

# Processing of a Silicon-Carbide-Whisker-Reinforced Glass-Ceramic Composite by Microwave Heating

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A calcium magnesium aluminosilicate-based glass that contained 10 wt% of silicon carbide whiskers ( $\text{SiC}_w$ ) as reinforcement was prepared by tape casting, followed by sintering either in a conventional furnace or in a microwave oven. The results were consistent with retardation of glass sintering through whisker bridging. The glass, by itself, was sintered to almost-full density at 750°C for 4 h by conventional furnace sintering; the best sintered composite, with an estimated density of ~90%, was obtained at 800°C with a dwell time of 4 h. Sintering at a temperature of >800°C did not improve the densification but rather resulted in severe whisker oxidation. A reduced densification rate was observed for the samples that were sintered in nitrogen. By contrast, in the microwave oven, almost-full density for the glass and ~95% of the theoretical density for the composite were obtainable at 850°C for 15 min, which represented a reduction of ~10 h of the total processing time and a reduced  $\text{SiC}_w$  oxidation.

## I. Introduction

WHISKER reinforcement has been identified as one of the major methods to toughen ceramics or glass matrices and improve their reliability. Whenever silicon carbide ( $\text{SiC}$ ) or silicon nitride ( $\text{Si}_3\text{N}_4$ ) whiskers are used in air sintering, they suffer from oxidation at temperatures of >700°C. Moreover, because of their particularly elongated shape, whiskers have a tendency to bridge during sintering, retarding or even stopping matrix densification. As a result, hot pressing is usually applied to effect the composite densification.

Microwave energy has been used increasingly in the past decade to sinter ceramics. Because the microwave energy is dissipated throughout the sample, which results in volumetric heating rather than through-surface thermal conduction, such as that in conventional heating, the temperature distribution inside the sample has a tendency to be more uniform and the interior of the sample has a tendency to be hotter than the surface.<sup>1</sup> These characteristics permit rapid heating with a reduced risk of cracking from thermal stress. However, many ceramics have low dielectric loss factors, absorb microwave poorly, and, hence, are difficult to heat; this is especially true in the low-temperature region. Therefore, it is not unusual that a combination of conventional and microwave heating is used.<sup>2</sup> This hybrid heating has an additional advantage of allowing the temperature profile inside a sample to be optimized. Because of

the varied dielectric loss factors of different materials, which leads to the preferential absorption of microwave energy by the more-lossy components, selective heating by microwave also is possible.

In the current work, we have studied a calcium magnesium aluminosilicate ( $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2$ , CMAS) glass that has been reinforced with silicon carbide whiskers ( $\text{SiC}_w$ ). In conventional furnace sintering, these whiskers act essentially as a mere inert filler. In a microwave field, however, because  $\text{SiC}$  has a very high dielectric loss factor, the whiskers are expected to heat up more rapidly than the glass matrix, which helps to heat the composite rapidly and sinter the composite in a reduced processing time. Moreover, the hot whisker surface may induce fast glass flow and adhesion, to avoid oxidation, even though no literature still exists on the topic. Some examples of microwave-processed alumina ( $\text{Al}_2\text{O}_3$ ) composites have been referenced by Sutton.<sup>3</sup>

## II. Experimental Procedure

The matrix was a CMAS-based glass-ceramic; 5 mol% of the  $\text{CaO}$  has been replaced by  $\text{BaO}$ . It was selected on the basis of its high softening and melting points (hence, good refractoriness).<sup>4</sup> The glass presented a natural tendency toward surface nucleation, which, in this case, has been enhanced by using very fine powders as matrix material. The glass powder contained 50 mol% of  $\text{SiO}_2$ , 5 mol% of  $\text{Al}_2\text{O}_3$ , 20 mol% of  $\text{MgO}$ , 20 mol% of  $\text{CaO}$ , and 5 mol% of  $\text{BaO}$ , with an average particle size of ~10  $\mu\text{m}$ , and had a glass-transition temperature ( $T_g$ ) of 710°C, a dilatometric softening point of 800°C, and a melting range of ~1250°C. The density of the glass powder was 2.93  $\text{g/cm}^3$ .  $\text{SiC}$  whiskers ( $\beta\text{-SiC}$ , Tateho, Tokyo, Japan) with a mean diameter of 0.4  $\mu\text{m}$ , an average length of 15  $\mu\text{m}$ , and a declared Young's modulus of 620 GPa were used. Poly(vinylbutyral) (PVB) (Butvar<sup>TM</sup> B76, American Cyanamid Co., Wayne, NJ) was used as a binder, and dioctylphthalate (DOP) (99%) was used as a plasticizer. Hypermer KD-1 (ICI, Kortenberg, Belgium) was added to stabilize the glass powder in acetone. The slip was highly unstable in the absence of any dispersing agents.

The dispersant was mixed with 80% of the total acetone that was used, and the glass powder was added into the mixed solution. Ball milling (Alubit<sup>®</sup> balls (Bitossi, Florence, Italy) in a polyethylene bottle) was applied for 5 h to allow for adequate absorption of the dispersant by the powder for a better particle dispersion. PVB and DOP were dissolved separately in the remaining 20% of acetone. The resultant viscous solution was blended thoroughly with the glass powder slip that was prepared previously. Finally, the  $\text{SiC}_w$  was added. The mixture was gently homogenized by ball milling for 3 h to ensure a good dispersion and minimum damage to the whiskers. After milling, the balls were removed and the slip was ultrasonically dispersed for 15 min to further disperse the whiskers and to allow any trapped gas bubbles to escape. The composition of the slip are listed in Table I.

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**Table I. Slip Composition for Tape Casting of Composites**

Glass	Composition (wt%)				
	SiC <sub>w</sub>	Acetone	Dispersant	PVB	DOP
50.5	5.5	33.0	2.0	4.0	5.0

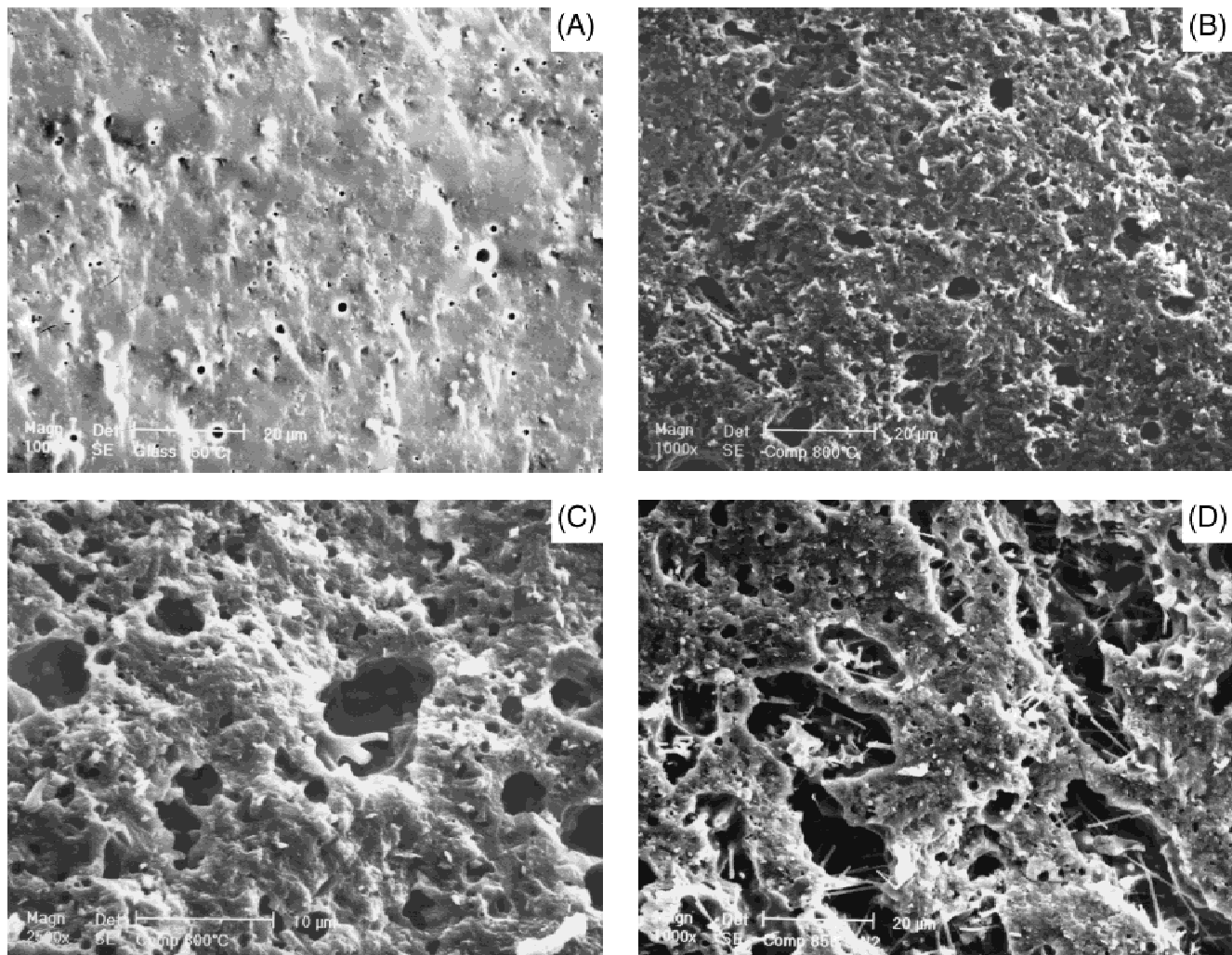
Tapes were cast onto acetate film using a doctor blade with a gap of 0.5 mm. Even though the stability of the slurry was not optimized, the thickness of the tape was uniform. Six layers of the dried tapes were stacked and cold pressed at 70 MPa for 60 s. In addition, tapes of glass powder without SiC<sub>w</sub> also were prepared to investigate the effect of the whiskers on sintering.

For conventional sintering, the specimens were fired in air in a muffle kiln (Model AT/9-17, Nannetti, Faenza, Italy), which had a temperature accuracy of  $\pm 3^\circ\text{C}$ , at a ramp rate of  $2^\circ\text{C}/\text{min}$  to  $550^\circ\text{C}$  and a soak time of 2 h, to allow the burnout of the organics, and then at  $5^\circ\text{C}/\text{min}$  to the set temperatures and, normally, a soak time of 4 h. Samples that were heat treated using microwaves were processed inside a microwave-transparent cavity (Model MAS 7000, CEM Corp., Matthews, NC) that was lined with SiC as susceptor material. This process is called hybrid heating, because the specimens are exposed to convection, infrared, and microwave radiation. A field homogenizer was installed to improve the microwave distribution in the cavity and, thus, minimize temperature gradients. The temperature was measured using a metal shielded thermocouple, and the cited temperatures were those of the cavity rather than

the specimens. As a consequence, a discrepancy between the measured and the actual values may exist. For sintering in air in the microwave oven, a ramp rate of  $19^\circ\text{C}/\text{min}$  to  $550^\circ\text{C}$  with a soak time of 30 min and then to the set temperatures with a soak time of 15 min were used, unless stated otherwise. For the sake of comparison, some samples also were sintered in the conventional muffle furnace, following the same program. The sintering atmosphere was considered to be the same for conventional and microwave treatments, independent of the number of cycles. In fact, the volume of the hot chamber was approximately the same for both furnaces, as were the sample volumes; moreover, the air was under static conditions.

The measurements of the temperature of the samples inside the microwave before and after the isothermal heating have been performed using an unshielded thermocouple (Type K, Omega Engineering, Stamford, CT) with the magnetron in the ‘‘off’’ condition. For more-rapid temperature measurement, the sensing head of the thermocouple was positioned on the sample surface until equilibrium was attained. A few minutes were necessary to detect the surface temperature of both the matrix and the composite. The calibration of the thermocouple was performed by inserting the thermocouple inside the conventional furnace during the isothermal firing of the samples at  $850^\circ\text{C}$ .

The apparent density was measured by the water immersion method. Phase identification was performed using powder X-ray diffractometry (XRD) (Model PW 1050, Philips Research Laboratories, Eindhoven, The Netherlands) on the samples that



**Fig. 1.** SEM fractographs of conventionally treated samples ((A) glass treated at  $750^\circ\text{C}$  for 4 h in air, (B) composite treated at  $800^\circ\text{C}$  for 4 h in air, (C) enlargement of a region of the composite depicted in Fig. 1(B), and (D) composite treated at  $850^\circ\text{C}$  in nitrogen for 4 h).

**Table II. Densities of Glass and Composites for Different Sintering Conditions in Air**

Temperature (°C)	Density (g/cm <sup>3</sup> )				
	Conventional heating			Microwave heating	
	Glass	Composite	Composite <sup>†</sup>	Glass	Composite
710	2.72	2.50 (2.56 <sup>‡</sup> )			
750	2.96	2.72 (2.63 <sup>‡</sup> )			
800	2.95	2.74 (2.70 <sup>‡</sup> )			2.13
820	2.95	2.74 (2.70 <sup>‡</sup> )			
850	2.86	2.74 (2.73 <sup>‡</sup> )	2.65	2.97	2.78
870					2.76
900	2.83	2.73			2.71

<sup>†</sup>Sintered following the same program as in the microwave oven. <sup>‡</sup>Value in parentheses is for the composite that was recrystallized at 900°C for 2 h.

were finely ground, to be representative of the bulk materials. Microstructural characterization was performed using scanning electron microscopy (SEM) (Model XL-40, Phillips Research Laboratories) either on freshly fractured surfaces or on polished samples.

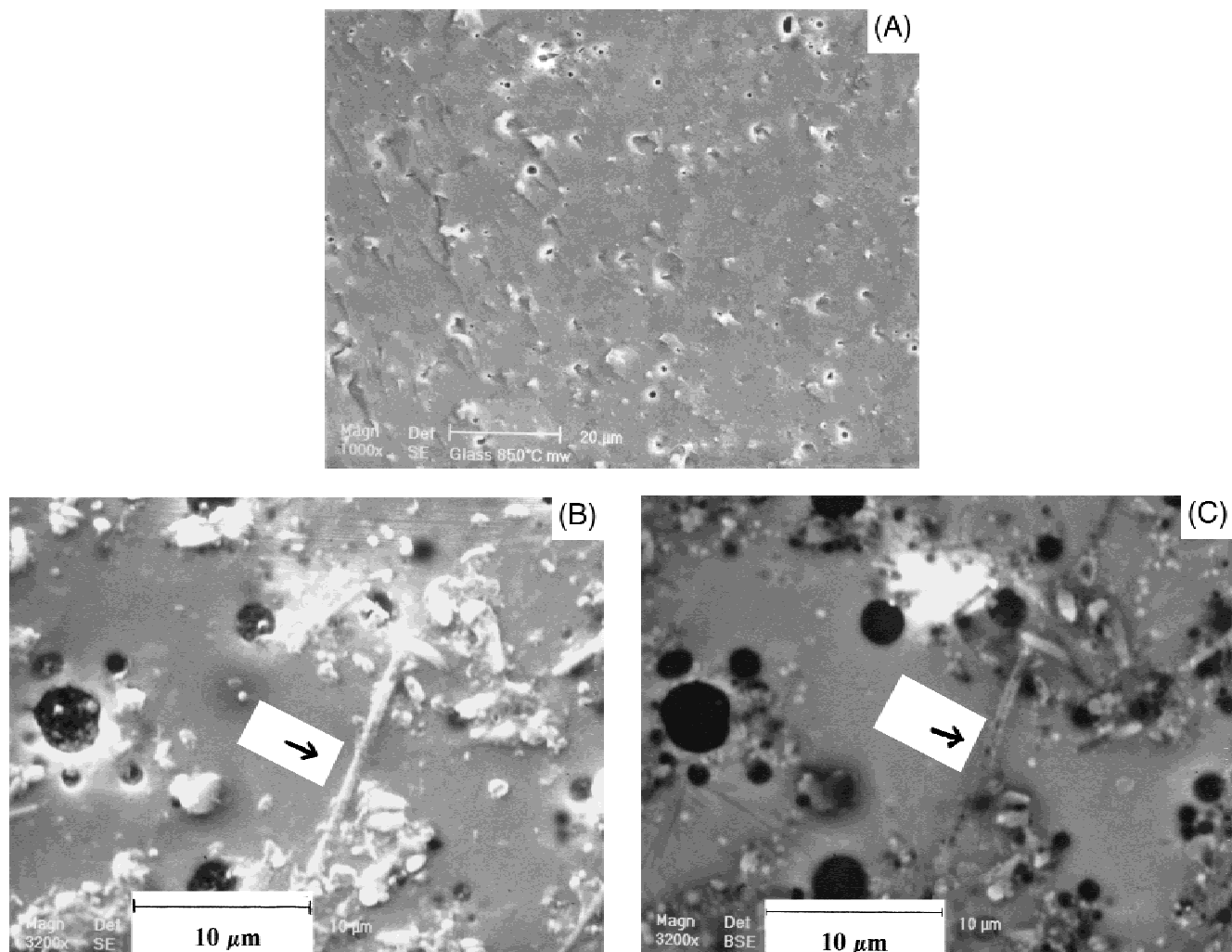
### III. Results and Discussion

#### (1) Sintering Behavior

The sintering behavior was evaluated mainly by using the density measurements and the SEM images. The samples that were only composed of the glass powder could be sintered to

almost-full density at 750°C for 4 h in a conventional furnace, as shown in Fig. 1(A). Recrystallization at a higher temperature results in glass-ceramics. If the sintering is performed at a temperature of >850°C, glass crystallization occurs (see Fig. 3) and a lower density always results (see Table II). The SEM micrographs and the density data both indicated that the addition of 10% of SiC<sub>w</sub> retarded the glass densification considerably. When a double heating (sintering plus glass crystallization at 900°C for 2 h) was applied to the composite, even lower densities were obtained, as a result of severe whisker oxidation (visible as a decrease in the peak height of the β-SiC diffraction signal).

Because the density of the matrix is a function of the crys-



**Fig. 2.** SEM fractographs of microwave-heated samples ((A) glass (secondary-electron image) and composite sintered in air at 850°C for 15 min ((B) secondary-electron image and (C) backscattered-secondary-electron image)).

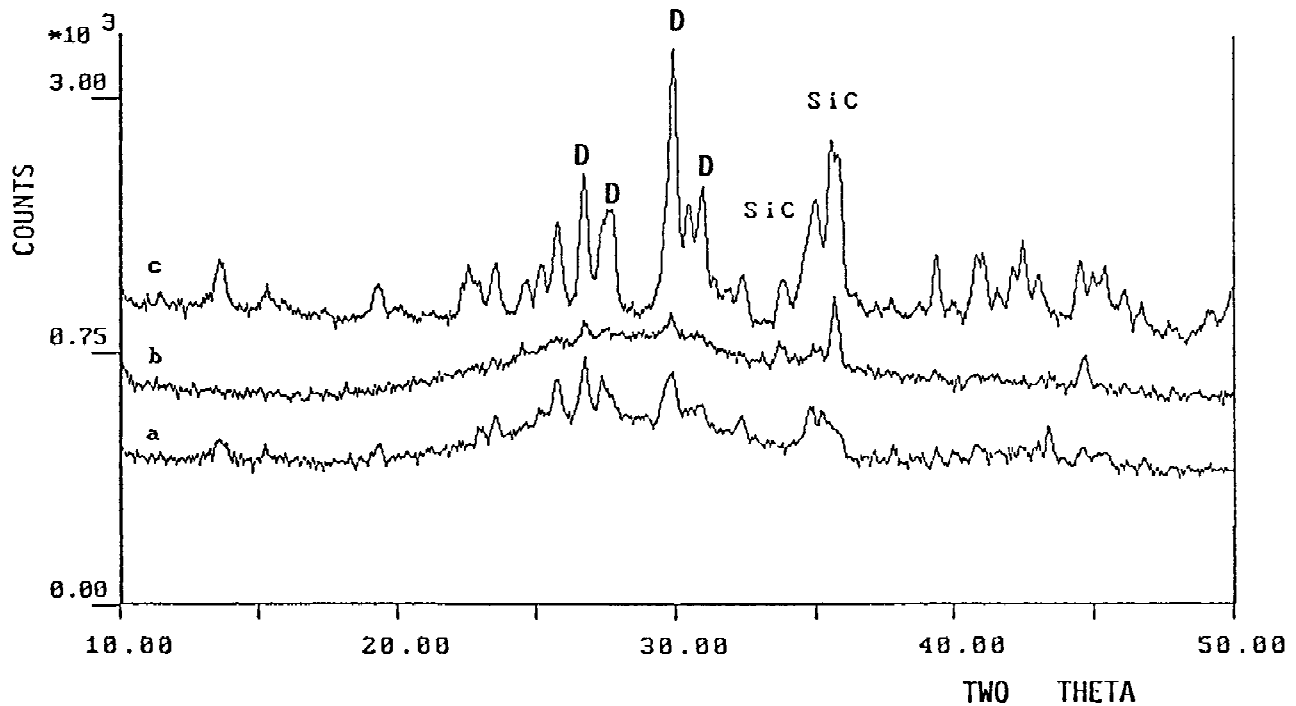


Fig. 3. XRD profiles of the glass (pattern "a") and the composites sintered in air at 900°C for 4 h (pattern "b") and in nitrogen at 910°C for 4 h (pattern "c").

tallinity, the theoretical density of the composite is difficult to determine. However, a good estimation from the SEM micrographs can be made. The best density that is attainable for the composite is 2.74 g/cm<sup>3</sup> at 800°C, which is estimated to be ~90% of the theoretical value from the SEM micrographs (Figs. 1(B) and (C)). Whiskers can usually be found in the inside walls of the holes, which suggests that whisker bridging

has impeded the matrix from shrinking (Fig. 1(C)). It is a well-known phenomenon that whisker reinforcements slow or even stop glass densification during conventional furnace sintering.<sup>5</sup> The fact that only few whiskers, which are evidently covered with glass, are clearly observed in this SEM image indicates that the glass wets the SiC<sub>w</sub> well.

To prevent whisker oxidation, sintering also has been con-

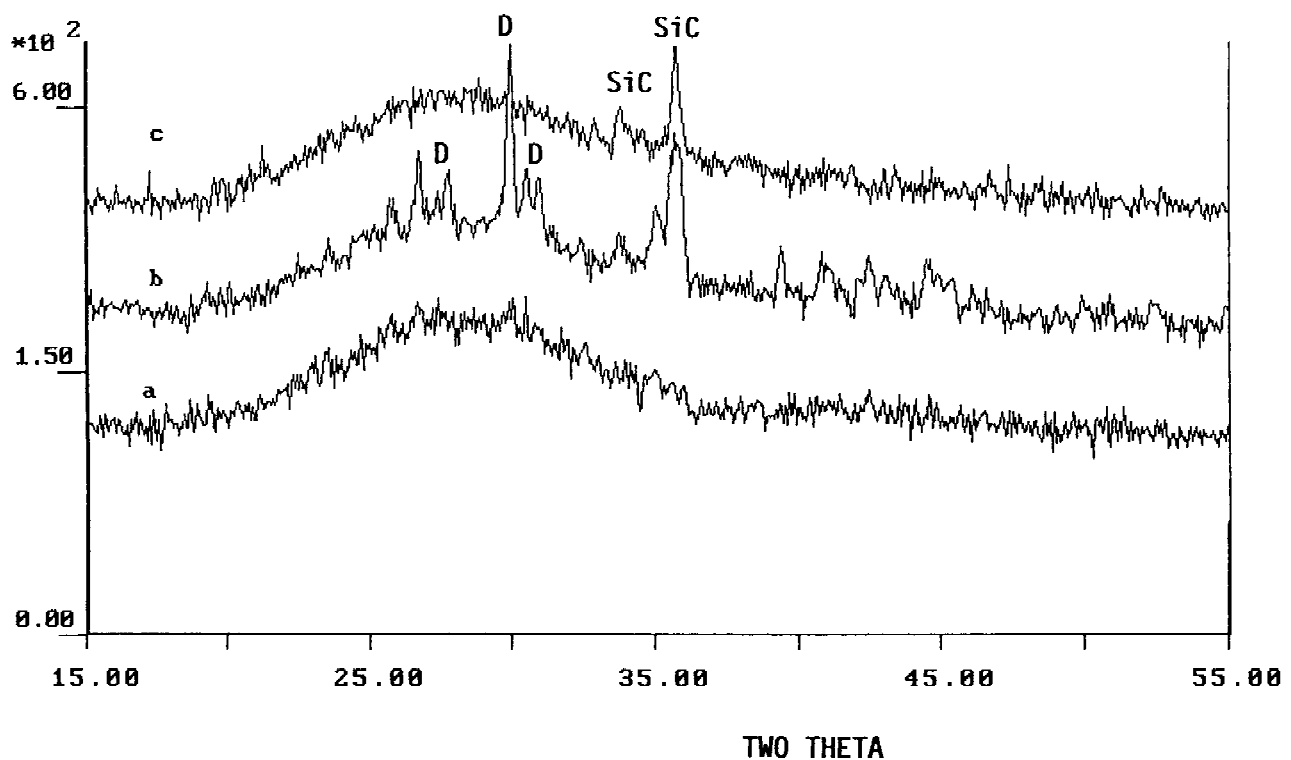


Fig. 4. XRD profiles of the glass (pattern "a") and the composites sintered in the microwave oven (pattern "b") and in the conventional furnace (pattern "c"); sintering was performed at 850°C for 15 min in air (the letter "D" represents a diopside peak).

ducted in nitrogen; however, lower densities are recorded for all the sintering temperatures, from 750°C to 950°C. The sintered samples are too porous (open porosity) and deformed for an accurate density determination (Fig. 1(D)); therefore, no density values are presented in Table II. The exact reasons for the poor performance in nitrogen are unknown; however, it is speculated to be due to a reduced wettability of the glass to the whiskers in nitrogen, in comparison to those in air. This hypothesis may be supported by the much-cleaner surfaces of the whiskers and the significantly delayed glass crystallization, as shown in Fig. 4.

With the microwave oven, no appreciable densification occurred at temperatures of <800°C. However, the density attained the maximum value at 850°C: almost-full density for the glass and ~95% of the theoretical density for the composite, as estimated from the SEM micrographs (Fig. 2). The total processing required ~1.5 h; >12 h were required for conventional sintering to attain similar densities. Higher sintering temperatures adversely affected the densification. From a comparison between Figs. 2(B) and (C), good adhesion of the glass on the whisker surface can be observed. No whisker pullout at the fracture surface or the crack is present, which shows that the whiskers are strongly bonded to the matrix.

Because of the rapid heating rate in microwave processing, incomplete organic removal has been observed if the samples are heated directly to the set temperatures. To burn out the organics completely, a dwell time of 30 min in air in a conventional furnace at 550°C has been used. For a meaningful comparison to be made between microwave and conventional sintering, a sample has also been fired in the furnace, which simulated the sintering schedule of the microwave oven. The resultant density is lower (Table II), which suggests that microwave sintering does have a positive effect on the densification of the composites.

## (2) Crystalline-Phase Evolution

The glass and the composite that was prepared at a temperature of <800°C were amorphous by XRD. Appreciable crystallization occurred after 850°C for the samples that had been sintered in the conventional furnace in air and after 900°C for the samples that had been sintered in nitrogen (Fig. 3). The crystalline phases consisted of diopside (ICDD<sup>†</sup> File Card No. 11-654) and a mixture of calcium and barium feldspar, anorthite (ICDD File Card No. 12-301), and celsian, which possess very similar diffraction patterns. The last component also was present in the hexagonal polymorphs as hexacelsian (ICDD File Card Nos. 12-725 and 12-726), which is not easily distinguishable from the monoclinic form, celsian (ICDD File Card No. 38-1450), because of the overlapping of some peaks and the small amount of BaO in the glass-ceramic. The peak at 3.95 Å (0.395 nm), which undoubtedly was attributed to hexacelsian, decreased from 800°C to 900°C, whereas the peak at 3.79 Å (0.379 nm), which was ascribed to the monoclinic form, increased as the temperature increased. In nitrogen, the crystalline phases were the same as those in air, with a slight tendency for hexacelsian; however, the  $\beta$ -SiC peaks at 2.65 Å (0.265 nm), which were absent in air, were always observable. This fact can be an indication of the different wetting of SiC<sub>w</sub> by the glass.

The effect of microwave heating on the crystallization of the glass and the composite is shown in Fig. 4. The pure glass matrix does not exhibit any diffraction peak, whereas, for the composite, some diopside peaks appear at 850°C, together with the  $\beta$ -SiC phase. To verify the effect of microwave heating, the

composite has been treated for 15 min in a conventional furnace at 850°C, after a conventional binder burnout at 550°C. The diffraction pattern (pattern "c" in Fig. 4) presents only the  $\beta$ -SiC phase, but to a minor extent, with respect to the composite that has been treated by microwave heating, which indicates oxidation (pattern "b" in Fig. 4). These observations were somewhat expected, because the highly microwave-absorbing SiC additive would make the composite hotter. In fact, the temperature registration of the samples that were heated in the microwave furnace confirmed such an explanation. The surface of the composite attained a higher temperature (734° or 695°C, if measured before or after the matrix, respectively) than that of the matrix (676° or 636°C, if measured before or after the composite, respectively) during the soak at 850°C. Moreover, the surface of the microwave-heated samples attains temperatures that are lower than the 850°C temperature that has been measured for the conventionally treated sample, which indicates high heat dissipation for such thin samples. The effect of microwave-susceptor SiC has been proven by the global temperature increase, even though localized heating is a possible explanation for the different crystallization and sintering behaviors. Such heating may affect the mass-transport mechanism, which enhances diffusion in general or lattice diffusion.<sup>1,6</sup>

## IV. Conclusions

In the silicon-carbide-whisker-reinforced (SiC<sub>w</sub>-reinforced) glass composite, the reinforcement retarded the glass sintering through whisker bridging. The glass was sintered to almost-full density at 750°C by conventional furnace sintering; however, the best sintered composite, which was estimated to be ~90% dense, was obtained at 800°C with a dwell time of 4 h. Sintering at a temperature of >800°C did not improve the densification; instead, it resulted in severe whisker oxidation. A reduced densification rate was observed for the samples that were sintered in nitrogen, which might be due to poor wetting of the whiskers by the glass. By contrast, in the microwave oven, almost-full density for the glass and ~95% of the theoretical density for the composite were obtainable at 850°C for 15 min, which represents a reduction of ~10 h of the total processing time and reduced SiC<sub>w</sub> oxidation. The composite temperature during microwave processing was higher than that of the glass sample, because of the susceptibility of SiC at a frequency of 2.45 GHz. Such phenomenon enhanced glass crystallization in the composite matrix but did not modify the crystalline phase of the whiskers. Microwave sintering seems to compare favorably with conventional furnace firing in densifying these glasses and composites and preventing carbide oxidation.

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<sup>†</sup>International Centre for Diffraction Data, Newtowne Square, PA (formerly Joint Committee on Powder Diffraction Standards (JCPDS), Swarthmore, PA).