SINTERING OF MONOLITHIC CORDIERITE AEROGELS
H. Vesteghem, D. Fargeot, A. Dauger

To cite this version:

HAL Id: jpa-00229486
https://hal.archives-ouvertes.fr/jpa-00229486
Submitted on 1 Jan 1989

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
SINTERING OF MONOLITHIC CORDIERITE AEROGELS

H. VESTEGHEM, D. FARGEOT and A. DAUGER

CNRS UR-320, Laboratoire de Matériaux Ceramic, Ecole Nationale Supérieure de Céramique Industrielle, 47 avenue A. Thomas, F-87065 Limoges, France

Résumé - Des aérogels de composition cordierite ont été élaborés par séchage hypercritique de gels obtenus par hydrolyse-condensation d'une solution alcoolique d'alcoxydes de silicium, d'aluminium et de nitrate de magnésium. La structure des gels et aérogels a été comparée par diffusion centrale des rayons X.

La structure des aérogels qui résulte d'un mécanisme d'agrégation de particules élémentaires denses est étudiée en fonction de la concentration initiale puis en cours de densification.

Abstract - Cordierite aerogels have been elaborated by hypercritical drying of gels obtained by hydrolysis-condensation of silicon and aluminium alkoxides in alcoholic solution with magnesium nitrate. The structure of gels and aerogels is compared through small angle X-ray scattering measurements.

The structure of aerogels which derives from an aggregation mechanism of elementary dense particles is studied for different initial concentrations and during densification.

1- INTRODUCTION

Cordierite (2MgO-2Al₂O₃-5SiO₂) has been recognized as candidate material for various applications such as electronic packaging, carrier of catalyst or heat exchanger (1). However, elaboration of a pure cordierite ceramic is known to be difficult and adding of sintering aids or crystallisation agents (2) always results in an alteration of its physical properties, thermal expansion coefficient or dielectric constant.

Multicomponent glasses and glass-ceramics can be prepared using the alkoxides of various elements by the sol-gel process (3). We have previously shown that transparent homogeneous gels of the cordierite composition can be obtained, and that hypercritical drying leads to very reactive products (4). Compacts of aerogel powders are fully densified into a transparent glass at 860°C, before any spontaneous crystallisation (5). Further heat treatment of the aerogel derived glass gives a fine grained glass-ceramic without any nucleation agent (6).
We report here on structural results of small angle X-ray scattering experiments performed on aerogels before and during sintering heat treatments.

2- EXPERIMENTAL

Our sol-gel method of preparation has been already described (5). A transparent alcoholic solution with cordierite composition was prepared from partially hydrolysed silicon tetraethoxyde, aluminium sec-butoxide and magnesium nitrate. This solution was reacted by adding sufficient amount of water to completely hydrolyse the alkoxides. The catalyst used was the hydrochloric acid. A clear, crystallisation free, wet gel was obtained in a few days.

The polymeric solution or the alcogel was placed in the teflon container of an autoclave, together with an appropriate volume of additional solvent. Hypercritical drying was carried out (260°C, 75 bars), leading to monolithic bodies of cordierite aerogels.

The linear shrinkage was measured in a compensated vertical dilatometer with alumina as reference at a heating rate of 3°C/min.

Small Angle X-ray Scattering (SAXS) data were obtained with a slit type camera using a double crystal monochromator (Cu-Kα1 wavelength) and a sample to detector distance of 500 mm. The scattered intensities were detected with a linear position sensitive proportionnal counter with an effective length of 55 mm. In these conditions, the explored scattering vector $H$ ranges from 6.10^{-2} to 2 nm^{-1} ($H = 4\pi \sin \theta \ / \lambda$ where $\theta$ is the Bragg angle).

Experimental results were corrected for parasite scattering and normalised to equivalent sample thickness, incident intensity and counter efficiency.

3- RESULTS

We have followed the structure development during polymerisation, through the sol-gel transition and during the ageing of alcogels. SAXS studies have shown that gelation occurs through the formation of polymeric particles. The mean size of these particles is estimated by the radius of gyration $R_g$, as measured in the Guinier region (low angles) of SAXS curves using the following approximation (7):

$$I(H) = N \delta^2 V_1 \exp(-H^2 R_g^2/3)$$

where $N$ is the number of particles of volume $V$ and of excess electronic density $\delta$. $R_g$ grows up during polymerisation and saturates to 7 or 8 nm near the gelation time, about 200 h at 45°C.

Scattering in the Porod region defined as $1/R_g << H << 1/a$ (8), where $a$ is the monomer size, depends on the internal structure of the scattering entities: a power law ($I(H) \propto H^{-D}$) behaviour is expected. For homogeneous particles with a smooth interface, Porod law is obeyed with $D = 4$. For polymeric structures, mass fractal objects, then $1 < D < 3$ where $D$ is the fractal dimension relating the mass $M$ of the object to its size : $M \propto R^D$.

Figure 1A shows the Porod plot of the alcogel. A power law is observed, and the slope of -1.6 is interpreted as the fractal dimension of the scattering particles.
The corresponding aerogel exhibits a rather different structure (9). The radius of gyration is 13 nm, and two regimes are observed in the log-log plot of figure 1B with slopes of -1.8 and -4. The crossover appears at about 0.8 nm\(^{-1}\), corresponding to a length of 1.25 nm. The structure is built up by a hierarchical agglomeration of clusters consisting of small, homogeneous and smooth primary units of average size \(a=1.25\) nm. This aggregate \((R_g=13\text{ nm})\) is a mass fractal of dimension \(D=1.8\), consistent with a cluster-cluster aggregation mechanism (10).

![Porod plots for (A) the wet gel and (B) the aerogel of Cordierite composition, showing power law regimes.](image)

The same hierarchical structure is observed for aerogels of different apparent densities (Figure 2) obtained from initial gels of different concentrations. However, all three structural parameters are slightly modified:

<table>
<thead>
<tr>
<th></th>
<th>apparent density</th>
<th>radius of</th>
<th>fractal</th>
<th>size of</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(d_a=250\text{ Kg/m}^3)</td>
<td>(R_g=13\text{ nm})</td>
<td>(D=1.6)</td>
<td>(a=1.8\text{ nm})</td>
</tr>
<tr>
<td>B</td>
<td>(d_a=120\text{ Kg/m}^3)</td>
<td>(R_g=18\text{ nm})</td>
<td>(D=1.9)</td>
<td>(a=1.25\text{ nm})</td>
</tr>
</tbody>
</table>

Assuming that the density of the elementary particles is the same for the two samples, the measured values are in good agreement since the apparent density of the aerogel is proportional to \(R_g^{D-3}\cdot a^3\) as expected.
Figure 2- Porod plots for two different Cordierite aerogels. The concentrations of alkoxides in the initial sol were (A) 0.13 and (B) 0.065 mole/l. Apparent densities of samples: (A) 250 and (B) 120 Kg/m³.

The linear shrinkage versus temperature of an aerogel bulk sample prepared from a gel (260 heures at 45°C) of initial concentration 0.13 mole/l, is shown in figure 3.

Figure 3- Densification curve for the cordierite bulk aerogel sample.
The aerogel begins to densify at a temperature which is appreciably lower than the temperature of sintering for conventional glass powders (6). Moreover, aerogel samples are able to reach nearly full densification before crystallisation starts, at about 960°C.

The internal structure, as studied by SAXS, is rather stable up to 830°C, where no significant change is observed. The first important modification occurring as the temperature is raised appears on figure 4. Since the X-ray absorption coefficient of the sample rapidly increases, the scattered intensity distribution is modified.

![Porod plot of cordierite aerogel samples after heat treatments of 15 mn at (A) 830°C and (B) 840°C.](image)

The region where Porod law is obeyed (slope -4) expands towards smaller scattering vectors indicating that elementary non fractal units are growing in size. Simultaneously, the fractal domain seems to disappear from the scattering curve indicating a collapse of the aggregated units. The scattered intensity rapidly decreases with the increasing density of the sample and the lack of porosity.

**CONCLUSION**

Cordierite gels have been prepared from aluminium and silicon alkoxides with magnesium nitrate in alcoholic solution. Hypercritical drying (260°C, 75 bars) leads to monolithic aerogels of high surface area which can be fully densified at 860°C since melting of pure cordierite composition requires a temperature of 1620°C.
SAXS studies show that the cordierite wet gel exhibits a polymeric structure made of mass fractal aggregates of about 8 nm in size and a fractal dimension $D=1.6$. The aerogel structure consists of mass fractal clusters (10 to 20 nm in size, $D=1.6$ to 1.9) resulting from the aggregation of small dense particles of 1 to 2 nm in size. Rapid growing in size of the elementary units and collapse of the aggregated structure yield to the densification of the aerogel, giving a transparent glass body at low temperatures.

REFERENCES