

Chapter II : Materials and Experimental Procedure

This chapter describes the steel grades that have been studied in this thesis and the various experimental procedures applied throughout this work. The chemical compositions of the materials will be described first, followed by the different thermo-mechanical treatments. Finally, the different techniques applied to measure the mechanical properties and to characterise the microstructures will be explained briefly.

II.1 Materials

Four different steel grades are investigated in the present study : two fully austenitic Ni-Cr stainless steels (AISI 301LN and 304) and two Fe-Mn-Si-Al alloys for which previous studies demonstrated the

excellent mechanical properties [Gräs98, Gräs00, From03]. The exact compositions of these steels, measured by atomic adsorption after dissolution, are presented in Table II.1. In the rest of this thesis, they will be called 301LN, 304, Mn15 and Mn20, respectively.

wt. %	C	Mn	Al	Si
301LN	0.027	1.3	< D. L.	0.43
304	0.02	1.85	< D. L.	0.56
Mn15	$1.6 \cdot 10^{-3}$	15.99	3.08	2.80
Mn20	$1.7 \cdot 10^{-3}$	19.66	3.11	2.88

wt. %	Cr	Ni	Mo	N
301LN	17.51	6.59	0.16	0.012
304	18.22	9.03	0.18	0.037
Mn15	< D. L.	< D. L.	< 0.005	$5.3 \cdot 10^{-5}$
Mn20	< D. L.	< D. L.	< 0.005	$5.7 \cdot 10^{-5}$

*Table II.1 : Chemical compositions of the different steel grades.
(D.L. stands for Detection Limit)*

II.1.1 Steels 301LN and 304

Both steel grades 301LN and 304 were provided by UGINE & ALZ, Isbergues (France). Steel 301LN was received as cold-rolled

and annealed metal sheets of 1.5 and 2.5 mm. Moreover steels 301LN and 304 were also provided as plates that were only roughed down to 32 mm.

II.1.2 Steels Mn15 and Mn20

The Fe-Mn-Si-Al grades were melted under vacuum then laboratory casted as ingots. After roughing, the 20mm-thick plates were homogenised for 24h at 1100°C. For the subsequent hot-rolling, the plates were first re-heated to 1200°C for 15 minutes, rolled down to 4mm in 4 passes then held at 600°C for 1h before furnace cooling in order to simulate coiling. They were finally re-heated at 1200°C for 15 minutes, hot-rolled again above 900°C down to a thickness of about 1.5 to 2 mm in 2 passes and air cooled to room temperature. After this last hot-rolling, the samples were annealed for one hour at 900°C, 1000°C or 1100°C in a muffle furnace then air-cooled to room temperature. In the rest of this work, the different samples will then be named “MnXX YY”, where “XX” refers to the Mn content and “YY” to the annealing temperature (*e.g.* Mn15 1000 stands for a sample of steel Mn15 annealed for 1h at 1000°C).

II.2 Experimental Procedures

II.2.1 Characterisation of the microstructure

II.2.1.1 Preparation of the surface

Prior to any observation of the samples, the surface was carefully prepared. Samples were first grinded with SiC papers of decreasing granulometry then polished with diamond pastes down to 1 μm . Due to the metastability of the austenite, these steps cause phase transformation in the surface layer. In order to remove the altered surface layer, a final treatment was applied. On the one hand, the surface layer of Fe-Mn-Si-Al alloys was removed by uniform chemical etching. The specimens were kept for 2 minutes in a solution of 100ml H_2O_2 (27%) + 100ml H_2O + 10ml HF (40%). They were then rinsed with ethanol. On the other hand, steels 301LN and 304 were electro-polished in a solution of 95% acetic acid + 5% perchloric acid kept in an optimum temperature range of 25°C to 35°C. The voltage was monitored to keep the current between 1.8 and 2.3A, depending on the sample size. The specimens were rinsed in ethanol after 2 minutes of electropolishing.

II.2.1.2 Metallography of the undeformed microstructure

After polishing, steels Mn15 and Mn20 were etched with a colour etching solution (1g sulfamic acid and 3g Na metabisulfite in 100ml of water) for 23 and 30 seconds, respectively [Vand84]. Figure II.1 presents an example of the microstructure of steel Mn15 revealed by colour etching. The ferrite appears in white while the austenite is

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darker. All grains are equiaxial and the austenite phase present evidence of annealing twins.



Figure II.1 : Colour etching of steel Mn15.

In the case of steels 301LN and 304, Figure II.2 illustrates that the microstructure was revealed thanks to the crystallographic contrast generated by the backscattered electrons in a scanning electron microscope (SEM) on the Fore Scatter Detector (FSD). The microstructure is fully austenitic and present a high proportion of annealing twins.

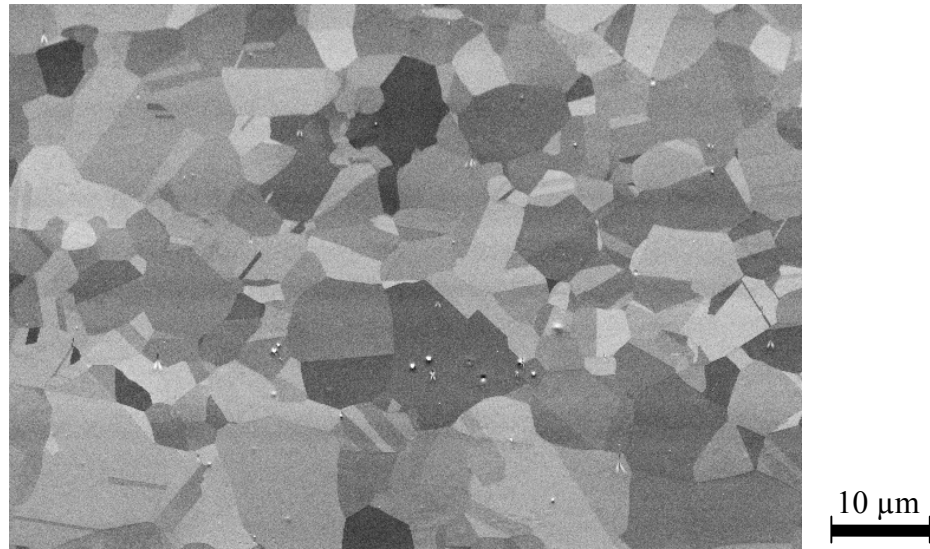


Figure II.2 : Microstructure of steel 301LN revealed by the FSD.

II.2.1.3 Phases proportions and compositions

II.2.1.3.1 X-Ray diffraction

The quantification of the phases present in different specimens was carried out by X-ray diffraction [Cull78] on polished and electropolished surfaces, using a Bruker D8 advance diffractometer. Figure II.3 shows the analysis of a X-ray diffraction pattern measured following a classical ' $\theta - 2\theta$ ' configuration using Cu $K\alpha_{1+2}$ radiation and a solid-state detector.

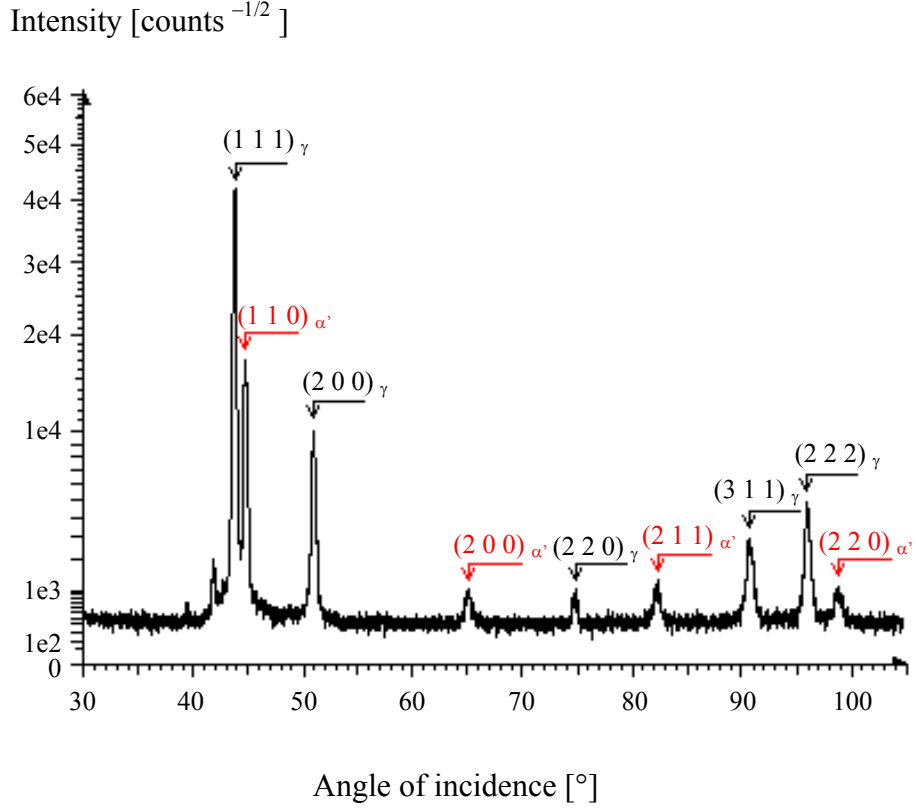


Figure II.3: X-ray diffraction pattern of steel 301LN.

Fitting was carried out by the Rietveld refinement method [Shan02], which allows a structural and quantitative analysis of the patterns. This method consists in a least-square refinement of the measured patterns (Pawley method [Shan02]) that minimises the difference between the observed diffraction pattern and a theoretical pattern calculated from a variety of parameters :

$$\text{Min}(R) = \sum_{\theta} |y(\text{obs}, \theta) - y(\text{calc}, \theta) - Bg(\theta)|^2 \quad (\text{II.1})$$

where $y(obs, \theta)$ and $y(calc, \theta)$ are the observed and calculated intensities at the angle θ , respectively, while $Bg(\theta)$ refers to the background at θ . The parameters are the peak position parameters (structural parameters and zero point), the peak shape parameters and the instrument parameters. The corresponding space groups were imposed for the different phases (α , γ , ϵ). The free parameters for each phase were the lattice parameters (initial values : $a = 2.86\text{\AA}$ for ferrite and α' -martensite ; $a = 3.61\text{\AA}$ for austenite ; $a = 2.54\text{\AA}$ and $c = 4.16\text{\AA}$ for ϵ -martensite) and the volume fraction.

II.2.1.3.2 Neutron diffraction

The volume fractions of the constitutive phases were also measured by neutron diffraction during *in situ* tensile tests carried out at the ISIS facilities¹. The analysis by neutron diffraction differs from X-ray diffraction by two main aspects :

- the penetration depth is different : about $5\mu\text{m}$ for X-rays against $800\mu\text{m}$ for neutrons [Hutc05].
- X-ray analysis was performed on unloaded samples, while neutron diffraction took place *in situ* during the course of the tensile tests.

Time of flight (ToF) diffraction patterns were analysed with the GSAS program using the identical Rietveld refinement method. The lattice parameters are obtained by fitting the neutron diffraction measurements. The average lattice strain is defined for each phase as :

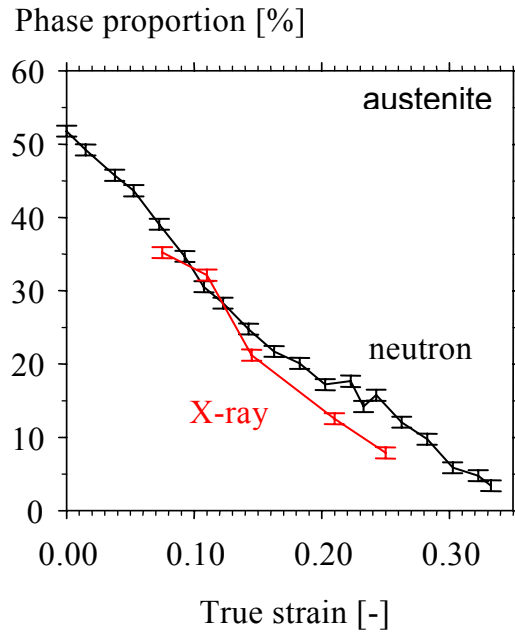
¹ Rutherford Appleton Laboratory, Chilton, OX11 0QX, United Kingdom.

$$\varepsilon^{lat.} = \frac{d^{lat.} - d_0^{lat.}}{d_0^{lat.}} \quad (II.2)$$

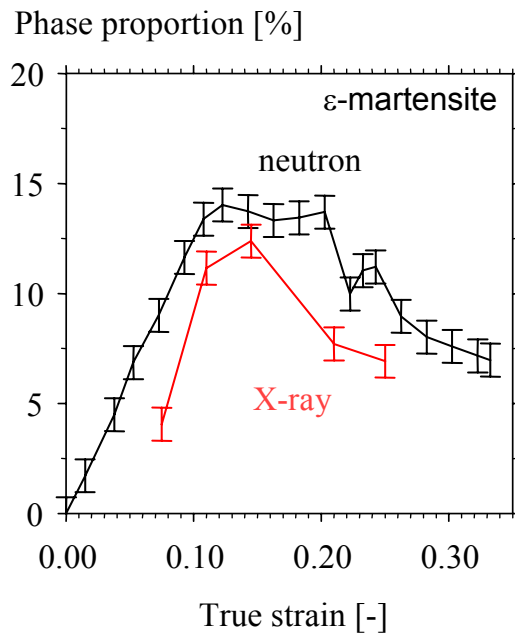
where $d_0^{lat.}$ represents the initial stress free lattice parameter and $d^{lat.}$ the instantaneous lattice parameter under loading.

II.2.1.3.4 Comparison between X-Ray diffraction and neutron diffraction methods to measure phase proportions

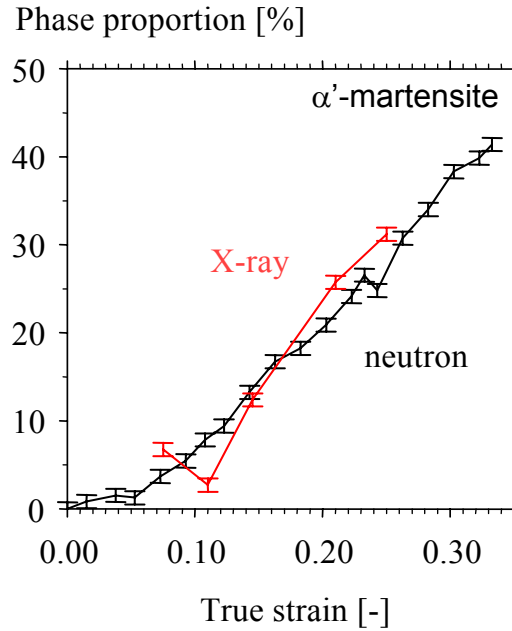
In this work, the evolution of the phase proportions during straining in steels Mn15 and Mn20 have been performed either by X-ray diffraction (XRD) or by neutron diffraction (ND). Figure II.4 shows the evolution of phase proportions of sample Mn15 1000 during tensile straining measured by XRD and ND techniques. It appears that the variation due to the measurement technique is minimal and can be neglected. The small differences that can be observed indicate that the proportions of austenite (Figure II.4 (a)) and ε -martensite (Figure II.4 (b)) are slightly lower while the amount of α' -martensite (Figure II.4 (c)) is slightly overestimated by XRD compared to ND. This can be due to the load state of the sample when the measurement is performed. Indeed, the specimen are unloaded for the XRD measurements while the load is kept constant during ND measurements. Residual stress concentrations could locally bring about an increase of the austenite and ε -martensite transformations.



(a)



(b)



(c)

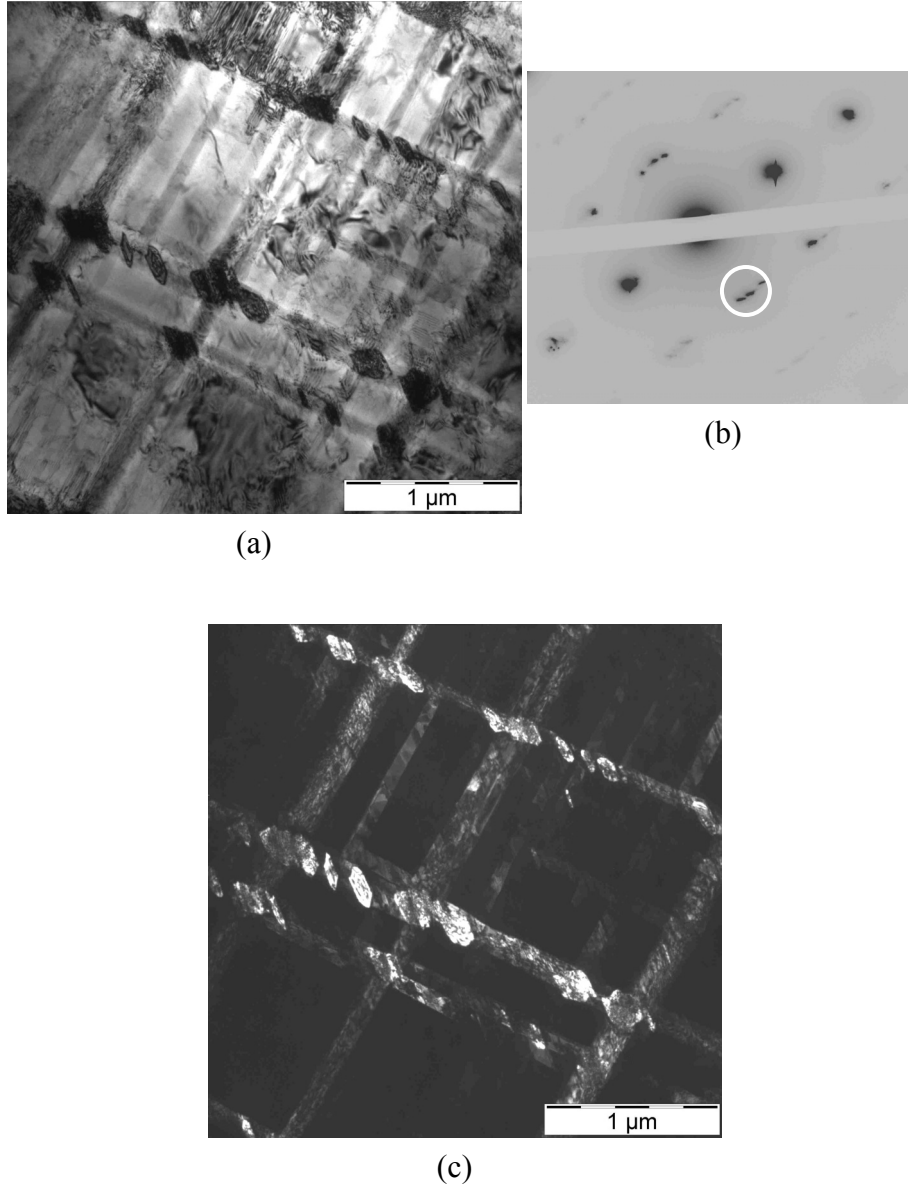
Figure II.4 : Evolution of the phase proportions during tensile straining in sample Mn15 1000, measured by X-ray and neutron diffractions :
(a) austenite ; (b) martensite and (c) α' -martensite.

II.2.1.3.4 WDX-microprobe

The chemical composition of the different phases was measured in steels Mn15 and Mn20 by WDX-microprobe analysis on polished specimens. The microprobe CAMECA was operated at 25kV. Each phase composition presented in this work consists in the average of 15 to 20 measurements.

II.2.1.4 Transmission electron microscopy

The observations were performed in a transmission electron microscope (TEM) Leo 922 operating at 200kV, equipped with an in-column Ω -filter [Will96, Bran99]. Zero-loss filtering mode was used in order to cut off any inelastic signal from images and electron diffraction patterns. Bright field / dark field TEM was carried out, as illustrated in Figure II.5. Samples were first mechanically polished down to a thickness of about 1 mm. They were then chemically thinned down to 50 – 70 μ m by immersion in a solution of 150ml H₂O₂ (27%), 150ml H₂O at 50°C and 21 ml HF (40%). Disks of 3mm in diameter were then cut out with a punching machine so the centre of the disks would not suffer from the preparation. Finally, these disks were electropolished with a twin jet electropolishing unit at room temperature. The electrolyte was 95% acetic acid + 5% perchloric acid and the tension was 20V. Electropolishing time was comprised between 60 and 90 seconds. The samples were then rinsed very carefully in ethanol. Great care was taken to avoid the application of any mechanical effort on the TEM sample that would induce some phase transformation prior to the observations.



*Figure II.5 : Example of TEM micrographs
corresponding to steel Mn20 :
(a) Bright Field ; (b) diffraction pattern
(c) Dark Field corresponding to (b).*

II.2.1.5 Orientation Imaging Microscopy

After they were prepared as described in section II.2.1, the microstructure of some samples was characterised by Orientation Imaging Microscopy (OIM) [Hump01, Wils01] using a Leo Supra55 Feg-SEM. This technique is based on the diffraction of back-scattered electrons (EBSD). The recorded Kikuchi patterns can be analysed to determine locally the nature and the crystallographic orientation of the observed phases. A “cleaning” procedure was applied by attributing to the non-indexed pixels (which proportion can vary from 0 to 35% depending on the considered microstructure) an orientation calculated from their neighbours. However, samples with a large unindexed proportion of the surface were not used for fine crystallographic analysis but only to distinguish different parts of the microstructure (such as recrystallised vs. non-recrystallised). Various features of the microstructures can then be characterised as illustrated on Figure II.6. Indeed, as shown in Figure II.6 (a), the general morphology of the microstructure is given by the Kikuchi bands contrast. Figure II.6 (b) presents the phase map (austenite γ in blue and ferrite α in red) while Figure II.6 (c) corresponds to the crystallographic orientation of the austenite represented with respect to the Inverse Pole Figure (with the Kikuchi band contrast for the ferrite).

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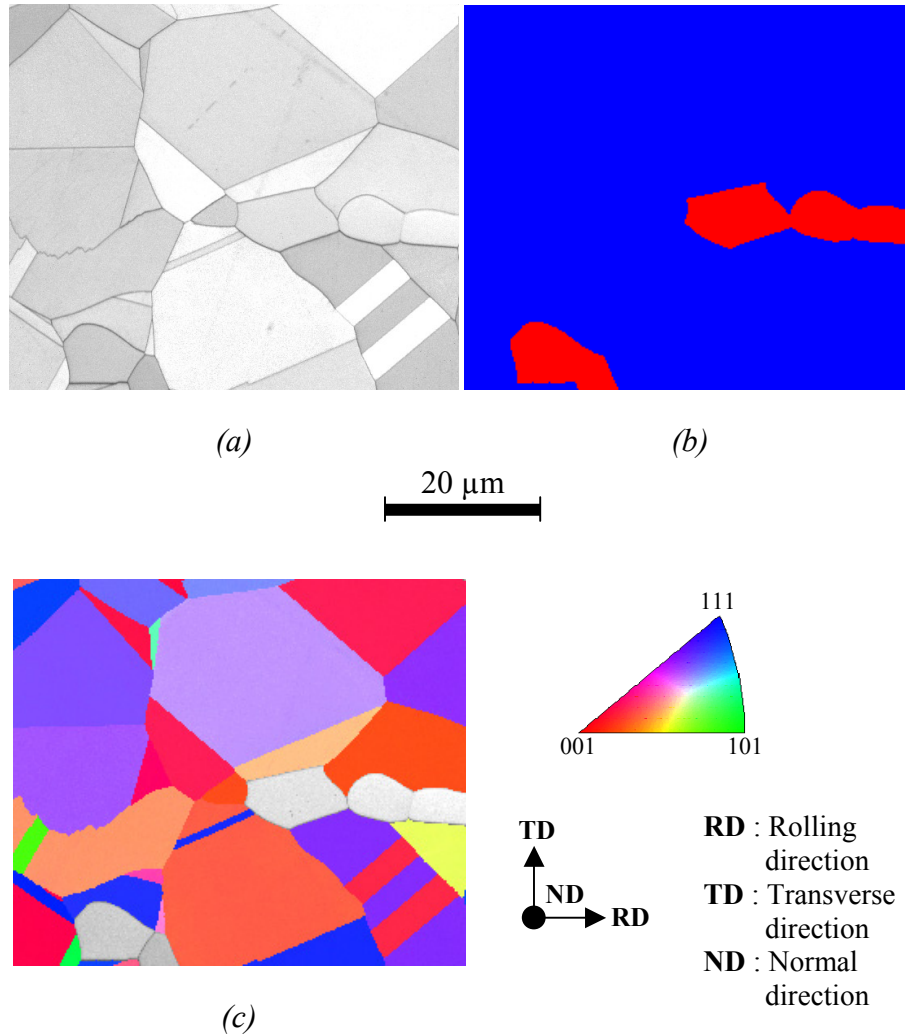


Figure II.6 : Typical EBSD maps of steel Mn20 :

(a) : Band contrast map ;

(b) Phase contrast map (austenite in blue and ferrite in red) ;

(c) Inverse pole figure (IPF) of the austenite along the rolling direction (R) with ferrite in grey.

II.2.1.6 Measurements on defect-free austenite

II.2.1.6.1 Proportion

A particular analysis of the EBSD data was applied to quantify the proportion of defect-free austenite in partially recrystallized microstructures [Hump01]. The analysis was carried out using VMAP², a Windows program for displaying and analysing data obtained using the HKL CHANNEL 4 or 5 systems.

After “cleaning” the maps, the grains and subgrains were defined based on misorientation criteria : if the misorientation between two points was larger than 15°, these points were considered being part of two different grains and they were separated by a high angle grain boundary (HAGB). If the misorientation between two points was between 2° and 15°, they were considered belonging to two different subgrains and their boundary was a low angle grain boundary (LAGB). Once the subgrains were reconstructed, the ones with an area smaller than 0.3µm² were reallocated to the adjacent subgrain with the closest orientation. Indeed, such small subgrains were artificially created by the reconstruction data analysis procedure. The defect-free austenitic fraction was calculated by setting 3 different conditions :

1. a minimum percentage of HAGB surrounding a grain (between 70 and 90%) ;
2. a grain size equal or higher to the average size of the subgrains with no HAGB ;

² developed by the research team of Prof. Humphreys, University of Manchester (United Kingdom).

3. a grain pattern quality of at least 80% of the whole map average pattern quality.

The proportion of defect-free austenite grains corresponds to the proportion of reconstructed grains meeting these 3 conditions.

II.2.1.6.2 Grain size

The austenite grain size was estimated by the mean linear intercept method. For large grains, the mean linear intercept was measured manually on micrographs obtained by the FSD method and the annealing twin boundaries were ignored. For smaller grains, it was measured through pre-existing routines in VMAP or Tango® (a Windows program for analysis of EBSD data acquired by HKL Channel 5 system), providing the proportion of twin boundaries $p(twins)$ and the mean linear intercept including the twin boundaries MLI_t .

$$p(twins) = \frac{I(twins)}{I} \quad (II.3)$$

$$MLI_t = \frac{L}{I-1} \approx \frac{L}{I} \quad (II.4)$$

where $I(twins)$ corresponds to the number of interception of twin boundaries (defined by a boundary between two subgrains with a misorientation of $60 \pm 2^\circ$ relatively to the $\langle 11-2 \rangle$ axis), I to the total amount of boundaries intercepted and L to the total length of the segments comprised between the intersections with boundaries. The MLI represents the mean linear intercept once the twin boundaries have been excluded and can be estimated by :

$$MLI \approx \frac{L}{I - I(\text{twins})} = \frac{L}{I(1 - p(\text{twins}))} = MLI_t \cdot \frac{1}{1 - p(\text{twins})} \quad (\text{II.5})$$

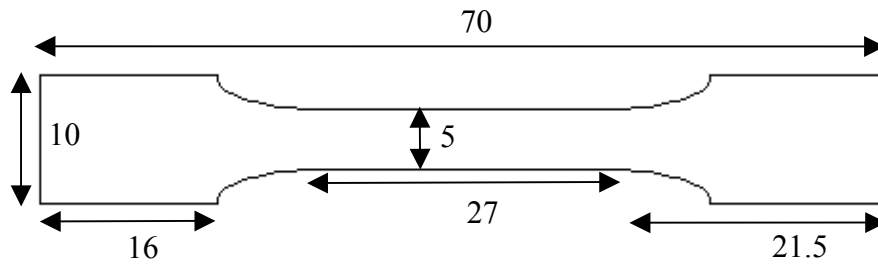
II.2.2 Thermo-mechanical processes

In order to characterise the mechanical properties or the modifications of the microstructure changes, several mechanical tests were applied : uniaxial tensile tests, rolling and rotary swaging. After rolling, annealing treatments have been performed on given samples to modify their microstructures.

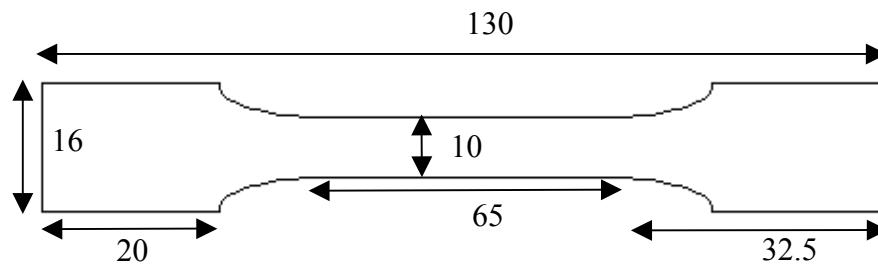
II.2.2.1 Uniaxial tensile tests

Tensile specimens were machined with the tensile axis parallel to the rolling direction. In the roughed plates, specimen with a circular section were machined with the tensile axis parallel to the roughing direction. The dimensions of the specimens are given in Figure II.7.

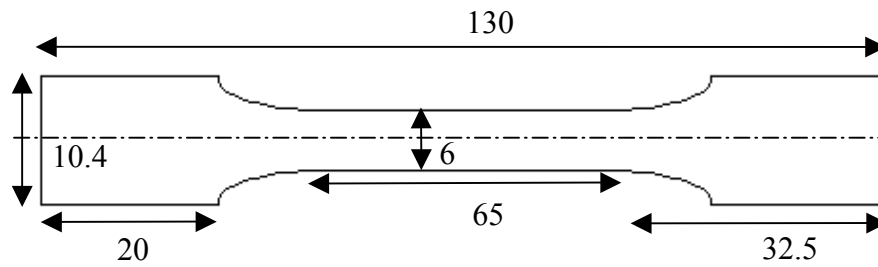
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(a)



(b)



(c)

Figure II.7 : Tensile test samples machined in the sheets (a) and (b) or in the plates (c). (all lengths are in mm).

Tests were performed at room temperature, on a 50kN screw-driven Zwick tensile testing machine, with strain rate comprised between 10^{-4} and $3 \cdot 10^{-3} \text{ s}^{-1}$. A thermocouple was spot-welded in the gage of some specimens in order to record the evolution of the temperature during straining. Measured loads and elongations were converted to true stress vs. true strain curves. The incremental strain hardening exponent ($n_{incr.}$) proposed by Sachdev [Sach83] was calculated for the different specimens. It writes

$$n_{incr.} = \frac{d \ln(\sigma)}{d \ln(\varepsilon)} \quad (\text{II.6})$$

The instability condition for the true stress vs. true strain curve is fulfilled when :

$$\sigma = \frac{d\sigma}{d\varepsilon} \quad (\text{II.7})$$

so that

$$n_{incr.} = \varepsilon_u \quad (\text{II.8})$$

II.2.2.2 Rolling

Samples of steel 301LN were rolled at two different temperatures : 20°C (room temperature) and 200°C. Samples rolled at 200°C were kept in an oven between each pass of deformation. Furthermore, in order to keep the temperature of the material as constant as possible,

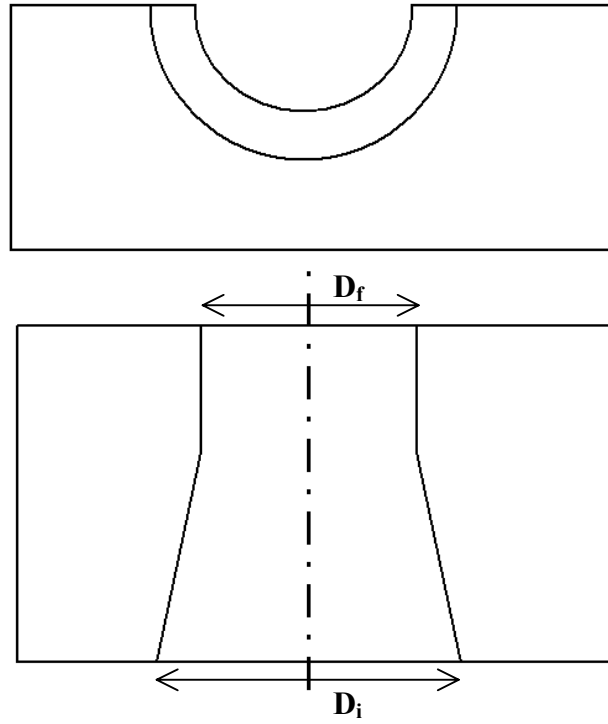
rolling was carried out in small steps. Thickness was reduced by 50%, which corresponds to an equivalent deformation (ε_{eq}) of :

$$\varepsilon_{eq} = \frac{2}{\sqrt{3}} \ln \left(\frac{t_s}{t_f} \right) = 0.83 \quad (\text{II.9})$$

with t_s and t_f the starting and final thicknesses, respectively.

II.2.2.3 Rotary swaging

Cylinders of steel 301LN with different initial diameters were deformed by rotary swaging. Swaging is a cold forming process allowing to reduce the section of bars, tubes and cables [Goff05]. In the rotary swaging machine used in this work, two matrices operate simultaneous high-frequency radial oscillations while turning around an axis. A cylindrical sample is pushed slowly through the die, with its axis aligned with the rotation axis of the matrices and every inward movement of the die-set reduces a small area of the sample section. Each matrix is shaped as presented on Figure II.8.



*Figure II.8 : Schematics of a swaging matrix
(D_i : initial diameter – D_f : final diameter)*

The initial and final diameters of the three different dies used in this work are presented in Table II.2, as well as the corresponding maximum equivalent deformations calculated as :

$$\varepsilon_{eq} = \ln \left(\frac{S_s}{S_f} \right) \quad (II.10)$$

with S_s and S_f the starting and final sections, respectively. During the tests, the actual equivalent deformation depends on the sample initial diameter.

Die	1	2	3
D_i [mm]	10.4	9.4	8.4
D_f [mm]	9.4	8.4	7.5
ϵ_{eq} [-]	0.20	0.22	0.23

Table II.2 : Initial and final diameters and corresponding equivalent deformation for the three dies used in rotary swaging.

Finally, it is worth noting that the rotary swaging consists in a very high number of cycles including redundant work and surface shears. The deformation rate is very high and the internal heat production induces a quick rise of the sample temperature to about 70°C.

II.2.2.4 Stress states

In order to compare the stress states induced by these three deformation techniques, macroscopic values can be used such as the stress triaxiality ratio (TR) and the Lode parameter (LP). Each stress state is characterised by a stress tensor $\underline{\underline{\sigma}}$, associated to a stress deviator tensor $\underline{\underline{s}}$ whose elements $\bar{s}_{ij}$ are defined as :

$$\bar{s}_{ij} = \bar{\sigma}_{ij} - \frac{1}{3} \bar{\sigma}_{mm} \quad (\text{II.11})$$

where $\overline{\sigma}_{ij}$ are the elements and $\overline{\sigma}_{mm}$ is the trace of the stress tensor $\underline{\underline{\sigma}}$. From these two tensors, several stress invariants can be described :

- the equivalent stress σ_{eq}

$$\sigma_{eq} = \sqrt{\frac{3}{2} \overline{s}_{ij} \overline{s}_{ij}} \quad (\text{II.12})$$

- the stress triaxiality ratio TR

$$TR = \frac{\overline{\sigma}_{mm}}{3 \sigma_e} \quad (\text{II.13})$$

- and the Lode parameter LP

$$LP = \frac{(2\sigma_{22} - \sigma_{11} - \sigma_{33})}{(\sigma_{11} - \sigma_{33})} \quad (\text{II.14})$$

The modes of deformation used here are then described by :

- *uniaxial tensile straining*

$$\sigma_{ij} = \begin{pmatrix} \sigma & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \Rightarrow \begin{cases} TR = \frac{\sigma}{3 \sigma} = \frac{1}{3} \\ LP = \frac{-\sigma}{\sigma} = -1 \end{cases} \quad (\text{II.15})$$

- *rolling*

Rolling is approximated by a plane stress compression (no stress in the rolling direction). The stress is only applied in compression along the direction normal to the rolling plane but in order to fit best reality, a stress along the direction transverse to the rolling direction has been added, representing the shear on the rolls surface which prevent the sample to deform transversally.

$$\sigma_{ij} = \begin{pmatrix} -2\sigma & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -\sigma \end{pmatrix} \Rightarrow \begin{cases} TR = \frac{-3 \sigma}{3 \sqrt{3} \sigma} = \frac{-\sqrt{3}}{3} \\ LP = \frac{3\sigma}{\sigma} = 3 \end{cases} \quad (II.16)$$

- *swaging*

The very complex stress state experienced in swaging has been assumed to be equivalent to biaxial compression, represented by the stress tensor, the *TR* and the *LP* presented in II.13.

$$\sigma_{ij} = \begin{pmatrix} -\sigma & 0 & 0 \\ 0 & -\sigma & 0 \\ 0 & 0 & 0 \end{pmatrix} \Rightarrow \begin{cases} T.R. = \frac{-2 \sigma}{3 \sigma} = -\frac{2}{3} \\ L.P. = \frac{-\sigma}{-\sigma} = 1 \end{cases} \quad (II.17)$$

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The stress triaxiality ratio (*TR*) and Lode parameter (*LP*) will be used to compare the different forming operations and are summarized in Table II.3.

Deformation mode	<i>TR</i>	<i>LP</i>
Uniaxial tensile straining	$\frac{1}{3}$	-1
Cold rolling	$-\frac{\sqrt{3}}{3}$	3
Rotary swaging	$-\frac{2}{3}$	1

Table II.3 : Estimation of the stress triaxiality ratio and Lode parameter for uniaxial tensile straining, cold rolling and rotary swaging.

II.2.2.5 Annealing treatments

The deformed samples of steel 301LN were annealed at different temperatures for different times. The specimens annealed at the lowest temperatures (between 700°C and 800°C) were heated in a fluidised bed furnace. The samples annealed at higher temperatures (between 900°C and 1100°C) were wrapped in a protective stainless steel sheet and heated in a muffle furnace. The samples were air-cooled to room temperature. Figure II.9 presents a typical annealing scheme. It is worth noting that the annealing times do not include the heating time, that was of the order of 1 to 2.5 minutes, depending on the furnace, on the annealing temperature and on the specimen size.

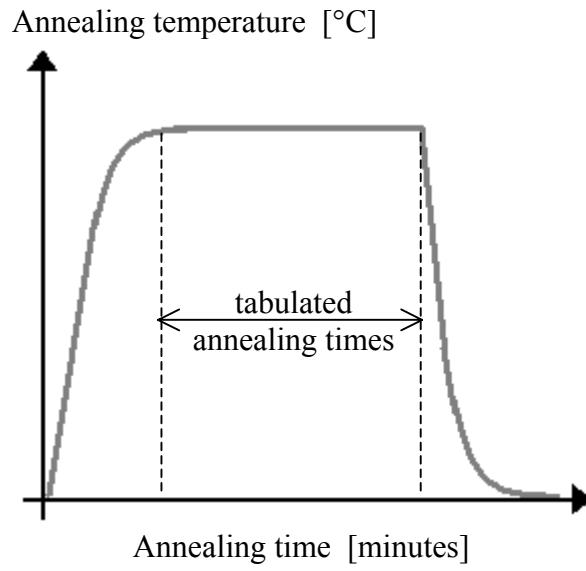


Figure II.9 : evolution of the sample temperature during annealing treatment.

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