Sintering characteristics of nano-ceramic coatings
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4. SILICA: VISCOUS SINTERING

This chapter concentrates on the sintering behavior of silica sol-gels. It starts with the description of different models that are used to predict the viscous sintering process (§ 4.2). In fact, silica forms an appropriate model system to study viscous sintering behavior, because it maintains its amorphous state at all temperatures during the sintering process. For a general description of the analysis of the microstructure reference is made to chapter 2. Only specific aspects for silica are summarized in section 4.3. The starting material contains small nanometer sized spheroids, called colloids, the preparation of this material is dealt with in § 4.4. Experimental results of furnace and laser treatments are the subject of the next section (§ 4.5 and § 4.6). The dependence of viscosity on temperature will be quantified by using the activation energy. Also the influence of the colloid size on the sintering time will be described. Both furnace and laser sintering results will be compared with the model of Chapter 3. In the last section the mechanical properties of the coatings will be revealed by nano-indentation (§ 4.7).

4.1. INTRODUCTION

The sintering process can be grouped into three different categories: Solid state sintering (type 1, see chapter 5); Liquid phase sintering (type 2); Viscous sintering (type 3). In this chapter the latter sintering type is investigated by studying the sinter process of layers of nano-crystalline particles of silica, using either a laser or a furnace. Porous SiO$_2$ film can be applied in large-scale uncooled IR detectors as a thermal-insulating layer$^{1,2}$. And a low dielectric constant material for an intermetal dielectric (IMD) is imperative to reduce power dissipation, cross talk, and interconnection delay in the deep submicron device regime$^3$. Because furnace sintering experiments with silica sol-gels have been reported in the past$^4$, the question should be addressed whether sintering with a laser would give similar results. Indeed, compared to the commonly applied furnace sintering, the energy input with a laser treatment is very localized and applied during a very short time lapse. In this work the focus lies on the size effect of the colloids and therefore the sol-gels were composed with
different initial colloid sizes. From previous experiments on micrometer sized ceramic compacts it is known that the final densification and maximum layer thickness depend on the particle size. The main challenge of this work is to compare sintering behavior of nanometer sized colloids with the conventional ceramic sintering processes. Because of the importance of material composition and morphology to the final layer thickness, the silica sol-gels contained spherical particles of equal size (the size distribution is ± 5%). The latter point is very important because sintering models rely on a monodisperse size distribution whereas most of the experiments in literature show a broad size distribution making a critical comparison with the model descriptions rather questionable.

4.2. MODEL DESCRIPTIONS

There are several approaches to formulate the kinetics of the viscous sintering process, both analytically and numerically. This section addresses only the problem encountered when modeling a viscous sintering process. As a starting point it is known that at high temperatures inorganic glasses behave as ordinary Newtonian liquids (sintering type 3). Due to surface tension, viscous flow takes place during sintering of a system of glass particles resulting in neck growth and approach of particle centers. This causes shrinkage. The work done by surface tension in decreasing the total surface area is equal to the total energy produced by dissipation of the flow of the viscous glass. As the flow of the amorphous silica plays a major role in the sintering process we start with the viscosity.

4.2.1. The viscosity

The viscosity of a glass ranges between 10 to $10^{13}$ Pa·s and is controlled by a number of factors, i.e., the connectivity of the structures, the strength of the bonds connecting the short range order, and the rate of change of the structure with temperature. Vitreous silica (or fused silica: glass consisting of almost pure silicon dioxide (SiO$_2$)) consists of a strongly bonded, three-dimensional network, which only slowly breaks down with increasing temperature. As a result, the viscosity decreases with increasing temperature. Each curve connects data points with the same hydroxyl content. From this graph one can see that when the silica contains more hydroxyls it becomes less viscous.
The reduction of the viscosity results from the creation of non-bridging bonds as silanol (Si-OH) groups that replace siloxane (Si-O-Si) bonds. Addition of small amounts of alkali oxides to vitreous silica also results in a rapid decrease in viscosity and a decrease in the slope of the curve. The replacement of alkali-oxides by alkaline earth oxides, which does not disrupt the network as much, results in a more viscous material. Analysis of viscous sintering is difficult because of the complex geometry of the porous body, but simple approximations yield satisfactory results.

4.2.2. Sintering of two spheres

The kinetics of initial stage sintering were described by Frenkel in an analytical form as early as 1945. He presented an analysis of the coalescence of a pair of spheres, which is a simple representation of the sintering of a body of packed powder. It was assumed ever since that the shape of the spheres changes in the neck region only and that at a given time of sintering the curvature over the neck regions is constant. This model leads to the following expression for the neck radius $x$ as a function of sintering time $t$:

$$\frac{x^2}{a^2} = \frac{3\gamma t}{2\eta a}$$  \hspace{1cm} (4.1)

Where $a$ is the particle radius (Figure 4.2), $\gamma$ is the surface energy and $\eta$ is the viscosity, at the sintering temperature. This equation was confirmed by Kuczynski, who measured the neck sizes of sintering pairs of glass spheres.
with a diameter of 500 μm. The mechanisms of sintering can be distinguished by the particular relationship of the radius of the neck $x$ found between two particles and the sintering time $t^8,9$ worked these out into a general equation:

$$\left(\frac{x}{a}\right)^n = \left(\frac{Bt}{(2a)^m}\right)$$

(4.2)

Where $n$, $m$ and $B$ can be assumed constant with the mechanism of mass transport.

**Viscous flow**

$$\left(\frac{x}{a}\right)^2 = \left(\frac{3\gamma t}{2\eta a}\right)$$

(4.3)

**Plastic flow**

$$\left(\frac{x}{a}\right)^2 = \left(\frac{9\pi\rho h D_{s,t}}{2kT a}\right)$$

(4.4)

**Evaporation-condensation**

$$\left(\frac{x}{a}\right)^3 = \left(\frac{3P\gamma Bt}{4\rho\alpha^2} \sqrt{\frac{\pi}{2}} \left(\frac{M}{kT}\right)\right)$$

(4.5)

**Volume diffusion**

$$\left(\frac{x}{a}\right)^5 = \left(\frac{10D_v\Omega t}{kT a}\right)$$

(4.6)

**Grain boundary diffusion**

$$\left(\frac{x}{a}\right)^6 = \left(\frac{5\delta D_b\Omega Bt}{4kT a^4}\right)$$

(4.7)

**Surface diffusion**

$$\left(\frac{x}{a}\right)^7 = \left(\frac{7D_s\Omega^2 t}{2kT a}\right)$$

(4.8)

Here, $D_v$ is the volume diffusivity, $D_s$ the surface diffusivity, $D_b$ the grain boundary diffusivity, $P$ the vapor pressure, $\Omega$ the atomic volume, $M$ the molecular weight, $\rho$ theoretical density and $T$ the absolute temperature.
Thus showing that viscous flow is the fastest sinter mechanism possible. In these relations are elaborated with the inclusion of plastic flow, lattice diffusion and grain boundary diffusion.

![Figure 4.2: Parameters for a two-sphere model.](image)

Because it is easier to measure the rate of approach of the centers of two spheres during sintering, an equation can be derived from the neck growth equations, making the usual assumption

\[
\frac{h}{a} = \frac{s}{a} = \frac{x^2}{4a^2}
\]  

(4.9)

This yields:

\[
\frac{h}{a} = \frac{3\gamma}{8\eta a}
\]  

(4.10)

Note that in the original work of Frenkel a numerical factor of ¾ has been calculated on the assumption \(s/a=x^2/2a^2\). Equation (4.10) can also be used to describe the rate of linear shrinkage of an array of spherical particles under the condition that the colloids stay at one line. Excellent agreement with these equations was claimed in experiments on the shrinkage of spherical glass powder arrays for shrinkage values up to 8%.

However, Exner pointed out that asymmetric neck growth and formation of new contacts during sintering makes a quantitative description of the shrinkage of irregularly packed particles by relations derived for only two particles questionable. Actually, the agreement between experimental results and the
shrinkage equation (4.10) for particle systems may be rather fortuitous. To prove this, he experimented with planar arrays with a larger number of spheres of 400 μm size. Rearrangement of particles and the formation of additional contacts during sintering were reasons to consider why the centre-to-centre approach of adjacent spheres and the shrinkage measured on an irregularly packed planar array of spheres differed from each other, thus limiting the validity of equation (4.10) to the first part of the sintering process until \(x/a = 0.33\).

Mackenzie and Shuttleworth (MS model) analyzed the shrinkage rate like Frenkel, but they used a shell model, where the void in the middle of a ball (shell) represents the pores in the sintering body. It has the advantage that the expressions for the change in surface area and the energy dissipated in viscous flow are exact, but its complexity does not invite to add any extra parameters such as temperature dependence to it. Furthermore the final state of full density can not be calculated. Comparing both models Frenkel’s still approaches the MS model very well. Bannister also shows that the usefulness of initial sintering equations like Frenkel’s can be extended beyond the conventional initial state into the intermediate stage of sintering. Coble focussed on solid state sintering but the cylindrical model proposed by Brinker and Sherer is based upon it. Further, German extended the analysis of Frenkel and Kuczynski towards a model for surface diffusion whereas Veringa presented a mathematical model to describe the densification and reorganization of a random stacking of particles due to internal transport of material. Rice presents a combination of models based on minimum solid areas of an idealized stacking of spherical particles partially bonded and spherical pores in a solid matrix. He compares the results with the material properties (like Young’s modulus and thermal conductivity) of the porous bodies of sintered glass powders and with foamed glasses. More recently Scherer developed the cylindrical model incorporating the influence of the pore size distribution, because Emmerling et al. together with Vorst showed that the change in surface area with density is inconsistent with the cylindrical model when the pore size distribution is not taken into account. The main features of the cylinder model are that the cylinders are not straight and that they are not fully connected.

Another way to model the viscous sintering behavior is by molecular dynamics. To understand what happens at the surface of the colloids, various methods of measuring porosity, density and surface area were performed.
4.3. MICROSTRUCTURE

4.3.1. Specimen preparation

For a general description of the experimental tools that were used for the analysis of the microstructure reference is made to Chapter 2. Here, only the relevant aspects for silica are mentioned. Silica’s structural evolution of the microstructure due to sintering can be studied in several ways. In order to increase the length scales Nuclear Magnetic Resonance Spectroscopy (NMR) is used to look at the kinetics of the hydrolysis and condensation reactions during gelation and the early stages of polymerization. Infra Red (IR) and Raman spectroscopic investigations are used to identify specific oligomeric species in different solutions and to follow the evolution of the inorganic framework. Zerda\textsuperscript{26} even coupled the Raman intensity to the particle radius. Small-angle-scattering (SAXS) was used in combination with light and neutron scattering by Shaefer\textsuperscript{27} to obtain quantitative information about pores in the xerogel and inter atomic spacings thus it may give information about the entanglement of the polymeric chains. Silica also has the disadvantage that due to the amorphous phase XRD-measurements cannot provide a value for the average grain size as is possible when analyzing zirconia.

Three commercially available (Merck) water based SiO$_2$ sol-gels containing monodisperse colloids with a diameter of respectively 25, 50 and 90 nm and one butanol based sol-gel were spin coated onto fused silica substrates with dimensions of 50x50 mm. The fused silica substrates were pre-treated by ultrasound in NaOH for 15 min, cleaned with demineralized water and dried at room temperature. The surface was wetted completely by spincoating.
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Figure 4.3: The spincoating process: A drop of the sol-gel is deposited on the center of a spinning (typically 1500 rev/min for 30 sec) substrate. Centrifugal forces drive the liquid outwards creating a coating of uniform thickness.

Figure 4.4: Thickness of the coating as a function the spinning speed. Three different sol-gels were spun with colloids with a diameter of 90, 50 and 25 nm.

Then the sample was dried for 2 h at 120 °C. Evaporation of the solvent and water to the atmosphere turns the sol into a porous xerogel material. Heating will drive off residual solvent, and sintering will produce a dense ceramic oxide.
Steel substrates were pre-treated by ultrasound in acetone for 15 min, for another 15 min in Kirolin Hydro (commercial cleaning agent for metals) and cleaned ultrasonically in demineralized water twice (changing water before second run) for 156 min. After drying at room temperature coating was performed in the same way as described for fused silica.

By adding 1,2- propanediole to the butanol based sol-gel the viscosity was adjusted for inkjetting at 7.5 mPa.s (it was observed that the viscosity of this sol-gel increases with time) and with this sol various substrates were also coated by inkjetting.

The application of a liquid film with solid particles onto a substrate is followed by a drying process, which should result in a homogenous material distribution without defects in the layer. The following problems can arise during drying:

Flow (of particles) in the liquid layer during drying will cause an uneven distribution of the solid in the dried layer. This flow can be induced by local differences in the surface tension. This so called Marangoni effect will present itself mainly when the sol has a low viscosity, and therefore so-called thickeners are sometimes added.

Tensile stresses in the film will arise during drying when the absence of sufficient liquid reduces the mobility of the particles. These stresses may eventually lead to cracks depending on the evaporation rate. Tensile stresses in the layer can only be avoided if the layer of particles shrinks anisotropically, perpendicular to the substrate. Thus there is an upper limit to the thickness of the layer without cracks. Thin cracks associated with small particles introduce higher stresses during drying. Although with larger particles thicker layers can be formed, they induce larger closed pores, which cannot be removed during sintering.

Flocculation of colloids in a sol-gel (Figure 4.5), will cause open structures with large pores, which usually nucleate cracks during sintering. This can be prevented by using non-aggregated and spherical particles and colloids with a high stability (see Figure 4.6).
Figure 4.5: Several ways in which colloidal particles aggregate or link together in: a) sol, b) coagulation (relatively close packed clumps) and flocculation (particles in clumps are linked) c) gel, where particles are linked together in branched chains that fill the whole volume.

Figure 4.6: Close packed dried silica colloids.

Inclusions of residual precursors, like water and additive organics, may cause additional shrinkage and extra stresses and even more problems during sintering, causing blistering and bubbles when heated.
Cracks in the dried coating were still recognizable after sintering, so if closed coatings are required from an application point of view, the dried layer should be homogeneous. Thus no cracks, no holes, no inclusions, no pollution and dust, and constant layer thickness across the whole surface area is desirable.

4.3.2. Heating

All furnace heat treatments were performed in air atmosphere. The temperature was monitored and controlled via a feedback loop by a thermocouple. If the drop in temperature by opening the furnace was significant, an alternative method of entering the sample into the furnace was used. A smaller sample was made and entered with a rod via a hole into the furnace. In-situ sintering experiments in the Environmental SEM were conducted under a water vapor atmosphere at a pressure of 7.5 Torr unless otherwise stated.

After heating the green (dried) samples at a constant temperature of 1100 °C for 4 to 68 hours the three sol-gels were compared. These sintered samples were used to give an indication of the densification and neck growth during sintering of the other samples. Next, to indicate temperature influence isothermal treatments were conducted for 30 minutes at temperatures between 500 and 1300 °C.

Considering the short interaction time of a laser treatment, the furnace treatments were drawn towards shorter sintering times. Sintering at a constant temperature was done for all three sol-gels, with different time intervals ranging between 5 minutes and 4 hours at 1100 °C. For the sol-gel containing 25 nm colloids, a treatment temperature of 1000 °C with the same time ranges was used as well. When putting the sample in the furnace, the entering time was kept short compared to the time the samples spent in the furnace, to avoid a drop in temperature when the furnace was opened.

Because the heating rate might be of influence to the build-up of strains during the treatment, the 50 and 90 nm sol-gels were put through heating rates of 1, 2.5 and 5 °C/minute up to 1200 °C. An overview of the experiments with short sintering times is listed in Table 4.1.
Table 4.1: Overview of experiments on silica sol-gels.

<table>
<thead>
<tr>
<th>Colloids</th>
<th>Short time sintering</th>
<th>Heating rates</th>
<th>Combination</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 nm</td>
<td>10, 20, 50 minutes and 2, 3, 4 hours at 1150°C</td>
<td>1°C/min, 2.5°C/min and 5°C/min up to 1200°C</td>
<td>1°C/min up to 1150°C and 50 minutes hold 2.5°C/min up to 1150°C and 20 minutes hold 5°C/min up to 1150°C and 10 minutes hold</td>
</tr>
<tr>
<td>50 nm</td>
<td>5, 10, 15, 20, 25, 45 minutes at 1100°C</td>
<td>1°C/min, 2.5°C/min and 5°C/min up to 1200°C</td>
<td>1°C/min up to 1150°C and 50 minutes hold 2.5°C/min up to 1150°C and 20 minutes hold 5°C/min up to 1150°C and 10 minutes hold</td>
</tr>
<tr>
<td>25 nm</td>
<td>5, 10, 15, 20, 25, 45 minutes at 1000°C</td>
<td>1°C/min, 2.5°C/min and 5°C/min up to 1200°C</td>
<td>1°C/min up to 1150°C and 50 minutes hold 2.5°C/min up to 1150°C and 20 minutes hold 5°C/min up to 1150°C and 10 minutes hold</td>
</tr>
</tbody>
</table>

Combined experiments of heating rate and isothermal sintering were conducted for the 90 nm particle sol-gel samples. The samples were heated up to 1150 °C with heating rates as before. The samples were kept for a certain amount of time at this temperature. The actual period of time depended on the heating rate, i.e., 10, 20 and 50 minutes for the 5, 2.5 and 1 °C/minute heating rates, respectively. The total treatment time was the same as the “rate-treated” samples.

The Environmental SEM enabled us to study the in-situ sintering behavior of the SiO₂ sol-gels. Changing the temperature in the microscope required a lot of adjustment of focusing. The best observations were obtained during isothermal treatment. In-situ sintering was conducted for 1 hour at 1100 °C. These samples were also observed with the HR FEG-XL30s SEM afterwards.

Laser sintering was performed with a CO₂-laser with 3 kW output power. The beam was imaged onto a polygon. Therefore the shape of the spot is elliptical with the large axis oriented in the direction of motion. With the rotation of the polygon the laser spot sweeps with at least 160 m/s across the substrate. Perpendicular to the motion of the beam the substrate was moved using a linear stage. The characteristic variable process parameters and their variation range are listed in Table 4.2
Table 4.2: Variable process parameters of the laser treatments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Power</td>
<td>W</td>
<td>1200 to 3000</td>
</tr>
<tr>
<td>Beam Widths</td>
<td>mm</td>
<td>4.6</td>
</tr>
<tr>
<td>Beam Lengths</td>
<td>mm</td>
<td>12</td>
</tr>
<tr>
<td>Scan Speed of Beam</td>
<td>m/s</td>
<td>10 to 160</td>
</tr>
<tr>
<td>Speed of Stage</td>
<td>mm/s</td>
<td>0.1 to 5</td>
</tr>
</tbody>
</table>

A CO₂ laser beam was put in a scanning mode to produce heat in a thin surface layer of the coated samples. Computer calculations of temperature distribution were performed to estimate the influence of scan and trace speed, laser power and laser spot size. Depending on those parameters two extreme-heating modes are possible:

- **Spot heating**, i.e. the laser spot has a much higher temperature than the scan line and the rest of the sample surface.

- **Line heating**, i.e. the laser spot has a similar temperature as the scanned line, which is much hotter than the rest of the sample.

Most experiments were carried out using a mixed spot and line heating where the temperature in the laser spot was a few hundreds of °C above the temperature of the scan line. Thereby sufficiently short heating times were achieved to prevent crack formation by thermal stresses.
Figure 4.7: SEM top views of the dried sols containing monodisperse 90, 50 and 25 nm sized colloids.
4.4. Furnace Sintering

Figure 4.7 shows a plane view of scanning electron microscope images of the xerogels containing monodisperse 25, 50 and 90 nm sized colloids. The packing density of the colloids can be extrapolated from these pictures to be in a range of 40% to 60% (maximum density for monodisperse spherical particles is about 70%). The basic material in the sol-gel is SiO$_2$/H$_2$O. The density of the colloids was measured to be 2.08 g/cm$^3$. The thickness of these layers was also investigated by scratching with a diamond tip and then breaking the glass substrates with the dried layer for a cross-section in the SEM.

Figure 4.4 showed the dependence of the thickness of the xerogel film on the spinning speed for the sols. The size of the colloids had no influence on the thickness of the coating, but increasing the viscosity of the gel by additives produced thicker layers. The coating thickness decreased proportional to (spinning speed)$^{-2/3}$. For lower spinning speeds the edge of the dried layers was thicker due to the spin-up process. When dried layers were too thick (> 1100 nm) they cracked. These cracks were still visible after sintering, showing the need for crack free dried coatings before sintering.

Experiments showed that sintering a sol-gel with colloids of 25 nm to full density took 3 hours at 1100 °C. For a sol-gel with 50 nm colloids it took 20 hours, a sol-gel with colloids of 90 nm needed 40 hours to fully densify.

Figure 4.8 shows the SEM pictures of the samples treated at different temperatures for 30 minutes. At 1100 °C there is a clear onset of sintering, and at higher temperatures the thin layers are for the greater portion sintered for all colloid sizes. However there is a clear difference, as seen before, between the different colloid sizes. The onset temperature for 25 nm colloids towards sintering appears to be lower than 1000 °C. The Environmental SEM enabled us to study the in-situ sintering behavior of the SiO$_2$ sol-gels. As a result of the beam charging the particles, locally the sintering was frozen, so to observe the sintering process it was necessary to observe different positions for several times. An advantage of this freezing effect was found as well: it was possible to freeze the sequential sintering stages and study them afterwards in the HR-FEG-XL30s SEM.
Figure 4.8: These SEM pictures show 3 columns containing resp. 90, 50 and 25 nm colloidal silica sol-gels treated from the top to the bottom row with resp. 1000, 1100, 1200, 1300 °C. The sintering time was 30 minutes.
Figure 4.9: Densification versus fluence. Different colloidal silica gels (25, 50 and 90 nm colloids) were laser sintered with different fluences. The relative thickness was measured by a profilometer.

4.5. LASER SINTERING

Figure 4.9 shows that a clear change for both the 50 nm and the 25 nm colloids occurs around the fluence of 600 J/cm$^2$, while for 90 nm colloids nothing happens.

The observations around a laser track were also fed into an existing image-processing program. In the case of silica sol-gel, several problems occur, such as blurry edges and the fact that the edges often are brighter than the centers, which makes it more difficult to apply a threshold to the image. To overcome these problems a new technique, called morphological image processing (MIP) was used to quantify the sintering process. The aim was also to measure the center-center distances of the grains during the process. But center-center distances were hard to calculate especially when individual colloids are not distinguishable anymore. More success was obtained by calculating the average perimeter and area, of the objects that were distinguished and by calculating the Euler number to quantify the sintering process. The Euler number is the number of objects minus the number of holes.

Figure 4.10 shows a typical temperature distribution around a moving laser spot on the sample surface.
Figure 4.10: Temperature distribution calculated for a laser treatment with a CO$_2$ laser beam scanning; laser beam velocity of 1.75 m/s and a power of 600 Watt.

Figure 4.11 shows the resulting calculations made by the MIP program. The average perimeter and area of the objects detected by the program were calculated as was the Euler number from pictures transverse to the laser track. The data in the graph show relative values that result from the actual data divided by the maximum value. For the average perimeter, $P$, and area, $A$, this was a fully sintered sample, for the Euler number an unsintered sample produced the maximum value. A fully sintered, non-porous sample has an absolute Euler number equal to 1, so the relative Euler number, compared with max Euler number, is almost 0.
Figure 4.11: Per picture normalized values for Euler number, area and perimeter. Calculation results from morphological image processing of the microstructure of laser treated silica sol-gel.

Figure 4.12: A characteristic number for the microstructure calculated by MIP for sintered silica was realized using the equation: \((P-E+1)/2\). This gives 0 for unsintered, 1 for fully sintered.
4.6. MECHANICAL PROPERTIES BY NANO-INDENTATIONS

The technique of nano-indentations provides a possibility to derive the mechanical properties of a thin film or coating. Deep indentations like those with Vickers hardness measurements are commonly used for thicker layers. On the other hand, indents made by nano-indentations are small and shallow enough to capture the mechanical properties of the coating and not of the substrate. In our experiments Vickers indentation was used to make a marker so as to find the locations of nano-indentations back for further investigations in SEM.

Figure 4.13: The hardness of the laser sintered silica coating, P= 800 W, v= 250 mm/s spot diameter = 1.7 mm. Each data point is the average of 8 measurements in the laser track. The highest hardness was measured in the middle of the track. The others are taken at steps of 100 µm increasing distance from the middle of the track.
4.7. DISCUSSION

As silica is a material that only sinters by viscous sintering it is an appropriate material to test the various sintering models. This is in contrast to other ceramic materials like zirconia that exhibits several phase changes during the process. Comparing sintering behavior of nano-meter sized colloids with the conventional ceramic sintering processes is feasible with scanning electron microscopy. Because of the importance of material composition and morphology of the layer, the silica sol-gels have to be monodisperse, enabling a good comparison with simplified models.

Coatings sinter more slowly than unconstrained gels, because films may shrink only in the direction perpendicular to the substrate but experiments have also shown the opposite.

To predict the densification of a thin film equation (4.10), can also be used to describe the rate of linear shrinkage of an array of spherical particles under the condition that the colloids stay at one line:

\[
\frac{L(t)}{L(0)} = 1 - \frac{3\gamma}{8\eta a} t
\]  

(4.11)
Where \( L(t) \) is the linear dimension at time \( t \) and \( L(0) \) the initial linear dimension, \( \gamma \) the surface energy, \( a \) the original particle diameter, and \( \eta \) the viscosity. Assuming \( \gamma = 0.3 \text{ J/m}^2 \), \( L(t)/L(0) \) was calculated for the M25 sol-gel at 1100 °C with different sintering times. See Figure 4.15. This resulted in: \( \eta = 1.3 \times 10^{11} \text{ Pa s} \).

Figure 4.15: Experiments to calculate the viscosity of the M25 silica sol-gel at \( T=1100 \text{ °C}, d=25 \text{ nm.} \rightarrow \eta = 1.3 \times 10^{11} \text{ Pa s.} \)

The temperature dependence of the viscosity\(^6\) can be described by:

\[
\eta = \eta_0 e^{\frac{\Delta}{RT}} \tag{4.12}
\]

with \( A, T_0 \) and \( \eta_0 \) constants, while \( T \) is temperature. But the viscosity of silica obeys the Arrhenius equation from liquidus to \( T_c \):

\[
\eta = \eta_0 e^{\frac{Q}{RT}} \tag{4.13}
\]

Where \( Q \) is the activation energy and \( R \) is the ideal gas constant. The activation energy increases as the hydroxyl content decreases. For silica\(^6\) the activation energy is \( 120 < Q \text{ (kcal/mol)} < 170 \). Thus with increasing temperature the decreasing viscosity results in a very high densification rate, much higher than the rate of densification of crystalline materials. The viscosity of silica is \( 10^7 \text{ Pa s} \) at 800 °C\(^{30} \). The sintering rate is also faster for bodies with smaller particles or pores, colloid diameters comparable to conventionally crushed powders, sinter typically orders of magnitude faster.

\[
y = -0.2436x + 1
\]

\[
R^2 = 0.9693
\]
The behavior of colloidal silica is based on its morphology and structure and on the chemistry of its surface. Bergna\textsuperscript{24} described the process of sintering of SiO$_2$ colloids as the condensation of silanol groups to form siloxane bridges. Siloxane bridges are formed on the hydroxylated silica surface by thermally induced condensation of hydroxyl groups up to about 500 °C. At higher temperatures the strained siloxane groups are converted into stable siloxane groups. The silica OH groups are the main centres of adsorption of water molecules; as mentioned by Zhuravlev\textsuperscript{23} the activation energy of desorption of physisorbed water is between 25 and 40 kJ/mol.

The silanol number $\alpha_{\text{OH}}$ being the number of OH groups per square nanometer surface of dehydrated but fully hydroxylated amorphous silica is a physicochemical constant independent of origin and structural characteristics of the silica. An $\alpha_{\text{OH}}$ of 4.6 OH groups per square nanometer is reasonable compared to the $\alpha_{\text{Si}}$ which is 4.55 Si atoms per square nanometer on the octahedral face of β-cristobalite (a crystalline silica which has a density similar to amorphous silica)\textsuperscript{24}. The concentration of the OH groups on the surface decreases monotonically with increasing temperature. At 200 °C all the physisorbed water is gone from the surface which is then made out of terminal silanol groups and siloxane bridges.(see Figure 4.16).

![Silanol groups and siloxane bridges on the surface of colloidal silicas.](image-url)
CHAPTER 4

Figure 4.17: This figure from Zhuravlev's article shows the silanol number as a function of the temperature. Curve A shows the surface silanols, curve B the surface siloxanes. In zone I the sol contains physisorbed $H_2O$, in zone II there are Vicinals, Geminals and Singles, in zone III Geminals and Singles are present at the surface and in zone IV only Singles are present. In the temperature region C coalescence takes place in region S sintering and at higher temperatures crystallization takes place.

At 450-500 °C all vicinal groups condense, yielding water vapor, and only terminal silanol groups and strained siloxane bridges remain. Internal silanols start to condense at about 600 – 800 °C. Up to temperatures of 1100 °C only isolated single silanol groups remain on the silica surface (see Figure 4.17).

The fewer OH groups at the surface of the silica and the more siloxane bridges the more hydrophobic the surface becomes. Brinker and Scherer show the temperature-viscosity relationship with the varying hydroxyl contents. For every one of these lines a combination of $\eta$ and $Q$ can be made. Putting these in one graph gives Figure 4.18.

90
The equation corresponding to the line through these points is:

\[ \eta_0 = 10^7 e^{-\frac{Q}{Q_e}} \]  

(4.14)

By using the calculated activation and Equation (4.11), the hydroxyl content of our \( \text{SiO}_2 \) gel can be calculated and the viscosity at other temperatures than 1100 °C can be predicted. The calculated values were: \(Q = 4.72 \times 10^5 \text{ J/mol.K} \) (=112 kcal/mol). The hydroxyl content was calculated to be 0.13 [wt%]. The resulting relationship between temperature and viscosity for our sol-gel is added to the Brinker and Scherer graph in Figure 4.18.

From Frenkel’s description an equation for the growth in radius of the neck between spheres during sintering can be derived\(^{10}\) (see equation (4.15) upon inserting the temperature dependence of the viscosity, the growth in radius of the neck between spheres during sintering becomes:

\[ \frac{x^2}{a^2} = \frac{3yt}{2\eta_0 e^{\frac{Q}{Q_e}} a} \]  

(4.15)

where \( \eta_0 \) and \( Q \) are taken as constants.
### Table 4.3: Necking of SiO$_2$ 90 nm colloids during sintering at 1150 °C at different sintering times, compared with calculated predictions.

<table>
<thead>
<tr>
<th>Sintering time [minutes]</th>
<th>Necking [L/L0]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measured</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>20</td>
<td>0.3</td>
</tr>
<tr>
<td>50</td>
<td>0.6</td>
</tr>
<tr>
<td>120</td>
<td>0.7</td>
</tr>
<tr>
<td>180</td>
<td>0.8</td>
</tr>
<tr>
<td>240</td>
<td>1</td>
</tr>
<tr>
<td>300</td>
<td></td>
</tr>
</tbody>
</table>

From a series of 7 sintered samples of SiO$_2$ at a temperature of 1150 °C the average necking area was measured (see Table 4.3). Once a necking of unity is reached this does not mean that the sintered coating is fully densified. Asymmetric neck growth, caused by the local packing and atmosphere, will cause a rearrangement of particles in regions of smaller packing and opening of larger pores$^{10}$. This process can be seen in Figure 4.19 and it was studied more closely in-situ where the subsequent stages of the rearrangement and pore growth were frozen and afterwards observed in the high resolution XL30s FEG Scanning Electron Microscope. Locally charging the sol-gel with the electron beam prevented further sintering at that point.

Because the experimental measurements of neck sizes after sintering showed a good match up to neck sizes of about 80% of the colloid radius, it is possible to extend the valid use of the Frenkel equations for nano-sized silica sol-gels beyond the initial sintering phase. For both 50 and 90 nm colloidal sol-gels this was verified.
Figure 4.19: Proceeding sintering stages in time of 90 nm colloids of silica.

With these observations it is possible to derive the temperature from the SEM pictures when the sintering time (for laser treatment this would be the interaction time) is known, according to

\[ T = Q R^{-1} \ln \left( \frac{\gamma a t}{\alpha^2 T_0} \right) \]  \hspace{1cm} (4.16)

Coupling between the temperature distribution model and these temperature calculations by observations of SEM pictures seems to be feasible. To improve this verification, a relation between necking percentage and the Euler number, determined by MIP, could be investigated.
4.8. Conclusions

Sintering experiments with nano-ceramic SiO$_2$ coatings show that models for viscous sintering of micro-ceramics are appropriate to predict the correlation between colloid size, necking and pore growth, and densification in these coatings. The observations, made with the Philips XL30s FEG SEM, gave an excellent insight in the nano-meter morphology via plane views and cross sections of an array of sintering experiments. Computer based image analysis was carried out to improve quantification of the observations for the sintering system. This turned out to be a feasible but still labor intensive. A much better insight in the development of the sintering process was achieved with the in-situ sintering experiments in the Environmental-SEM. In spite of some difficulties with the resolution and charging effects of the electron beam during observation, the observations clearly showed the densification and structural evolution that take place during the sintering process. Some adjustments have to be made to be able to use existing densification-kinetics models for sol-gels containing nanosized colloids.

If coatings are to be produced flexibly, laser treatments might be a very interesting alternative competing with the classical way of furnace sintering. To achieve a precise dimensioning of the coated patch care must be taken to apply an overall homogeneous coating with a similar thickness everywhere and a stable laser beam. Putting several laser tracks next to each other can produce these isolated coating patches anywhere on the substrate. Based on the analytical descriptions delineated in Chapter 3 calculations of the temperature fields were conducted to compare and predict the resulting microstructure of the finally sintered coatings and these were in good accordance with the results obtained from the experiments.

4.9. References

SILICA: VISCOS SINTERING
