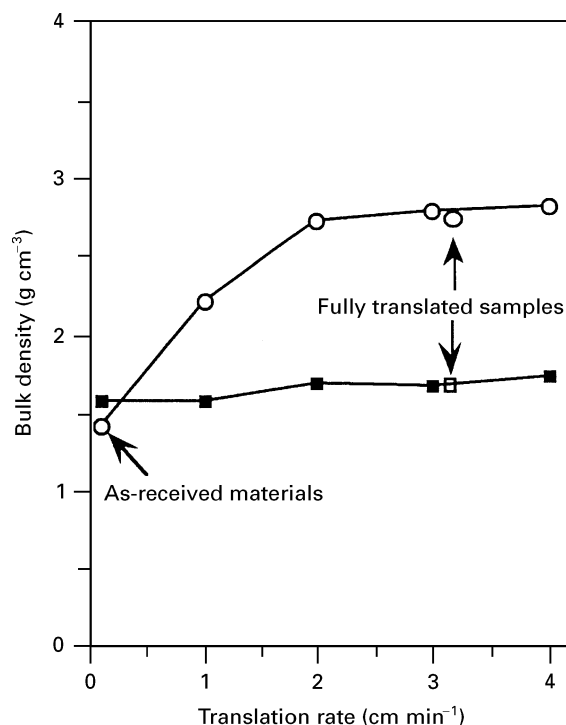


Figure 4 Effect of translation through RF plasma on densification of mullite and SiC whisker reinforced mullite matrix composite: ■ - SiC + mullite; —○— mullite.

shown in Fig. 5. EDS microanalysis showed that all of the silicon had been removed from this surface, so that the remaining composition was essentially aluminium oxide. Silicon depletion from the mullite sample was a superficial phenomenon, however. The interior of the sample was fully dense, and X-ray diffraction analysis of the sample produced Bragg reflections characteristic of mullite.

SEM examination of the SiC whisker reinforced mullite matrix composite after plasma treatment also showed that the surface was depleted of silicon. However, the depth of the depletion was greater and there was no densification of the interior of the sample. Fig. 6 shows the relative Al and Si compositions determined by EDS microanalysis across a fracture surface of the SiC/mullite composite after plasma treatment. Si depletion is noted at locations several mm from the exterior surface. The interior of the SiC whisker reinforced mullite composite was porous and retains the microstructure of the green compact. Fig. 7 is a scanning electron micrograph of the region of the fracture surface near the exterior surface. Sintering has occurred only within the outer 10 μm of the composite, and this region has not densified. Note that no SiC whiskers are visible in the region near the exterior surface, while in the interior of the sample, the structure is nearly unchanged from the condition after binder burnout as shown in Fig. 8.

3.3. Deposits

At the conclusion of the experiments, dark deposits were observed to have formed on the walls of the fused-silica reaction tube. Loose deposits were removed from the walls of the tube and subjected to

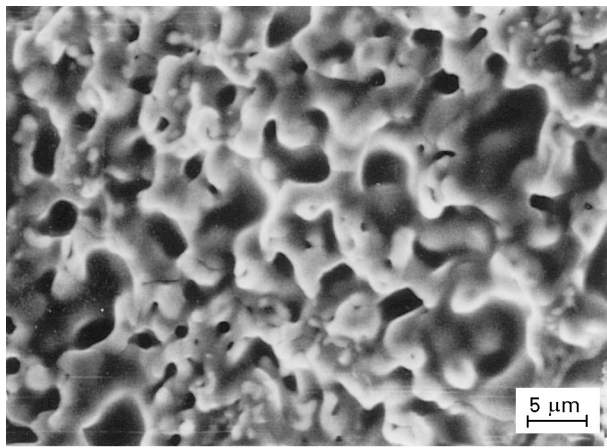


Figure 5 Scanning electron micrograph of surface of mullite specimen after plasma sintering.

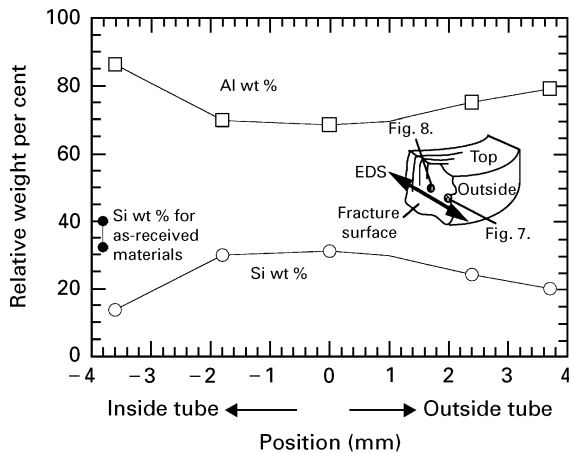


Figure 6 Relative Al and Si compositions across fracture surface of SiC whisker reinforced mullite matrix composite specimen after plasma treatment.

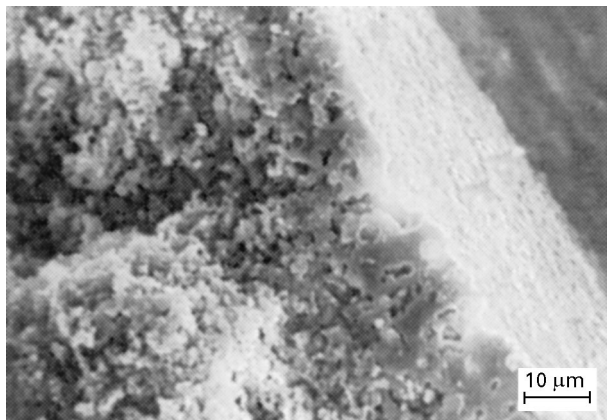


Figure 7 Scanning electron micrograph of near surface region on fracture surface of SiC whisker reinforced mullite matrix composite after plasma treatment.

analysis by X-ray diffraction and EDS. EDS analysis detected only silicon, and X-ray diffraction detected primarily Bragg reflections characteristic of cristobalite. After the deposits were held in an oxidizing environment at 900 °C for 24 h, they lost their dark colour. This suggests that the dark colour was due to

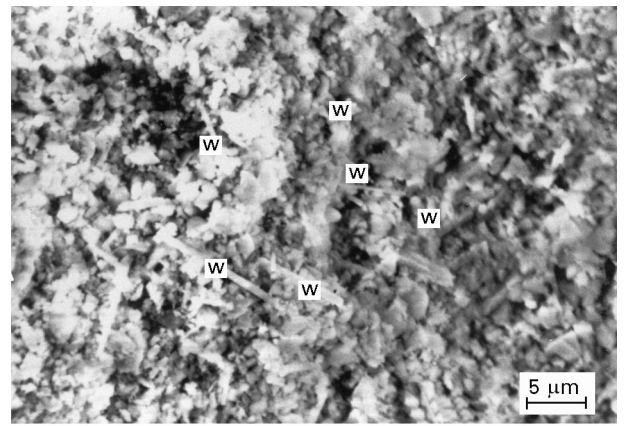
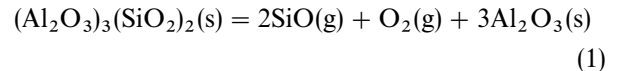


Figure 8 Scanning electron micrograph of interior of fracture surface of SiC whisker reinforced mullite matrix composite after plasma treatment.

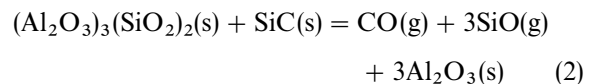
carbon in the deposits which was removed by the oxidizing treatment. The deposits consist largely of carbon and silica, which volatilize from the specimens during plasma treatment and deposit on the water cooled walls of the reaction chamber.

4. Thermodynamic considerations

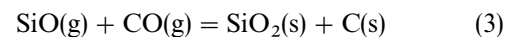
Plasma sintering of mullite is complicated by the possible thermal decomposition of the specimens according to Reaction 1:



EDS microanalysis indicated that this reaction had occurred on the surface of the mullite specimens. When the same process is applied to a SiC reinforced mullite matrix composite, the thermodynamic driving force for Reaction 2 exceeds that of Reaction 1:



In effect, the SiC reacts with the SiO₂ in the mullite to form the volatile species CO and SiO [15]. The activity of silica in the mullite is not sufficiently low to suppress this reaction. The failure of the composite to sinter under plasma conditions may be related to the chemistry of these reactions. The SiO and CO produced in Reaction 2 undergoes a reverse reaction when it diffuses to the water-cooled walls of the reaction chamber where it produces deposits according to Reaction 3



The endothermic nature of Reactions 1 and 2 may limit the effectiveness of plasma sintering under the low pressure conditions prevailing in the RF plasma reactor. The SOLGASMIX computer program was used to predict the effects of high temperature on the dissociation of mullite alone and in the presence of SiC [16]. The program was used in the form of the STEP-SOL program for IBM-based personal computers provided by the University of Missouri at Rolla.

Fig. 9 shows the results of calculations performed on mullite at temperatures between 1200 and 3000 K at a total pressure of 66.65 Pa (6.6×10^{-4} atm.). While mullite is stable at temperatures below 2300 K, at higher temperatures, it breaks down according to Reaction 1 leading to production of alumina and SiO vapour. Fig. 9 shows the partial pressures of the vapour species which are produced by the sintering

process under conditions prevailing in the plasma furnace. The calculations indicate that at temperatures above 2300 K, the vapour pressure of SiO and partial pressures of O₂ become significant in comparison to the total pressure in the system.

Fig. 10 shows the results of similar calculations performed for a mixture of mullite plus 10 mol % SiC performed under the same conditions. Fig. 10 shows

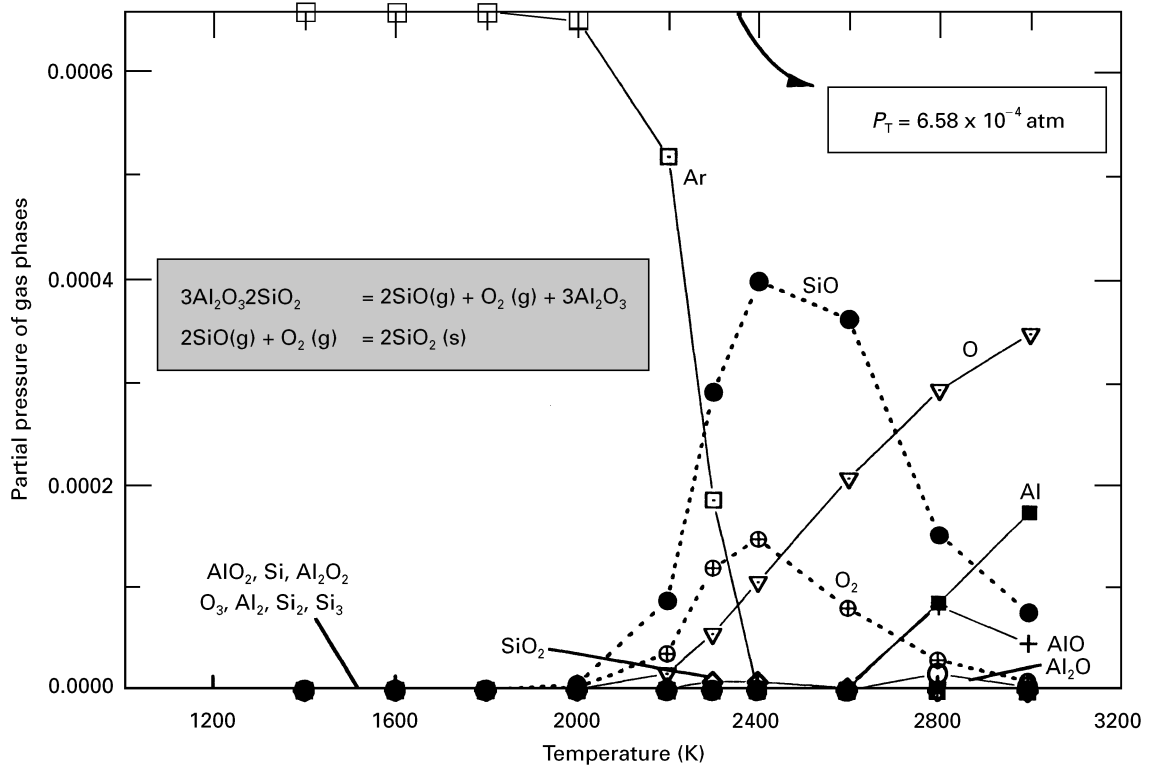


Figure 9 Vapour species formed during reaction of mullite with Ar plasma at temperatures between 1200 and 3000 K.

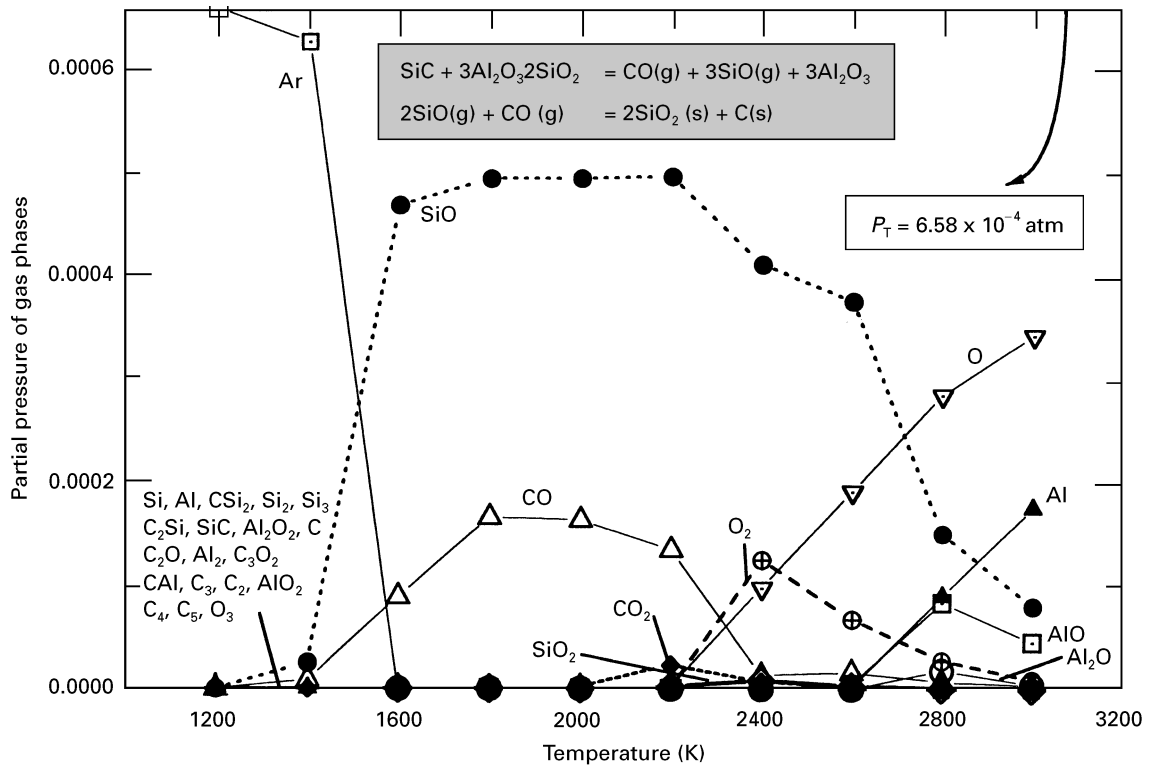


Figure 10 Vapour species formed during reaction of mullite and SiC with Ar plasma at temperatures between 1200 and 3000 K.

the partial pressures of the vapour species which are produced by the sintering process. In this case the SiO and CO contents of the gas phase rise sharply between 1400 and 1600 K, consistent with Reaction 2. Above 2300 K, the O₂ content of the gases rises and that of CO falls as Reaction 1 begins to occur and decompose the balance of the mullite.

The effect of SiC additions to the mixture can be interpreted as favouring the decomposition of mullite to form vapour species by providing excess silicon and carbon which reduce silica in the mullite to SiO vapour. Because both Reactions 1 and 2 are highly endothermic (Reaction 1 has an enthalpy change of 1530 kJ mol⁻¹ at 2300 K, while Reaction 2 has an enthalpy change of 1405 kJ mol⁻¹ at 1500 K), this has a drastic effect on the effectiveness of plasma sintering. Sintering occurs rapidly in plasma because energy can be transferred from the plasma into the sintering surfaces at a higher rate than in conventional processes. When decomposition of mullite occurs during plasma sintering, the energy absorbed by the endothermic reaction consumes the energy transferred by the plasma and effectively limits the maximum temperature which can be produced. In the case of mullite alone, the decomposition can only occur at temperatures above 2300 K, well above the melting point of mullite and high enough that it does not interfere with the rapid sintering process. In the case of composites containing SiC, the decomposition can begin at temperatures as low as 1500 K. This is too low a temperature to produce rapid sintering and therefore, no densification occurs until the reaction is complete and all of the SiC has been consumed by the reaction.

The successful fabrication of mullite matrix-SiC reinforced ceramic matrix composites by hot pressing can be explained by consideration of the effect of pressure on Reaction 2. While decomposition according to Reaction 2 would be expected to occur at 1400 to 1600 K under the low pressure conditions prevailing in the plasma furnace, increasing the total pressure to 1.013 × 10⁵ Pa (1 atm) would raise the temperature at which Reaction 2 is significant to 2000–2200 K, and raising the pressure to 253.25 × 10⁷ Pa typical of many hot pressing systems would raise the threshold temperature to 2400 K. These temperatures are sufficiently high to produce densification of the mullite. Therefore, these reactions would not be expected to hinder the fabrication of mullite matrix-SiC

reinforced CMCs by hot pressing or by conventional sintering at atmospheric pressure.

5. Conclusions

It is not feasible to plasma sinter SiC whisker reinforced mullite matrix CMCs because of chemical reactions between the mullite and the SiC in the plasma environment. The reaction leads to the consumption of the SiC and conversion of the mullite to alumina, and is sufficiently endothermic to limit the temperature of the system to a level too low to produce rapid sintering. The high pressures used in hot pressing systems suppress this reaction up to temperatures high enough to produce densification.

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