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Atmospheric-Induced Stress Corrosion Cracking of Grade 2205 Duplex Stainless Steel—Effects of 475 °C Embrittlement and Process Orientation

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Abstract: The effect of 475 °C embrittlement and microstructure process orientation on atmospheric-induced stress corrosion cracking (AISCC) of grade 2205 duplex stainless steel has been investigated. AISCC tests were carried out under salt-laden, chloride-containing deposits, on U-bend samples manufactured in rolling (RD) and transverse directions (TD). The occurrence of selective corrosion and stress corrosion cracking was observed, with samples in TD displaying higher propensity towards AISCC. Strains and tensile stresses were observed in both ferrite and austenite, with similar magnitudes in TD, whereas, larger strains and stresses in austenite in RD. The occurrence of 475 °C embrittlement was related to microstructural changes in the ferrite. Exposure to 475 °C heat treatment for 5 to 10 h resulted in better AISCC resistance, with spinodal decomposition believed to enhance the corrosion properties of the ferrite. The austenite was more susceptible to ageing treatments up to 50 h, with the ferrite becoming more susceptible with ageing in excess of 50 h. Increased susceptibility of the ferrite may be related to the formation of additional precipitates, such as R-phase. The implications of heat treatment at 475 °C and the effect of process orientation are discussed in light of microstructure development and propensity to AISCC.

Keywords: duplex stainless steel; 475 °C embrittlement; atmospheric-induced stress corrosion cracking; electron backscatter diffraction; X-ray diffraction; residual stress

1. Introduction

Duplex stainless steels (DSSs) are used as corrosion-resistant materials for marine, off-shore, and nuclear applications [1,2]. DSSs provide superior mechanical and electrochemical properties to most of their austenitic and ferritic counterparts, which is related to the complementary nature of both crystallographic phases [3,4]. However, service temperatures in excess of 250 °C or welding can result in embrittlement and loss of corrosion resistance [5–7].

Exposure to the 250–550 °C low temperature embrittlement window, also known as "475 °C embrittlement", can cause loss of toughness and ductility, primarily related to phase reactions in the ferrite [5,7,8]. Spinodal decomposition in ferrite (δ) to form Fe-enriched (Cr-depleted) α' and Cr-enriched (Fe-depleted) α'' structures, or the nucleation and growth of α'' -particles embedded in an α' -matrix can occur, typically followed by the formation of further precipitates, such as χ , Frank-Kasper R-phase, τ , or Mo-Si enriched G-phase [5,7,9–15]. The phase separation products ($\alpha' + \alpha''$), in general, do not exceed dimensions larger than 100 nm, whereas precipitates such as G- or R-phase can grow

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to sizes larger than 500 nm [6,10–14]. It should be noted that similar phase reactions have also been reported in austenite, which, however, requires further investigations to make clear statements about their origin [8,9,16,17].

There has been extensive research on the characterisation of 475 °C embrittlement, which predominantly focused on investigating microstructure development and mechanical property changes [6,7,14,18–20]. It is common that embrittlement gradually increases with ageing, reaching saturation after prolonged exposure times. Corrosion properties and associated atmospheric chloride-induced stress corrosion cracking (SCC) performance of 475 °C embrittled microstructures, however, have not been studied in detail, and the understanding of their SCC propensity is lacking. So far, most research to better understand SCC was carried out in extremely aggressive environments [21–31], often at temperatures in excess of 100 °C [23,29,30,32,33]. The low-temperature SCC performance (<100 °C), in particular under atmospheric exposure conditions, has not been elucidated, but is certainly important for engineering applications.

In this work grade 2205 DSS was heat treated to investigate the effect of 475 °C embrittlement on the atmospheric chloride-induced SCC behaviour. U-bend samples were manufactured along RD and TD to assess the effect of process orientation on microstructure AISCC susceptibility. The key focus of this study was the effect of 475 °C heat treatment on microstructure propensity to AISCC, and the work reported here is part of a larger research project on understanding the effect of 475 °C embrittlement on DSS performance [34–38].

2. Experimental Section

A solution-annealed (as-received) sheet of grade 2205 DSS (EN 1.4462, UNS S32205) manufactured by OutoKumpu (Torshälla, Sweden) of 2 mm thickness was used in this study. The sheet had a chemical composition (in wt. %) of 22.44Cr, 5.75Ni, 3.32Mo, 1.41Mn, 0.42Si, 0.015C, 0.155N, 0.006Nb, 0.21Cu, 0.12Co, and Fe (bal.). The sheet was then cut along RD and TD to produce rectangular strips with dimensions of 70 mm \times 20 mm \times 2 mm (L \times W \times T). Two holes of 5.2 mm diameter each were drilled on both sides of the strips, with samples exposed to heat treatments at 475 °C \pm 5 °C for 5, 10, 20, 50, and 255 h, followed by water quenching. The surface of all specimens was ground to 4000-grit using SiC paper. A schematic illustration of the strips, including their orientation with respect to RD/TD, and how these were further shaped into U-bend samples is shown in Figure 1. Bending was carried out using an Instron 5569 testing machine (Instron, Norwood, MA, USA) under compression with a load cell of 50 kN and a crosshead displacement rate of 10 mm/min. The U-bend samples were tightened using stainless steel bolts and nuts.



Figure 1. (a) U-bend shaping jig with (b) sheet dimensions and bending orientation in RD and (c) in TD. The circle in the centre of each specimen indicates the position of XRD stress measurements before and after bending. The angles indicate the measurement direction in 0° and 90° .

2.1. Microstructure Characterisation

Two as-received strip specimens were cut along RD and TD. The samples were then ground and polished to $1/4 \mu m$ finish using diamond paste, followed by an OP-S end-polishing treatment for one hour. Microstructure characterisation was carried out on both specimens before and after bending using electron backscatter diffraction (EBSD).

EBSD analysis was performed over a scan area of 711 μ m × 622 μ m of the samples before bending, and 728 μ m × 728 μ m of the bent specimens using an FEI Quanta 650 scanning electron microscope (SEM, Hillsboro, OR, USA) interfaced with a Nordlys EBSD detector (Oxford Instruments, Abingdon, Oxfordshire, UK) and AZtec V2.2 software for data acquisition from Oxford Instruments (Abingdon, Oxfordshire, UK). A 20 kV accelerating voltage with step sizes of 527 nm and 773 nm was used for microstructure analyses. Both EBSD maps were acquired over approximately the same area in both samples, located towards the centre of the strips, schematically shown in Figure 1b.

EBSD data processing was undertaken with HKL Channel 5 software (version 5.12.62.0 64-bit, Oxford Instruments, Abingdon, Oxfordshire, UK). High-angle grain boundaries (HAGBs) were defined with misorientation $\geq 15^{\circ}$ and low-angle grain boundaries (LAGBs) between $>1^{\circ}$ and $<15^{\circ}$. The grain size was determined by the mean linear intercept method, as the mean of vertical and horizontal directions, with 50 intercept lines used for grain boundary detection. The aspect ratio of the average grain size of ferrite and austenite was determined for the as-received and U-bend microstructures. The aspect ratio was defined as the quotient of the average grain sizes obtained from vertical linear intercepts (V) and those obtained from horizontal linear interception (H). The phase fractions of ferrite and austenite were also extracted.

Local misorientation (LMO) maps (Kernel average misorientation) were generated by using 3×3 pixel binning with a 5° sub-grain angle threshold. This analysis gives the average LMO below the pre-determined sub-grain angle threshold, and this method was used to locate regions with higher concentrations of misorientation in the microstructure. The latter is typically associated with local micro-deformation in the form of elastic/plastic strain [39].

2.2. Hardness Measurements

Macro-hardness measurements were carried out on a Georg Reicherter Briviskop 1875 Vickers hardness machine (Esslingen a.N., Baden-Württemberg, Germany) on all samples. Measurements were undertaken on flat strips and U-bend samples. For the samples before testing, 10 hardness indentations were produced with five indentations on each end of the samples, as seen in Figure 2a. Three indentations were placed on the apex of the U-bend samples after bending, as shown in Figure 2b. The corresponding hardness was then calculated from the mean of the hardness measurements.



Figure 2. Schematic representation of the location of hardness indentations in (**a**) flat strips and (**b**) U-bend samples.

2.3. XRD Stress Measurements

XRD stress measurements were carried out using the Proto iXRD Combo testing machine (Proto Manufacturing Inc., Oldcastle, ON, Canada), which is equipped with a two-detector system. Cr and Mn X-ray sources were used to measure the strain in ferrite and austenite, respectively. All setup parameters are listed in Table 1. Prior to each test, the X-ray diffractometer was calibrated to determine the zero stress positions of the peaks of the diffracted X-rays. Stress-free and stressed standard samples,

provided by the manufacturer, were used for calibration. The multiple exposure technique with 11 angles was applied for inter-planar d-spacing measurements. Two X-ray measurement orientations, i.e., 0° and 90° , aligned to the RD and TD process orientation, were chosen. Each measured orientation corresponds to the stress direction specified in Figure 1b,c. The measurement position was in the centre of each specimen, measured at the same position before and after bending.

Parameter	Measure		
X-ray type	Cr-Kα	Mn-Ka	
Source voltage, current	20 kV, 4 mA	20 kV, 4 mA	
Aperture size	2 mm	2 mm	
Bragg angle, 2θ	156.4	152.8	
Diffraction plane	(211)	(3 1 1)	
Wavelength	2.291 Å	2.1034 Å	
Max. measurement angle, β	27°	27°	
Number of β angles	11	11	
β angles	27	27	
β oscillation angle	3°	3°	
Phi angles	0° and 90°	0° and 90°	
Exposure time	2 s	2 s	
Number of exposure profiles	10	10	
Number of exposures gain	30	30	
X-ray elastic constant $S_1^{(hkl)}$	$1.28 \times 10^{-6} \text{ MPa}$	$1.2 \times 10^{-6} \text{ MPa}$	
X-ray elastic constant $1/2$ S ₂ ^(hkl)	$5.92 \times 10^{-6} \text{ MPa}$	7.18×10^{-6} MPa	
Peak fit	Gaussian Gaussian		

Table 1. X-ray measurement conditions.

2.4. Atmospheric-Induced Stress Corrosion Cracking Tests

AISCC tests were performed by exposing samples at a temperature of 75 °C \pm 3 °C and a relative humidity (RH) of 35% \pm 5% for 35 days. Three water droplets containing MgCl₂ were applied onto the surface of all U-bend samples, yielding an initial MgCl₂ deposition density of 20 µg/cm² (Drop 1), 332 µg/cm² (Drop 2), and 3835 µg/cm² (Drop 3). Drops 1, 2, and 3 correspond to a chloride deposition density of 15 µg/cm², 247 µg/cm², and 2856 µg/cm², respectively. An Eppendorf micropipette was used to dispense the droplets with volumes of 0.5, 1.5, and 2.5 µL, producing an overall droplet radius of 1.8, 2.3, and 2.8 mm, respectively. The effect of secondary spreading of the droplet during the test was not considered, therefore the exposed chloride concentrations should be regarded as "initial" chloride densities. The samples were placed in a Perspex box, and the humidity controlled by a saturated solution of MgCl₂, which was placed into the box together with the specimens. The box was sealed with a special temperature-resistant sealant and placed in a heating cabinet at 75 °C. The temperature and RH over the entire testing time was recorded with an EL-USB-2+ data logger from Lascar (Lascar Electronics Ltd., Salisbury, UK).

At the end of all tests, the exposed samples were imaged with a Zeiss stereo microscope (Jena, Thüringen, Germany). The samples were then cleaned in \approx 70 °C citric acid solution for 2 h to remove all corrosion products without attacking the metal substrate. A photograph of a U-bend specimen deposited with salt-laden droplets and a stereo-microscopic image of a deposit after 35 days exposure is shown in Figure 3.

The corrosion morphology was analysed with an FEI Quanta 650 SEM and Zeiss Ultra V55 SEM (Jena, Thüringen, Germany). Ferrite could easily be distinguished from austenite, by its darker channelling contrast and morphological appearance. When this was not obvious, energy-dispersive X-ray spectroscopy (EDX, Oxford Instruments, Abingdon, Oxfordshire, UK) was used to inform about the chemical composition of each phase. Ferrite is typically richer in Cr and Mo, whereas the austenite is richer in Ni and Mn. The corrosion area and volume of each deposit was measured with a Keyence VK-X200 3D laser scanning confocal microscope (LSCM, Keyence Corporation, Osaka, Japan) using

20× and 50× lenses in stitching mode. Corrosion area calculations were further performed on SEM micrographs by converting the image into a binary matrix and determining the area of corrosion by threshold segmentation using the open source ImageJ image processing programme (version 1.6.0_24 64-bit, Wayne Rasband from National Institutes of Health, Bethesda, MD, USA).



Figure 3. (a) Photograph of a U-bend specimen with salt-laden droplets containing MgCl₂; (b) stereo-microscopic image of one of the deposits after AISCC testing.

The microstructure propensity towards AISCC was assessed without disassembling the U-bend samples. The extent of SCC damage was determined as crack length per measured nominal corrosion area, and plotted against 475 $^{\circ}$ C exposure time. For the latter analysis, only the longest crack was considered, which was measured using SEM images and the ImageJ analysis program.

3. Results

3.1. Microstructure Characterisation

The as-received microstructure consisted of $54\% \pm 1\%$ austenite (γ) and $46\% \pm 1\%$ ferrite (δ). The average grain size of ferrite and austenite was $4.2 \ \mu m \pm 2.3 \ \mu m$ and $2.2 \ \mu m \pm 1.4 \ \mu m$, respectively. The austenite grains are arrayed in a band-like structure and embedded in the ferritic matrix, as shown by the EBSD phase map in Figure 4a. The microstructure has elongated grains along RD, with no intermetallic phases observed. The aspect ratio of ferrite and austenite was 0.84 and 0.93, respectively. Numerous LAGBs were present in the microstructure, and a summary of all EBSD results is listed in Table 2.

After bending the sample in TD, the phase fraction of austenite to ferrite changed to $48\% \pm 1\%$ versus $52\% \pm 1\%$, highlighting a clear reduction of the austenite content. The apex microstructure was heavily deformed with elongated ferrite and austenite grains towards the bending direction, as shown in Figure 4b. The band-like austenitic structure seemed disrupted after the bending process. The average grain size of ferrite and austenite increased to $5.1 \ \mu m \pm 2.3 \ \mu m$ and $3.7 \ \mu m \pm 1.7 \ \mu m$, respectively, with the aspect ratio of ferrite and austenite increasing to 1.61 and 1.71, respectively. This shows that austenite and ferrite grains were highly deformed in the bending direction (TD). The microstructure bent in TD shows far more disrupted grain morphologies, compared to the microstructure bent in RD.



Figure 4. EBSD phase maps of (**a**) as-received 2205 DSS, and (**b**) after bending in TD and (**c**) in RD. Black lines are phase boundaries and HAGBs. The arrows indicate normal direction (ND), rolling direction (RD), and transverse direction (TD).

Sample	Phase	Fraction (%)	G _S (μm)	σ (μm)	Aspect Ratio (X_V/X_H)
As-received	δ	46	4.2	2.3	0.84
	γ	54	2.2	1.4	0.93
	Total	100	2.8	1.8	0.91
Bent in RD	δ	53	5.1	2.3	0.80
	γ	47	2.5	1.4	0.92
	Total	100	3.4	1.9	0.89
Bent in TD	δ	52	5.1	2.2	1.61
	γ	48	3.7	1.7	1.71
	Total	100	4.3	1.7	1.67

Table 2. EBSD grain geometry and morphology data.

 G_S : Average grain size; σ : standard deviation.

After bending in RD, the phase fraction showed a similar change to 47% \pm 1% austenite versus 53% \pm 1% ferrite, supporting observations of a clear reduction in the austenite content. Large deformations can be noticed along the bending direction, as shown in Figure 4c. The band-like austenitic structure had an even more elongated appearance. The average grain size of ferrite and austenite slightly increased to 5.1 µm \pm 2.3 µm and 2.5 µm \pm 1.4 µm. The aspect ratio of ferrite and austenite decreased slightly to 0.80 and 0.92, respectively, indicating no significant change in grain morphology of both ferritic and austenitic grains.

The LMO analysis of both U-bend samples showed the presence of elastic-plastic strain and deformation in austenite and ferrite, summarised in Figure 5a–c. The degree of local misorientation changed to values up to 5° , indicating the presence of large strains across the entire microstructure due to the bending deformation. The microstructure bent in TD had nearly twice the degree of LMO compared to RD, indicating a far stronger effect on microstructure changes when samples are bent in TD. The austenite seemed to have a somewhat larger LMO distribution in comparison to ferrite, which was observed in both bending directions. In the microstructure bent in RD, a local region with accumulation of high LMOs, indicative of elastic/plastic strain, was observed in austenite.



Figure 5. EBSD local misorientation maps of (**a**) the as-received microstructure, (**b**) after bending in TD, and (**c**) after bending in RD. Black lines are phase boundaries only. Note that the misorientation profiles of ferrite and austenite in (**a**) overlap with each other. The arrows indicate normal direction (ND), rolling direction (RD), and transverse direction (TD).

3.2. Hardness Behaviour

The hardness results of all samples as a function of ageing time at 475 °C are shown in Figure 6. The hardness increased from 285 HV30 \pm 5 HV30 to 369 HV30 \pm 5 HV30 after 255 h ageing. The same trend, but with significantly higher hardness values, was also observed for all U-bend specimens. The hardness after bending in RD and TD was 510 HV30 \pm 15 HV30 and 529 HV30 \pm 5 HV30, respectively. The hardness measured on U-bend specimens with 475 °C ageing treatment up to 10 h followed similar trends, as the hardness measured on as-received samples with the same heat treatment. This indicates only a minor effect of bending deformation on the hardness for short-term ageing treatments at 475 °C. Heat treatments in excess of 10 h showed a clear difference in hardness after bending.



Figure 6. Hardness of flat strips (pre-bend) and U-bend samples in (RD) and (TD) as function of ageing exposure at 475 °C.

3.3. XRD Surface Stress Measurements

The surface stresses of ferrite and austenite before and after bending in RD and TD as a function of ageing time at 475 °C are shown in Figure 7a–d. Bending deformation of the as-received specimens led to the formation of tensile stresses in austenite with respect to both measurement directions $(0^{\circ} \text{ and } 90^{\circ})$.



Figure 7. In-plane surface stress development in ferrite and austenite as a function of ageing at 475 °C: (**a–b**) before (pre-) and after bending in RD; (**c–d**) before (pre-) and after bending in TD.

The surface stresses of austenite of the flat specimen (Figure 7b) decreased with ageing from 232 MPa \pm 20 MPa in 0° to 15 MPa \pm 10 MPa, whereas in 90° no significant stress changes were noticed. The in-plane stress of ferrite increased from 44 MPa \pm 23 MPa to 194 MPa \pm 15 MPa in 90°, with no significant changes in 0°. The measurement orientation 0° in RD corresponds to 90° in TD and vice versa, and obtained data in the different process orientations always showed similar trends with only small variations. In summary, the austenite seemed to be the phase with the highest stress in the as-received microstructure, but the stress in ferrite grew with ageing to values similar to those measured in the austenite after long-term ageing.

After U-bending, the surface stresses of all microstructures increased significantly. The stresses in austenite after bending in RD were 980 MPa \pm 33 MPa and 671 MPa \pm 29 MPa in 0° and 90°, respectively. The stress in austenite in the microstructure aged for 5 h was higher than the stress measured in the as-received condition, reaching tensile stresses of 1203 MPa \pm 55 MPa (0°) and 787 MPa \pm 51 MPa (90°). No significant change of the stress in austenite was seen with longer ageing times. The stress of ferrite, however, showed a steady increase as a function of ageing time, increasing from 437 MPa \pm 31 MPa (0°) and 247 MPa \pm 24 MPa (90°) to 984 MPa \pm 73 MPa (0°) and 595 MPa \pm 44 MPa (90°) after 255 h ageing, in line with expected microstructure changes in ferrite with 475 °C embrittlement. The highest stress was clearly concentrated along the bending direction for both, ferrite and austenite.

The stress of austenite and ferrite after bending in TD showed a similar increase with the austenite reaching slightly higher stress values than ferrite. The stress measured in austenite showed a steady increase from 1042 MPa \pm 80 MPa (0°) and 605 MPa \pm 20 MPa (90°) to 1348 MPa \pm 51 MPa (0°) and 878 MPa \pm 44 MPa (90°), as a function of ageing up to 10 h. This was followed by a decrease to 1046 MPa \pm 47 MPa and 735 MPa \pm 39 MPa with longer ageing (255 h). The in-plane stress of ferrite rose steadily from 612 MPa \pm 40 MPa (°0) and 325 MPa \pm 15 MPa (90°) to 962 MPa \pm 37 MPa (0°) and 463 MPa \pm 44 MPa (90°) with ageing exposure.

3.4. Atmospheric-Induced Stress Corrosion Cracking Behaviour

3.4.1. As-Received (RD vs. TD)

The corrosion morphology in (RD) after exposure to 20 μ g/cm² MgCl₂ (Drop 1) is shown in Figure 8a. Numerous nanometre-sized corrosion sites were present on deformed austenitic sites, whereas, the ferrite seemed unaffected. The deposit with 332 μ g/cm² of MgCl₂ (Drop 2) also resulted in nanometre-sized corrosion sites, which selectively nucleated in the austenite, possibly associated with deformation sub-structures (slip bands), as can be seen in Figure 8b,c. Furthermore, cracks were observed in the ferrite of 5–20 μ m length, either oriented parallel or ~45° inclined to the stress axis, as shown in Figure 8b,c. Under the droplet containing 3835 μ g/cm² MgCl₂ (Drop 3) far more corrosion attack was observed as well as small micro-cracks (Figure 8d–f). Selective dissolution of ferrite occurred at the droplet periphery, with dissolution of both ferrite and austenite observed in the droplet centre. Most cracks propagated along grain boundaries and stopped after encountering other grains, shown in Figure 8e. However, connected cracks of up to 100 μ m in length were found.



Figure 8. Corrosion morphology of as-received microstructure (in RD) with (**a**) "nano-pits" preferentially nucleated in austenite under Drop 1 (BSE-SEM image); (**b**) a micro-crack in ferrite with "nano-pits" in austenite under Drop 2 (SE-SEM image); (**c**) another micro-crack in ferrite under Drop 2 (SE-SEM image); (**d**) the entire attacked area under Drop 3; (**e**, **f**) small SCC cracks and crack-like regions under Drop 3. Bending direction is vertical to the images.

On the U-bend specimen (TD), two corrosion sites with 50–60 μ m diameters were observed beneath Drop 1 (Figure 9a). Selective dissolution was identified as the main corrosion mechanism at those sites, shown in Figure 9a, especially at the circumference of the corroded region. Some intergranular corrosion and micro-cracks were also observed. These micro-cracks were branched with very narrow crack openings, and a maximum length of 10 μ m. Under Drop 2, minor selective attack on ferrite with disintegration and fracture of austenite grains was observed, as shown in Figure 9b. Corrosion and SCC was observed under Drop 3, with dissolution of both phases and numerous cracks in austenite. The micro-cracks in austenite were indicative of chloride-induced SCC, showing transgranular cracks with branching (Figure 9d). The cracks were perpendicular to the stress axis. In ferrite, however, multiple closely-spaced, parallel-arrayed crack-like morphologies were observed, indicating a hydrogen-embrittlement type of attack, as shown in Figure 9c.



Figure 9. Corrosion morphology of the as-received microstructure (in TD) showing (**a**) corrosion sites with intergranular corrosion and some cracks emanating from the circumference of the pit wall under Drop 1 (BSE-SEM image); (**b**) cracked, disintegrated, and possibly fractured austenite grains under Drop 2 (SE-SEM image); (**c**) closely-spaced crack-like corrosion morphology in ferrite (BSE-SEM image), and (**d**) a branched transgranular micro-crack in austenite (SE-SEM image), both under Drop 3. Bending direction is vertical to all images.

3.4.2. Ageing at 475° C for 5 h (RD)

Multiple closely-spaced corrosion and crack sites were observed, primarily in the austenite under Drop 1, as can be seen in Figure 10a. No selective dissolution was observed, indicating no difference between the anodic and cathodic corrosion behaviour of both phases. A filiform-like corrosion pattern was found under Drop 2, as shown in Figure 10b. This corrosion morphology was neither associated with microstructure nor process orientation. Dissolution of ferrite and austenite with SCC cracks in austenite were observed under Drop 3 (Figure 10c). The maximum crack length found was ~120 μ m.



Figure 10. Corrosion morphology of microstructure aged at 475 °C for 5 h (in RD) with (a) closely-spaced micro-cracks and corrosion sites in austenite and ferrite under Drop 1 (BSE-SEM image), (b) filiform-type corrosion appearance under Drop 2 (SE-SEM image), and (c) corrosion with cracks in austenite under Drop 3 (BSE-SEM image). Bending direction is horizontal to all images.

3.4.3. Ageing at 475 $^{\circ}$ C for 10 h (RD)

Neither corrosion nor cracking was observed under Drop 1 and 2. Selective corrosion of ferrite had occurred with preferential dissolution along RD under Drop 3. Transgranular SCC was observed in austenite, with examples given in Figure 11a. Some SCC cracks had penetrated into ferrite grains, as shown in Figure 11b. Localised corrosion on slip bands and fractured austenite grains were observed (Figure 11c), suggesting slip-band dissolution-assisted SCC of the austenite.



Figure 11. Corrosion morphology of microstructure aged at 475 °C for 10 h (in RD) under the deposit containing 3835 μ g/cm² magnesium chloride showing (**a**) multiple micro-cracks in austenite with selective dissolution of ferrite; (**b**) selective dissolution of ferrite and attack on γ/δ interface; (**c**) a fractured austenite grain (all SE-SEM images). Bending direction is vertical to these images.

3.4.4. Ageing at 475 $^{\circ}$ C for 20 h (RD)

A few corroded nano-sites were found on ferrite and austenite grains with exposure to Drop 1. Under Drop 2, both austenite and ferrite seemed to have dissolved, as can be seen in Figure 12a. Multiple closely spaced and densely arranged micro-cracks were observed in the austenite. The dissolution of ferrite occurred beneath Drop 3 (Figure 12b). Multiple micro-cracks with transgranular pathways were observed in austenite, with a maximum length of ~100 μ m.



Figure 12. Corrosion morphology of microstructure aged at 475 °C for 20 h (in RD) showing (**a**) multiple closely-spaced fine-scale cracks formed in austenite under Drop 2 (SE-SEM image); (**b**) micro-cracks in austenite and selective dissolution of ferrite under Drop 3 (BSE-SEM image). Bending direction is horizontal to the images.

3.4.5. Ageing at 475 $^{\circ}$ C for 50 h (RD)

Corrosion and cracking in ferrite and austenite was observed under Drop 1 (Figure 13a). Despite the large number of micro-cracks, a maximum crack length of only 5 μ m was measured. In contrast, longer cracks were seen in the austenite under Drop 2, as shown in Figure 13b. The cracks seemed to be primarily of an intergranular nature, with a maximum crack length of 25 μ m. Severe SCC with multiple transgranular cracks were found all over the corroded region under Drop 3 (Figure 13c), with a maximum length of ~100 μ m.



Figure 13. Corrosion morphology of microstructure aged at 475 °C for 50 h (in RD) showing (**a**) small cracks in ferrite and austenite under Drop 1 (SE-SEM image); (**b**) intergranular attack in austenite under Drop 2 (SE-SEM image); (**c**) transgranular micro-cracks with γ - δ - γ crack path (SE-SEM image). Bending direction is vertical to the images.

3.4.6. Ageing at 475 $^{\circ}$ C for 255 h (RD)

The specimen aged for 255 h showed the strongest corrosion attack response. The corrosion morphology observed under Drop 1 is shown in Figure 14a–d, with localised corrosion on austenite grains, in the vicinity of partially dissolved ferrite regions (Figure 14a), indicating preferential dissolution of ferrite. However, an increased susceptibility to localised corrosion was noticed in the austenite, associated with long-term ageing at 475 $^{\circ}$ C.



Figure 14. Corrosion morphology of microstructure aged at 475 °C for 255 h (in RD) showing (a) localised corrosion in austenite adjacent to a partially dissolved ferrite grain under Drop 1 (BSE-SEM image); (b) partially attacked austenite and embrittlement of ferrite under Drop 1 (SE-SEM image); (c) fractured ferrite grains (SE-SEM image); (d) localised corrosion on austenite underneath a ferrite grain under Drop 1 (BSE-SEM image); (e) cracks under Drop 2 (SE-SEM image); (f) multiple cracks in ferrite grains (SE-SEM image); (g) numerous corrosion pits in ferrite (BSE-SEM image); (h) precipitates at the crack wall under Drop 2 (SE-SEM image). Bending direction is vertical to all images.

In some areas, partially dissolved austenite grains and cracked ferrite regions were observed (Figure 14b). These cracks are clear evidence of the embrittlement of ferrite, with a preferred crack orientation towards the processing orientation. Moreover, in some austenite grains, local corrosion sites were observed beneath fractured ferrite grains (Figure 14c). This observation is supported by the SEM image in Figure 14d. The maximum crack length was ~250 μ m. The extent of corrosion and SCC was more pronounced under Drop 2. The maximum crack length was ~700 μ m, orientated perpendicular to the bending axis. The cracks could be noticed at low magnification, which can be seen in Figure 14f. Cracks were preferentially formed in the ferrite. Fractured ferrite grains were seen with multiple cracks, indicating microstructure embrittlement. The number and severity of cracks

in ferrite were higher than those formed in austenite. Numerous corrosion pits also nucleated in the ferrite and at interphase boundaries, indicating enhanced local corrosion propensity (Figure 14g). No SCC could be seen in the austenite. At the bottom of the main crack, protruding precipitates were seen at the surface of ferrite regions in the form of bright speckles, shown in Figure 14h. These precipitates seemed to have net cathodic character with respect to the decomposed ferrite matrix, and are believed to be associated with R-phase. Severe corrosion and cracking was observed under Drop 3. General dissolution of both ferrite and austenite beneath the entire exposed area was seen. Wide and long cracks with a maximum crack length of ~1500 µm were found.

3.4.7. Ageing at 475 °C for 5 h (TD)

No corrosion attack was observed under Drop 1, clearly showing better corrosion resistance of the specimen aged for 5 h only. Beneath Drop 2, only nanometre-sized corrosion sites were observed in both ferrite and austenite. However, SCC was found under Drop 3 (Figure 15a,b), with a preferential pathway of cracks aligned along the microstructure process orientation. Cracks seemed to have nucleated in ferrite, and either propagated transgranularly through ferrite grains or along interphase boundaries. No selective dissolution of either phase was observed, indicating a more balanced net anodic and net cathodic character of both phases. Long SCC cracks were observed with a maximum crack length of ~1700 μ m, oriented perpendicular to the stress axis.



Figure 15. Corrosion morphology of 2205 DSS aged at 475 °C for 5 h (in TD) showing (**a**,**b**) long cracks in ferrite under Drop 3 (both SE-SEM images). Note that (**b**) is a magnified view of the highlighted region in (**a**). Bending direction is horizontal to the images.

3.4.8. Ageing at 475 $^{\circ}$ C for 10 h (bent in TD)

Corrosion and SCC was observed beneath Drop 1, but with only shallow corrosion sites. A number of transgranular micro-cracks were found in the austenite with a maximum crack length of ~30 μ m. Filiform-type corrosion morphologies were observed under Drop 2 (Figure 16a), with transgranular SCC in austenite under Drop 3 (Figure 16b,c). The maximum crack length was ~50 μ m, oriented perpendicular to the stress axis.



Figure 16. Corrosion morphology of microstructure aged at 475 $^{\circ}$ C for 10 h (in TD) showing (a) filiform-like corrosion of ferrite and austenite under Drop 2; (b,c) micro-cracks in austenite under Drop 3 (all SE-SEM images). Bending direction is vertical to the images.

3.4.9. Ageing at 475 $^{\circ}$ C for 20 h (TD)

On the specimen aged for 20 h two corrosion sites with maximum lateral sizes of 10 μ m were seen underneath Drop 1 (Figure 17a). Significant surface attack was observed under Drop 2, indicating corrosion of both ferrite and austenite (Figure 17b). A few fine-scale micro-cracks were seen in austenite, but no cracks in ferrite. Under Drop 3, numerous fine-scale cracks were also found in austenite, whereas the ferrite seemed to have corroded only superficially (Figure 17c). In austenite, multiple SCC-containing sites were found (Figure 17d).



Figure 17. Corrosion morphology aged at 475 °C for 20 h (in TD) showing (**a**) pits formed under Drop 1 (SE-SEM image); (**b**) filiform-like corrosion with micro-cracks in austenite under Drop 2 (BSE-SEM image); (**c**) numerous closely-spaced fine-scale cracks in austenite under Drop 3 (SE-SEM image); (**d**) cracks in austenite under Drop 3 (SE-SEM image). Bending direction is horizontal to all images.

3.4.10. Ageing at 475 $^{\circ}$ C for 50 h (TD)

Selective corrosion occurred on austenite grains under Drop 1 with slip planes acting as preferential nucleation sites, as shown in Figure 18b. General corrosion of ferrite and austenite was observed under Drop 2, with numerous crack-like features in the austenite (Figure 18b). Severe corrosion was observed under Drop 3, with cracks in ferrite and austenite (also summarised in Figure 18c). Bright features at the surface of ferrite were observed, indicating R-phase precipitates.



Figure 18. Corrosion morphology of microstructure aged at 475 °C for 50 h (in TD) showing (**a**) localised corrosion along slip planes on austenite under Drop 1 (SE-SEM image); (**b**) crack-like features in austenite under Drop 2 (SE-SEM image); (**c**) precipitates in ferrite (bright speckles) with cracks in ferrite and austenite under Drop 3 (SE-SEM image). Bending direction is vertical to the images.

3.4.11. Ageing at 475 °C for 255 h (TD)

The specimen aged for 255 h showed localised corrosion in austenite under Drop 1 (Figure 19a), and selective dissolution of ferrite along the process orientation was also observed. This observation was different to the corrosion morphology observed on the specimen aged for 255 h and bent in RD. Multiple closely-spaced crack-like features were seen in austenite, as shown in Figure 19a, with numerous transgranular micro-cracks under Drop 2 (Figure 19b). Corrosion was observed

under Drop 3, with dissolution of both ferrite and austenite, as well as cracks seen in both ferrite and austenite (Figure 19d).



Figure 19. Corrosion morphology aged at 475 °C for 255 h (in TD) showing (**a**) selective dissolution of ferrite and multiple closely-spaced crack-like features in austenite under Drop 1 (BSE-SEM image); (**b**) transgranular cracks through ferrite and austenite under Drop 2 (BSE-SEM image); (**c**,**d**) cracks in ferrite and austenite under Drop 3 (both BSE-SEM image). Bending direction is horizontal to the images.

4. Comparison and Quantification

The measured corrosion area and corrosion volume as a function of ageing time and process direction are summarised in Figures 20 and 21, respectively. In general, the area and volume of corrosion increased with increasing chloride deposition density, and with 475 °C embrittlement heat treatment exposure time. Most corrosion was observed on specimens aged for 255 h. Furthermore, corrosion attack on specimens bent in TD was in general larger than those bent in RD. No corrosion was observed under Drop 1 for all heat treatment conditions and both process orientations. Only very little attack was present under Drop 2, with corroded areas in the order of ~ $10^5 \mu m^2$ and corrosion volume of ~ $10^6 \mu m^2$. The area of corrosion attack beneath Drop 3 was typically ~ 10^6 – $10^7 \mu m^2$, with a volume of ~ $10^7 \mu m^3$.



Figure 20. Measured surface area of corrosion as a function of ageing time at 475 $^{\circ}$ C of microstructures bent in (**a**) RD and (**b**) TD.

The extent of corrosion showed the lowest volume of corrosion for the 10-h-aged specimens bent in RD and the five-hour-aged specimen bent in TD. Corrosion under Drop 3 did not seem to have stopped or saturated, even for a microstructure aged for 255 h. The corrosion volume on the 255 h aged specimens was ~5-times larger compared to the as-received samples.



Figure 21. Measured volume of corrosion as a function of ageing time at 475 $^{\circ}$ C bent in (**a**) RD and (**b**) TD.

SCC cracks were also measured as a function of ageing time (Figure 22). The shortest cracks were found on the specimen aged for 10 h (in RD), indicating the best SCC performance. Severe SCC occurred on the 255-h-aged specimen, with maximum crack length measured under Drops 1, 2, and 3 of ~250, ~700, and ~1500 μ m, respectively. However, the U-bend specimens in TD showed a somewhat different crack length distribution. The longest crack with 1700 μ m length was measured under Drop 3 for the specimen aged for 5 h.



Figure 22. Measured maximum SCC crack length of 2205 DSS microstructure bent (a) in RD and (b) TD.

5. Discussion

5.1. Microstructure Characterisation

The fraction of austenite decreased from 54% to 47% in the microstructure with bending in RD and to 48% in TD. This can possibly be attributed to the formation of deformation-induced martensite, which is typically indexed as ferrite due to its similar crystallographic structure. Deformation-induced martensite in 2205 DSS has been reported after plastic deformation by cold rolling (ϵ = 3.38), which supports this assumption [40–42].

The bending deformation resulted in an increase of grain sizes of both ferrite and austenite, with the latter being more affected in the TD direction. All grain structures were apparently more affected after bending in TD than after bending in RD. The microstructure resembled a sandwich-like appearance consisting of bands of ferrite and austenite. As a consequence of the deformation of the ferrite, the surrounding austenite grains were also constraint.

LMO development clearly showed that the austenite contained larger proportions of elastic-plastic strain than the ferrite after bending in RD, whereas the opposite was apparent after bending in

TD. The structural change and strain response clearly demonstrated the effect of microstructure on bending. Similar results have been recently reported in cold-rolled 2205 DSS in which the fraction of HAGBs and LAGBs increased with cold reduction, causing micro-deformation and, hence, strain in the microstructure [36,43]. Severe strain localisation in austenite grains was observed, resulting in localised corrosion [36,43].

5.2. Hardness Behaviour

Bending increased the hardness of the stainless steel strips resulting in a higher dislocation density in the microstructure. The hardness also increased with ageing, indicating an effect of the 475 °C embrittlement treatment. The latter is known to impede dislocation motion in ferrite [44]. The hardness increased gradually up to 20 h of ageing exposure, with a steep rise after 50 h, reaching a maximum hardness after 255 h. Larger precipitates were seen after 255 h of ageing. These are also believed to be responsible for the additional hardness increase, and they may even play a larger role than spinodal decomposition for the observed hardness changes [45,46].

5.3. XRD Stress Development

The surface stress of austenite was not substantially affected by ageing alone, whereas the stress in the ferrite became more tensile after 255 h of ageing. The latter was even more pronounced after bending in RD. Precipitates formed at the interface between austenite and ferrite can hinder dislocation motion, forcing ferrite grains to distort along RD. The effect of 475 °C embrittlement on the stress state of both phases can clearly be noticed after bending in RD and TD. Both phases became tensile in all directions with ageing exposure, which is the response of the microstructure due to the applied strain. The observed stress in austenite was higher than the stress in ferrite in the as-received microstructure, as well as in all conditions aged for up to 50 h. This is related to larger plastic strain, which can be accommodated in austenite, most likely accompanied by strain-induced martensite formation. Martensite formation is typically accompanied by a volume expansion resulting in strain hardening, which in turn is associated with retardation of dislocation motion. Both phases had similar tensile strength after 255 h of ageing, indicating a balanced stress state.

5.4. Corrosion and AISCC Behaviour

Temperature and RH play a key role in atmospheric corrosion, and the highest susceptibility to AISCC has been reported to occur on stainless steels at RHs at or close to salt deliquescence [47]. Up to 12 M chloride can be formed at the deliquescence point of MgCl₂ at room temperature [48,49], and this can be 15 M or even higher for \geq 50 °C [24,50]. Large droplet sizes (diameter, thickness) have also been reported to increase the extent of atmospheric corrosion [51,52]. There is a relationship between the extent of corrosion with the droplet size (ranking order Drop 3 > Drop 2 > Drop 1). Increasing the chloride deposition density from 15 µg/cm² (Drop 1) to 247 µg/cm² (Drop 2) increased the corrosion by more than six orders of magnitude, with a further increase of the chloride deposition density to 2856 µg/cm² (Drop 3) the extent of corrosion increased approximately by one order of magnitude (see Figures 20 and 21).

Ferrite and austenite have different electrochemical corrosion potentials, therefore a different form and extent of corrosion attack can be expected [53–56]. In most 2205 DSSs, ferrite usually dissolves in chloride-bearing media [34,35,54–59], which is due to a higher corrosion potential of austenite deriving from its higher nickel and nitrogen contents [54–56]. Furthermore, ferrite and austenite show inherently different mechanical behaviour during plastic deformation due to their different crystal structure [3,36,38,60]. The corrosion mechanism was clearly affected by the ageing time, bending deformation, and also process orientation (RD, TD).

Short-term ageing in the 475 °C embrittlement temperature window of duplex stainless steels is typically associated with an increase of the corrosion resistance, but then a decrease with further ageing time has been observed [35,59,61]. After these short 475 °C embrittlement treatments, an improvement

of the passivation behaviour of the ferrite has been observed with no selective attack on either the ferrite or the austenite [35,59,61]. Spinodal decomposition of the ferrite has been postulated as the reason for an increase of the corrosion resistance of ferrite. Longer exposure periods, in excess of 10 h at 475 °C, results in further precipitates formed within ferrite regions and at interphase boundaries, such as R-phase. These are believed to be the reason for the reduced corrosion resistance of the ferrite [35].

The AISCC behaviour was compared to corrosion area and corrosion volume measurements in Figure 22. The extent of SCC (length, number) in the microstructures along RD increased with ageing time, with the lowest susceptibility to cracking observed, in line with the smallest corrosion attack. The microstructure bent in TD, however, showed severe cracking beneath Drop 3 after ageing for 5 h. The extent of SCC and the corrosion volume of the microstructure after bending in TD did not seem to correlate with those after bending in RD, showing that microstructure plays a key role in the extent of atmospheric corrosion and SCC.

In the as-received condition and after bending in RD, ferrite was preferentially attacked by localised corrosion. Cold deformation causes strain heterogeneity in the duplex microstructure, with austenite accommodating most plastic strains and forming strain hotspots, which have been reported to become electrochemically active sites [36]. Localised corrosion in austenite was observed under Drops 1 and 2. Localised corrosion can govern the corrosion mechanism for heavily deformed microstructures [36,60]. The austenite was more deformed after bending in RD, with strain heterogeneities observed to cause localised attack, whereas ferrite was more strained in TD.

SCC occurred primarily in the austenite, which may be considered as the phase primarily responsible for cracking. However, the propensity to SCC increased with ageing time and reached maximum susceptibility after 255 h, with numerous ferrite grains also showing fractures. Ferrite became prone to SCC with an increasing degree of 475 °C embrittlement. The crack morphology observation of ferrite would suggest chloride-induced SCC or hydrogen-assisted embrittlement/cracking, since multiple closely-spaced, fine-scale cracks arrayed in crystallographic manner are typically signs of hydrogen embrittlement [62–64]. The crack morphologies in austenite suggest that chloride-induced SCC was most likely the cause of cracking. Despite the quantitatively larger number of cracks in the microstructure bent in TD, the maximum crack length observed was only 40 μ m, while longer cracks of ~100 μ m were measured in microstructures bent in RD. This suggests that bending in RD is more critical than in TD regarding the corrosion and SCC susceptibility of 2205 duplex stainless steel.

6. Conclusions

In this study, the effect of process orientation and ageing at 475 $^{\circ}$ C on microstructure development and atmospheric chloride-induced stress corrosion cracking was investigated.

- The extent of 475°C embrittlement increases with increasing ageing time and is mainly caused by microstructural changes in the ferrite. All microstructures were rendered susceptible to AISCC with exposure to 475 °C, with improved AISCC performance observed for microstructures aged for 5 or 10 h at 475 °C.
- 2. The austenite phase was mainly susceptible to AISCC in microstructures aged up to 50 h, whereas the ferrite became more susceptible after ageing in excess of 50 h.
- 3. The samples manufactured in TD had highest propensity towards AISCC. This was in line with higher strain and stress in both ferrite and austenite in TD. Bending along TD results in larger strain and stresses in the microstructure and higher propensity to corrosion and AISCC. The direction of bending deformation determines the extent and distribution of strain in the duplex microstructure.

4. XRD measurements confirmed the development of stresses in ferrite and austenite with ageing at 475 °C. The austenite showed larger stresses with exposure up to 50 h, whereas the stress in ferrite increased with ageing time.

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