Effect of cold rolling on microstructure, corrosion and electrochemical response of the lean duplex stainless steel LDX 2101® by a correlative EBSD–SKPFM investigation

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Abstract
This study elucidates the effect of cold rolling on the microstructure, corrosion and electrochemical response of the lean duplex stainless steel LDX 2101®. With thickness reductions of 0%, 20% and 40%, three different specimens are investigated in terms of microstructure (electron backscattered diffraction [EBSD] and energy-dispersive X-ray spectroscopy [EDS]), corrosion properties (ASTM G150, ASTM G61 and field testing), passive film properties (X-ray photoelectron spectroscopy) and electrochemical response (scanning Kelvin probe force microscopy [SKPFM]). It is shown that deformation of LDX 2101 leads to changes in the microstructure such as mechanical twinning and martensite formation. The combination of EBSD, EDS and SKPFM maps shows that the work function is clearly dependent on composition, deformation and local misorientation, but not on the crystallographic orientation of the grains in the microstructure. Zones with low work function are seen to have the highest pitting susceptibility, which includes deformed ferritic, martensitic phase and areas with a high concentration of dislocations such as grain boundaries and mechanical twins. The overall conclusion is that cold deformation up to a 40% thickness reduction has a significant influence on the microstructure, but a small impact on the corrosion resistance of LDX 2101.

KEYWORDS
cold rolling, corrosion, deformation, EBSD, LDX 2101, martensite, SKPFM, stainless steels, work function

1 | INTRODUCTION

Stainless steels are well known for their excellent corrosion resistance, good mechanical properties and formability. They are often subjected to plastic deformation in fabrication processes or intentionally cold worked to increase the strength. This deformation can lead to changes in the microstructure, passive film protectiveness and corrosion resistance.

Various aspects of the effect of deformation on the microstructure of stainless steels have been reported in the literature. It is recognised that cold deformation can increase local misorientation (LMO), and it can also instigate strain-induced martensite formation for some specific
stainless steel grades. The stainless steel grades most studied after deformation are austenitic,[1-5] but several studies have also been published on the duplex grades 2205 and LDX 2101.[7,9] Duplex grades have a two-phase structure, comprising a face-centred cubic (FCC) phase, austenite, and a body-centred cubic (BCC) phase, ferrite. Plastic deformation introduces local strain in the material that is distributed heterogeneously within the microstructure, depending on the crystallographic structure and the composition of the phases. For instance, Feng et al.[10] compared the effects of deformation on LDX 2101 and 2205, and showed that the deformation of the two phases in the duplex grade 2205 was almost equal, whereas for lean duplex LDX 2101, the ferritic phase was more deformed than the austenitic phase. Other preferred known sites for strain and dislocation concentrations are grain boundaries, as reported by Kamaya.[5]

Plastic deformation of duplex stainless steels can also lead to the transformation of the austenite phase into strain-induced martensite (also denoted as deformation martensite). The stacking fault energy (SFE) is one parameter that governs the stability of austenite, and it is dependent on the chemical composition and can be estimated using Equation (1) developed by Schramm and Reed.[11] A lower SFE favours the formation of martensite.[8]

\[
SFE (\text{mJ/m}^2) = -53 + 6.2(\%\text{Ni}) + 0.7(\%\text{Cr}) + 3.2(\%\text{Mn}) + 9.3(\%\text{Mo}).
\]

Another important factor related to the metastability of austenite is the martensite formation temperature (Ms), which is estimated using the following equation[13]:

\[
Ms(\text{°C}) = 1302 - 42(\%\text{Cr}) - 61(\%\text{Ni}) - 33(\%\text{Mn}) - 28(\%\text{Si}) - 1, 667([\text{C} + \text{N}]).
\]

When plastic deformation is applied, energy is supplied to the metal and the temperature of martensite formation can be increased. This is can be assessed by the Ms30 temperature according to Equation (3) developed by Nohara.[13]

\[
Ms30(\text{°C}) = 551 - 462([\text{C} + \text{N}] - 9.2(\%\text{Si}) - 8.1(\%\text{Mn}) - 13.7(\%\text{Cr}) - 29(\%\text{Ni} + \%\text{Cu}) - 18.5(\%\text{Mo}) - 68(\%\text{Nb}) - 1.42(\text{GS} - 8),
\]

where GS is the ASTM grain size number.

A relevant technique used in several studies for investigating the relation between strain concentration, grain orientation and the presence of martensite is electron back-scattered diffraction (EBSD).[1,8,9] Bassani et al.[8] investigated LDX 2101 after a 10–80% thickness reduction using EBSD and found that martensite formation appeared after 20% deformation. Örneke et al.[9] used EBSD to correlate the LMO of the microstructure to the Volta potential maps and corrosion properties of the duplex stainless steel 2205 after deformation. In addition to changes in the microstructure, the deformation and introduced stresses in the material can also affect the overall corrosion response of the stainless steel. It has been reported that cold deformation can decrease the critical pitting temperature (CPT) of stainless steels.[14,15] The reduction of corrosion resistance after deformation can differ, depending on the composition and crystallographic structure of the steel. Low alloyed austenitic and duplex grades appear to be more susceptible to a reduction of corrosion resistance than high alloyed grades. This has been attributed both to the formation of martensite[14,16] and to the presence of small cavities in the deformed austenite acting as initiation points for pitting.[2] For the duplex grades, lean duplex grades such as LDX 2101 and 2304 have been shown to be more sensitive to corrosion attack after deformation, compared with more alloyed grades such as 2205 and 2507[14,17]. However, it has also been reported that cold deformation can improve the corrosion properties of stainless steels. For instance, Schöning et al.[18] showed an increased CPT for AISI 304L after 30% deformation. This was explained by a finer microstructure after deformation with low amounts of martensite and a better protective passive film than the original material, as suggested by Jinlong et al.[19]

Although deformation-induced martensite in stainless steels may have a negative effect on the corrosion properties, in recent years, there has been an increased focus on developing stainless steels that form deformation martensite due to the beneficial effect on the mechanical properties. Forta FDX 25® (UNS S82012) and Forta FDX 27® (UNS S82031) are examples of stainless steel grades that have improved formability properties, compared with other stainless steel duplex grades, and can be used in demanding applications such as plate heat exchangers.[16,20,21] The increased formability of the Forta FDX grades is attributed to the transformation of some of the austenite to martensite during cold deformation. Schöning et al.[21] showed that this phase transformation in Forta FDX alloys did not affect the corrosion resistance of the studied materials.

Scanning Kelvin probe force microscopy (SKPFM) has proved to be a valuable tool to elucidate the link between microstructure, deformation and corrosion properties.[9,22-24] With SKPFM, the electron work function (EWF), defined as the energy needed to remove an electron from the surface, can be mapped with a nanoscale lateral resolution. A zone with high EWF is correlated to a cathodic potential and thus a higher corrosion resistance, compared with a zone with low EWF, anodic potential, which is linked to a more unstable and electrochemically reactive surface.[9,25-27] Studies have shown that the EWF decreases when plastic
deformation is applied, and this is due to a higher dislocation density after deformation and more oxygen and cation vacancies in the passive film.[9,22,23,28] Wang et al.[24]

investigated the effect of elastic and plastic deformation on 2205; they stated that EWF increased during elastic deformation but decreased during plastic deformation, which is attributed to the increase of roughness, dislocations and slip bands during plastic deformation. Similar results on the austenitic grade 301LN using scanning Kelvin probe were reported by Fuertes et al.[20]

The investigations performed using SKPFM have focused on the duplex grade 2205 to date.[9,24] The purpose of the present study is to investigate the effect of cold rolling on the microstructure and electrochemical response of lean duplex stainless steel LDX 2101. This is a low nickel duplex stainless steel that was developed to perform better than the standard austenitic grades such as 304L. Nickel is partially replaced in LDX 2101 by nitrogen and manganese to give a duplex microstructure at a lower overall cost. LDX 2101 is used in a broad range of applications where deformation and corrosion are relevant. Thus, understanding the effect of deformation on corrosion properties of LDX 2101 is crucial to ensure the successful use of steel.

2 | EXPERIMENTAL SECTION

2.1 | Material and sample preparation

A 5-mm thick plate material of the lean duplex steel LDX 2101 (UNS S32101) provided by Outokumpu Stainless AB was investigated. The chemical composition of the plate according to the manufacturer’s certificate is given in Table 1. The alloy was investigated in the as-received (annealed) condition and after cold rolling with thickness reductions of 20% and 40%. The specimens obtained after each rolling condition will be denoted in this study as LDX 2101-0%; LDX 2101-20% and LDX 2101-40%, where % indicates the thickness reductions.

2.2 | Microstructure and passive film characterisation

Microstructure examinations were performed on the rolling plane of the specimens using a scanning electron microscope in the backscattered electron mode and the EBSD Nordlys detector in an LEO 1530 field emission. Specimens were cut, then successively ground to 4,000 mesh, polished to 0.25-µm diamond paste, followed by silica suspension (OPS-AA) polishing to achieve a finely polished surface free from residual stresses from the sample preparation process.

The software used for acquiring and processing EBSD data were Aztec V2.2 and HKL Channel 5 from Oxford Instruments. The parameters used for EBSD acquisition were as follows: an acceleration voltage of 20 kV, step sizes ranging from 0.035 to 0.27 µm and scanned areas from 741 × 741 µm to 900 × 900 µm. Grain boundaries were defined as high and low angle, depending on whether the misorientation was higher or lower than 10°. Noise reduction was not performed in any of the figure presented in this study. Simultaneous energy-dispersive X-ray spectroscopy (EDS) mapping was performed during the EBSD measurements for investigating the composition of the materials. The distribution of phases present in the microstructure, grain size and LMO were investigated. The latter, LMO maps, can be used for studying the distribution of plastic microdeformation in the different phases of the microstructure due to the presence of dislocations.

Passive film thickness and composition were determined using small spot X-ray photoelectron spectroscopy (XPS). Before testing, the specimens were prepared as for microstructure examination, then degreased with ethanol and kept overnight for repassivation.

2.3 | Corrosion testing

The corrosion resistance of the specimens was evaluated by CPT testing, cyclic potentiodynamic polarisation measurements, immersion testing and field testing in natural seawater.

CPT was carried out according to ASTM G150,[29] in an aerated 1 M NaCl solution using a flushed port cell. A circular surface section of 1 cm² of the specimen was exposed to the electrolyte and the solution was heated from 0°C to 100°C at 1°C/min and +700 mV saturated calomel electrode (SCE). The current density was monitored during the test and the CPT was defined as the temperature when the current density was above 100 µA/cm² for 1 min. This time delay was to ensure stable pit growth and exclude short current peaks.

Potentiodynamic polarisation measurements were carried out using the procedure described in ASTM G61 standard,[30] in 1 M NaCl using a flushed port cell. Constant air bubbling was maintained during the measurement. As for CPT testing, a surface section of 1 cm² of the specimen was exposed to the electrolyte. The temperature of the electrolyte...
was kept constant at 15°C. The potential was increased at a rate of 10 mV/min from the open-circuit potential (OCP) to a potential where the current density was 5 mA/cm² and then reversed to −55 mV SCE.

According to the ASTM G150 and ASTM G61 standards, before testing, the specimens are ground to 600 mesh. Such grinding will introduce surface stresses in the specimens that could interfere with the evaluation the effect of deformation stress due to rolling. Thus, the specimens were instead successively ground to 4,000 mesh, polished to 0.25 µm diamond paste, followed by silica suspension (OPS-AA) polishing.

To evaluate the susceptibility of the different microstructural components to pitting, immersion testing was performed according to the method developed by Bianchi et al., which is frequently denoted as BCMT testing, the designation being the authors’ initials. The specimens were immersed for 30 s in a 40°C heated solution of 15 g ferric chloride, 15 g aluminium chloride, 100 ml ethanol and 100 ml glycerol. The specimens were tested with a surface prepared as for metallographic examination and ASTM G150 and ASTM G61.

Long-term exposures were performed in natural seawater at 30°C for 15 days. During the exposure, the OCP (mV SCE) of the specimens was constantly logged.

### 2.4 EWF analysis

The distribution of the EWF, also denoted as Volta potential, on the microstructure of the investigated alloys was evaluated using SKPFM. This technique quantifies in situ the electron work function (EWF, \( \phi \)) of the alloy relative to a reference electrode. The EWF is defined as the difference between the alloy potential \( (\mu_e) \) and the alloy–air interface potential \( (\chi) \):

\[
F = \mu_e - \chi,
\]

where \( e \) is the electron charge.

The EWF can differ, depending on the crystallographic structure, interatomic distance and composition of the phases in the alloy. The thickness of the passive film and external loads can also lead to variations of the EWF. The EWF can be used as an indicator of the corrosion resistance of the phases in the microstructure, as a higher EWF indicates a nobler phase.

The EWF analyses in this study were carried out with a probe of PtIr-coated Si using a cantilever from Bruker (SCM-PIT), 200–250 µm long with a nominal constant spring of 1–5 N/m, and a resonance frequency of 60–100 kHz.

Before testing, the specimens were ground to 80–4,000 mesh and gradually polished to 0.25 µm diamond paste. With the aim of removing the zone deformed during grinding and polishing, Ar ion milling was performed on the specimen’s surface for 10 min. The SKPFM measurements were carried out before EBSD measurements. Both analyses were performed in the same area of the microstructure of the specimens, located by nanohardness indentations.

The software NanoScope analysis 1.5 was used to analyse the SKPFM data. The topography maps were flattened using first-order flattening, and the potential maps were plotted relative to the work function of the specimen, meaning that high and low potential values indicate, respectively, cathodic and anodic behaviour.

### 3 RESULTS

#### 3.1 Effect of deformation on microstructure

Table 2 provides the composition of the phases of LDX 2101 obtained by equilibrium calculations using Thermo-Calc TCFE9 database and the measured phase fractions (Table 4). Higher nitrogen, manganese and nickel contents are predicted in the austenitic phase, compared with the ferritic phase, whereas the ferritic phase has a considerably higher chromium content. These trends are experimentally confirmed by EDS analyses. The composition of the phases can be used to calculate the pitting resistance equivalent number (PREN) that gives an indication of the resistance to pitting corrosion. The austenitic phase exhibits a slightly higher PREN, and thus a predicted higher resistance to pitting corrosion than the ferritic phase.

The effect of cold rolling on the microstructure is shown in the EBSD maps of Figure 1 where phase maps and orientation maps for LDX 2101-0%, and LDX 2101-40%, are displayed. From the phase maps, ferrite (red) and austenite (blue) can be distinguished. Other phases which may occur in duplex stainless steels, such as sigma, chi or nitrides, were not detected. Table 3 provides the amount of each phase in vol%, calculated from the EBSD maps. It can be seen that increased cold rolling decreases the amount of
FCC phase (austenite). It apparently also decreases the measured amount of BCC phase (ferrite and martensite), but there is an increase of nonindexed pixels from 0.8% for the LDX 2101-0% to 10% for the LDX 2101-40%. This is most probably due to the difficulty in indexing zones with high deformation on LDX 2101-40%, which correspond to the deformed austenitic phase and martensitic phase. However, it is apparent from the micrographs in Figure 1 that there has been an increase in the amount of BCC phase within the FCC austenite areas. Cold rolling also causes some size reduction for the phases of the microstructure. When comparing LDX 2101-0%, with 2101-40%, it has been observed that there is a decrease in the mean diameter of FCC phase from 2.85 to 1.74 µm, whereas there is a decrease in the mean size of BCC from 2.81 to 1.41 µm. This may be directly correlated to the increase in the amount of BCC phase within the FCC austenite areas, as commented above.

The saturation magnetism (Satmagan method) was measured to quantify the content of martensite in the investigated specimens. However, the amount of martensite measured was under the detection limit of the test and no measurable difference was detected between the LDX 2101-0% and LDX 2101-40%.

Slip and mechanical twinning are observed in the austenitic phase of LDX 2101-20% and LDX 2101-40% and deformation-induced martensite are identified for the most deformed specimen, LDX 2101-40%. Mechanical twins have a different orientation, corresponding to a <111> 60° rotation. Examples of mechanical twins observed in the LDX 2101, 20% and LDX 2101, 40%, are

**FIGURE 1** Electron backscattered diffraction (EBSD) phases (upper) and IPF ND (lower) figure of (a) LDX 2101-0%, and (b) LDX 2101-40%. The circled zones indicate examples of mechanical twinning. For the EBSD figure (top), blue corresponds to austenite and red to ferrite/martensite, and for the IPF ND figure, the colour indicates the orientation of the grains, where blue grains are (111) planes, green grains (101) and red grains (001)
circled in the phase and IPF ND orientation maps in Figures 1 and 3.

Visualisation of the distribution of deformation-induced martensite can be done by comparing the EDS chromium maps with EBSD phase maps and identifying the zones with FCC crystallographic structure and similar chromium content as austenite. This is described in conjunction with the SKPFM of LDX 2101-40%, in the next section.

Despite the effect of deformation on microstructure, no major consistent impact on the thickness or composition of the passive film was observed from the XPS analysis, as shown in Table 4. However, the presence of Mo and a slightly higher content of Cr was detected for the most deformed material LDX 2101-40%.

### 3.2 Effect of deformation on work function

To investigate the effect of cold rolling on the electrochemical response of the specimens, SKPFM was used to produce the work function maps shown at the top right of Figures 2–4. The work function, EWF, is correlated to phase-type, crystallographic plane parallel to the sample surface and LMO maps obtained by EBSD measurements. All the maps correspond to the same region in the microstructure. The maps for LDX 2101-20%, are taken at a higher magnification than the other two specimens.

For all the specimens, the EWF of austenite was higher than the ferrite, indicating the austenite to be the more noble phase, in agreement with the PREN values from Table 2. For the LDX 2101-0% Figure 2, the EWF varied within the grains, being higher at the centre of the austenitic grains than at the border. This was not observed in the ferritic grains, but instead, some lower work function zones were spotted inside the grains. There was no effect of the grain boundaries or of the presence of annealing twins on the work function level. The small changes in LMO appeared not to affect the work function of LDX 2101-0%.

The LMO map of LDX 2101-20% given in Figure 3, confirmed higher deformation compared with LDX 2101-0%. The highest misorientation was found in the austenitic phase, at the slip planes and at the mechanical twins. These zones with highest LMO had lower EWF than the corresponding nondeformed zones of the equal phase. Thegrey zones in Figure 3 correspond to non-indexed zones, but they interestingly show a morphology that is similar to that of martensite. Variations of work function depending on the crystallographic orientation could not be distinguished in the austenitic areas. Notably, the ferritic grains with low LMO and (111) parallel to the sample surface had higher work function than the adjacent ferritic grains with a similar level of deformation but (101) parallel sample surface (see circled zones in Figure 3).

The specimen with the highest degree of cold rolling, LDX 2101-40% exhibited the largest LMO concentration and the lowest work function in comparison with the other specimens, as shown in Figure 4. To identify the zones where austenite has transformed to martensite, the EDS Cr maps of Figure 4 were used. This was performed by distinguishing the grains that have a BCC crystallographic structure and the same Cr content than the austenitic grains. The martensitic regions identified in the microstructure picture of LDX 2101-40% are indicated with arrows in Figure 4 and have a typical acicular shape. These zones exhibited also the largest LMO measured and

### Table 3 Amount and size of phases (vol%) in LDX 2101-0%, and LDX 2101-40%, measured by EBSD

| Material      | FCC vol% ± | µm | BCC vol% ± | µm | Nonindexed |
|---------------|------------|----|------------|----|------------|
| LDX 2101-0%   | 58.1 ± 2.9 | 2.9 ± 3.1 | 41.1 ± 2.8 (ferrite) | 2.8 ± 2.5 | 0.8 |
| LDX 2101-40%  | 54.1 ± 1.6 | 1.7 ± 1.9 | 35.9 ± 2.9 (ferrite/martensite) | 1.4 ± 1.8 | 10 |

Note: Four different zones sized 100 × 100 µm were analysed for each material.
Abbreviations: BCC, body-centred cubic; EBSD, electron backscattered diffraction; FCC, face-centred cubic.

### Table 4 Chemical composition and thickness of the oxide (% cations) for LDX 2101-0%, LDX 2101-20% and LDX 2101-40% measured with XPS

| Material      | Thickness (nm) | Cr (at%) | Fe (at%) | Mo (at%) | Mn (at%) |
|---------------|----------------|----------|----------|----------|----------|
| LDX 2101-0%   | 1.8            | 42.8     | 50.7     | –        | 6.5      |
| LDX 2101-20%  | 1.9            | 40.4     | 52.7     | –        | 7.0      |
| LDX 2101-40%  | 1.7            | 50.4     | 41.4     | 1.5      | 6.7      |

Abbreviation: XPS, X-ray photoelectron spectroscopy.
the lowest EWF. Variations of work function were also observed within the austenitic grains linked to the level of LMO. As observed for LDX 2101-20% zones in the austenitic grains with the highest LMO exhibited lower work function than zones of the same phase with lower LMO.

### 3.3 Effect of deformation on corrosion properties

The effect of deformation on corrosion properties was investigated by immersion testing (BCMT), CPT testing, polarisation curves and field testing in seawater. Immersion
test according to BCMT revealed pitting predominantly in the ferritic phase in LDX 2101-0%, and in the ferritic and martensitic phase in LDX 2101-40%, as shown in Figure 5. This is in agreement with the results obtained from SKPFM analysis, showing a lower EWF in ferrite than in austenite, and with the calculated PRE values.

Similar results to BCMT were obtained after CPT testing according to the ASTM G150 standard. As shown in
Figure 6, pitting attack predominantly occurred in the ferritic phase for LDX 2101-0% and LDX 2101-40%. For the most deformed material, LDX 2101-40% pits also occurred in the austenitic phase, but it was, however, difficult to distinguish if these were associated with the martensitic phase. A small effect of deformation was seen on the CPT, as shown in Figure 7. A decrease of CPT, from 16°C to 13°C, was seen for the specimens with higher thickness reduction, LDX 2101-20% and LDX 2101-40% compared with LDX 2101-0%.

Potentiodynamic polarisation curves according to ASTM G61 were also used to investigate the effect of deformation on the corrosion potential, as shown in
A higher critical pitting potential for LDX 2101-0% than for LDX 2101-40% was seen in some of the tested specimens. However, the results also showed that an increased deformation increases the scatter in the measured pitting potentials at both 10 and 100 µA/cm².

There was no major effect of deformation on the OCP values during long-term testing in natural seawater, as the OCP for LDX 2101-40% was 240 mV SCE, and for LDX 2101-0% it was 280 mV SCE.

4 | DISCUSSION

4.1 | Effect of cold deformation on microstructure

The observed effect of cold deformation on the microstructure of LDX 2101 after a thickness reduction of 0%, 20% and 40% is in agreement with published works on duplex stainless steels.⁸,⁹ Cold rolling led to the formation of slip bands and mechanical twins in the austenitic phase after a 20% thickness reduction. For the specimen with the highest thickness reduction, 40%, the high deformation in the austenite led to the transformation of this phase into martensite, which is in agreement with studies performed on LDX 2101 by Bassani et al.⁸

Table 5 provides the predicted martensite formation temperatures, Ms and M₄₃₀. M₄₃₀ corresponds to the temperature at which 50% of austenite transforms into martensite after 30% deformation. The values were obtained using Equations (2) and (3) and the composition of austenite from Table 2. The ASTM grain size for the austenitic phase was 13. The Ms and M₄₃₀ temperatures indicate that austenite in LDX 2101 will not transform to martensite at room temperature.
The calculated $M_{d30}$ is in agreement with the $M_{d30}$ temperatures calculated for LDX 2101 by Outokumpu, but it is well below experimentally determined values, which indicated deformation martensite formation at room temperature. This suggests that $M_s$ and $M_{d30}$ formulae are not applicable to duplex stainless steel with high Mn and N.

Higher LMO was observed in the austenitic phase than in the ferritic phase as well as at the grain boundaries. This result differs from the work presented by Örnek et al. on the duplex grade 2205, in which the LMO of 2205 was found to be similar in the ferritic and austenitic phases after cold rolling. This may be explained by the fact that LDX 2101 is lower alloyed than 2205, so ferrite and austenite have different stability, SFE and deformation behaviour. The interface between phases was also described in previous works as a preferred zone for sites of strain and concentration of dislocations.

The interpretation of the effect of deformation on the thickness and the composition of the passive film is not as clear as that on the microstructure. The increased chromium and molybdenum content for the highest deformed specimen most likely reflects the enhanced transportation of these elements to the passive film due to the increased presence of dislocations after deformation.

#### Table 5

| Material | $M_s$ (°C) | $M_{d30}$ (°C) |
|----------|------------|---------------|
| LDX 2101 | -510       | -20           |

4.2 Effect of cold deformation on corrosion properties

Although cold deformation on LDX 2101 had a strong impact on the microstructure, the results from this study showed that it has a small impact on the overall corrosion properties. The pitting corrosion resistance of the non-deformed material, LDX 2101-0% is in agreement with the steel data sheets published by Outokumpu. A decrease in CPT after cold deformation has been reported by a previous study on 2304 and 2101. This was attributed both to the formation of martensite and to the presence of small cavities in austenite acting as initiation points for pitting. The dislocation motion in the slip bands and the formation of martensite can initiate cracks in the passive film and thus initiate pitting corrosion in the underlying metal, causing a decrease in CPT. A small negative effect of martensite on the corrosion resistance of lean duplex grades is corroborated by the observation that higher alloyed duplex grades do not suffer from a decrease of corrosion resistance after deformation and are not susceptible to martensite formation.

The martensitic phase was a preferred location for pitting after CPT and BCMT testing. After 40% thickness reduction, pits were observed in the martensitic and ferritic phase, whereas for the nondeformed specimen, pits were observed in the ferritic phase and grain boundaries. The higher pitting susceptibility for the ferritic phase compared with the austenitic phase can also be explained by the higher PREN calculated from their elemental composition. The increased concentration of dislocations and strain sites in the grain boundaries could also decrease the corrosion resistance.

The higher pitting susceptibility of the most deformed specimen is also reflected by the increased pitting...
potential and increased scatter of the corrosion potential values compared with the nondeformed specimen. However, there was no effect on the OCP from long-term exposures.

4.3 | Effect of cold deformation on the electrochemical response

The combination of EBSD and SKPFM was useful to elucidate the relation between deformation, work function and corrosion resistance.

The selective corrosion attack after BCMT and CPT testing can be explained by the difference of work function in the phases present in the microstructure. The higher work function measured on the austenite compared with the ferrite has been previously reported by several authors.\[9,26,27\] However, the effect of martensite on the work function has not been previously reported. The results from this study show a clear decrease in work function in the zones where martensite was formed, with martensite exhibiting the lowest work function of all the present phases. As the composition is the same as the austenite, this indicates an effect of deformation and/or grain orientation on the work function. However, it is shown in this study that annealing twins in austenitic grains do not have a different work function than the surrounding grains, suggesting that the work function is affected more by the presence of dislocations than by the grain orientation. This is manifest as a decrease in work function for annealing twins, slip bands and mechanical twins. In previous works, it has been found that the work function decreased significantly in slip bands zones, which could facilitate electron transfer at such locations, leading to corrosion.\[22,24\]
The grain boundaries, previously described as zones susceptible to pitting corrosion and confirmed as such by BCMT testing, had a lower work function than the surrounding matrix. This can also be explained by the increased concentration of dislocations.[14]

In Figure 9, it can be seen that high LMO corresponds in most of the cases to a low work function and low LMO to a high work function. Studies have shown that there is a decrease in work function when plastic deformation is applied, and this is attributed to a higher dislocation density after deformation and more oxygen and cation vacancies in the passive film.[22,23,28] A low work function is also linked to a more unstable and electrochemically reactive surface, and thus to generally lower corrosion resistance of the stainless steel. Figure 9 also shows a higher work function measured on the austenite than on the ferrite for all the materials. This work function gradient between the austenite and ferrite decreases for higher degrees of deformation, indicating a more homogeneous work function over the microstructure. This could be attributed to a higher dislocation concentration throughout the material from the cold deformation.

To investigate the correlation between work function and crystallographic orientation, Figure 10 has been plotted by using the Euler angles from the EBSD analyses and the work function values of all the grains in the analysed EBSD/SKPFM microstructural zone. The figure interestingly shows that there is remarkably a little correlation between the work function level and grain orientation. For LDX 2101-20% a slightly higher EWF is observed for (101) in austenite and for (111) in the ferrite, and for LDX 2101-40% a marginally higher EWF is seen for (101) in austenite, for (001) in ferrite and for (001) in martensite. These results agree with Lindell and Pettersson[19] who showed that there is a small effect of crystallographic orientation on pitting corrosion resistance, but a larger effect on the corrosion rate in sulphuric acid to crystallographic orientation.

5 | CONCLUSIONS

The main observations from this investigation are summarised as follows:

1. Deformation on LDX 2101 induces mechanical Twinning and martensite formation for the specimen with the highest thickness reduction.
2. The effect of deformation on the thickness and composition of the passive film is minor.
3. The work function is clearly dependent on composition, deformation and LMO, but not on the crystallographic orientation of the grains in the microstructure.
4. The lowest work function and highest pitting susceptibility are seen for the most deformed ferritic phase and deformation-induced martensitic phase. A lower work function is also seen at the grain boundaries and at mechanical twins.
5. Cold deformation up to a 40% thickness reduction has a significant influence on the microstructure of LDX 2101, but a small impact on the overall pitting corrosion resistance of the material.

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