

**EFFECT OF ADDITIVES ON THE DENSIFICATION PROCESSES AND PROPERTIES OF SILICA-BASED CMCs**

The effect of additives on the densification behavior and mechanical properties of pure and additive (Zr, B and Mg)-added silica ceramics were investigated for their application to the matrix phase of a silica fiber reinforced silica ( $\text{SiO}_2/\text{SiO}_{2f}$ ) composite. The additives affected the rate of densification and crystallization (or transformation) of the amorphous silica. Among the compositions, pure silica ceramics sintered at 900°C for 1 h showed the maximum flexural strength. Based on the results,  $\text{SiO}_2/\text{SiO}_{2f}$  was fabricated by a repeated vacuum-assisted infiltration method followed by the heat treatment at 900°C for 1 h. The relative density of the composite was 78.2% with a flexural strength of 22.4 MPa. Fractography revealed that the composite was damaged by strong bonding at the fiber/matrix interface and the fracture of fiber.

*Keywords:* Ceramic matrix composite (CMC), Silica, Densification, Mechanical properties

**1. Introduction**

Silica ( $\text{SiO}_2$ ) ceramics have a high thermal shock resistance, high chemical inertness and excellent thermal stability, as well as a low dielectric constant (3.1-3.8) with tangent loss (0.004) [1,2]. Because of these properties, amorphous silica is a promising candidate material for many engineering applications, such as high-temperature microwave-transparent materials and thermal shielding materials in the aircraft industry. However, catastrophic fracture behavior due to the relatively low strength and fracture toughness of silica in the monolith form has limited their wide applications in structural materials [3,4]. Thus, continuous fiber is generally used as the reinforcement. In particular, with the use of silica fibers in the form of a unidirectional state or a 2- or 3-dimensional preform in the silica matrix, the fracture strain and fracture work can be increased, and thus catastrophic fracture can be avoided [5].

SiC-based ceramic matrix composites (CMCs), such as C/SiC and SiC/SiC, are usually fabricated at relatively high temperatures (typically, ~1300°C in the PIP process and even higher in the melt infiltration method) [5]. In the case of silica-based CMCs, the high temperature process leads to serious degradation of the silica fiber, so it is difficult to pack the matrix densely into silica fiber preforms to acquire high strength composite materials. Recently, several research groups have reported a fabrication process (silica-sol-infiltration-sintering, SIS) with silica-based CMCs [4]. Compared with conventional methods, the SIS method has several advantages: relatively low heat-treatment temperature (450°C), low shrinkage and reduced

drying stress. In the CMC system, the shrinkage of the matrix phase evidently plays an important role in the final density of the CMC due to the dimensional rigidity of reinforcements. However, due to the low heat treatment temperature of the SIS method, it is difficult to achieve a fully dense CMC. Li et al. fabricated a CMC with a relative density of 77% at a temperature of 450°C in an infiltration processes repeated 15 times [4]. Their lower than expected strength values might have been due to the low relative density of the final CMC. Thus, it is important to achieve a higher relative density in the matrix phase to improve the mechanical properties of the CMC system.

In this study, the shrinkage and densification behavior of the matrix phase was analyzed to determine the optimal densification conditions of silica-sol. In order to improve the densification and mechanical properties of the matrix phase, sintering additives Zr, B and Mg were incorporated in the silica-sol. The effects of the additive on the densification and mechanical behavior of silica-based composite were investigated.

**2. Experimental**

The raw materials used for the matrix phase was colloidal silica (Sigma-Aldrich, St. Louis, USA). Zirconyl chloride octahydrate, boric anhydride and magnesium acetate tetrahydrate (Sigma-Aldrich, St. Louis, USA) were used as additive materials. Silica-sol was dried in an oven at 80°C for 72 h to obtain powders and each powder was weighed according to the formula of 5 mol% added silica. The powders were mixed and ball-milled

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in DI water for 24 h. The slurry was dried in an oven at 80°C for 48 h and sieved. The powder was pressed into cylindrical compacts, and then cold isostatically compressed at 200 MPa for 5 min. The compacts were annealed in air as functions of temperature and time.

Silica fabric (purity >99%) woven 2-dimensionally with thicknesses of 8-10 mm and stacked 6 times was used as a pre-form for the CMC. The preforms were vacuum infiltrated using colloidal silica and dried in an oven at 80°C for 48 h. Then the dried preforms were heated in a furnace at 200°C for 2 h to remove the coupling agent and bound water. The whole process was 10 times repeated to enhance the density of the composite. Finally, the composite was sintered in a furnace at 900°C for 1 h to sufficient shrinkage of the matrix phase.

The thermal properties of silica-sol were analyzed by TGA/DSC (LABSYS Evo, Setaram, France) and dilatometer (DIL402, Netzsch, Germany). The density of the samples was calculated by measurement of volume and mass. The phase constitution was identified using X-ray diffraction with CuK $\alpha$  radiation (D/MAX-RB, RIGAKU, Japan). The flexural strength of the matrix phase and the composite was measured by ring-on-ring testing (ASTM C1499) and the three-point-bending method (ASTM C1341), respectively, with a computer controlled test machine (5882, Instron, America). For each condition, at least three samples were prepared and measured, and their average value was presented as the measured data. The fracture surface of the CMC was observed by a scanning electron microscope (Quanta 650, FEI, America).

### 3. Results and discussion

TGA/DTA curves of the dried silica-sol (matrix phase) are shown in Fig. 1. In the temperature range from 25 to 200°C, a weight loss of about 4.5% and one endothermic peak (~95°C) were clearly observed. These were likely due to the vaporizing of the residual water in the dried-sol. For the temperature higher than 200°C, there was no significant weight loss. We considered

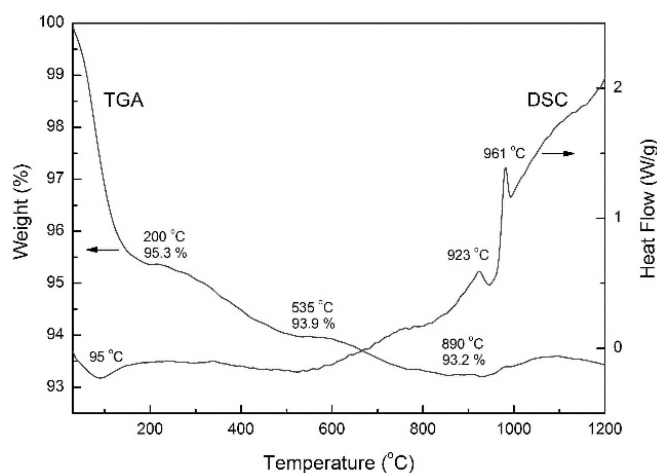


Fig. 1. TGA and DSC curves of dried silica-sol in the temperature range from 25 to 1200°C

that two exothermic peaks at 923 and 961°C might be related to the crystallization of amorphous silica particles (analyzed below).

Fig. 2 plots the shrinkage curve of the matrix phase from dried silica-sol as a function of temperature. The shrinkage of the silica occurred very slightly below 800°C, but the shrinkage rate increased drastically at around 900°C. The values of the relative shrinkage (%  $\Delta L/L_0$ ) were 3.6% and 6.2% at 850°C and 900°C, respectively, and the final value increased up to 14% at 945°C. The relative density curve of the matrix phase sintered at various temperatures for 10 h are also displayed in the inset of Fig. 2. Below 800°C, little densification occurred, which was similar result to shrinkage curve of dilatometric analysis, and significant densification began around 900°C. The relative density of the matrix phase sintered at 900°C increased from 65.9% to 90.4% with sintering time from 30 min to 10 h (Fig. 3). Based on the densification results from the dilatometric analysis and density measurement, the following heat treatment processes were performed at 900°C.

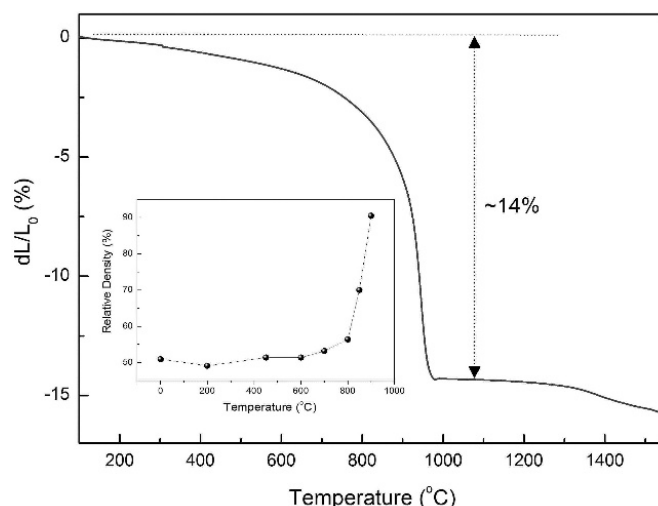


Fig. 2. Dilatometric and relative density (inset) curves of the matrix phase (dried silica-sol) as a function of temperature

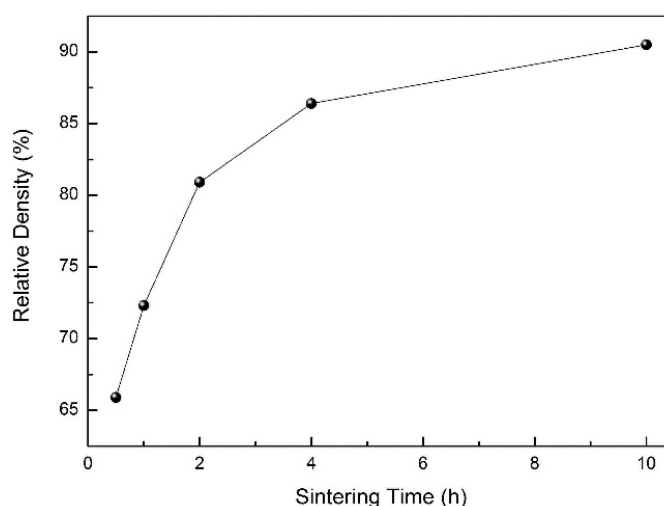


Fig. 3. Relative density of the matrix phase (dried silica-sol) sintered at 900°C for various times

Fig. 4 shows the XRD patterns of the matrix phase sintered at 900°C for various times. For the samples sintered for 30 min and 1 h, there was only a single broad peak, indicating the pure amorphous phase. With the increase in sintering time, however, the shape of the diffused peak become sharp and crystalline peaks were observed in the sample sintered for 4 h. These peaks can be identified by  $\alpha$ -cristobalite silica.

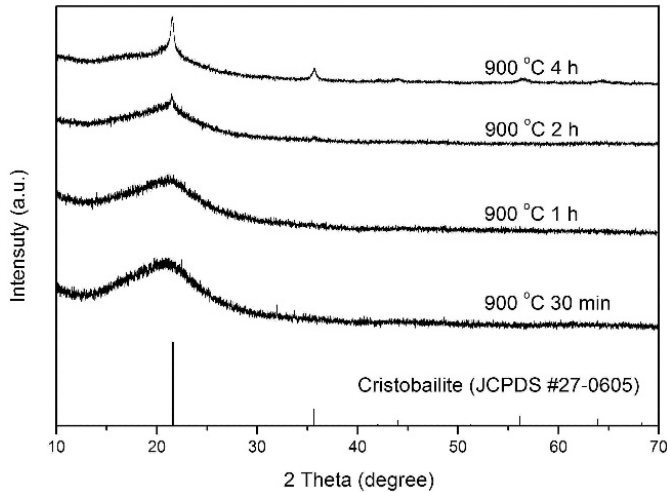


Fig. 4. X-ray diffraction patterns of the matrix phase (dried silica-sol) sintered at 900°C for various times

The effects of the additives (Zr, B and Mg) on the bulk density are shown in Fig. 5 with respect to sintering time at 900°C. All the samples with the additives had higher density than the sample of pure silica-sol in the early stage of sintering at 900°C. B and Mg added samples were rapidly densified, and the bulk density of the samples were 1.75 and 1.65 g/cm<sup>3</sup>, respectively, though they were sintered for 30 min. These values were higher than the values of the pure silica samples sintered for 1 h. However, these samples did not shrink significantly with an increasing sintering time. Although pure silica had a low initial density, it shrank continuously with increasing sintering times and had the highest final density.

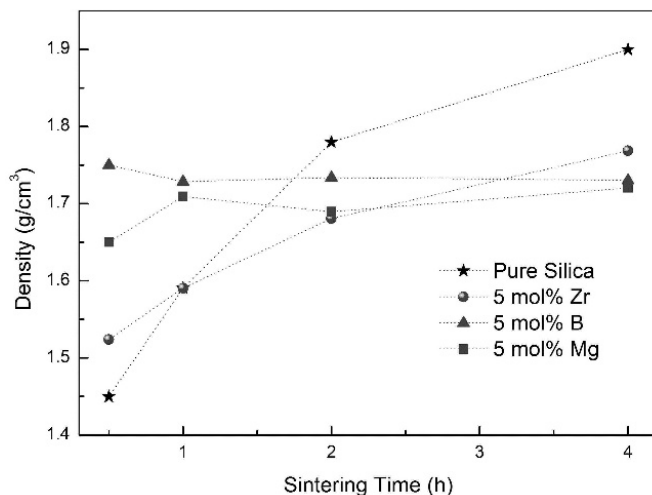


Fig. 5. Bulk density of silica and 5 mol% Zr, B, and Mg-added silica samples sintered at 900°C for various times

Fig. 6 shows the XRD patterns of silica with additives sintered at 900°C. In the Zr-added silica sample, both crystalline and diffused peaks are observed. All of the crystalline peaks can be identified by ZrO<sub>2</sub>, and the silica still remains as an amorphous phase. These data indicate that crystallization of silica can be retarded by adding Zr. (Figs. 4 and 6) and these results are consistent with a previous study [6]. Zr in the silica diffuses into the surface layer of silica particles to form a solid solution, resulting in a lattice distortion, which may generate a compression stress on the surface region and finally retard crystallization of the silica. On the other hand, the B and Mg-added silica samples sintered at 900°C for 30 min already present crystalline peaks of cristobalite silica. These crystalline peaks are much stronger than those of the silica sample sintered at the same temperature for 4 h. It is known that B<sub>2</sub>O<sub>3</sub> stimulates crystallization through heterogeneous nucleation, where B<sub>2</sub>O<sub>3</sub> acts as an impurity [7,8,9].

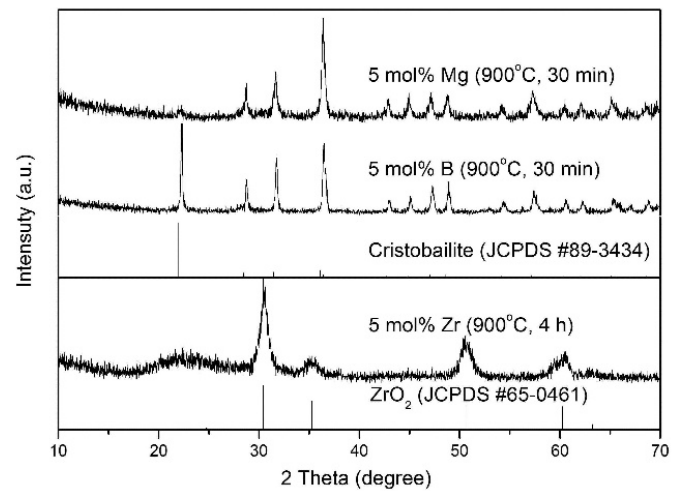


Fig. 6. X-ray diffraction patterns of 5 mol% Zr, B and Mg-added silica samples sintered at 900°C

The effects of the additives and sintering time on the flexural strength of the matrix phase are listed in Table 1. According to the Fig. 3, the relative density of the matrix phase increases with sintering time at 900°C, but the flexural strength decreases after 1 h for the sintering shown in Table 1. These results can be explained by the crystallization behavior of silica-sol in Fig. 4. The flexural strength of silica decreases due to creation of crystalline cristobalite and its increasing content. Similarly, B and Mg-added silica samples show low flexural strength (Table 1) because these samples, which were sintered at 900°C for 30 min, already included a high content of cristobalite as shown in Fig. 6. It is well known that microcracks are created on the microstructure by crystallization of amorphous silica because the crystalline phase of silica has a high anisotropic thermal expansion coefficient and volume change during the  $\alpha$  to  $\beta$  phase transformation of cristobalite [2,10]. Therefore, maintaining the amorphous phase is as important as improving the density to achieve high mechanical properties for silica ceramics during the sintering process.

TABLE 1

Flexural strength of silica and 5 mol% Zr, B and Mg-added silica matrix

Sample	Flexural strength (MPa)			
	Sintering time (at 900°C)			
	30 min	1 h	2 h	4 h
Silica	23.2	34.2	20.0	13.9
5Zr	14.9	—	—	20.7
5B	7.5	—	—	7.6
5Mg	4.5	—	—	4.3

We designed the fabrication of the silica-based CMC based on the results of densification and mechanical properties of the matrix phase. Fig. 7 shows the SEM micrograph of the fracture surface of the silica-based CMC via a vacuum-assisted infiltration method. As shown in the figure, the CMC is consist of a reinforcing phase and a matrix phase. It appears that the matrix phase successfully infiltrated into the narrow channel of the reinforcing phase.

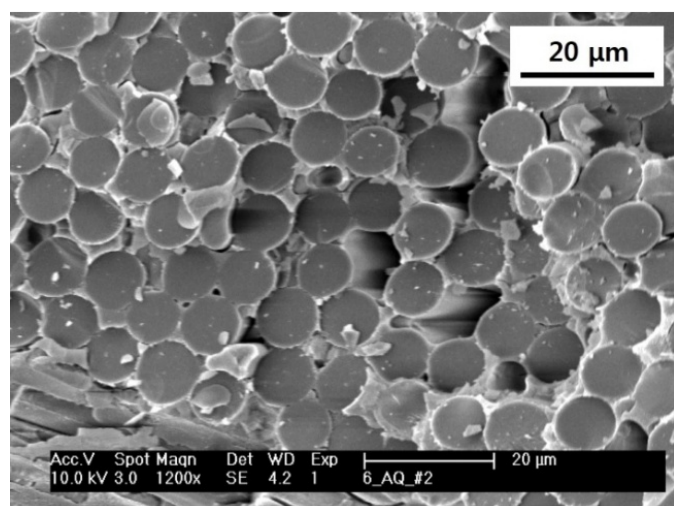


Fig. 7. SEM micrographs showing fracture surface of the fabricated CMC

The empty space between filaments was filled with silica-sol successfully. However, larger cavities were observed between the reinforcing materials, it seems that the silica-sol flowed in the spaces between filaments by osmotic pressure and flowed out of the CMC when the silica-sol dried. In addition to the presence of a larger cavity in the matrix phase, there was no fiber pull-out with brittle behavior, suggesting strong interface bonding between the fiber and matrix. The relative density and flexural strength of the CMC were 78.2% and 22.4 MPa, respectively. The strength values were not much improved due to the relatively low density and brittle behavior of the CMC. We believe that

the characteristics of the CMC can be improved by performing process optimization, such as interfacial control at the matrix/fiber or preparation of delicate 3D preform.

#### 4. Conclusions

We investigated the densification and crystallization behaviors of amorphous silica and also studied the influences of sintering additives (Zr, B and Mg) on densification and mechanical properties. The mechanical properties were not much improved by the additives due to the delay of densification and crystallization of silica. The pure silica sintered at 900°C for 1 h exhibited the maximum mechanical properties with 34.2 MPa. Based on those results, we prepared a  $\text{SiO}_2/\text{SiO}_2f$  composite by a vacuum-assisted infiltration method using 2D woven and stacked silica fabric and colloidal silica at a temperature of 900°C for 1 h. The relative density of the composite was 78.2% with 22.4 MPa. SEM observation revealed that the fracture surface of the CMC encompassed brittle behavior with no fiber pull-out but there were large cavities. Our future work will focus on optimizing the interface properties and making a more delicate 3D silica-based preform.

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