2 Experimental techniques

This chapter summarizes the basic concepts of the principal techniques that are used in this work. The focus of the chapter is on microscopy techniques, hardness and wear tests that are employed for the investigation of the thick metallic coatings produced by laser cladding. The laser cladding technique is discussed in detail in Chapter 3. Since x-ray diffraction techniques are much used in this work for the determination of residual stresses, these methods are highlighted in Chapter 5.

2.1 Electron microscopy

Since its advent in the early 1930s, the electron microscope has become an invaluable tool in materials research. Using very short wavelengths of the electrons it is possible to obtain the information about the microstructure of materials that would not be revealed if only the light microscope was used. Electron microscopy techniques are intensively used in this work for the characterization of the laser clad layers produced. The following microscopes were used and each of these microscopes is equipped with Energy Dispersive Spectrometry (EDS) to perform the chemical analyses.

- SEM Philips XL-30-FEG (Field Emission Gun) equipped with EDS and EBSD (Electron Back-Scattered Diffraction) patterning analysis system.
- SEM Philips XL-30s-FEG with EDS and EBSD patterning analysis system.
- Environmental-SEM Philips XL-30S-FEG with EDS.
- Jeol 2010F analytical TEM with GIF (Gatan Imaging Filter) and EDS.

In this section the electron microscopy techniques are briefly described. Detailed explanation on the electron microscopy techniques can be found in several textbooks [1-6].
2.1.1 Scanning electron microscopy

The basic parts in an SEM are schematically depicted in Figure 2.1. In an SEM, electrons are focused by electron lenses to a beam of 1-1000 nm diameters that influences the resolution of the microscope. The electron beam scans the surfaces by means of deflecting coils. At the position of incidence, secondary electrons (SE) with energies of 1-100eV are emitted. These electrons are accelerated by a 10 kV potential onto a detector. The secondary-electron signal is rather sensitive to topographical details and gives a good lateral resolution. The incident electrons can also be backscattered (BSE), the higher the atomic number the more BSEs are generated. These electrons have energies up to the incident beam and need no pre-detection acceleration. The deflection of the beam of a display cathode-ray tube is synchronized to the probing beam and its intensity is modulated with the signal of the detectors. The magnification is affected by the ratio of deflections on the display tube to those on the specimen. The resolution of low-magnification images is limited by the size of the beam of the display tube. At higher magnification, the limitation is determined by the size of the probing beam.

Figure 2.1: Schematic representation of the scanning electron microscope.

An incident electron may interact also inelastically with atoms of the investigated material causing x-ray radiation. An electron of sufficient energy may ionize an atom by ejecting an inner-shell electron. When the electron decays it may produce either an Auger electron, or an x-ray photon with a characteristic energy for this transition and therefore, and as a consequence it characterizes the ionized element. X-ray photons may be detected by an energy dispersive spectrometer (EDS). In such a detector a liquid-nitrogen cooled Si(Li) detector is used, which may be positioned at a few millimeters away from the specimen. In the Si crystal, a quantum produces conduction electrons in an amount that is proportional to its energy. The current produced is converted to a voltage proportional to the current. The occurrence of such steps is counted in a multichannel analyzer in which for each voltage step an appropriate channel is allocated. When a heterogeneous specimen is analyzed, one should
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keep in mind that the investigated volume will vary depending on the atomic weight of the element. Light elements, like B and C, have a high absorption of low energy x-rays and the accuracy in the quantitative analysis of these elements is lower than for heavier elements.

2.1.2 Electron Backscattered pattern microscopy

Electron Backscattered Diffraction (EBSD) is also known as Kikuchi diffraction (KD), or electron backscatter pattern technique (EBSP). EBSD can give information about the crystal structure and orientation of the grains in a crystalline material. Consider an electron beam irradiating a crystal as illustrated in Figure 2.2. The primary electrons are diffusely scattered in all directions, and consequently part of them impinges on a given set of lattice planes \{hkl\} at the Bragg angle, \( \theta \) [7, see also Chapter 5 of this thesis]. Although the Bragg angle depends on the wavelength of the electrons, see equation 2.1, the relative change in wavelength due to inelastic scattering in an electron microscope is relatively small and therefore both elastically and inelastically scattered electrons may contribute to Bragg diffraction at approximately the same angle.

\[
n\lambda = 2d_{hkl} \sin \theta \tag{2.1}
\]

Here \( \lambda \) is the De Broglie wavelength, \( d_{hkl} \) is the plane distance and \( \theta \) is the half angle between the incident and the scattered beam. The trajectories of these electrons constitute two cones on either sides of the diffraction set of planes with an apex half-angle of 90°- \( \theta \) to the plane normal \(<hkl>\). These are known as Kossel cones. When the backscattered electrons are recorded on a phosphor screen, the interception of a pair of Kossel cones with the screen is seen as a pair of hyperbolas, which approximate to straight lines (Kikuchi lines) because the Bragg angle is relatively small.

![Figure 2.2: Set up in SEM equipped with phosphor screen to detect Kikuchi lines and determination of crystal orientation.](image)
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Figure 2.3 shows a typical indexed EBSD pattern. The distance between a pair of Kikuchi lines is related to the interplanar distance of the corresponding lattice planes and the angles between different pairs of Kikuchi lines represent the angular relationships in the crystal. The pattern therefore contains many important characteristics of the crystal and the orientation of the crystal can be determined from the position of the lines.

Figure 2.3: Indexed EBSD pattern of bcc lattice performed by OIM.

The principle of EBSD has been implemented into the SEM for phase determination and orientation mapping. The most popular commercial names for the automation include the Orientation Imaging Microscopy (OIM) and Automated Crystal Orientation Mapping (ACOM). The specimen surface is oriented about 70° tilted with respect to the electron beam in order to promote backscatter diffraction. The electron beam subsequently scans across the area of interest on the surface, and at each position the backscatter is recorded and analyzed. This allows for a fast mapping of the texture of polycrystalline materials, together with the phase identification from a limited number of pre-selected phases. The orientation resolution that can be obtained from the pattern is of the order of 1°.

2.1.3 Transmission electron microscopy

When a higher resolution is necessary the analytical Transmission Electron Microscope (TEM) is used. The schematic representation of a TEM is depicted in Figure 2.4. A field emission gun emits the electrons that are focused by using several electromagnetic lenses and electrical deflectors. The most straight-forward way to obtain information is to form an image of the transmitted beam [8]. This is called bright-field imaging. Some of the electrons, however, are elastically scattered leading to diffracted beams. In the normal bright-field mode, diffracted beams are not allowed to pass through the objective aperture.
The information of an image of the sample is not the only way to obtain structural information. Another possibility is to use the diffracted beams more explicitly. Some applications of the electron beams can be found in [9]. This technique, that resembles other diffraction techniques, can provide information about the atomic structure of the sample. A diffraction pattern is obtained in the following way. For the directions in which the Bragg’s law is satisfied, constructive interference of scattered electrons may lead to a diffracted beam. The intensity of these beams is proportional to the lattice structure factor $|F|$ for the unit cell, where:

$$F(g) = \sum_j f_j \left(\frac{\sin \theta}{\lambda}\right) e^{-2\pi g \cdot r_j},$$  \hspace{1cm} 2.2$$

in which $g$ denotes the reciprocal lattice vector, equals to $k - k_o$, i.e. the difference between the diffracted and the incident beams, and $r_j$ is the position of the atoms in the lattice. The summation is over the atoms in the unit cell. $f_j (\sin \theta / \lambda)$ is the atomic scattering factor. For the typical electron case, Bragg angles must be very small for considerable diffraction to take place. This is not the case for x-ray and neutron diffraction. The result of such calculation is that for most crystals not all reflections are present. For instance, in fcc lattice only those reflections for which $h, k$ and $l$ are all even or uneven are actually present.

All beams for which the structure factor (and the transmitted beam) is not equal to zero are focused in the back-focal-plane of the objective lens. By suitable settings of the intermediate lenses, an image of this diffraction pattern can be obtained on the viewing screen or on a photographic plate. By placing an aperture in the image plane of the objective lens, only that part of the specimen that is located inside of this aperture will contribute to the diffraction pattern. This technique is called Selected Area Diffraction (SAD) and it is used to
obtain certain information of a single grain or large precipitate in a specimen. If a material is polycrystalline with a grain size much smaller than the beam, many grains will contribute to the diffraction pattern and a ring pattern, instead of points, is formed.

Making use of a diffracted beam instead of a transmitted beam is called dark-field imaging. Since the diffracted beams usually do not coincide with the optical axis of the microscope, the image will not be of maximum quality, as far as spherical aberration is concerned. To overcome this problem the beam is tilted in such a way that the desired diffracted beam passes along the optical axis. Application of this technique leads to high contrast images of several types of defects. Whenever an image of a lattice is formed by diffraction contrast, the specimen is tilted into a so called two-beam condition. In this way only one set of diffracting planes contributes to the image formation, which makes interpretation of the micrograph easier.

When dislocations are to be imaged, it is often better to tilt the crystal slightly further by such an amount that the Bragg condition is fulfilled within a small region near the dislocation. The deviation from the exact Bragg condition \((s)\) for a perfect crystal is then given by \(k - k_0 = g + s\). This way a high resolution image is obtained, in which the dislocation shows up as a white line. This is called weak beam imaging for \(|g| \approx 0.3\) nm\(^{-1}\). The amount of extra tilting can be determined accurately by the relative position of the Kikuchi lines with respect to its associated diffraction spot, which is determined by the direction of the incident beam. As a consequence, the exact deviation from the Bragg condition is specified, and a numerical value of \(s\) can be obtained. In laser treated samples, the internal stresses can be so high that the Kikuchi patterns become faint or are not resolved. In such cases \(s\) cannot be determined, and one should tilt the sample until a reasonable contrast is achieved. The magnitude of \(s\) is related quantitatively to the resolution of a dislocation image in the following way. The width of a dislocation image is approximately \(0.3\xi_g\). Here \(\xi_g\) is the extinction distance for a certain reflection, and is in the order of 15 to 200 nm for most metals. If the lattice is tilted away from the exact Bragg condition the effective extinction distance, \(\xi_{g_{\text{eff}}}\), is reduced and the width of a dislocation image can be decreased to values of 1 to 5 nm.

Application of the kinematical theory for electron diffraction, which assumes that the crystal is so thin or \(s\) is so large that the intensity of the diffracted beam is small compared to the intensity of the transmitted beam, results in the following expression for the amplitude of the diffracted beam:

\[
\Phi_g = \frac{m}{\xi_g} \Phi_0 \int_0^t e^{-2\pi g} dz,
\]

where \(t\) is the thickness of the foil. Evaluation of the integral yields the following expression for the diffracted intensity as a function of the foil thickness:
provided that $s_g \gg \xi_g^{-1}$, i.e. the kinematical theory is applicable. It is easy to see that the diffracted intensity oscillates as a function of depth, giving rise to the so called thickness fringes. These fringes, occurring with a periodicity $\xi_g^{eff}$, can be used to estimate the foil thickness. Such an estimate must be done carefully, because of a small deviation from the Bragg condition already results in a significant effect on the extinction distance. Therefore, the value obtained must be regarded as an upper limit rather than a precise value. Contrast of lattice imperfection is given by a modified version of equation 2.4 [10]:

$$\Phi_g = \frac{m}{s_g} \Phi_0 \int_0^f e^{-2\pi(s g z^r + \xi_g^{-1} z)} dz,$$  

where $\vec{r}$ describes the displacement of a particular atom from a perfect lattice, in the vicinity of an imperfection. The displacement can be calculated using isotropic linear elasticity theory [10]. Although a precise calculation of the image contrast of dislocation is quite complicated, this equation allows one to predict the visibility of a dislocation.

In TEM the diffraction pattern is sometimes not sufficient for the complete characterization of a material because the measurement of lattice parameters is not as accurate as in x-ray diffraction. In such a case, EDS can be used to describe the material. For that, in transmission microscopy, the sample holder has to provide a low background to avoid disturbances in the spectra. In this work, the phase analysis of the clad layers performed by XRD is complemented with TEM-EDS to characterize the various phases.

### 2.2 The white light confocal microscopy

The principle of the confocal microscope is rather simple and was presented by Minsky [11,12]. Light emitted from a laser or white light source passes an illumination pinhole, a beam splitter and an objective lens, which converges the beam onto the sample. The setup is chosen in such a way that only when the beam is focused on the surface the reflected light, converges again by the objective lens and is redirected by the beam splitter, passes the confocal or detector pinhole after which it is collected by a detector. When the surface is slightly out of focus, less reflected light will pass the pinhole and reach the detector.
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Figure 2.5: Schematics of basic construction of a confocal microscope [13].

In a modern confocal microscope, the principle of Minsky is slightly modified. Figure 2.5 shows the schematics of such a microscope. A collimator lens creates a parallel beam, which passes first through a splitter and then through a rotating Nipkow disk, which acts as a multiple point source scanning the surface. The light from a single hole in the disk is focused on the surface by the objective lens. When the specimen is exactly in focus, the reflected light will be refocused onto the same hole in the Nipkow disk, after which the beam splitter and an imaging lens will form an image on the detector. The Nipkow disk, which is in fact both the illumination and detector pinhole, makes it possible to get topographic information from a fixed grid of points with a single capture of the CCD detector. The objective lens can be moved very accurately using a piezo-device, bringing the different parts of the specimen in focus.

The intensity of the beam at the detector can be described by the simple formula:

\[ I(z) = I_0 \left( \frac{\sin(kz(1 - \cos \alpha))}{kz(1 - \cos \alpha)} \right)^2, \]

2.6

where \( \alpha \) is the aperture angle of the objective lens, \( k \) is the wavenumber of the radiation, \( z \) is the defocusing coordinate and \( I_0 \) is the intensity at the detector when the sample is exactly in focus (\( z = 0 \)). The variation of \( I \) with \( z \) is given in Figure 2.6.
Since all points in the grid are moved through focus, the problem of finding the height at a point $x, y$ is reduced to calculating the center of gravity of the peak in equation 2.6:

$$h(x, y) = \frac{\sum_{Z_k \text{FWHM}} I(X, Y, Z_k) \cdot Z_k}{\sum_{Z_k \text{FWHM}} I(X, Y, Z_k)}$$  \hspace{1cm} 2.7$$

where the summation is only taken over those $Z_k$ values within peak’s full width at half maximum to reduce noise effects occurring in the profile’s tail.

2.3 Mechanical testing

2.3.1 Vickers indentation hardness test

Hardness measurements are used in this work to obtain information on the mechanical properties of the clad layers, substrate and hardened material.

The Vickers hardness test method consists of indenting the test material with a diamond indenter, in the form of a pyramid with a square base and a top angle of 136 degrees between opposite faces subjected to a load of 1 to 3 N. The full load is normally applied for 10 to 15 seconds. The two diagonals of the indentation left in the surface of the material after removal of the load are measured using a microscope and their average calculated. The area of the sloping surface of the indentation is calculated. The Vickers hardness is the quotient obtained by dividing the load by the area squared of indentation. The measurements are performed in cross sections of the materials that have been ground and polished to eliminate the macro-roughness. The depth of the work hardened zone is negligibly small as compared to the depth of the indentation so that it does not influence the measurement. These kinds of measurement reveal the strength of a material due to a combined effect of yield strength and strain hardening.
2.3.2 Wear dry sliding test

The principal goal of laser surface treatments is to create a hard, strong and wear resistant surface. The theory of wear is quite complicated, since wear may manifest in several ways. Depending on the nature of the counteracting bodies, on the environmental conditions, and on the applied contact pressure, one or more of the following plasticity dominated wear mechanisms will usually operate: adhesive, abrasive or surface fatigue [14]. At high sliding velocities, oxidation or even melting may play a role. For a more detailed description of the mentioned wear mechanisms, reference is made to the textbook by Halling [15], who also paid attention to the effect of lubrication, different material combinations, stress distribution, surface roughness etc.

In this work the CSM High-Temperature Tribometer is used to perform the pin on disk test to investigate the wear properties of laser deposited clad layers. The instrument can perform on the following ranges of parameters: temperature, up to 800 °C; load, up to 60 N; friction force, up to 10 N; rotation speed, between 0.3 - 500 rpm and sensitivity of the lever of about 20 nm. Dry sliding test, Figure 2.6, is performed with a flat or a sphere shaped indenter loaded on to the test sample. A pin is mounted on a stiff lever, designed as a frictionless force transducer and the sample is always sliding, resulting frictional forces acting between the pin and the sample, which are measured by very small deflections of the lever. Wear coefficients for both the sample and material are calculated from the volume of the material lost during a specific friction run. This simple method facilitates the determination and study of friction and wear behavior of almost every solid state material combination, with varying time, contact pressure, velocity, temperature, humidity, lubricants, etc.

![Diagram of pin on disc test](image)

*Figure 2.7: Schematics of pin on disc test used for dry sliding wear test.*
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References