Chapter 2 Experimental

This chapter gives an overview of the materials investigated, the experimental techniques employed and the sample preparation procedures used for each technique. In the first section, the compositions and manufacturing process of the two investigated steels are introduced. The following sections focus on the various characterization techniques, including visible light microscopy (VLM), scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), scanning/ transmission electron microscopy (S/TEM), matrix dissolution, small angle neutron scattering (SANS), Vickers hardness measurements and tensile tests. First each technique is briefly explained, including their application and basic principle, then the sample preparation procedures, instruments and testing parameters for each experiment are described.

2.1 Materials

2.1.1 GO electrical steel

The investigated GO electrical steel was provided by Tata Steel, IJmuiden. The steel was hot rolled, hot-band annealed and cold rolled to the final thickness of 0.23 mm. The cold-rolled steel was first decarburized at 830 °C and then nitrided at 850 °C for one minute. The chemical composition (wt%) for the most relevant elements of the decarburized and nitrided (D-line) steel is show in Table 2.1. The detailed annealing cycles are described in Chapter 3.

<table>
<thead>
<tr>
<th>Si</th>
<th>Mn</th>
<th>C</th>
<th>Al</th>
<th>N</th>
<th>Cu</th>
<th>S</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.106</td>
<td>0.192</td>
<td>0.023</td>
<td>0.034</td>
<td>0.025</td>
<td>0.1</td>
<td>0.0055</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

2.1.2 HSLA steel

The investigated cold-rolled Ti-V HSLA steel was provided by Tata Steel, IJmuiden. The steel was hot rolled, coiled below 600 °C and cold rolled with a reduction of 60% to the final thickness of 1.5 mm. The composition ranges for the most relevant elements (wt%) are shown (Table 2.2). The cold-rolled steel samples were annealed at different temperatures and times (see Chapter 4 for isothermal annealing and Chapter 6 for continuous annealing).

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>N</th>
<th>Ti</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03-0.07</td>
<td>0.8-1.2</td>
<td>0.002-0.006</td>
<td>0.03-0.08</td>
<td>0.05-0.12</td>
</tr>
</tbody>
</table>
2.2 VLM

The visible light microscope, also referred to as optical microscope, is a type of microscope that uses visible light and a range of objective lenses with different magnifications to generate magnified images of small objects. The maximum magnification is limited to around 1000 times due to the limited resolving power of visible light. The diffraction limited resolution is about half a micrometer. It is widely used in the field of microelectronics, nanophysics, biotechnology, microbiology and mineralogy. For metals and alloys, surfaces and polished/etched cross sections are usually examined, through which grain size and shape, inclusions and internal stress patterns can be investigated.

In the present work, for both types of steels, samples (with a dimension of $10 \times 10 \times 0.23$ mm$^3$ for GO electrical steel and $10 \times 10 \times 1.5$ mm$^3$ for HSLA steel) were hot mounted in Bakelite, ground using silicon carbide papers (500, 1000 and 2000-grade) and polished with diamond paste (6 μm, 3 μm, 1 μm and 1/4 μm) with standard procedures. 3% Nital solution was used to etch the sample surface after final polishing and microstructures were investigated with an Olympus VANOX-T visible light microscope.

2.3 SEM

An SEM is a type of microscope that produces images by scanning the sample surface with a focused beam of electrons. Various types of signals generated from different regions within the sample can be obtained by SEM due to the interaction between the electrons and atoms (see Fig. 2.1). These signals carry different kinds of information and are used for different purposes. Of the most commonly used signals, secondary electrons offer the best resolution and carry information about the surface topography. X-rays carry the best information about the sample composition but have poor spatial resolution. Backscattered electrons occupy the middle ground offering a medium resolution image carrying (by Z-contrast) significant but non-specific compositional information. Compared to VLM, SEM offers superior performance, particularly in resolution (using electrons instead of visible light), depth of field (due to the very narrow electron beam) and microanalysis [1].

Fig. 2.1 Various types of signals and their generated positions for SEM observation.
In the present work, an FEI Nova NanoSEM650 with (ideally) a resolution of 0.9 nm was used to investigate the morphology (grains and precipitates) of the GO steels after surface etching at 30 kV. This SEM is also equipped with a high angle annular dark field (HAADF) detector and can thus be operated as an STEM for very thin specimens.

The STEM-in-SEM is based on two principles. On one hand, as in an SEM, the beam focuses on a small spot that scans over the sample. The image is formed by mapping some signal intensity synchronously with the scan. On the other hand, as in a TEM, image information is extracted from electrons that have passed through a thin sample. The STEM-in-SEM is also referred to as “low-voltage STEM” because it uses a low voltage of 20-30 kV which generates electrons with lower energy limit to go through the sample [2]. This technique has its own advantages over separate SEM and TEM. It enables imaging with even higher resolution compared with its host SEM due to the very small beam-sample interaction volume [3]. Moreover, the low accelerating voltage allows for enhanced contrast compared with TEM due to the absence of chromatic aberration since no projection lens are needed [2].

For elements with a higher atomic number Z, more electrons are scattered at higher angles due to greater electrostatic interactions between the electron beam and nucleus. The HAADF detector is used to collect the high off-axis (> 50 mrad) incoherently scattered electrons and therefore collects more signals from atoms with a higher Z. Fig. 2.2 schematically shows the position of the HAADF detector and the general electron scattering angles gathered by each detector in a STEM. In a HAADF-STEM image, heavier atoms exhibit higher brightness, making HAADF a very useful way to identify small areas of an element with a high Z in a matrix of material with a lower Z. This technique is especially suitable for determining the size of nano-particles and their distribution on carbon extraction replicas.

In addition, the Nova NanoSEM650 allows image stitching, where a large area can be observed to derive the overall precipitate distribution, while still maintaining the high resolution present in an individual image.

In this thesis, the precipitate non-uniformity and size distribution (especially the non-uniformly distributed precipitates between 10 -100 nm) were investigated on carbon replicas under HAADF-STEM mode at 30 kV. Image-Pro Plus software was used to measure effective precipitate radius from stitched HAADF-STEM images.
Fig 2.2 The position of the HAADF detector and the general electron scattering angles gathered by each detector in a STEM. Adapted from Williams and Carter [4].

2.4 EBSD

EBSD is an SEM-based microstructural-crystallographic characterization technique by collecting elastically backscattered electrons (BSEs) which have undergone coherent Bragg scattering when they leave the specimen [5]. It is widely used in the analysis of crystalline or polycrystalline materials, for instance, which crystal structures are present and their orientation, sizes and morphology of individual grains, the collective texture of alloys, and crystallographic relationships between phases [6].

Fig. 2.3 shows a schematic diagram of a typical EBSD installation [7]. A well-polished crystalline specimen is placed in the SEM chamber at a highly tilted angle (usually 70° from horizontal) towards the CCD camera in order to increase the contrast in the resultant electron backscatter diffraction pattern. The phosphor screen is located within the specimen chamber of the SEM at an angle of approximately 90° to the pole piece. The diffracted electrons, which satisfy the Bragg diffraction condition after hitting the titled sample, can be detected when they impinge on a phosphor screen and generate visible lines called Kikuchi lines. With EBSD software, Kikuchi lines are typically detected via a mathematical routine using a modified Hough transform, in which every pixel in Hough space denotes a unique line. The detected individual Kikuchi line can be used to identify the phase, to index the pattern, and to determine the orientation of the crystal.

In this thesis, an FEI Nova NanoSEM 650, equipped with an EBSD detector, was used to conduct EBSD measurements in particular of the HSLA steel (Chapter 5). The RD-ND plane was investigated after standard sample preparation process with the final step of polishing with OPS for 40 min. In each EBSD measurement, first an area of 100 × 140
µm$^2$ was measured at 20 kV accelerating voltage at a step size of 0.20 µm. TSL OIM analysis software was used to analyze collected data for grain size and recrystallization fraction. Then an area of 30 × 40 µm$^2$ in the already measured area was scanned at a step size of 0.08 µm with the same recrystallization fraction as in the large area. The collected data have been used to estimate the geometrically necessary dislocations (GND) density with Matlab and Mtex software [8–10].

Fig. 2.3 Schematic diagram of a typical EBSD installation [7].

2.5 TEM

Specimens for TEM investigation were prepared with three distinct methods: electrochemical polishing, focus ion beam (FIB) and carbon replica extraction. The three methods have their own advantages and disadvantages. Thin foils produced by electrochemical polishing allows the real microstructure observation, such as grain boundaries, dislocations and precipitate distribution, and obtaining the orientation relationship between the matrix and the precipitates. However, the steel specimens investigated are quite magnetic, making it difficult to get clear images, especially at high magnification modes, because the electrons shift when going through the magnetic specimens. Moreover, grain boundaries, dislocations and artifacts like bend contours introduced by electrochemical polishing interfere the characterization of precipitates. In addition, only small areas of the thin foil samples are sufficiently thin, not enough to give quantitatively results when precipitates are not uniformly distributed. FIB lamellas are essentially thin foils and therefore have almost the same pros and cons as specimens produced by electrochemical polishing. The difference lies in the much smaller size and more site-specific location of FIB lamellas, such as from a crystal with a certain orientation or a specific feature. Besides, the magnetism of a FIB lamella is so small that it disturbs the TEM analysis much less. In contrast, carbon replica extraction only extracts the precipitates, avoiding all the disadvantages of the thin foils. However, the orientation relationship between the matrix and the precipitates is lost. There is also a risk that precipitates do not
Chapter 2  Experimental

show the real distribution due to precipitate aggregation during their extraction. The detailed preparation procedures of each method are described below.

2.5.1 Electrochemical polishing

Electrochemical polishing can only be used for electrically conducting samples, such as metals and alloys. This method is relatively quick (a few minutes) and can produce thin foils without mechanical damage. The schematic diagram of a twin-jet electrochemical polisher is shown in Fig. 2.4. The positively charged specimen is held in a Teflon holder between the jets. A certain applied voltage results in anodic dissolution of the specimen with a polished surface. A light pipe (not shown) detects sample transparency (hole formation) and terminates the polishing when the light intensity passing through the sample exceeds a certain setpoint.

In this thesis, 3 mm sample discs were cut and ground to 80 μm thickness (using 500, 1000, 2000 and 4000-grade silicon carbide papers) with a Gatan disc grinder. Electrochemical polishing was performed in a solution of 5% perchloric acid (HClO₄) and 95% acetic acid at the temperature of 15 °C and a voltage of 25 V with Struers Tunepol 3.

Fig. 2.4 Schematic diagram of a twin-jet electrochemical polishing. Adapted from Williams and Carter [4].

2.5.2 FIB

FIB is a technique for site-specific analysis, allowing deposition and ablation of materials used in the semiconductor industry, materials science and biological field [11]. An FIB resembles an SEM, except that a focused beam of ions (mostly gallium (Ga) ions) is used in FIB whereas the SEM uses a focused beam of electrons. FIB can also be incorporated in a system with both electron and ion beam columns, allowing the same feature to be investigated using either of the beams. The angle between the (vertical) electron column and the (tilted) ion column is normally 52°.
FIB is commonly used to prepare TEM specimens, taking advantage of choosing site-specific region, such as in a grain with a certain crystal orientation or on a certain grain boundary [12].

In this thesis, FIB lamellas were primarily produced for grains with <100> axis perpendicular to the surface in GO electrical steels. They were papered with an FEI Helios G4 CX Dual Beam Electron Microscope. These lamellas were used to record selected area electron diffraction (SAED) patterns in TEM, through which the precipitate (with a mean size of 3 or 4 nm) type and their orientation relationship with the matrix was identified. The detailed procedures are described below.

Before FIB lamella preparation, an EBSD measurement was first performed on the well-polished samples, through which grains with <100> axis perpendicular to the surface were found and marked by extensive electron beam exposure. Then the sample was transferred into the dual beam system. In the first step, the marked grain was found and moved to eucentric height (Fig. 2.5a). The second step is the deposition of a protective platinum (Pt) layer using the ion beam and a precursor gas (Fig. 2.5b). The third step involves bulk milling and U shape cutting (Fig. 2.5c), after which the sample is ready for lift out. In the fourth step, the milled lamella is attached to a needle and lifted out (Fig. 2.5d). In the fifth step, the lamella is transferred to a dedicated TEM grid (Fig. 2.5e). Finally, the lamella is thinned using 30 kV ion and cleaned with 5 kV and 2 kV ions to a final thickness of around 100 nm. The bottom edge of the thinned lamella in the (30 kV) HAADF-STEM image (Fig. 2.5f) shows bright contrast, indicating the specimen is thin enough for TEM observation (at 200 or 300 kV).

2.5.3 Carbon replica extraction

The general procedures for carbon replica extraction are shown in Fig. 2.6. The sample is first polished metallographically. Then an appropriate etching process is used to slightly remove the matrix such that the particles stand proud of the matrix surface. Next a layer of thin carbon film is evaporated onto the surface and cut into 2 mm squares. The etching is continued until the squares of carbon film that carry the particles float to the surface of the etching liquid. Finally, these carbon film squares are caught on a grid and ready for TEM investigation.

In this thesis, for both types of steel, the preparation procedure is the same. The well-polished (with the final polishing using 1/4 μm diamond paste) samples were lightly etched with 3% Nital solution before being placed into a carbon coater for depositing a layer of carbon with a thickness of about 5 nm. After carbon deposition, samples were etched in 3% Nital solution for several minutes until the carbon film started to detach from the steel surface. Nickel TEM grids were used to pick up the carbon replicas.
Fig. 2.5 (a) the marked grain was found and moved to eucentric height, (b) deposition of the protective Pt layer with the ion beam, (c) lamella bulk milling and U shape cutting, (d) lamella lifting out, (e) lamella transformation to TEM grid, (f) lamella thinning and cleaning to a final thickness of around 100 nm.

Fig. 2.6 Schematic diagram showing the procedures of carbon replica extraction. Adapted from Williams and Carter [4].
2.5.4 S/TEM observation

S/TEM is a very powerful microscopy technique that forms an image by making use of a high energy electron beam that is transmitted through a thin specimen. The features such as morphology, size, crystallographic structure and chemical information inside of the specimen can be obtained through the interaction between electrons and atoms. Due to the small de Broglie wavelength of electrons (2.5 pm at 200 kV), TEM has a very high resolution to characterize fine structure, even a single atom. In the past the point resolution was severely limited by spherical aberration (of the objective lens) to values above 100 pm, but nowadays with an aberration corrector inserted in the TEM column, resolution can go down to 50 pm. STEM resolution is particularly determined by the diameter of the electron beam (waist) interacting with the sample, which can nowadays be clearly smaller than the distance between atoms and with an aberration corrector (for the probe) can also lead to resolutions well below 100 pm. S/TEM has been a major characterization technique for biomedical research, material science, nanotechnology and semiconductor research.

In TEM, the electron beam generated from the electron gun can be operated in two principal modes: parallel beam and convergent beam [4]. The former is primarily used for TEM imaging and selected area diffraction (SAD), whereas the latter is mainly used for STEM imaging, and convergent beam electron diffraction (CBED), and chemical composition analysis via X-ray and electron spectrometry.

Fig. 2.7 illustrates the basic operation modes of diffraction (left) and imaging (right) in TEM. In diffraction mode, the strength of the intermediate lens is set automatically in such a way that it takes the back focal plane of the objective lens as its object and allows the diffraction pattern of the sample to be projected on to the viewing screen with high magnification. The SAD aperture (that can be selected with various diameters) can be used in diffraction mode in order to have a diffraction pattern from a particular region of the sample. The sample can be titled to a certain orientation so that a particular diffraction pattern under a certain axis can be obtained. In imaging mode, the intermediate lens takes the image plane of the objective lens as its object and allows the image of the sample to be projected on to the viewing screen of the system. The objective aperture is typically inserted to enhance image contrast (or improve signal-to-noise ratio in atomic resolution images).

In STEM, two extra pairs of scan coils (double deflection scan coils) are employed to guarantee that the scanning beam is always parallel to the optic axis when it scans across the specimen surface (see Fig. 2.8). The STEM associated to TEM is similar to the STEM associated to SEM, which has been introduced in section 2.3. However, the STEM in TEM can be equipped with an aberration correction, which enables the probe to be focused to sub-angstrom diameter, such that the resolution nowadays can be improved down to 50 pm.
In this thesis, a JEOL 2010 (a 200 kV TEM equipped with a LaB$_6$ electron source) was used to obtain the bright-field TEM images for precipitate size measurement. A JEOL 2010F (a 200 kV TEM equipped with field emission gun) was used to obtain the SAD pattern (for GO electrical steel with FIB lamellas) to identify the precipitate type and their orientation relation with the matrix. An FEI Themis Z, a double aberration corrected TEM and STEM which is equipped with two large race-track EDS detectors (Dual X system), was operated at 300 kV to obtain (i) precipitate chemical composition, especially precipitates of several nanometers, (ii) high resolution TEM (HRTEM) images, (iii) EDS elemental mapping under STEM mode.
2.6 Matrix dissolution

Matrix dissolution is a method to selectively dissolve the matrix while leaving the precipitates unattacked [13]. The precipitates can then be extracted and analyzed by different techniques, such as SEM, TEM and XRD, whereas the supernatant can be investigated with inductively coupled plasma (ICP) tests, from which elements concentration can be obtained and thus the precipitate composition and volume fraction are derived. Matrix dissolution is a very promising technique to quantify precipitates in steels, as it provides samples that are more representative of the steel strip. Relatively large volumes of the material (a few cm³) are analyzed, so that statistically significant quantities of precipitates are collected.

In this thesis, matrix dissolution experiments were performed on the cold-rolled and the annealed HSLA steel samples. Matrix dissolution refers to the whole process, i.e., chemical dissolution, filtering, centrifuging and inductively coupled plasma - optical emission spectroscopy (ICP-OES) measurements. The schematic diagram of matrix dissolution is shown in Fig. 2.9. After weighing the sample (the dimension is about 10 × 10 × 1.5 mm³) using an analytical balance with an accuracy of 0.1 mg, 12 ml HCl acid solution (1:1 mixture by volume of distilled water and HCl acid with a density of 1.19 g/cm³ [14]) was used to dissolve the steel matrix at 55 °C. In order to separate precipitates from the solution,
vacuum filtration with a 20 nm pore size filter was first conducted, followed by centrifuging performed with a Beckman Coulter Avanti-20 XP. The solution after filtering was quickly rotated up to 21500 rpm at 4 °C and held for 50 min. ICP-OES measurements were conducted on the supernatant obtained after filtering of the CR sample and after both filtering and centrifuging for all samples to determine the Ti and V concentrations in the matrix. The Ti and V concentration in the precipitates can then be obtained by subtracting the Ti and V concentrations in the matrix from the known overall Ti and V concentrations in the steel. The precipitate volume fraction is then calculated using the densities of the various phases (matrix and precipitates) involved.

Fig. 2.9 Schematic diagram of the matrix dissolution method, including filtering, centrifuging and ICP-OES measurements on the obtained supernatants. TEM is employed to verify the filtering and centrifuging efficiencies.

2.7 SANS

SANS is a powerful technique that uses elastic neutron scattering at small scattering angles to investigate the structure of materials with size ranges from 1 nm up to 100 nm for large sample volumes [15]. Fig. 2.10 shows the schematic representation of a SANS experiment. A beam of neutrons is directed at a sample, which can be an aqueous solution, a solid, a powder, or a crystal. The neutrons are elastically scattered by nuclear interaction with the nuclei or interaction with the magnetic moments of unpaired electrons. The initial output of SANS measurements is a 2D scattering pattern. It can be transformed into 1D data following the methods described in [16], giving the relationship between scattering intensity $I(q)$ and scattering vector $q$. This data then can be further analyzed to obtain information on particle size, number density and volume fraction.

In this thesis, SANS experiments were performed at room temperature on the LARMOR Instrument at ISIS Neutron and Muon Source (STFC Rutherford Appleton Laboratory) [17]. Sample dimensions for the SANS measurements are $10 \times 10 \times 1 \text{ mm}^3$ (each side of the 1.5 mm steel plate was ground away by 0.25 mm). A $5\times5 \text{ mm}^2$ neutron beam and a wavelength range of 0.42 - 1.33 nm were used. A 3473-70 GMW electromagnet was used to generate a transversal magnetic field of 1.65 T, perpendicular to the neutron beam. This strong magnetic field is necessary to magnetically saturate the specimens, to avoid any
contribution to the scattering signal from magnetic domains, and to separate the nuclear and magnetic scattering contribution from the SANS pattern [16]. The SANS detector is a 600 \times 600 \text{mm}^2 \text{ } ^3\text{He tube array with an } 8 \times 8 \text{mm}^2 \text{ pixel size. The sample-to-detector distance was 4.3 m. Exposure time of each sample was 25 min. The SANS data were analyzed with Mantid software [18].}

![SANS experiment](image.png)

**Fig. 2.10** Schematic representation of a SANS experiment [19].

## 2.8 Vickers hardness measurement

The Vickers hardness test is a versatile hardness test method, used for both macro and micro hardness testing. It has a broad load range (1 to 100 kgf) and is suitable for a wide range of applications and materials. The Vickers hardness measurement consists of indenting the test material with a diamond indenter, in the form of a right pyramid with a square base and an angle of 136º between opposite faces subjected to a load that applied for 10 to 30 s [20]. The two diagonals of the indentation left in the surface of the material after removal of the load are measured using a microscope. The area of the sloping surface of the indentation is calculated. The Vickers hardness is then obtained by dividing the kgf load by the square mm area of indentation.

In this thesis, the Vickers hardness measurements were performed on the polished surface of the sample with a Leitz Wetzlar hardness tester. At least 5 different sample locations were tested for each sample with a load of 200 g for 30 s.

## 2.9 Tensile test

Tensile test is a fundamental materials science and engineering test in which a sample is subjected to a controlled tension until failure. The basic idea of a tensile test is to place a sample of a material between two fixtures called "grips" which clamp the material. The material has known dimensions, like length and cross-sectional area. Load was applied to the material gripped at one end while the other end is fixed. The load was kept increasing while at the same time measuring the change in length of the sample until the material break down. Properties that are directly measured via a tensile test are yield strength,
ultimate tensile strength, breaking strength, maximum elongation, reduction in area and strain-hardening characteristics [21].

In this thesis, the tensile tests were performed on the HSLA samples after continuous annealing. Samples for tensile tests were machined with the dimensions shown in Fig. 2.11. Tensile tests were performed on an MTS 810 Universal Testing Machine with a strain rate of 1 mm/min.

![Fig. 2.11 Schematic diagram of the sample dimension for tensile tests.](image)

2.10 References


