2.

EXPERIMENTAL

In this chapter the main experimental tools that have been used for the sintering experiments will be summarised. Scanning Electron Microscopy (§ 2.2) plays a predominant role in the analysis of nano-ceramic coatings. The use of this instrument will result in information on the surface quality in terms of morphology, roughness and density. Extra equipment added to the SEM like a high-resolution (HR) lens and a hot-stage are described in § 2.3. When even higher resolutions and magnifications are required Transmission Electron Microscopy is an appropriate tool (§ 2.4). Digital image manipulation techniques have been used to quantify the data obtained from the micrographs (§ 2.5). Films and coatings have also been examined with ellipsometry, to obtain porosity and thickness measurements (§ 2.6). The role of X-ray diffraction equipment in determinations of phases and grain sizes is described in § 2.7. In section § 2.8 equipment for mechanical testing, e.g. the nano-indentor, is described. In the final section, § 2.9, the laser systems used are described.

2.1. INTRODUCTION

The evolution of the microstructure due to sintering of nano-ceramics can be studied in several ways. Nuclear magnetic resonance Spectroscopy (NMR) has been applied to examine the kinetics of the hydrolysis and condensation reactions during gelation and the early stages of polymerisation. 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 skeleton. Zerda\(^1\) investigated the relationship between the Raman intensity and the particle radius. Small-angle-scattering (SAXS) has been used in combination with light and neutron scattering by Shaefer\(^2\) to obtain quantitative information about pores and interatomic spacings in a xerogel. Thus SAXS may provide information about the coherence length in the entanglement of the polymeric chains. The principal tools employed in this thesis are rather direct observations via high-resolution microscopy. In addition ellipsometry has been applied as well.
2.2. SCANNING ELECTRON MICROSCOPY

To observe densification and even necking of fusing colloids at the nanometer scale, it is impossible to use a conventional light microscope. Its resolution is limited to about 300 nm. The Philips high resolution XL30s FEG Scanning Electron Microscope is able to display pictures with a resolution of 2 nm at low accelerating voltage. Due to the character of the Field Emission Gun (FEG), a heated tungsten hairpin that emits monochromatic electrons, a very well-resolved image can be made. In Figure 2.1 a schematic cross-section of the SEM is visible with all its lenses.

![Figure 2.1: A schematic cross section of an SFEG XL 30 SEM (Courtesy of FEI company).](image)

The generated probe current is approximately $10^{-8}$ to $10^{-7}$ Amperes. The gun accelerates the electrons down the column towards the sample with energies typically ranging from hundreds to tens of thousands of eV. The electrons
emerge from the gun as a divergent beam. The condenser lenses, objective lens and several apertures in the column converge and focus the beam on the sample surface. A set of scanning coils deflects the beam in a scanning pattern over the sample surface. The beam exits from the column into the specimen chamber, which incorporates a stage for manipulating the sample and one or more detectors. The signals, emitted from various positions of the specimen surface as the specimen is scanned by the electron probe, are detected by a detector (located near the specimen) and the signal induced in the detector is sent to the video amplifier. The interaction volume between the incoming primary electrons and the sample can be divided into regions associated with a specific signal type, as schematically illustrated in Figure 2.2. Secondary electrons (SE) are caused by inelastic collisions with the atoms in the target area and generally have a low energy (by convention less than 50 eV). Because of their low energy, they can escape only from a shallow region at the sample surface. As a result, they offer the best imaging resolution (in the order of 5-20 nm). The contrast arises primarily from sample topography. This makes the interpretation of secondary electron images very intuitive.

![Image](image.png)

*Figure 2.2: Different types of signals originating from the volume interaction of the primary electron beam.*

Backscattered electrons (BSE) are primary electrons that have been scattered out of the sample by elastic collisions with the nuclei of sample atoms. They have a high energy resulting in a large specific interaction volume and subsequently resulting in a lower resolution (10-100 nm) of backscattered images. Contrast in these images comes primarily from point to point differences in the average
atomic number of the sample. High atomic number nuclei backscatter more electrons and create bright areas in the image, which are not easy to interpret.

X-rays excited by the electron beam form two types of spectra, the Bremsstrahlung (electromagnetic radiation emitted by electrons when they pass through matter) with a continuous spectrum, and the characteristic radiation with a distinct line spectrum. The line spectrum can be analysed by Energy Dispersive Spectrometry (EDS) to reveal the atomic composition.

Each component of an SEM has its own resolution and noise characteristics. Lenses exhibit certain kinds of aberrations. Two of the most important are spherical and chromatic aberrations. Spherical aberrations result when electron paths away from the optical axis are bent more than those close to the axis. Chromatic aberrations are caused by the fact that slower electrons are bent more than the faster electrons. Because of aberrations, all electron paths originating from a given point in the crossover do not converge perfectly on the same point in the image.

Due to the interaction of the electrons with the sample the current signal of electrons reaching the detector is smaller than the probe current and has to be amplified by direct electron multiplication and conventional electron amplifiers, causing background noise to be the main reason of blurred images.

Image quality has been improved the last decades due to noise reduction, more precise scanning devices, more powerful electron emitters and additional image processing units. Factors to be optimised by the operator include the intensity and the accelerating voltage of the primary beam, the size of the apertures inside the column, the working distance, spot size and scan parameters.

In conventional SEMs insulating materials build up a space charge region by accumulation of absorbed electrons. This charging deflects the incident beam, leading to image distortions, and significantly causes local variations in the emission of secondary electrons.

**Specimen preparation**

Good imaging necessitates contamination-free surfaces, resistance of the specimen to high vacuum and to the electron beam, absence of electrical charging and a sufficiently high electron yield.
Charging effects can be avoided by operating at a low accelerating voltage or applying conductive coatings, which is a widely used technique. The coating layer must be thick enough to provide a conductive path, but should be as thin as possible to avoid obscuring fine details. The minimum thickness depends on the surface roughness. The coating can be applied by cathode sputtering under vacuum during a certain time. The investigated samples in this thesis have been coated by sputtering palladium.

2.3. **HIGH RESOLUTION, EDS, ESEM AND HOT-STAGE**

The microscopes used to produce the micrographs in this investigation are the Philips XL30s-SEM for pictures with high resolution, Philips XL30-SEM for EDS and XL30 Environmental SEM (ESEM) for in-situ sintering experiments. All microscopes produce primary electrons using a field emission gun.

The XL30s microscope is equipped with a special electromagnetic lens, which generates a magnetic field surrounding the specimen. It deflects the secondary electrons towards the detector, increasing the efficiency of the secondary electrons dramatically. Therefore, good images can be obtained at low voltages, despite the low secondary electron yield. The maximum obtainable resolution at 1 kV is about 2.5 nm in this so-called ultra high-resolution mode.

The width of the electron beam $d_p$ mainly determines the lateral resolution of the scanning electron microscope and can be described by equation (2.1). In order to achieve the smallest spot size, all contributions should be as small as possible.

$$d_p^2 = \frac{1}{\alpha^2} \left[ \frac{i}{B} + (1.22\lambda)^2 \right] + \left[ \frac{\Delta E}{E_0} C_s \right]^2 + \left[ \frac{1}{2} C_c \right]^2 \alpha^5$$  \hspace{1cm} (2.1)

$B$ is the brightness of the source, $i$ is the beam current and $\alpha$ its divergence angle. A field emission gun (FEG) has a very high brightness $B$ thus decreasing the spot size. The second part is the contribution due to diffraction of the electrons of wavelength $\lambda$, by the size of the final aperture. The energy spread $\Delta E$ in the electron energies is small. Decreasing the accelerating voltage will not only cause the wavelength of the electrons to increase but will also increase the chromatic aberration ($C_c$). This increases the spot size and as a consequence decreases the resolving power of the microscope. But chromatic and spherical ($C_s$) aberration coefficients can be reduced by optimising the lenses for low-energy.
Although FEG-SEMs have superior resolution, depth of field and micro-analytic capabilities, they also have a number of limitations. Almost all of these limitations derive from the high vacuum an SEM must maintain in its specimen chamber. Firstly, the column requires a high vacuum in order to generate and focus the electron beam. Otherwise, gas molecules could scatter electrons and degrade the beam. Secondly, the specimen chamber demands a high vacuum to permit the use of Everhart-Thornley secondary electron detectors, because of their high voltage elements.

The usual design is to allow the column and chamber to share a common vacuum environment. However, in the FEG XL30 Environmental SEM (ESEM), multiple pressure limiting apertures separate the chamber from the column. The column remains at a high vacuum while the chamber may sustain a relatively high pressure in the order of several Torrs.

In the chamber scattering of the electrons by gas molecules occurs, decreasing the intensity of the beam reaching the sample. But the intensity profile does not broaden within a certain scattering regime, corresponding to a range of operational conditions (pressure, gas path length, temperature, gas type and accelerating voltage).

The detector used in the ESEM is a gaseous secondary electron detector, using gas ionisation to detect and amplify the secondary electron signal. Gas ionisation also suppresses charging of insulating samples. In our experiments the gas used was water vapour.

To heat up a specimen in the microscope a heating stage was used. The heater assembly is essentially a micro-furnace, schematically illustrated in Figure 2.3, in which samples are heated from the sides and from the bottom. This allows for more uniform temperature gradients around the sample. The surface area of the sample exposed provides much heat loss through radiation. Therefore, the exposed surface will be cooler than the bottom, thus a heat shield is added to minimize this effect. Also, high chamber pressures will cause more heat loss through convection.

Sintering by employing the hot stage makes it necessary to use the ESEM for two reasons. Firstly, the high temperature causes evaporation from the sample, making a high vacuum impossible. Secondly, in-situ experiments make a conduction layer, usually a sputtered layer of palladium, unpractical. Therefore, a gaseous environment is needed to prevent charging.
X-rays result when an energetic electron, usually from the beam, removes an inner shell electron from a sample atom. When a higher energy, outer shell electron of the same atom fills the vacancy, it releases energy as an X-ray photon.

![Figure 2.3: The hotstage with schematic picture of the heater.](image)

The XL30 SEM is provided with an X-ray spectrometer collecting the X-rays, characteristic for the elements present in the specimen. The spectrometer counts and sorts the X-ray photons on the basis of energy (energy dispersive spectrometry-EDS). Peaks in the spectrum correspond to the elements present, while the intensity level of the peak indicates its concentration.

2.4. **TRANSMISSION ELECTRON MICROSCOPY**

Transmission electron microscopy allows for the observation and analysis of materials down to the sub-nanometer scale. The image contrast is mainly formed by elastic scattering of electrons with matter and can be used to obtain real space as well as diffraction information.

Lattice imaging with a High Resolution Transmission Electron Microscope (HRTEM) provided structural information better than 0.2 nm spatial resolution. With this technique the positions of individual atomic columns can be resolved. When recorded under optimum conditions, electron micrographs can be directly interpreted in terms of the projected crystal potential. In other cases,
image simulations are necessary to match proposed structures to image features. Lattice imaging has been performed on a JEOL TEM 4000EX/II and on a JEOL 2010F to observe the zirconia grains in the xerogel before sintering (see chapter 5).

The inelastic scattering of the electrons can be helpful in obtaining chemical information from very small regions in the specimen. To obtain specific elemental information and also to improve the resolution of the microscope Energy Filtered Imaging has been used. In standard transmission electron microscopy the image is formed from the entire range of electron energies transmitted through the sample including those electrons that have been scattered elastically (zero-loss) and those electrons that have been scattered inelastically (energy loss). In energy filtered imaging the image is formed only by electrons transmitted within a certain energy window.

![Figure 2.4](image.png)

*Figure 2.4: Preparation of a TEM sample: 1) out of one sample with a sintered coating several pieces 2) have been cut and 3) 4 were glued together with 3 quartz plates in between them, to keep the coating in place while cutting and polishing it in slices of 1 mm thickness. 4) These slices have been thinned by polishing with diamond paper with a final grain size of 1 µm and in the middle a small hole has been made with an ion beam (PIPS).*

To perform this a JEOL 2010F TEM, operating at 200kV, is equipped with a post column filter. This Gatan Imaging Filter (GIF) is a magnetic prism spectrometer, which is positioned behind the projector lens spreading the electrons into a spectrum of energies. The GIF is tuned to pass only the desired range of energies through a slit which blocks electrons outside that energy range. The results of this energy filtered imaging can be found in section § 5.3.7.
To be able to study the cross sections of the sintered coatings, TEM samples were made as depicted in Figure 2.4. The sandwiched samples had the advantage that the area that has been electron transparent usually contained the coating and the boundary between the coating and the substrate. For samples with a steel substrate TEM samples were the only possible way to look at the cross section of coating and the attachment to the substrate.

2.5. DIGITAL IMAGE PROCESSING

The SEMs used in this project are equipped with a CCD camera so the question has been posed whether the images could be analysed digitally to extract quantitative information to indicate the stage of sintering of the depicted microstructure. In this thesis this problem has been examined with respect to plane-view SEM-pictures of samples with sintered zirconia and silica. Using the features of zirconia grains to set up selection rules, a program has been developed to calculate the grain size distribution for this system providing a good representation of the status of the sintering process. The features of a crystalline grain were used to recognise a zirconia grain by the computer.

![Figure 2.5: Typical SEM picture of a crystalline zirconia microstructure.](image)

Figure 2.5 shows the following features:

The grey value of the grain is brighter than the boundaries. And there is a large change in grey value at the border of a grain. Grains are large; the little grey variations in the grains are sputtering islands. The program should ignore these islands.

The image taken by an SEM has 256 grey values. For every pixel it can be said that it belongs to a grain or is part of the boundary between grains. The goal is
to go from an 8-bit image (256 grey values) to a 1-bit black and white image. The white represents a grain and the black the space between the grains. The easiest way is to threshold an image. Let $A = \{a_{ij}\}$ be a grey-scale image. Let $t$ be a threshold. The result of the thresholding is a binary image obtained by: $a_{ij} = 0$, if $a_{ij} < t$; $a_{ij} = 1$, if $a_{ij} \geq t$. As can be seen, the main task involved is to choose the value of $t$ by using a certain criterion. This threshold can be chosen for the whole image (global thresholding), or a different threshold can be chosen for different parts of the image (local thresholding). If the values of objects and those of the background are fairly consistent over the entire image, then global thresholding is the most appropriate for the binary system.

$$\begin{array}{ccc}
a_{i-1,j-1} & a_{i-1,j} & a_{i,j+1} \\
a_{i,j-1} & a_{i,j} & a_{i+1,j} \\
a_{i+1,j-1} & a_{i+1,j} & a_{i+1,j+1}
\end{array}$$

*Figure 2.6: Pixel numbering when applying a jump-function.*

A second method of creating a black and white image is the method of jumps. The boundary of a grain is identified by a large derivative of the grey value. The derivative needs to be taken in several directions. If only one of the directions is larger than the *jump* value the maximum difference between one pixel $a_{ij}$ and one of its neighbours is (Figure 2.6):

$$a_{ij} = 1, \text{ if } \max(\text{abs}(a_{ij} - \text{neighbour pixel})) < \text{jump}$$

$$a_{ij} = 0, \text{ if } \max(\text{abs}(a_{ij} - \text{neighbour pixel})) \geq \text{jump}$$

This function makes grains bright and the borders black. If the space between the grains is larger than 2 pixels the space in between the grains will also turn bright. A contour is an array of $n$ points $(x,y)$ which encloses an area of black or bright pixels. If a contour is closed the first point of the array is the same as the last point. If a black and bright image are created by the addition (logical OR) of both binary images (threshold and jump), then it is time to remove the small black and white areas (noise). This can be done in several ways, but working with contours is easier. When the grains are large, short contours can be removed. But also the contours with a small inner area are of no value.
Figure 2.7: Two grains which need to be split up.

Because the created binary image is not a perfect representation of the image, grains will merge with only one or two pixels (see Figure 2.7). The minimum distance between two points in a contour are taken into account when two grains are to be split. Secondly the length of each of the two contours must be larger than a minimum length \(l_{\text{min}}\). This is due to the fact that two neighbouring contour points have a distance of one pixel. If \(P(x_i,y_i)\) is the \(i^{th}\) point in the contour array the distance \(d_{ij}\) between points \(P(x_i,y_i)\) and \(P(x_j,y_j)\) can be written as:

\[
d_{ij} = \sqrt{(x_i - x_j)^2 + (y_i - y_j)^2}
\]  

The minimum distance \(d_{\text{min}}\) is:

\[
d_{\text{min}} = \min \{d_{ij}, i = 1 \ldots n - l_{\text{min}}, j = i + l_{\text{min}} \ldots n\}
\]

If the minimum distance is smaller than a certain value, the contour will be cut in two at the position \(P(x_i,y_i)\) and \(P(x_j,y_j)\) where \(i\) and \(j\) are the indices where the distance is at a minimum. It can be seen that the total number of calculations is quadratic with the number of points in the contour. All other calculations (jump and threshold) are linear with the number of pixels. As a consequence this part of the contour calculation will take most of the calculation time.

These image processing steps are demonstrated on an original SEM picture of a sintered zirconia coating as is displayed in Figure 2.8, from which the grain size distribution can be calculated. Some grains were not detected by the contours, because their area or contour length has been too small. A few grains with an unclear boundary were not recognised as individual grains.

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 centres, which makes it more difficult to apply a threshold to the image. To overcome these problems a new technique, called Morphological Image Processing (MIP) has been used to quantify the sintering process and to measure the centre-to-centre distances of
the grains during the process. Morphology refers to the study of the shape and structure.

Figure 2.8: a): Original image, b): After threshold, c): After jump, d): Combining jump and threshold, e): Final contours of figure, f): Grain size distribution of 506 grains in 51 groups.

In Figure 2.9 a human eye can distinguish the separate colloids, even for heavily sintered silica, but a threshold-based program cannot. MIP analyses a picture by comparing how some predetermined geometric shape fits into the picture.
This form determines the structure. In our case this is a sphere of appropriate size. There are two sets of two morphological operators that play an important role. These are dilating, eroding, opening and closing.

Dilation “rolls” the structuring element around the border of the various objects, creating new objects that contain the border plus the structuring element. Eroding creates new objects for which the structuring element is fully contained in the original object. Thus dilation tends to expand the subject with the structuring element while erosion tends to shrink the subject. This is shown in Figure 2.10. When opening, the image is first eroded and then dilated, when closing first dilation then erosion takes place. Intuitively opening an image is obtained by “rolling” the structuring element about the inside of the image while closing is obtained by rolling the structuring element around the outside of the image.

Opening and closing an image with an appropriate structuring element can free an image from internal and external noise as is illustrated in Figure 2.11.

The program that has been used for performing morphological image processing at the various pictures is called Minko2d and has been developed by the department of Theoretical Physics in Groningen by dr. K. Michielsen and professor H. De Raedt.
It provides the user with the complete set of morphological operators, such as dilation, erosion, opening and closing, both for grey-valued pictures and for black-and-white pictures. A script of a collection of these operators can be made. First the grey-valued picture is treated, then the picture is converted into a black-and-white picture and finally the number of objects, Euler number, average area, average perimeter, minimal and maximum centre-to-centre distance of detected objects are calculated. The Euler number is the number of objects minus the number of holes. For a series of pictures a log-file could be made which contained all the numbers for each picture. The aim is a script that can analyse and quantify all stages of sintering of a silica sol-gel, and prove the relation between sintering parameters like time and temperature with the centre-to-centre distance of the colloids.

It has been found rather difficult to create a script that could deal with the separate colloids in the first stage of sintering as well as with the large structures of the final stages. It turned out to be convenient to choose much smaller structural elements in the case of separate colloids than with heavily sintered structures. Several series of images have been analysed. All of these
series are images of a laser track, where images are taken from sites where no sintering has taken place to sites in the middle of the track.

Figure 2.12: The original sintered silica sol-gel picture and the resulting MIP processed picture.

The Euler number (number of objects minus number of holes) gives a quantitative value for the microstructure and can be related to the porosity of the coating. MIP did not allow a more precise measurement of the centre-to-centre distance of the colloids to improve the comparison of the SEM pictures with material properties. The size of the structuring elements, defined in the templates in concurrence with the magnification and resolution of the SEM pictures, turned out to be crucial to the successful processing of the pictures.

2.6. ELLIPSOMETRY

Ellipsometry is based on the fact that materials may change the polarization of light through reflection and refraction\(^5\). It is an experimental method that can detect certain properties of thin films by looking at the change in polarization. In our case ellipsometry has been applied to examine the samples with thin zirconia layers to determine the thickness and the porosity quickly and easily. The measurements have been carried out at the Physical Laboratory of Philips in Waalre/Eindhoven. Ellipsometry derives its sensitivity from a relative phase change in a beam of reflected polarised light and it is more accurate than intensity reflectance measurements because the absolute intensity of the reflected light does not matter. In ellipsometric experiments it is common to use the so-called \(p\)- and \(s\)- directions as the two orthogonal base vectors used to express beam polarisation states. The basic setup of an ellipsometer is schematically displayed in Figure 2.13. The \(p\)- direction is defined as lying in the plane of incidence, defined as the plane containing the incident and the reflected beams. \(s\) is the vector normal to the plane. From the difference of these
two polarisation states the ellipsometer collects its experimental data. The actual values detected are $\Psi$ and $\Delta$, which are coupled to the polarisation states which are related to the changes in amplitude and in phase of the reflected beam in comparison to the incident beam (see Figure 2.14).

Figure 2.13: The set-up of the ellipsometer. A linearly polarized light beam (1) reflects off the sample (2). At the detector an elliptically polarized beam is detected (3). Note the name convention: the p-component of the polarized beam is the component in the plane of incidence, the s-component is the component perpendicular to it.

Figure 2.14: Output of the ellipsometer: $\Psi$, the amplitude change and $\Delta$, the phase change in the reflected beam.

An important parameter in ellipsometry is the ratio of two complex reflection coefficients (Fresnel reflection coefficients); $R_p$ and $R_s$ for p- and s- polarized light, respectively. Because of the fact that the two Fresnel coefficients are complex, their ratio can be written as a constant times an exponential function;
namely $\tan(\psi)$ times $e^{i\Delta}$, the so-called ellipsometric parameter. The connection between the Fresnel coefficient and the ellipsometric parameter is:

$$\rho = \frac{R_e}{R_i} = \tan(\psi) e^{i\Delta}$$

(2.4)

For more theory on the principles of ellipsometry we refer to 5.

For a general polarisation, of which linearly and elliptically polarised are special cases, the detected signal is sinusoidal with a DC offset of the form:

$$V(t) = DC + \alpha \cos(2\omega t) + \beta \sin(2\omega t)$$

(2.5)

Where $\omega$ is the frequency and $t$ is the time. The two important quantities measured by the ellipsometer are $\alpha$ and $\beta$, which are normalised Fourier coefficients of the signal. They can be represented in terms of the $\psi$ and $\Delta$ values of the specimen and the (known) polariser azimuthal angle by:

$$\alpha = \frac{a}{DC} = \frac{\tan^2 \psi - \tan^2 P}{\tan^2 \psi + \tan^2 P}$$

(2.6)

$$\beta = \frac{b}{DC} = \frac{2 \tan \psi \cos \Delta \tan P}{\tan^2 \psi + \tan^2 P}$$

(2.7)

$P$ is the input polariser azimuth with respect to the plane of incidence ($P = 0^\circ$ is the plane of incidence). The above equations may be converted to obtain $\psi$ and $\Delta$ from the measured $\alpha$ and $\beta$ and the known $P$.

There are different detection mechanisms. At the Philips’ Physical Laboratory we used a VASE ellipsometer. It is displayed in Figure 2.15.

A random beam enters the monochromator and is polarised by a polariser under an angle $P$. Next the beam is reflected by the sample and enters a rotating polariser under an angle $A(t) = \omega t$. A semi-conductor detector converts the light intensity to a voltage. Care is taken that this detector is polarisation insensitive and extremely linear.
First the optical constants of fully sintered layers have been determined by measuring well-defined samples of fully sintered zirconia on fused silica. Then a simple model has been used to generate data consisting of the substrate, a composite layer (zirconia + voids) and a certain roughness layer. The calculations were done within the effective medium approximation. The latter represents a linear combination of the refractive indices of the constituents of a composite layer. This formulation calculates the total refractive indices of the layer by computing the different percentages of constituents present. A reference sample has been used with a monoclinic zirconia layer on fused silica (FS), with a thickness of 103 nm, obtained by SEM. It has been furnace treated for 30 min at 1200 °C. Figure 2.16 shows that the calculated data of the model is almost identical to the experimental data. It means that the rather simple model is confirmed. After the fit in Figure 2.16 it is possible to derive the optical constants of the fully sintered layer and refer to a sintered monoclinic layer. The same calculations were done for a tetragonal zirconia layer. Here, the reference sample is a tetragonal layer on fused silica (FS), with a layer thickness of 136 nm, determined by SEM. It has been heat treated for 30 min at 500 °C.
Figure 2.16: Calculated and experimental values of $\Psi$ for zirconia film on fused silica sintered at 1200 °C for 30 min. With values of $\theta$ of 50, 55 and 60°.

2.7. X-RAY DIFFRACTION (XRD)

X-ray diffraction can be used for phase identification, texture determination and stress analysis. Here we focused on phase identification. X-rays are produced when high-speed electrons collide with a metal target. Therefore a X-ray tube contains an electron source, a high accelerating voltage and a metal target. When the voltage on an X-ray tube is raised above a certain critical value, certain characteristic lines appear. One of the inner electrons (e.g. K-shell) is kicked from the atom by the incoming electron, leaving the atom in an excited, high-energy state. One of the outer electrons decays into the hole, emitting energy in the form of radiation with a definite wavelength. The K-shell hole may be filled by an electron from any of the outer shells, thus giving rise to a series of K lines; K$\alpha$ and K$\beta$ for example. The XRD-machine used had a tube with a Cu anode, emitting a K$\alpha$ wave length of 0.154 nm. K$\beta$ radiation is also present, which is filtered with a Ni-filter so as to obtain nearly monochromatic radiation.
The monochromatic X-rays are used in Bragg diffraction. A possible crystallisation can be detected by scanning the sample over a certain \( \theta \)-range. If the sample contains crystallised grains, sharp peaks in the intensity are observed for particular values of \( \theta \), which correspond to a set of crystal planes \([hkl]\) for which Bragg’s law is satisfied. From the position and relative intensity of the peaks, it can be determined which phase of the material is present. When no peaks are observed the coating is assumed to be amorphous or highly textured. A textured microstructure can imply that there are preferred crystal orientations, which do not diffract the X-rays towards the detector. In addition there will be background radiation caused by inelastic (Compton) scattering and fluorescent radiation.

The analysis of sintered silica sol-gels with this method is not useable due to silica’s amorphous nature. For the zirconia coatings XRD-measurements can give the phase of the material and the average grain size, derived from the peak broadening, which is only possible when the grains are smaller than 150 nm.

The X-ray equipment used in this report consisted of a Philips X’Pert MPD with a Cu anode. Copper radiation has been chosen because of the small penetration depth. The copper tube operates at 40 kV and 30 mA. A special configuration for thin coatings has been used.

### 2.8. Mechanical Testing

To obtain the mechanical properties of the sintered coatings, micro hardness measurements and nano-indentations have been performed. These measurements reveal the strength of the coating in a rather complex manner because it is a combination of yield strength and strain hardening. For micro hardness measurements Vickers Hardness tests are applied. The applied force varied from 1 to 3 N, but for almost all coatings this load turns out to be too high as can be seen in Figure 2.17. Therefore an MTS Nano Indenter XP set-up has been chosen for measurements of the hardness and strength of the coatings. As an indenter the Berkovich tip has been used, this is a triangular pyramid instead of a square pyramid, as is used with Vickers hardness tests. For a triangular tip the radius can be made sharper, which improves the accuracy of the measurements.

When measuring substrate-independent properties of thin films literature \(^{8-11}\) mentions, that the contact depth should be less than 10% of the total depth of
the coating. In several of our measurements the thickness of the coating can be determined, from the point at which the substrate first starts to influence the measurements.

The MTS nano-indentor works with a technique called Continuous Stiffness Mode (CSM), which makes it possible to measure hardness as a function of depth during one indentation. The CSM technique imposes an oscillating force on the indenter while monitoring its response displacement. The phase and amplitude of this response are characteristic of the materials properties because it is a direct measure of the stiffness of contact and the damping by the material at the frequency of the oscillation. All nano-indentations are performed several times to obtain a statistically significant volume of data.

Figure 2.17: Vickers harness test (left), punctured through the coating, effectively measuring the hardness of the substrate. (right) the resulting indentation of the Berkovich tip after a nano-indentation measurement.

2.9. LASER SYSTEMS

Sintering with a laser makes use of the particular advantages of a laser system. These include the capability to focus the beam onto a very small spot and to position the beam accurately. As a consequence treatment of small areas (mm²) at specific places are possible. Laser sintering requires a laser with a high energy density with a specific wavelength that is well absorbed by the material. A CO₂ laser uses an active medium of a mixture of N₂ and CO₂ gasses. The vibrational transitions in the CO₂ molecule give rise to the amplifying effect with a wavelength λ of 10.6 μm. This kind of laser has a 9% efficiency which
necessitates an efficient cooling system, but it is still far better than other non-
semi-conductor lasers. The laser systems used in this project were both-
laboratory and industrial lasers. At the University of Groningen use is made of-
a Spectra Physics - Rofin Sinar 820 laser. This is a transverse flow continuous-
CO\textsubscript{2} laser with a maximum power of 1500 W at the sample surface, operating in-
a TEM\textsubscript{00} mode, which means that the beam is nearly Gaussian. The initial-
diameter of the laser beam is 19 mm, which is focused by a water-cooled ZnSe-
 lens (focal length 127 mm) onto the surface of the sample. Argon is the-
shielding gas that is used to protect the lens as well as to prevent oxidation of-
the sample. The sample is mounted on a (computer numerical controlled) CNC-
X-Y table which can move with a maximum speed of 0.25 m/s. By varying this-
speed the power density, the fluence and the interaction time could be-
controlled. This laser system is used both to sinter silica sol-gel coatings onto a-
silica substrate, as well as to cut small samples from fused silica samples for-
heat treatment in the ESEM.

![Image](image.png)

*Figure 2.18: Polygon laser system sintering printed sol-gel-ink logo's.*

At Philips CFT-laboratories in Eindhoven also a CO\textsubscript{2} laser (max 3.5 kW) has-
been used for the densification process. A polygon system has been built, where
a polygon-wheel rotates fast, scanning the beam very fast over the sample while the sample moves slowly in the indicated direction (Figure 2.18).

Table 2.1: Relevant laser process parameters.

<table>
<thead>
<tr>
<th>Type</th>
<th>Process Parameter</th>
<th>Symbol</th>
<th>Dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate:</td>
<td>Substrate dimension</td>
<td>L x W x H</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>Heat conduction coefficient</td>
<td>$\lambda_H$</td>
<td>W/mK</td>
</tr>
<tr>
<td></td>
<td>Specific heat</td>
<td>$c_p$</td>
<td>J/kgK</td>
</tr>
<tr>
<td></td>
<td>Density</td>
<td>$\rho$</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td></td>
<td>Absorption coefficient</td>
<td>$A_{\lambda}$</td>
<td>a.u.</td>
</tr>
<tr>
<td>Laser Beam:</td>
<td>Laser power</td>
<td>$P_l$</td>
<td>W</td>
</tr>
<tr>
<td></td>
<td>Beam dimensions</td>
<td>$d_a \times d_h$</td>
<td>m</td>
</tr>
<tr>
<td>Motion:</td>
<td>Speed</td>
<td>$v$</td>
<td>m/s</td>
</tr>
<tr>
<td>Process:</td>
<td>Fluence</td>
<td>$F_l$</td>
<td>J/m$^2$</td>
</tr>
<tr>
<td></td>
<td>Interaction time</td>
<td>$t_i$</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>Heat diffusion length</td>
<td>$d_{h}$</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>Temperature change</td>
<td>$\Delta T$</td>
<td>K</td>
</tr>
</tbody>
</table>

Further, at Philips CFT-laboratories in Eindhoven also a Rofin-Sinar Nd-YAG laser has been used. It has a wavelength of $\lambda=1064$ nm. The laser beam is directed through a fibre and as a consequence the energy distribution converts from Gaussian to a top-hat distribution. The Nd-YAG has a spot of 10 mm under unfocussed conditions, a power of 50 to 180 Watt a speed of up to 75 mm/s. The overlap between separate pulses could be programmed but has mostly been 90%. The laser operates in a pulsed mode. The pulses of less than 2 ms have been placed in an array with a frequency of 20 to 750 Hz and have been focussed to a spot width of 1.1 mm. The Nd-YAG laser has been used because spectroscopic investigations of stainless steel indicated that the radiation from a CO$_2$ laser (10.6 $\mu$m) is reflected by 95% at perpendicular incidence. While the radiation of a Nd-YAG laser (1064 nm) and an Excimer laser (248 nm) show more absorption in the steel substrate material. (Figure 2.19).

The absorption at the wavelength of a Nd-YAG laser is about 0.3 to 0.4; at the wavelength of an Excimer laser the value is twice as high, about 0.7.

The reason for this higher absorption in the UV range may be the excitation of the oxide bonds in the surface layer of the stainless steel.
Figure 2.19: Spectral characterisation of the used stainless steel substrate material in the UV/VIS range.

2.10. REFERENCES