Sintering characteristics of nano-ceramic coatings
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5.

ZIRCONIA: CRYSTALLINE SINTERING

In this chapter the sintering behavior of zirconia sol-gels coatings deposited on fused silica and steel is analyzed. It starts with the description of the experimental set-up for both substrates and precursors (§ 5.2). Experimental results of furnace and laser treatments are the subject of the next section. Attention is paid to the densification behavior and the grain growth in the layer. Also, the different crystal phases observed are addressed (§ 5.3) followed by a discussion of the differences between furnace and laser sintering in § 5.4. We conclude with a formulation that predicts the grain size and densification both for the initial fast sintering of the process, at all sintering temperatures, and for the final slow sintering, only at the higher sintering temperatures (§ 5.5).

5.1. INTRODUCTION

Applications of zirconia (ZrO₂) have grown very fast and at present ZrO₂ has become one of the most industrially important ceramic materials. The traditional applications of ZrO₂ and ZrO₂ containing materials are foundry sands and flours, refractory ceramic and abrasives. Due to its high oxygen ion conduction and high refractive index it is also used in a broad range of novel applications including catalysts, oxygen sensors, fuel cells and jewelry. Since the publication of the famous paper on ‘ceramic steel’ transformation toughened zirconia by Garvie et al., zirconias have also been utilized in many structural applications. Along with high strength and toughness, zirconia also possesses adjustable hardness, wear resistance and thermal shock resistance. These properties have led to the use of zirconia-based components in a number of engineering applications such as automobile engine parts, wire drawing dies and cutting tools. The low thermal conductivity together with a relatively high coefficient of thermal expansion makes zirconia a suitable material for thermal barrier coatings on metal components.
At atmospheric pressure zirconia has three crystalline polymorphs, namely cubic, tetragonal and monoclinic. The stable phase at room temperature and at atmospheric pressure of pure coarse-grained zirconia is monoclinic which transforms martensitically at 1170 °C to tetragonal and at 2370 °C to a cubic structure. The martensitic transformation from tetragonal to monoclinic structure has great importance for mechanical applications because it forms the basis for transformation toughening.

5.2. EXPERIMENTAL

This investigation was focused on short and long sintering times in the furnace, and with ESEM on sintering times shorter than 10 minutes, mainly aimed at examining the first sintering phase. Experiments indicated that the principal changes in the sol-gel structure occurred within the first minutes. After this laser experiments were performed.

5.2.1. The substrates

The zirconia sol-gels were prepared from precursors, which reacted with each other to form monodisperse zirconia particles of about 3 nm (consisting of zirconium hydroxide) that are suspended in an aqueous fluid (the sol-gels were provided by Merck-Germany). The layers of zirconia sol-gel were deposited on both polished fused silica substrates and stainless steel substrates, and the desired thickness was achieved by spin coating. After coating the samples were dried in air at ambient temperatures. The spincoating rotational speeds were set to produce 350 nm green layers, because experiments indicated that this was the maximum layer thickness for a coating without cracks.

Zirconia sols were deposited onto polished fused silica samples of 50x50x1.5 mm and on steel substrates. The coatings applied to the steel substrates appeared to crack much easier than the layers on fused silica, although the sinter process seems to be identical. Some cracks already occurred during the drying process. The cracking was found to be related to the surface roughness of the substrate. In Figure 5.1 plane view images are depicted of zirconia sol-gel layers deposited on different steel substrates. The sample with the highest roughness (the ground substrate) exhibits more cracks, whereas the least rough substrate (polished) shows only a few cracks. These cracks are probably due to local stresses.
5.2.2. Preparation of samples for furnace sintering

The fused silica samples covered with a dried zirconia sol-gel layer were dried for a few days at room temperature and were then put in a furnace with an atmosphere of air. These specimens were isothermally sintered under normal air atmosphere with different sintering times ranging from 1 minute up to 6 hours and at temperatures ranging from 150 °C to 1200 °C. Subsequently, the samples were cooled down to room temperature in ambient air. The sintering variables were temperature and time, resulting in zirconia coatings with different particle sizes, layer thickness and densities.

Because the green coating is very thin (approximately 350 nm), it will heat up so fast that the coating is almost instantly at the same temperature as the furnace atmosphere (calculations predict within 2 microseconds).
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For temperatures higher than 1200 °C quartz becomes rather soft and sintering temperatures much higher than 1200 °C were not possible on quartz as a substrate.

To make layers with a larger thickness the zirconia sol was hydrothermally treated (1 hour at 110 °C). The primary particles in the sol clog together forming clusters of 2 nm to 75 nm. As a result of the different size and properties of the hydrothermally treated zirconia a green layer thickness of 1 μm could be obtained without cracking. Also with hydrothermally treated zirconia all tests were performed with quartz as a substrate. Both furnace and laser sintering experiments with a large range of heat inputs were performed.

The samples were examined using ellipsometry, scanning electron microscopy, transmission electron microscopy and X-ray diffraction. With the use of an ellipsometer (VASE Ellipsometer at Philips Physical Laboratory-Eindhoven, a rotating analyzer type measuring the spectral range between 185 and 1700 nm) layer thickness and density were studied. An SEM equipped with a special electromagnetic lens in order to obtain higher resolution (Philips XL30-S FEG SEM) was used to study the layers (see Chapter 2). Grain size from plane view images and layer thickness from cross section images were determined. A TEM (JEOL 4000 EX/II) was used to obtain high resolution images so as to study the original sol-gel particles and a TEM JEOL 2010 F was used for an analysis of the chemical composition and sub-grain boundaries as well as the wetting of the zirconia by the substrate at high temperatures.

For SEM preparation, the heat-treated samples were glued onto an aluminum holder with silver paint and then coated with a thin Palladium layer to prevent sample charging. As a result, small islands can be seen at very large magnifications, but because they are smaller than 5 nm, it is still possible to see the individual zirconia grains. All pictures in this chapter were taken with the Philips XL30s SEM at an acceleration voltage of 3.0 kV, with a spot size of 2 or 3 and a working distance between 1 and 5 mm.

5.2.3. Zirconia Sol-Gels

In Table 5.1 the possible phases of zirconia are listed. Five different precursors of zirconia were sintered and studied, see Table 5.2.
Table 5.1: Phases of zirconia with their dimensions, starting temperatures densities and Bragg reflections (CuKα-radiation).

<table>
<thead>
<tr>
<th>Monoclinic</th>
<th>Tetragonal</th>
<th>Cubic</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>5.31</td>
<td>5.12</td>
<td>5.1</td>
</tr>
<tr>
<td>b</td>
<td>5.2125</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>5.14</td>
<td>5.25</td>
<td>5.1</td>
</tr>
<tr>
<td>h k l</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>-1 1 1</td>
<td>100</td>
<td>28.198</td>
<td></td>
</tr>
<tr>
<td>1 1 1</td>
<td>68</td>
<td>31.494</td>
<td>100.30.193</td>
</tr>
<tr>
<td>2 0 0</td>
<td>21</td>
<td>34.188</td>
<td>25.35.337</td>
</tr>
<tr>
<td>0 2 1</td>
<td>11</td>
<td>34.412</td>
<td></td>
</tr>
<tr>
<td>Start Temp [°C]</td>
<td>0</td>
<td>1170</td>
<td>2370</td>
</tr>
<tr>
<td>density [g/cm³]</td>
<td>5.56</td>
<td>6.1</td>
<td>5.7-5.9</td>
</tr>
</tbody>
</table>

Table 5.2: Five different precursors of zirconia sol-gel were used in this project.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>ZrO₂ precursor</th>
<th>layer thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AH013</td>
<td>Hydrothermally treated for 3 hours at 110 °C</td>
<td>300±15</td>
</tr>
<tr>
<td>AH015</td>
<td>Hydrothermally treated for 3 hours at 130 °C</td>
<td>360±15</td>
</tr>
<tr>
<td>AH018</td>
<td>ZrO₂ stabilized with NO₃⁻</td>
<td>280±15</td>
</tr>
<tr>
<td>AH025</td>
<td>ZrO₂ original sol</td>
<td>220±15</td>
</tr>
<tr>
<td>AH026</td>
<td>Hydrothermally treated for 3 hours at 140 °C</td>
<td>300±15</td>
</tr>
</tbody>
</table>
5.2.4. Sintering

Because a non-isothermal sintering process is different from isothermal sintering and the actual temperature influences the sintering results, it is very important to assure that the temperature is correct and can be kept constant. Therefore a chromel-alumel thermocouple was used to monitor the temperature for calibrating, testing and selecting the furnaces. Sintering experiments at temperatures up to 1100 °C were done with a Hereaus furnace [K 1252-F max 1250 °C]. Fast sintering at these temperatures was carried out in a cylindrical Hereaus furnace [TIK/R 11/12 max 1300 °C], while the experiments at 1200 °C and 1300 °C were executed in Thermoline High Temp Furnace [type 46100 max 1700 °C].

Two different samples were heated in the furnaces at two different temperatures: the samples with an initial particle size of 9.5 nm were sintered at 800 °C and 1200 °C, whereas the samples with an initial particle size of 30 nm were sintered at 1000 °C and 1200 °C. These samples were fabricated from the original sol-gel by heating at a relatively low temperature, i.e. far lower than the sintering temperature, excluding influences on the investigated sintering behavior. It even diminishes the effects of processes like aging and drying.

Inserting the samples in a furnace for short sintering times is a problem, because opening and closing the furnace caused a reduction of the temperature of several tens of degrees up to about 60 °C at a sintering temperature of 1100 °C. It took several minutes to attain the originally set temperature (Figure 5.2). A higher temperature corresponded to a larger drop in temperature and a longer time to restore. Because this would affect the values and reliability of the results, especially those obtained after short sintering times, another method of inserting the samples was necessary.
Therefore a quartz rod was used having a cavity near the top for small samples. Through a small opening in the front or backside of the furnace, the rod was inserted in the furnace, which could maintain a nearly (± 5 °C) constant temperature in this way. After completion of the sintering time, the rod was pulled back out of the furnace and its top end including the sample was cooled by quenching in demineralized water at room temperature. In this way sintering temperature and time could be controlled to a great extent.

It can be assumed that the ZrO$_2$ is heated up so fast, that the time to reach the furnace temperature for the whole cross section of the layer can be neglected. This has been confirmed by calculations with the model of chapter 3.

5.2.5. Environmental SEM in-situ sintering preparation

To execute in-situ sintering experiments the previously described XL30 environmental SEM with hot-stage was used (see Chapter 2). Various samples with different average particle sizes (14, 28, 46 and 75 nm) were heated to several sintering temperatures (800, 1000 and 1200 °C) and times. Some of the experiments have been recorded by video. Cooling took place.
inside the ESEM, until the pressure within the SEM allows opening of the door and the sample was cooled in air to room temperature. Before and after the experiment micrographs were made by the XL30S SEM to compare and determine the influence of the sintering process.

Figure 5.3 illustrates the resolution of the ESEM at large magnifications while making use of the hot-stage. It is impossible to determine the average particle size reliably and changes in the sol-gel structure are practically not observable. At higher sintering temperatures and for longer times imaging was even worse, probably caused by the smoothing of the layer during the sintering process. Although the micrographs from the XL30s clearly showed changes in the structure of the zirconia coating, it was impossible to observe the development in-situ with a great degree of precision.

An additional problem was the difficulty to focus continuously on the same location of the sample because of the drift caused by the extension of the zirconia layer during the in-situ experiments. The hot-stage has a maximum heating rate of 300 °C/min, but the standard setting for all measurements was 5 °C/min to avoid any substantial drift. Other variables such as stigmatism and alignment also had to be adjusted continuously.

![Figure 5.3: Typical image obtained from in-situ experiments of zirconia sintering, making use of the hot-stage.](image)
5.2.6. X-ray diffraction measurements

X-ray equipment (Philips PW 1820 with a Cu anode) was used to determine crystal phases in the layer. The X-ray diffractograms were recorded for both the furnace treated and the laser treated samples. These diffractograms show several properties of the coatings. The sizes of the grains were calculated with the Scherrer equation:

$$D = \frac{K\lambda}{B\cos\theta_g}$$

(5.1)

where $K$ is a factor ~0.9-1.0, $\lambda$ is the wavelength of the radiation used (1.54056 Ångstrom for CuKα) and $B$ the broadening of the profile. The broadening $B$ has to be corrected for the instrumental broadening due to slit sizes and X-ray source characteristics. To measure the instrumental broadening, a reference diffractogram was recorded from a standard specimen. This specimen should not show broadening of the line profiles. Therefore, the crystallite size should be larger than 1 μm and the grains should not be strained. As a standard specimen, a Fe₃O₄ sample was used. The APD program was used to calculate the Full Width at Half Maximum (FWHM) of the peaks. The instrumental broadening with this experimental set-up was measured and calculated to be 0.098.

5.2.7. Mechanical properties testing preparations

Pre-sintered samples had to be cut into smaller sizes to fit into the ESEM. At first this was done by ultrasonically cutting pieces out of the samples or grinding with a diamond grindstone. Afterwards the samples were rinsed with demineralized water, ethanol or acetone. To check the results of these machining processes, pictures were taken by the XL30s SEM in order to compare with unprepared original samples. To illustrate the results a picture of the unprepared sample and of the ground sample rinsed with water are shown in Figure 5.4. All of the six combinations of preparing appeared to have the same effect on the zirconia coating: space has been developed between the grains and the open porosity has increased.
The exposure of the coating to ultrasonic vibrations turned out to be the cause of the surface morphology. Figure 5.5 shows a representative part of the structure of a sample with an average grain size of 69 nm after having been ultrasonically vibrated for 300 minutes. Large areas of the zirconia coating have disappeared, leaving a pattern on the boundary between coating and quartz substrate. This pattern is due to quartz material, which has lifted between the zirconia grains during the sintering process.

The development of space between the grains under the influence of ultrasonic vibrations, as can be seen from Figure 5.4, implies that the bonds between the grains is not very strong and these were broken due to the vibrations. This suggests that at their boundaries the grains are not well adhered. Actually nano-crystalline materials have a very large grain boundary area which gives them special properties. For instance, a nanophase...
material with an average grain size of 5 nm has about 50% of its atoms within the first two nearest-neighbor planes of a grain boundary, in which significant atomic displacements from their normal lattice positions are exhibited. To fully understand the properties of nanophase materials also other structural features must be taken into account, such as pores, larger flaws, grain boundary junctions, and other crystal lattice defects.

Because ultrasonic cutting generated harmful vibrations we chose to scratch the back of the samples using a diamond tip and then break them. This had no influence on the microstructure of the coating and or its sintering behavior.

5.3. RESULTS

5.3.1. The dried coating

The non-sintered sol-gel coating consists of clustered agglomerates with a non-regular shape. Inter-agglomerate pores were difficult to visualize with the SEM, but are evidently present. Inter-particle pores seemed to have disappeared in the preliminary process of sample producing, or they are too small to be detected. The ZrO$_2$ particles in the green layer were too small to be visible in the SEM. In the TEM (see Figure 5.6) the particles could be made visible, but they were obviously affected by the electron beam so that most particles crystallized almost immediately. That the green particles were amorphous was inferred from the X-ray diffractograms. The particles have a spherical shape with a radius of about 2 to 3 nm. Clusters of particles can also be found. These clusters easily form larger conglomerates, which indicates that the material is very reactive.

The clusters show a colloid-like behavior allowing for all colloid-influencing forces (e.g. electric, magnetic and electromagnetic fields can be used to manipulate the packing of the particles).
5.3.2. Results of furnace sintering

The decrease of the layer thickness due to the sintering process is the phenomenon that is most easily studied. In Figure 5.7 the layer thickness as measured on the pictures of the cross sections is plotted as a function of the sintering temperature, with a sintering time of 30 minutes for all samples.

There was good agreement between the results obtained with the SEM and those obtained by ellipsometry. Only at very low sintering temperatures...
(less than 300 °C) there appeared to be a difference. At those temperatures the layer thickness values obtained with the ellipsometer were less than half of those obtained with the SEM. The values obtained with SEM can be assumed to be correct and the differences with the ellipsometry results can be explained by the high degree of porosity in the layer and the fact that probably still some hydroxyl groups are present. It is obvious that the layer will shrink when heat is applied. In this study the layer shrinks from about 350 nm to 100 nm (approximately 70%).

All samples were also examined in plane view to observe the development of the zirconia structure during sintering. By the activity of minimisation of surface energy the particles have acquired a rounder shape and, on average, a larger size. Interface formation results in a higher density of the sol-gel structure, in which the particles fit better with respect to each other, in addition to an observable correlated decrease of the porosity. This is accompanied by pore rounding. A higher sintering temperature and/or longer sintering time magnify these phenomena, as can be seen in Figure 5.8. Some particles show various stages in the process of pore formation, in which eventually small round pores are enclosed by apparently one zirconia particle. Upon further sintering the smaller pores disappear, increasing the average pore size while the total porosity diminishes.
Figure 5.8: Developing structure at increasing sintering times of zirconia sol-gel coating with an initial particle size. a: not-sintered b: 10 sec c: 30 sec d: 1.5 min e: 3.5 min f: 10 min g: 15 min h: sub grain structures of 9.5 nm, sintered at 1200 °C (a-g). Distinctive sub grain structures at higher magnifications (h).
Open porosity is the situation, where pores are present in the top layer (see Figure 5.9). However, when the layer is heated further, the open porosity almost disappears, especially at higher sintering temperatures, and pores primarily remain inside the coating or within the grains. It can be observed that the layers heated below 1000 °C show a lot of open pores, but for higher sintering temperatures almost all open pores disappear. So, if there is any porosity it must be due to micro-pores within the grains, which cannot be seen by SEM.

Related to the change in thickness of the coating is the change in density. In Figure 5.10 the density is plotted as a function of the sintering temperature. At a temperature of 1200 °C a completely densified zirconia layer is achieved. This can be observed with the SEM (Figure 5.13) and detected by ellipsometry. It is clear that the density increases continuously with...
increasing temperature. The green layer density is very low, about 30%. The density values at low temperatures are obtained from SEM-images, assuming that the 1200 °C layer is completely dense and that all layers had the same green layer thickness (those obtained with ellipsometry are too high due to the high degree of porosity).

Figure 5.10: Density measured by ellipsometry and SEM as a function of furnace sintering temperature for 30 minutes sintering of zirconia sol-gel. The W stands where all physisorbed water is removed, the T indicates the transformation from the monoclinic to the tetragonal phase.
Figure 5.11: Top view of a zirconia surface layer heated for 30 minutes at 300 °C.

Figure 5.12: Top view of a zirconia surface layer heated for 30 minutes at 800 °C.

Figure 5.13: Top view of a zirconia surface layer heated for 30 minutes at 1200 °C.

The grain size as a function of sintering time is displayed in Figure 5.14 for different sintering temperatures. At the lowest temperatures (300 °C or...
less) no, or almost no grain growth took place (this can be seen in Figure 5.11). XRD measurements showed that no crystal phases were present, even at longer sintering times.

![Graph showing grain size of zirconia surface layer as a function of sintering time at various sintering temperatures.](image)

*Figure 5.14: Grain size of zirconia surface layer as a function of the sintering time at various sintering temperatures.*

When the sintering temperature gets higher (between 500 and 1000 °C) the curves show two distinct regions. Instead of a continuous growth of the grains, the grains seem to attain a certain size very quickly. The grain size depends on temperature. After that hardly any grain growth takes place as is depicted in Figure 5.14. In these samples the XRD measurements show a mixed composition of tetragonal and monoclinic phases. This can be explained by the fact that part of the grains are still very small, which favors the tetragonal phase instead of the monoclinic phase normally stable at room temperature. When the sintering temperature is even higher (1100 and 1200 °C) there is an additional slow grain growth after the initial rapid growth (see Figure 5.13). In this case the XRD results show only the monoclinic phase for all samples.

Figure 5.10, in which the densification is plotted as a function of sintering temperature, shows that complete densification is possible. The structure in the layer is demonstrated in Figure 5.15. A completely dense layer is observed with a grain size of about 120 nm. The cross section shows that the thickness of the layer consists out of a single grain and is thus also about 120 nm.
Figure 5.7 shows an almost linear decrease of the layer thickness with temperature, which cannot be explained using only a single thermally activated process. Obviously, more than one process takes place, replacing the previous one as the temperature increases. For amorphous ceramic systems it is known that when heated three regions can be observed. At the lowest temperatures physically absorbed water will be removed, but the shrinkage is usually small. For silica this has only a small influence (approximately 0.5%), but in this case with even much smaller particles the influence is observed at very low temperatures. For temperatures to 150 °C a value of approximately 15% is calculated. In the next regimes (to approximately 500 °C) polymerization (both within and on the surface of the inorganic skeleton) and structural relaxation (an irreversible process in which the free energy decreases through reformation of grain boundaries) result in a large shrinkage. Finally at very high temperatures related to the glass transition temperature viscous sintering may yield satisfactory results (around 800 °C). This results in a very high densification rate, much higher than the densification rate of crystalline materials.

The process seems to be quite similar when heat-treating with a laser. With low heat input no sintering takes place. The layer shrinks considerably to about one third of the original thickness, but no grain growth is detected. At higher heat input the particles in the layer sinter, where the maximal attainable grain size is of the same order as the thickness of the layer due to the directional dependence of the diffusion.
5.3.3. Results of hydrothermally treated ZrO$_2$ precursors.

In order to make layers with a larger thickness the zirconia sol was hydrothermally treated (1 hour at 110 °C). As a result the primary particles in the sol grow from 2 nm to 75 nm. As a result of the different size and properties of the hydrothermally treated zirconia a green layer thickness of 1000 nm can be obtained without cracking. After sintering the layer thickness is still 400 to 500 nm thick, much thicker than the layer made from the original zirconia particles. In the case of crystallized particles the sintering will be much slower and the resulting layer will contain more pores. In the case of hydrothermally treated zirconia sol-gel (particle size ranging from 15 to 70 nm), i.e. large particles, which are partly crystallized, cause an incomplete densification. When the particles are smaller and less crystallized the layer seems to become more densified than when using crystallized large particles (see Figure 5.16).

All tests on hydrothermally treated zirconia were also performed on quartz substrates. Both furnace and laser sintering experiments with a large range of heat inputs were performed. Figure 5.16 shows some typical structures that were obtained.

![Figure 5.16: Laser treated ZrO$_2$-sol on quartz a) 15 nm hydrothermally treated zirconia sol-gel 1950 W, 75 mm/s, b) 70 nm hydrothermally treated zirconia sol-gel 1950 W/ 0.94 mm/s.](image)

From these observations it is concluded that the optimum in the production of a completely densified zirconia layer is reached if a sol-gel existing of small amorphous particles is used. As a result the original Merck and ISC sols are good candidates as well as the hydrothermally treated sol-gels, when treated on a low temperature.
5.3.4. In-situ results

The results of Figure 5.14 posed the question what the behavior of the zirconia would be when we keep the sintering time very short. To execute these short sintering experiments both a specially prepared furnace and the hot-stage in the XL30 environmental SEM were used. As was already described in the experimental part of this chapter the longest heating time was 15 minutes. Various samples with different starting particle sizes (14, 28, 46 and 75 nm) were heated up to several sintering temperatures (800, 1000 and 1200 °C) and several sintering times. Some of the experiments were recorded by video. Before and after the experiment pictures were made with the XL30s SEM. In Figure 5.18 the results of these short sintering experiments are shown. It is very clear that the microstructures were reproducible, even the difference in starting size only played a part during the first few minutes, after that the sintering temperature turned out to be the main parameter to influence the resulting grain size.

Figure 5.17: All sintering experiments on zirconia in a furnace where the resulting grain size is displayed versus sintering temperature. Larger grain sizes result from longer sintering times.
5.3.5. Laser sintering results

Of course sintering with a laser results in very short interaction times. In Chapter 3 a model was developed in which the laser is allowed to heat both the sol-gel layer and the substrate. Depending on the wavelength of the laser beam, the coupling of the laser energy into the sol-gel coating could be neglected. When the layer is sufficiently small (about 0.2 μm) the absorption of the laser energy in the substrate is more important. With this “frying pan” assumption, the results obtained with laser sintering were comparable with the results obtained with furnace sintering. It turned out to make a complete dense layer, which was, like the furnace treated
zirconia coating, one grain thick. Also with the laser the maximal obtainable thickness was in the order of 100 to 150 nm.

Figure 5.19: Laser treated ZrO$_2$-sol on quartz $d_0 = 300$ nm a) 4000 W/ 1.88 mm/s, b) 4000 W/ 0.94 mm/s, c) 4000 W/ 0.46 mm/s, d) 4000 W/ 0.46 mm/s.

With increasing heat input the layer changed from a situation, where only densification but no grain growth occurs towards a completely sintered sample. Figure 5.19 shows SEM images of the laser treated samples. The images show some difference: but in all cases the zirconia coating shows densification. An increase in the grain size with increasing heat input of the laser can be found. In Figure 5.19a (cross section) a layer is visible which is not very well attached to the substrate. It is also visible that the layer is a number of grains thick. Figure 5.19b (cross section) shows the layer after medium heat input. Some grains have already grown to a larger size, but also some grains are still rather small. Figure 5.19c and d (both cross sections and plane views) show the layer after high heat input. The thickness of the layer and the grain size are about the same.
The hydrothermally treated zirconia sol-gel gave different results. The green layer could be made thicker without cracks appearing, but this layer was much more open. Starting with a green layer of at least 1000 nm the sintered layer thickness was 500 ±50 nm and the layer was still very open. In Figure 5.20 some typical obtained laser sintered structures of hydrothermally treated zirconia are shown.

![Figure 5.20: Laser treated hydrothermally treated zirconia sol on quartz. a) Fluence 226 J/cm², b) Fluence 226 J/cm².](image)

After the initial step the sinter process is dominated by diffusion, thus a higher heat input of the laser did not change the structure of the layer significantly. The process time was too short to densify the layer completely.

In Figure 5.21a (cross section) the layer is shown after a low heat input. Almost no sintering has taken place and the particles are the original ones, due to hydrothermal treatment, clogged particles, i.e. only slightly connected to each other.

Figure 5.21 b and c (cross section and top view) the layer is shown after a medium heat input. The grains have grown considerably, but the pores in the layer are still numerous and of considerable size.

Figure 5.21d (cross section) shows the layer after high heat input. The layer shows very large grains, with pores included in one grain and it shows that the process can be well controlled. Thus when the heat input of the laser is low there is no sintering, but the layer reaches very quickly the maximum density. At intermediate heat input the grains in the layer grow, but the size of the grains depends on the heat input. When the laser impact is high the layer sinters completely to a layer, with a thickness of one grain only.
5.3.6. XRD results

Figure 5.22 shows the typical CuKα Bragg reflections of a monoclinic zirconia at 2θ angles of 34.4 and 35.3 degrees. Due to the texture in the coating the [111] planes are not visible in this direction. The higher the temperature the higher the diffraction peaks in the noted angles, this shows the increase of the grain sizes with temperature. As explained in § 5.2.6 via the FWHM the grain size can be calculated. In Figure 5.23 the grain size was plotted against the fluence of a laser treatment. Several series of samples were made. One series had two constant speeds, one series a constant power of the laser. Thus the same fluence but with different speed and power were comparable. With XRD measurements the difference between the same fluence samples can be analyzed.
Figure 5.22: Diffractograms of a hydrothermally treated zirconia that was sintered from 800 up to 1300 °C for 30 minutes.

Figure 5.23: The grain size is calculated from the peak broadening in XRD measurements of a laser treated zirconia samples with a different fluence. Figure 5.24 shows that a constant fluence is not always determining the grain size of the resulting coating. But that speed has its specific influence. The constant power with variable speed seems to give very reliable sintering predictions. Constant fluence is not as precise but gives a good approximation. Low fluences are not reliable at high powers.
It is possible to formulate an equation by multiplying the fluence and the interaction time with a factor to approach the sintering degree required. One problem is still present: the XRD-measured grain size is smaller than observed with the SEM. This may be due to different sensitivities with respect to particle length.

5.3.7. TEM observations

In the SEM subgrain boundaries can be observed. In Figure 5.25 the corresponding TEM pictures specially made for this purpose are shown.
Figure 5.25: Subgrain boundaries are visible in the larger grains.

Figure 5.26 TEM bright field images on the left show a porous layer with a thickness of approx. 150 nm at 800 °C for half an hour, which densified towards 100 nm at 1200 °C. SEM pictures at the right show surface topology of the cross sections.
At 900 °C no interaction of the fused silica and the zirconia coating is observed, while at 1200 °C there is a wetting of grain boundaries (see Figure 5.26). The boundaries with high energy have a higher tendency to be wetted by the silica. Lattice image pictures in the top right of Figure 5.27 show two geometrically (energetically) different boundaries where the clear difference in wetting can be seen. At 800 °C the coating is not fully sintered, the carbon distribution shows the pores in Zirconia. The difference in intensity of the zirconia map alone would not be enough because it is also affected by the local thickness of the sample.

Figure 5.27: Elemental mapping was done by Energy Filtered TEM. Red - Silicon on L23 edge at 99 eV, blue - Zirconia on M45 edge at 130 eV, green - Carbon on K edge at 284 eV.
5.4. Discussion

Amorphous materials sinter by viscous flow and crystalline materials sinter by diffusion. Consequently, the dynamic paths for the material and the relationship between the rate of transport and the driving force are quite different. However, very little information is available on the kinetics of thin film sintering. It was shown previously that films densify faster than bulk material, even though the film has lower surface area. This is contrary to a well accepted model, which predicts that a film will sinter more slowly than an unconstrained gel, since a film can shrink only in the direction perpendicular to the substrate.

For amorphous systems it is known that upon heating three regions can be observed. At the lowest temperatures physically absorbed water will be removed, but the shrinkage is only small. This may be due to the linear strain caused by changing of the surface energy:

$$
\varepsilon = \frac{(1-v)S \rho \Delta \gamma}{E}
$$

where $v$ is the Poisson’s ratio, $E$ the Young’s modulus, $S$ the surface area, $\rho$ the skeletal density and $\Delta \gamma$ the change in specific surface energy. For silica this has only a small influence (approximately 0.5%), but with zirconia and its much smaller particles the influence is even observed at very low temperatures. For temperatures to 150 °C, values of $v=0.2$, $E=15$GPa, $S=2 \times 10^6 \text{m}^2/\text{g}$, $\rho=1.31 \text{g/cm}^3$ and $\Delta \gamma=0.001 \text{ J/m}^2$ result in a value of approximately 15%. At higher temperatures continued desorption that increase surface energy should result in additional capillary strain of less than 1%, which represents a minor contribution to the shrinkage.

In the temperature range up to 500 °C, polymerization, both within and on the surface of the inorganic skeleton, and structural relaxation, an irreversible process in which the free energy decreases through bond restructuring or rearrangements result in a large shrinkage. According to XRD graphs already some crystallization starts around temperatures of 600 °C and at higher temperatures this is followed by grain growth and a density increase towards 100%.

Given a microstructural model, it is possible to relate the change in surface area to the overall change in dimensions. Frenkel suggested that the rate of densification could be found by equating the rate of change in surface area...
energy to the rate of energy dissipation as was described in Chapter 4. The viscosity of a material decreases, and the coupled shrinkage rate of the layer increases upon increasing temperature. This results in a very high densification rate, much higher than densification of crystalline materials. Because the values after 1 minute of sintering already show some crystalline phases the viscous flow must have taken place earlier. At a temperature of 800 °C this leads to a value for the viscosity (using $\gamma$ is 0.3 J/m$^2$) between $10^{-7}$ and $10^{-10}$ Pa.s, depending on the initial shrinkage rate. These values are rough estimates because of the lack of measurements with shorter sintering times, but the values are of the right order of magnitude (e.g. $10^{-7}$ Pa.s for silica at 800 °C). Also from silica it is known that the viscosity decreases as the hydroxyl content increases, which could be of importance because the zirconia layer loses its hydroxyl groups during the process.

During the first part the zirconium hydroxide is transformed to zirconium oxide and water, and concurrently, the particles may grow together to larger grains. This second part of the process is the growth of the crystalline grains. Crystallization within grains of the layer can be concluded from XRD-measurements. The grain growth can be described by:

$$G_t^n = G_0^n + BD_0^n \exp \left( -\frac{Q_{GB}}{kT} \right)$$

where $G_t$ is the instantaneous grain size at time $t$, $G_0$ the initial grain size and $n$ a constant dependent on the agglomerate size, $B$ a constant close to unity, $D_0$ diffusivity and $Q_{GB}$ activation energy for grain boundary diffusion.

The constant $n$ must be determined experimentally (theoretically considerations yield a value of 2$^{14}$). Fitting the equation to the measured data can lead to the determination of $n$. Previous experiments$^4$ have shown that it usually lies between 2 and 4. With the use of this relation (with $Q_{GB}$ is 350 kJ, $D_0$ is $4.85\times10^{-5}$ m$^2$/s$^{13}$) the value for $n$ can be calculated. This is done for the second part of the 1100 °C and 1200 °C curves (at lower temperatures the grain growth is too slow to be observed). The value for $n$ is 2.3 and 2.1, respectively. These values agree reasonably with the theory, which predicts a value of 2 for very homogeneous materials.

A model was developed in which the laser is allowed to heat both the sol-gel layer and the substrate. One conclusion that can be made is that the
coupling of the laser into the sol-gel surface layer can be neglected when
the layer is sufficiently small (about 0.2 μm).

5.4.1. Particle growth

The average grain size in the samples was determined by applying a
method known as the linear intercept method. It makes use of a line of
known length L drawn over the surface of the samples. The average grain
radius \( \bar{R} \) is a direct measure from the number of intersections N of this line
with a grain boundary, according to

\[
\bar{R} = \frac{3L}{4N} \quad (5.4)
\]

The systematic relative error \( \frac{\Delta R}{R} \) made by the fact that the lines mostly
start and end within a grain is approximated by

\[
\frac{\Delta R}{R} = \sqrt{\frac{20.25}{N^2}} \quad (5.5)
\]

To reduce the systematic error a number of \( N' \) lines have to be drawn over
the surface of the samples, each resulting in a particular value \( R_i \) and error
\( \Delta R_i \) for the particle size. The most probable error or standard deviation
\( \Delta \bar{R} \) in the average particle size is then given by

\[
\Delta \bar{R} = \frac{\left( \sum (\Delta R_i)^2 \right)^{1/2}}{N'} \quad (5.6)
\]

The grain sizes as a function of the temperature are plotted in Figure 5.14.
Two regimes can be distinguished in the sintering process: the first in
which particle growth takes place very fast and final sizes are reached, and
the second regime with slow growth, if occurring at all.

Reason for the growth to slow down after a certain sintering time cannot be
the arrival at a 100% density, which would stop the viscous flow.
Measurements show that before and after the transition of the first to the
second regime the density nearly has the same value. For both pre-sintered
starting samples with an initial size of 9.5 nm and 30 nm, the density
difference between before and after the transition respectively is just a few percent.
The transition cannot be caused either by a changeover from the intermediate to the final sintering stage, because at least the samples with an initial particle size of 30 nm already have passed the intermediate stage during the pre-sintering for their production.

Furthermore, transformation of tetragonal zirconia to the monoclinic phase cannot result in the transition, as can be observed from diffraction measurements. These measurements show that after 30 minutes sintering at a temperature of 800 °C, both phases coexist in comparable concentrations. So from this point of view there is no reason for the grain growth to slow down that dramatically in the second regime of the sintering at 800 °C. Additionally, the starting sample with a size of 9.5 nm already has undergone the t-m transformation before it has reached the second regime. Measurements in the next paragraph show that zirconia, sintered for 30 minutes at 1000 °C, mainly has the monoclinic phase, while the average grain size is smaller than that of zirconia in the first regime sintered at 1200 °C.

A possible explanation is to assign the first and second regime to fast amorphous particle growth by viscous flow and slow crystalline grain growth by diffusion, respectively. The reason of the transition from the first to the second sintering regime is probably the loss of hydroxyl groups in the zirconia by condensation after which crystallization takes place.

However, the boundaries between different particles are not visible in the case of a 100% dense amorphous material as can be seen in chapter 4. Brinker\textsuperscript{15} shows that in the first regime the boundaries are visible between the particles in locally fully dense locations in the material.

The length of the first regime is of the order of a few minutes and appears to be longer for higher sintering temperatures, but the dependence is not strong. The length is independent of the initial particle size.

A faster particle growth in the first regime seems to be achievable by using a smaller initial size and a higher sintering temperature. Nevertheless, the initial size does not influence the final size. The final average particle size is according to the figure exclusively dependent on the sintering temperature, where a higher temperature results in a bigger average size.

The transition from the first to the second regime is not abrupt, which indicates that in the zirconia layer not all the material undergoes the
transformation simultaneously. Low concentrations of substrate ions diffusing into the film may influence the diffusion of ions in the film considerably. The assumption that the second sintering regime corresponds to crystalline sintering can be verified by fitting the data in the theoretical model of crystalline sintering in the final sintering stage, as described in Chapter 2. For that purpose, the graphs of Figure 5.18 are plotted in Figure 5.28, but for longer sintering times in the second regime and with the most probable errors in the grain size.

The slope of the 1100 °C line is $(4.4 \pm 1.0) \times 10^{-2}$ m$^3$/s. Using equation (5.3) with $n=3$, the activation energy for grain boundary diffusion can be computed: $Q_{GB} = 395$ kJ/mol. The slope of the 1200 °C line is $(22.0 \pm 1.5) \times 10^{-2}$ m$^3$/s and $Q_{GB} = 404$ kJ/mol, which agrees very well with the literature value of ZrO$_2$: 300-400 kJ/mol. The constant $B$ in equation(5.3) was taken 1 and is not very important since it is outside of the exponent so it does not influence $Q_{GB}$ much.

![Figure 5.28: $G^3$ versus sintering time(minutes) to verify the law for grain growth.](image)

For a sintering temperature of 1200 °C steady grain growth is observable, whereas for the lower temperatures the growth is too small or insignificant within one hour of sintering. The value of $n$ can be calculated using relation (5.3) with $Q_{GB} = 350$ kJ, $D_0 = 4.85 \times 10^{-5}$ m$^2$/s, $T = 1473$ K, and $B = 1$. $G^n(t)$ can be described by a linear equation in $t$. The found value of $n$ is $2.25 \pm 0.05$. 

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This value agrees with theory, predicting a value of two for very homogeneous materials where grain growth is the result of grain boundary diffusion. The second period can thus be explained by crystallization of the zirconia layer.

5.5. CONCLUSIONS

Ellipsometry can be used to calculate layer thickness and density in sol-gel derived zirconia layers, but only when the density is high enough and the material is free of hydroxyl groups. Constant power with variable laser beam velocity gives very reliable sintering predictions. Constant fluence is not as precise but allows a good approximation. Low fluences are not reliable at high powers.

Full density in sol-gel derived coatings can be obtained when applying temperatures higher than 1000 °C. The sintering of sol-gel coatings can be divided into two parts: The initial part is governed by viscous sintering. The densification rate is very quick, resulting in an almost instantaneous growth of the grains. At the end of this first period most of the hydroxyl groups will be lost and crystallization has taken place. The second part exists of grain growth in the zirconia coating. This grain growth is governed by grain boundary diffusion.

5.6. REFERENCES:

14 J. G. Byrne, Recrystallization and Grain Growth (Macmillan, 1965).