Conventional and microwave sintering of condensed silica fume

Jan Majing and Peter Znasik
Department of Ceramics, Slovak Technical University, 812 37 Bratislava, Slovakia

Dinesh Agrawal, Jiping Cheng, and Rustum Roy
Intercollege Materials Research Laboratory, Pennsylvania State University,
University Park, Pennsylvania 16802-4801

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Condensed silica fume, a by-product from the production of silicon alloys, was sintered by (i) conventional heating in a dilatometric furnace, both at constant heating rate and isothermal heating, and (ii) by the microwave heating. The dense products with relative density up to 95% of theoretical can be obtained only by short runs at high heating rates, preferentially accomplished by the microwave treatment. Prolonged heating leads to the devitrification of the original glassy phase to cristobalite, accompanied by an arrest of densification.

The condensed silica fume from the silicon or ferrosilicon alloys industry is a voluminous, high tonnage by-product consisting of amorphous, spherical, and submicron particles. This is predominantly used as an active additive to cement pastes and concrete mixtures. The chemical composition of condensed silica fume varies according to the type of silicon alloy produced in the furnace, the design of the furnace, and the chemical composition of the raw materials. All condensed silica fumes, however, have some chemical characteristics in common. The iron content fluctuates between 0.1 and 2.0%. The alumina, lime, magnesia, alkali, and SO$_3$ contents are quite low, being lower than 2% in each case. The carbon content is less than 1.5%. The glassy state of the silica powder makes it a suitable candidate for possible preparation of ceramic-shaped articles by viscous flow sintering. Though the literature on sintering of pure glassy silica or related powders of different origin is quite large, there is no information available on sintering of silica fume used in this study.

It was shown in a previous study that a commercial silica fume of high purity (Degussa Aerosil Ox 50) sinters nearly to the theoretical density at 1450 °C without devitrification. Samples of commercial soda-lime glass remained vitreous during sintering. The crystallization of cordierite glass powder was detected only after sintering, and the presence of alkalis and water vapor accelerates crystallization of glass. As-received diatomite, for example, devitrifies at 1000 °C, whereas leached material, composed practically of SiO$_2$, devitrifies at 1100 °C after 8 h of exposure. Leaching of alkalis from silica foam produced from commercial SiO$_2$ sol, and stabilized by Na$_2$O, significantly retarded devitrification of the system.

Devitrification occurring during the reheating of glassy powders is largely an uncontrolled process depending also upon chance effects such as the presence of foreign particles which can act as nucleation catalysts. The silica fume used in this study is rather an impure glassy powder. It is expected to sinter well similarly to other mentioned powders or powder compacts, its “impure” form may be, however, the cause for devitrification.

The objective of this contribution is to ascertain the basic processing conditions under which powder compacts of silica fume with varying green densities can be controllably sintered to lightweight or dense structures.

The Elkem C50 silica fume (Elkem Chemicals Inc., Pittsburgh, PA; shipped to IMRL in 1988) was used in this study. Its density was measured pycnometrically. The specific surface area of the powder was measured by BET (Quantachrome, model Autosorb-I). Its carbon content was deduced from DTA/TG analysis (Derivatograph 3427). X-ray analysis was performed using a Dron 2.0 diffractometer (Cu K$_\alpha$ radiation).

All samples investigated were in the form of disks of constant volume (diameter = 12 7.6 mm, thickness = 5.54 mm) prepared by pressing the loose powder in a steel die. They differed in amounts of powder taken for pressing (0.28, 0.30, 0.38, 0.51, 0.64, and 0.70 g, respectively). The nonisothermal and isothermal sintering runs were performed using a Harrop dilatometer. The stress induced in the sample by the push rod of the dilatometer was 0.5 N.

The microwave sintering was performed in a modified multimode microwave oven (Amana RC/205E, 2200 W). Six pellets of silica fume, pressed to the same bulk (green) density, were placed on a thin alumina sheet inside a porous zirconia cylinder of 60 mm diameter and heated in the microwave oven in a single run. The samples in each run were always placed inside the oven at identical positions separated by equal distances. After reaching the desired temperature of 1000 °C at a rate
TABLE I. Chemical composition of silica fume (oxides in wt. %)

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>MnO</th>
<th>SO₃</th>
<th>P₂O₅</th>
<th>L.O.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>95.93</td>
<td>0.52</td>
<td>0.20</td>
<td>0.18</td>
<td>0.40</td>
<td>0.12</td>
<td>0.05</td>
<td>&lt;0.05</td>
<td>0.024</td>
<td>0.10</td>
<td>0.07</td>
<td>2.90</td>
</tr>
</tbody>
</table>

![Graph](image)

FIG. 1. DTA and TG traces of the silica fume powder heated at a rate of 5 °C/min.

of approx. 200 °C/min, the samples were soaked at 1000 °C for 3 min.

The chemical composition of the silica fume is shown in Table I. It can be seen that alkalies, both as Na₂O and K₂O, are present in appreciable amounts. The gray color of the powder is caused by the presence of an elementary carbon. Its amount is determined by the DTA/TG analysis (Fig. 1). An oxidation of the carbon in the lightly pressed powder, heated at a rate of 5 °C/min, occurred as observed in Fig. 1 in the temperature range of 500–600 °C.

The powder density was determined as 2.22 g · cm⁻³, and the calculated relative green densities of individual disks were (a) 0.18, (b) 0.19, (c) 0.24, (d) 0.32, (e) 0.41, and (f) 0.445, respectively. The equivalent diameter of the particles, calculated from BET surface area (23.52 m²/g) data, is 0.11 μm.

In the dilatometric runs, only those samples with relative green densities of 0.19 and 0.445 were taken into analysis, and they are referred to in the text as lower density (LD) and higher density (HD) compacts, respectively.

Dilatometric results for heating rates of 2 °C/min and 10 °C/min for the HD and LD samples are given in Table II. The table also lists the onset temperatures of shrinkage, temperatures at which the shrinkage ended, and the time period of densification, respectively. These data have been determined from the dilatometric measurements.

The recorded curves were very similar in appearance, in spite of the differences in initial relative density and heating rate. The curve for sample No. 4 (HD) is shown in Fig. 2, as a typical example. It follows from this curve that the shrinkage of the samples is accomplished at a high constant rate until the arrest temperature is reached (1164 °C). The shrinkage at this temperature has suddenly halted with no sign of further linear (volume) change upon further heating. From the sudden cessation of shrinkage of the sample and only its moderate densification, it was deduced that the devitrification of the original glassy phase to cristobalite had occurred. At temperatures in question cristobalite is essentially a nonsinterable phase. Its presence was confirmed by x-ray analysis. X-ray diffraction patterns in Fig. 3 belong to the samples with thermal treatment corresponding to (b) and (d) positions on the dilatometric curve of Fig. 2.

From the x-ray diffraction pattern (d) in Fig. 3, it can be seen that cristobalite starts to crystallize at temperatures lower than 1164 °C. The growth of cristobalite crystals is enhanced with temperature, but it halts the process of densification suddenly. It is interesting to note that the diffraction peak of β-quartz (denoted as Q) is the first one to appear in the corresponding diffraction pattern. The well-crystalized samples [Figs. 3(a) and 3(b)] contain also the diffraction peaks of tridymite (T). The rest of the diffraction peaks in the diffraction patterns belong to the low cristobalite.

The LD and HD samples were isothermally sintered at 1000 and 1050 °C, respectively. The heating rate of 10 °C was kept constant in all cases. No appreciable shrinkage occurred during heating up of the samples.

Characteristic time periods, from beginning of deflection to the end of shrinkage, are given in Table III. The dilatometric curve for the sample No. 8 is shown in Fig. 4. It is seen from this figure that the rate of shrinkage decreases continuously. Similar to the previous case,

TABLE II. Characteristic temperatures for the constant heating rate.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Heating rate (°C/min)</th>
<th>Temperature (°C)</th>
<th>Time period of densification (min)</th>
<th>Final relative density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Onset</td>
<td>Arrest</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>LD</td>
<td>2</td>
<td>914</td>
<td>1132</td>
<td>110</td>
</tr>
<tr>
<td>2</td>
<td>HD</td>
<td>2</td>
<td>925</td>
<td>1120</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>LD</td>
<td>10</td>
<td>956</td>
<td>1146</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>HD</td>
<td>10</td>
<td>965</td>
<td>1164</td>
<td>20</td>
</tr>
</tbody>
</table>
TABLE III. Results of isothermal heating.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Temperature of isothermal run (°C)</th>
<th>Time period of densification (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>LD</td>
<td>1000</td>
<td>190</td>
</tr>
<tr>
<td>6</td>
<td>HD</td>
<td>1000</td>
<td>300</td>
</tr>
<tr>
<td>7</td>
<td>LD</td>
<td>1050</td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>HD</td>
<td>1050</td>
<td>70</td>
</tr>
</tbody>
</table>

FIG. 2. Dilatometric curve for sample No. 4 heated at a rate 10 °C/min up to 1175 °C followed by an isothermal heating at this temperature.

FIG. 3. X-ray patterns of silica fume compacts treated correspondingly to (a), (b), (c), and (d) positions in Figs. 2 and 4, respectively.

FIG. 4. Dilatometric curve for sample No. 8 heated at 10 °C/min up to 1050 °C followed by an isothermal heating at this temperature.

terms of duration in which the shrinkage took place. In HD samples the shrinkage was accomplished in a substantially long time.

It was reported previously that the presence of oxygen enhances the crystallization of reduced vitreous silica by providing a proper stoichiometry to form crystalline phases. It may, therefore, be concluded that the reason for this observation, is the difference in oxygen deficiency between HD and LD sample, caused by the originally present remnant carbon. The crystallization may have been retarded more for HD samples than LD samples. The same applies also to the samples heated at the constant rate. A separate experiment conducted had substantiated this inference. A sample embedded in the powder carbon when subjected to the thermal treatment corresponding to position (a) (Fig. 4), had remained completely black and undevitrified.

Microwave sintering of silica fume was attempted because published data showed its effectiveness in sintering of various ceramic powders. Of special interest is the heating of low density compacts with low thermal conductivity because in the case of microwave sintering the heat is homogeneously generated in the bulk of the material.

Six pellets of silica fume, of the same green density, which were sintered simultaneously in a single run, differed in density depending upon their location on the alumina support. This phenomenon is attributed to
the uneven distribution of the microwave energy in the cavity of the oven. The results are shown in Fig. 5. The upper curve (No. 1) corresponds to the samples with the highest density, and the bottom curve (No. 2) to the samples with the lowest density in individual runs. The sintered densities of the remaining four samples lie between the curves 1 and 2. The general trend of achieving higher density with increasing green densities, as is normally observed in conventional method, was observed in the microwave sintering also. In spite of the limitations of conducting these experiments, it was clearly shown that silica fume compacts sinter very rapidly in a microwave field. All microwave-sintered samples were fully glassy.

The fracture surface of highly dense samples contained black cores, a characteristic of firing of traditional (brick) ceramics in a reducing atmosphere. The heating of ceramics at a very high rate, such as in a microwave field, is accompanied only by the partial oxidation of carbon present in the outer layer and no oxidation of the carbon present inside the samples, resulting into a black core. It has been demonstrated that carbon alone is a good microwave absorber. Therefore, the presence of carbon impurity in the silica fumes may have a positive effect in enhancing the microwave absorption efficiency. Measurement of carbon oxidation of the denser and less dense samples and of the amount of the residual carbon were beyond the scope of this work.

It has been found that the "waste" condensed silica fume is quite a flexible system for the mechanically and thermally induced densification. Compacts of the silica fume can be prepared with varied green densities. The compacts start to sinter at the temperatures around 914 °C. A high heating rate, as exerted in microwave treatment of the green samples, leads to the dense and nondevitrified microstructures. Prolonged heating leads to the devitrification of the system (to cristobalite). The presence of elementary carbon has a beneficial influence in microwave sintering as well as in the conventional heat treatment. In the latter case, it is believed, that carbon retards the devitrification.

The chemistry of the system is rather complex and many of the observed changes could not be studied and explained in detail. Only the basic features have been identified for the processing of the silica fumes. Our results show that this particular kind of the condensed silica fume deserves some attention in the area of its thermal processing thus far not explored.

**ACKNOWLEDGMENT**

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**REFERENCES**

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