Chapter 2

2 Basic Concepts

In this chapter, the experimental techniques that have been used to process, test or characterise the highly porous ceramics are described. These include extrusion, mechanical testing, acoustic emission, Atomic Force Microscopy (AFM) and low voltage Scanning Electron Microscopy (LV-SEM).

2.1 Processing

The precursor powder is produced by a spray drying process. A solution made of small precipitates of SiO$_2$ or Al$_2$O$_3$ is made, where the size of the particular precipitates can be controlled using a number of processing parameters. These precipitates are called the primary particles, which can be as small as 13 nm. Next, the solution is atomised into a hot gas stream and depending on the temperature, the temperature gradient and the velocity of this gas stream, the primary particles will cluster together to form the secondary particles. Typical sizes of these secondary particles are of the order of 150 µm.

After the spray drying process, the powder is mixed with water and, depending whether it is SiO$_2$ or Al$_2$O$_3$ powder, a base or an acid is added to the mix. The charged OH$^-$ or H$^+$ groups connect to the
secondary particles and create a surface charge on these particles causing the particles to break up again. The mixing process takes place in a so called mix-muller. Two heavy wheels compact the mix while turning around. After a while the mix starts to form agglomerates and it becomes ready for extrusion.

The extruder is usually a screw extruder which forces the mix through a hole in a die plate, shaping the extrudate. Extrusion pressures can be as high as 100 bar. Usually the extrudate is shaped as a cylinder, but other shapes are possible as well. After extrusion, the extrudates are dried and subsequently sintered. During firing the primary particles will sinter together and form a three dimensional network.

The process parameters involved in the mixing process are of importance to the extrudability of the mix and also to the physical and catalytic properties. When designing a catalyst carrier, the operating window can be enlarged using additives, consisting mainly of polymers, that can control the amount of water bound to the mix.

2.2 Mechanical Properties

2.2.1 Mechanical Testing

The mechanical properties of the catalyst carriers are characterised using an indirect tensile test. In this test, the Side Crushing Strength test (SCS), the cylinder is slowly uni-axially deformed, at a constant strain rate of 0.5 mm per min., using a HOUNSFIELD 5000E tensile testing machine. The tensile stress has its maximum in the plane between the contact points (figure 2.1) and shows an almost homogeneous distribution. This tensile stress at failure can, as will be shown in § 4.2.1, be calculated in the case of a perfect, homogeneous cylinder. The tensile failure stress can then be expressed in terms of
the maximum force experienced by the specimen during testing, the length of the specimen and its diameter. The procedure of the SCS test is to stop mechanical loading after the force on the specimen has dropped to 60% of the maximum force. A typical experiment consists of 100 tests on individual extrudates. These 100 tests are statistically treated in order to get a good description of the failure distribution.

Beside this Side Crushing Strength test, where failure occurs under pure tensile stresses, we also developed a test that involves compressive stresses (§ 4.3), by increasing the number of contact points (figure 4.5). Due to the fact that we abandon the SCS geometry where all contact points are in line, and apply a geometry with the contact points not in line, a second stress component perpendicular to the first one is introduced. The two stress components together result in both a tensile and compressive stress area.

**Figure 2.1** The side crushing strength (SCS) test and its tensile stress distribution in-between the points of contact.
Since these disordered materials are brittle in nature, fluctuations in the mechanical strength are to be expected. Actually, the failure strength does not only depend on the microstructural features, but also on the macroscopic size of the specimen. So, instead of investigating the average strength, we describe the mechanical strength by a complete failure distribution. A typical example of a failure distribution is displayed in figure 2.2.

In literature the Weibull distribution is commonly used. This distribution describes the statistical size effects as follows:

\[ F_V = 1 - \exp\left(-c V \sigma^m\right) \]  

(2.1)

Where \( F_V \) represents the cumulative chance on failure, \( \sigma \) is the stress at failure, \( V \) is the volume of the particle, \( m \) is the Weibull modulus and \( c \) is
a constant. The semi-empirical relationship between $V$, $\sigma$ and the chance to failure has been tested with numerous experimental data. There are however some non-physical assumptions made in this distribution. The $\sigma$ dependency arises from mathematical convenience and it is assumed that the shape of the stress field and its intensity can be separated. The Weibull distribution can only be used for predicting crack-initiation behaviour, not to describe the crack-propagation. Another problem is that it is only applicable to homogenous systems and that failure occurs under pure tensile stresses.

More recently, Duxbury and Leath (D-L) proposed another type of failure distribution\textsuperscript{3}. The principal difference with the Weibull statistics is that here a different volume dependence is introduced by considering explicitly a distribution function of the size of the cracks. While the Weibull approach is based on the weakest link principle, that is to say the chance on a larger crack scales with the volume, D-L's model implies a 'hottest spot' criterion where failure occurs at the site of the largest local stress. A concise summary is as follows:

In the beginning of this century, Griffith\textsuperscript{4} explained the low strength of glass by relating the failure strength of the specimen to the crack size $a$ in the material:

\[
\sigma \sim \frac{1}{\sqrt{a}}
\]  

(2.2)

This stress field at the tip of the crack is the most important parameter rather than the macroscopic applied stress. Due to the geometry of the crack, the stress at the crack tip itself can be amplified, which is characterised by the stress intensity factor $K_I = \sigma \sqrt{\pi a}$ (see also § 3.2). If the stress at the crack tip exceeds a critical value, failure will occur and the crack will propagate. This critical value is characterised by the critical stress intensity factor $K_{IC}$. 
Another important parameter in characterising fracture is the energy release rate $G$. In general a crack will propagate if the energy released upon propagation (quasi-statically) is at least equal or larger than the energy needed for creating a new surface. The (elastic) energy release rate of a propagating crack under tensile stress can be derived by minimising the total energy of a crack with respect to its length. The stress intensity factor, the energy release rate and dynamic crack propagation will be discussed in more detail in chapter 3.

Duxbury and Leath combined the observations of Griffith with a defect size distribution and derived a failure distribution for lattice models:

$$F_V = 1 - \exp \left[ -cV \exp \left( \frac{-k}{\sigma \mu} \right) \right] \quad (2.3)$$

Where $k$ is the Duxbury-Leath constant and $\mu$ a screening constant. There are several assumptions made in this Griffith approximation. In the case of stationary crack growth and an elliptical crack-shape, the failure stress depends on the crack-length (eq. (2.2)). If however crack-growth is regarded as a dynamic process, the failure stress depends also on the radius of the crack.

Van den Born has shown that the Duxbury-Leath distribution describes the failure distribution of highly porous ceramics better than the Weibull distribution. Especially the lower strength particles, which are extremely important in practical use, are better described using the Duxbury-Leath distribution. Also the determination of the Duxbury-Leath parameters proved less difficult and better reproducible than in the Weibull case.

Both distributions, the Weibull and D-L, assume that global failure occurs when fracture is initiated. However, this would only be the case for ideal brittle materials and in practice we see damage being built up
before global failure occurs. The strength of a batch of material can be characterised by the expectation value, $\sigma_{1/2}$, which is the stress at which a specimen of standardised volume (so we can compare results of different batches) has a 50 % chance on failure.

### 2.2.2 Acoustic Emission

Acoustic Emission$^5$ (AE) is based on the generation of transient elastic waves due to rapid changes in displacement fields and stress fields, $\dot{u}$ and $\sigma$. Crack propagation and initiation, for example can cause release of the stress waves, as can moving dislocations. AE has been know for a long time. The well know "cry of Tin" is such a AE phenomenon, induced by moving dislocations during the phase transformation. Kaiser$^6$ pioneered in this field in the early fifties, recognising the importance of these effects also in other materials.

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**Figure 2.3** The experimental setup with the Hounsfield 5000E tensile testing machine and the PAC Locan 320 acoustic analyser.
The main advantage of AE techniques are that nucleation and growth of cracks can be observed in time and in addition not only on the fracture surface, but also within the bulk of the sample. It is also a time resolving technique because the AE source strength is rather a function of the rate of change of cracks than of absolute size. So brittle materials with their high crack velocities are an ideal case for AE techniques.

Basically an Acoustic Emission set-up consists of a piezoelectric transducer and a signal processor. The transducer converts the movements on the surface of the specimen into an electric signal. This signal is amplified using a high-pass preamplifier and finally sampled by a PAC LOCAN 320 acoustic emission analyser (figure 2.3). It does not analyse the complete wave packet, but only its main characteristics, which are described in figure 2.4.

![Figure 2.4](image)

**Figure 2.4** The main features of an acoustic emission wave package.

The interpretation of AE signals is rather complex. Unless very well defined samples are used and the AE system is well calibrated, dispersion, reflection and attenuation of the signals will remove most of the characteristics of the AE signal. Consequently, it is very difficult
to make a full quantitative evaluation of the signals and link them to specific fracture processes. Because of these difficulties, usually resonant Piezo transducers with a higher sensitivity are used rather than the non-resonant transducers. Its very important to realise that, as a result of the fact that the transducer is resonant, this will remove all kinds of frequency information from the AE signal. This leaves us with only a few characteristics of the signal to be measured (figure 2.4). Because this type of transducer is resonant, most of the stored characteristics are linked to each other. If the resonance frequency of the piezo is known, and we assume it to be a damped oscillator, we may calculate the duration and number of counts from the amplitude of the signal. This leaves us only with the total number of acoustic events during a test and the amplitude distribution to use for gaining physical insight into the failure mechanism.

2.3 Structure and Morphology

2.3.1 Local Probe Microscopy

In the early 1980's Binnig and Rohrer\textsuperscript{10} introduced the scanning tunneling microscope\textsuperscript{11} (STM). With the ability to study structural as well as electronic properties at a very local scale, the advent of this new microscopy enables observations with atomic resolution at a wide range of materials. Its operation is based on tunneling of electrons between two (semi-) conducting materials, separated by a vacuum as is schematically displayed in figure 2.5. Maintaining a bias voltage between the two (semi-) conductors will effectively lower the Fermi energy level with respect to each other and will bring some empty energy levels in correspondence with filled ones, enabling a tunneling current. This tunneling current is very sensitive to the distance between tip and surface and in order for the tunneling phenomenon to occur, the distance between specimen and tip has to be in the
sub-nanometer range. Since the place where tunneling takes place is localised, we may scan the surface at several discrete points in order to get a picture of the electronic properties near the Fermi surface of the specimen from which topographic information is derived. Considering that a tunneling current will only occur in a (semi-) conducting material, Binnig kept searching for a local probe technique that could be used on a wider range of materials, including non-conducting \(^{12}\) (AFM).

Atomic Force Microscopy \(^{13}\) (AFM) is based on measuring the forces acting on a tip in the vicinity of a surface. Most of the times the attractive van der Waals forces dominate the interaction between tip and specimen, but frictional, capillary, magnetic or electrostatic forces may be predominant as well.

The tip is mounted on a flexible cantilever with a very low spring constant. The deflection of this cantilever can accurately be measured using electrical (capacitive, tunneling) or optical (interferometry,
optical beam deflection) methods. Several types of cantilevers exist. The most popular cantilever is equipped with a standard pyramidally shaped silicon tip. The tip is etched along the <100> plane of silicon and has a top angle of 60°. Also cantilevers with sharper Si₃N₄ tips are available. The main advantage is the much sharper top angle of 15°.

A schematic set-up of the AFM is shown in figure 2.6. A piezo electric scanner is used to scan the specimen surface. At each discrete (x,y) co-ordinate, the deflection of the cantilever (and hereby the force on the tip) is measured using a laser diode set-up. The laser beam is reflected from the cantilever onto a split photo diode. A shift in intensity from one section of the photo diode to the other can be used to measure the deflection of the cantilever. It can be shown that this relative simple method of measuring the deflection, is just as accurate as the interference method. The accuracy (in the order of 0.01 nm) can be improved by increasing the distance between cantilever and photo diode. This system can also be used for frictional measurements when using a detector with photo diodes divided in four segments.

Figure 2.6 A schematic set-up of the AFM.
In this study a Digital Instruments Nanoscope II equipped with AFM-3 head was used. Two scanners were to our disposal, a 12 µm - and a 1 µm scanner.

Modes of operation

Keeping the AFM tip within a few nanometers of the surface is not an easy task and operating an AFM became only possible due to the development of high speed control electronics. The AFM can be operated in two different modes: the constant height - or constant force mode. In the constant force mode the piezo is used to keep the force interaction between tip and specimen constant. The electronic feedback-loop keeps the deflection of the cantilever constant by correcting each deviation using the piezo. This means that the piezo z voltage can be used to mimic the topography of the surface.

The constant height mode can be used to measure the changing interaction between tip and surface and to create a force plot. In this mode the feedback loop is very slow and is only used to keep the average deflection constant. The actual deflection signal can be used to mimic the force field.

2.3.2 Scanning Electron Microscopy

Scanning Electron Microscopes (SEM) offer particular advantages over conventional (light) microscopes. The resolution of microscopes in general is limited by the wavelength of the beam used. Depending on the acceleration voltage used, the De Broglie wavelength of the electrons is substantially smaller than the wavelength of visible light. Also depth of field is much larger, making it the perfect instrument for studying fracture surfaces.
The electron source is generally a heated hair pin filament or a heated LaB₆ crystal, the latter giving a higher yield of electrons within a narrower energy range. More recently, field emission guns (FEG) came commercially available. These FEG sources generally make use of a single crystal of tungsten. A very high electrostatic field (in the order of $10^{10}$ V/m) at the surface enables electrons to tunnel through the potential barrier. The high brightness and high spatial coherence make these sources excellent for use in high resolution electron microscopes.

The basic set-up of an SEM is schematically displayed in figure 2.7. Electromagnetic lenses are used to focus the beam on the surface and this beam is swept across the surface. As the primary electrons enter the surface, several processes will be initiated. The most important processes are schematically drawn in figure 2.8. Some valence electrons, excited from the conduction band, can escape from the surface. Coming from a very small region of the solid (the mean free path of these electrons is in the order of nanometers), makes these

**Figure 2.7** The basic set-up of a Scanning Electron Microscope.
secondary electrons (SE) ideal for a study of the topography of the surface. The small volume from which SE's can escape, results in a very good lateral resolution (in the order of nm's). The primary electrons can also be backscattered (BE) by atoms in the surface of the specimen, depending on characteristics of the material at the surface. Due to the larger volume of solid contributing to the BE's, the resolving power is much lower (in the order of micrometers). These SE's and BE's can be observed using appropriate detectors and combining the position of the electron beam with the intensity of SE’s or BE's gives us a spatial picture of the surface.

Conventional SEM's use high voltage electrons in order to increase resolution and the lens systems of these microscopes are optimised for high acceleration voltages (typically 20 - 30 kV). The penetration depth of the electrons however, will also increase with increasing acceleration voltage. When studying non-conducting materials, this will lead to charging of the specimen surface. The electrostatic charge on the
surface will deflect the electron beam, giving rise to distortion of the image. Sputtering a metal layer on top of the surface (usually 10-20 nm) will help to avoid charging, but will also decrease the resolving power of the microscope.

**High Resolution Low Voltage Scanning Electron Microscopy**

Another solution to the charging effects is balancing the number of electrons coming in, with respect to the number of electrons emitted from the surface. If we look at the emission of secondary electrons versus incident beam energy (figure 2.9), we can generally see two crossover points, where the electron yield per incoming electron equals unity. Two different regions can be distinguished: if the electron yield is < 1 then negative charging will occur which will manifest itself as a very bright region. If the electron yield is > 1, positively charging will occur, resulting in a darkened region. If the electron yield equals unity, we can avoid charging and keep the surface neutral. The second

![Graph showing electron yield per incoming electron versus incident beam energy.](image)

**Figure 2.9** Secondary electron yield per incoming electron versus incident beam energy. This example is based on carbon.
crossover voltage $E_2$ for non-conducting materials is typically in the order of 3.0 keV. Reducing the accelerating voltage however, has its disadvantages. The following equation shows the principal factors determining the resolution limit\(^{14} \):

$$d = \left( \frac{i}{B \alpha^2} \right)^2 + \left( \frac{a \lambda}{\alpha} \right)^2 + \left( \frac{\Delta E}{E} C_c \alpha \right)^2 + (b C_s \alpha^3)^2$$

The first term deals with the beam itself, $B$ is proportional to the brightness of the source and $i$ is the beam current and $\alpha$ the beam divergence. The second term represents the diffraction limit, $\lambda$ being the electron wavelength. The third and last term concern the effects of aberration. If we now decrease the acceleration voltage, not only the wavelength of the electrons increases, but the chromatic aberration increases as well.

This is why a low voltage high resolution SEM (LVSEM) uses a Field Emission Gun to generate their low energy electrons. When using a FEG, the first term of eq. (2.4) becomes very small since the brightness $B$ is much larger than for a conventional source. Also the contribution of the chromatic aberration will decrease, since the energy spread $\Delta E$ of the electrons is much smaller than in the conventional case. Also optimisation of the lenses for low energy electrons can decrease the aberrations $C_c$ and $C_s$. All this together makes a FEG LVSEM ideal for studying small features.

### 2.3.3 Mercury Porosimetry

Mercury Porosimetry is used to characterise the pore structure of the material. It is based on the resistance of a liquid on entering a small volume. If we assume all pores to be cylindrical, we may estimate the pore diameter, using eq. (2.5), from a plot of applied pressure against the cumulative volume of the specimen that has been intruded by the
mercury. A typical measurement is shown in figure 2.10. We can link the applied pressure with the pore-diameter $P_d$ (if we have cylindrical shaped pores) using the following equation:

$$P_d = \frac{2\Gamma_{st}\cos \theta}{A_p}$$

(2.5)

where $A_p$ is the applied pressure, $\Gamma_{st}$ the surface tension of mercury and $\theta$ the wetting angle of mercury on our materials. The resolution of this technique depends on the maximum pressure that can be applied on the mercury. The main drawback of mercury porosimetry is the assumption that the pores are of a specific shape. A comparative study with TEM however\textsuperscript{17}, has shown that the outcome of mercury porosimetry can be related to the actual microstructure.
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