Toward Understanding the Effects of Strain and Chloride Deposition Density on Atmospheric Chloride-Induced Stress Corrosion Cracking of Type 304 Austenitic Stainless Steel under MgCl_2 and $\text{FeCl}_3\text{:MgCl}_2$ Droplets

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Towards Understanding the Effects of Strain and Chloride Deposition Density on Atmospheric Chloride-Induced Stress Corrosion Cracking of Type 304 Austenitic Stainless Steel under MgCl_2 and $\text{FeCl}_3\text{:MgCl}_2$ Droplets

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Abstract

Type 304 (UNS S30400) austenitic stainless steel was exposed for 6 months under elastic (0.1%) and elastic/plastic (0.2%) strain to MgCl_2 and mixed $\text{MgCl}_2\text{:FeCl}_3$ droplets with varying chloride deposition densities (1.5-1500 $\mu\text{g}/\text{cm}^2$) at 30% relative humidity (RH) and 50°C. The occurrence of pitting corrosion, crevice corrosion, atmospheric chloride-induced stress corrosion cracking (AISCC) and hydrogen embrittlement (HE) was observed, and the average crack growth rates estimated. Exposure to elastic/plastic strain resulted in longer and more severe cracks. AISCC was found at chloride deposition densities down to 14.5 $\mu\text{g}/\text{cm}^2$, whereas no cracks were seen at lower deposition densities, with cracks developing at pit or crevice corrosion sites. More severe cracks were seen under MgCl_2 droplets as contrasted to mixed $\text{MgCl}_2\text{:FeCl}_3$ salt droplets, which were seen to promote more localized corrosion sites with deeper penetration and in conjunction with shorter crack lengths. Differences in AISCC propagation rates and associated crack morphologies are discussed in relation to understanding long-term atmospheric corrosion exposures.

1. Introduction

The UK's intermediate level radioactive waste (ILW) is immobilized in containers made from type 304/316 austenitic stainless steel and stored in above-ground waste repositories until deep geological disposal becomes available.¹⁻⁵ Most waste repositories are located at near-coastal regions and, therefore, it is very likely that the container will be subjected to the deposition of chloride-containing aerosols onto the surface, which can lead to the formation of aggressive thin-film electrolytes, a phenomenon known as atmospheric corrosion.¹⁻⁸ Residual stresses in the material originating from material processing, near-net shape deformation, and welding can lead to an increased propensity towards AISCC, which is by far the most detrimental form of corrosion for thin-walled ILW containers.^{1, 4, 5, 7-13} The specimen design and the loading regime can, therefore, have a significant influence on AISCC, with most long-term AISCC results so far being obtained using highly-stressed U-bend or C-ring specimens.^{10, 14-21}

Atmospheric corrosion and/or AISCC typically occurs under thin-film electrolytes in the presence of humidity, varying from a few monolayers of water, sufficient to form an aggressive corrosive electrolyte, to the formation of large droplets.^{17, 18, 22-24} The chloride concentration is, unlike in bulk aqueous conditions, dependent on the ambient RH, with the deliquescence relative humidity (DRH) forming the most aggressive electrolytes.^{4, 5, 8-11, 25-28} Seawater is

mainly composed of NaCl and MgCl₂ compounds, and the latter plays vital role in low humidities since NaCl is dry at 72% RH.²⁹ Chloride concentrations up to 10-12 M have been reported to form under MgCl₂ deposits at 30% RH at room temperature (DRH of MgCl₂ is 27-35% RH at room temperature^{4, 26, 30, 31}), promoting local anodic dissolution reactions.^{17, 25-28} Moreover, oxygen is typically abundantly present all over the entire exposure area and less-likely depleted if the thickness of the electrolyte is thin enough to sustain oxygen reaction kinetics, further enhancing the corrosion amenability. At and around (also below) the DRH, deposited salts can remain solid and semi-wet³²⁻³⁴, favoring crevice corrosion at the salt/metal interface.^{35, 36} The pH can drop to very aggressive low values and further promote corrosion.^{26, 37}

For corrosion to occur at such atmospheric exposure conditions is a matter of time. The corrosion kinetics and morphology determine the long-term integrity of the material, both information being scarcely reported. Atmospheric corrosion is usually localized independent whether the material has a passive film or a loosely-attached, non-protective surface oxide. In stainless steel, corrosion beneath droplets is either localized at grain boundaries or forms corrosion pits, with the rates often being incomparable with data obtained from bulk aqueous exposure tests.^{4, 8-11} For a successful application of long-term storage of radioactive waste in stainless steel canisters, there is more experimental data about atmospheric corrosion as well as AISCC in various exposure conditions with different metallurgical scenarios (strain, deformation etc.) needed to understand the corrosion behavior and to increase statistical certainty for a safe application.

Austenitic stainless steels are by far one of the most studied materials in atmospheric conditions, and a very good understanding of the corrosion kinetic behavior as well as stress corrosion cracking (SCC) already exists, with quantitative data being often available for end-users enabling reliable life-time estimation.³⁸⁻⁴¹ However, data often derive from bulk aqueous corrosion tests, and most corrosion has been reported in concentrated, boiling, or high-temperature exposure conditions, and therefore the data are less relevant for ILW storage. The latter needs information under atmospheric, thin-film electrolyte conditions, with low-chloride deposition densities (typically <10 µg/cm²) at temperatures typically not exceeding 50°C.^{3, 5, 8, 10, 11}

Some grades of austenitic stainless steels, including 304 and 316, have long been recognized as less susceptible to AISCC below 60°C, which encouraged end-users to expose these materials to corrosive environments below the believed threshold temperature.^{9, 11, 42, 43} However, SCC at ambient temperatures has been reported in harsh corrosive environments and has questioned the “threshold” temperature concept.^{14-16, 44, 45} The threshold concept has not been revisited, however, instead the temperature under which pitting corrosion may not occur (critical pitting temperature), which is around 0°C and 10°C for 304 and 316 stainless steel respectively⁴⁶, has been argued as a safe approach for ILW storage.⁹ Lower storage temperatures certainly reduce the probability to induce pits and cracks, however, the classic notion that SCC initiates from pits may not always be true since SCC, in particular under atmospheric conditions, can also initiate from crevices.^{9, 13, 47}

In this work, the effect of applied tensile strain in the elastic (0.1% strain) and elastic/plastic (0.2% strain) regime on the AISCC behavior of 304 austenitic stainless steel has been elucidated, using exposed chloride coverage per unit area (deposition density) of 1.5 - 1500 µg/cm². The existing understanding of austenitic stainless steel corrosion has been revisited, and is discussed in light of atmospheric exposures of up to 6 months.

2. Experimental

2.1. Microstructure Characterization

A Type 304 (UNS S30400) austenitic stainless steel was studied in this work, with the chemical composition of the plate given in Table 1. The microstructure was assessed for grain size and secondary phases using electron backscatter diffraction (EBSD) for which the sample was ground to 4000-grit using SiC grinding paper, then polished using 3, 1, $\frac{1}{4}$ μm diamond paste, followed by an electrolytic etch in 10 wt.-% oxalic acid at 5 V for 30 seconds. An *FEI Magellan* scanning electron microscope (SEM), interfaced with a *Nordlys* EBSD detector from *Oxford Instruments*, was used. The EBSD data was acquired with *AZtec V3.1* program from *Oxford Instruments* with 15 kV accelerating voltage, 6.4 nA probe current, 4x4 binning of the CCD camera for pattern readout, and a step size of 650 nm over an area of 1540 x 856 μm^2 . *HKL Channel 5* software was used for data post-processing. For grain size analysis the mean linear intercept method was used in X and Y directions with 100 lines. Twin grain boundaries were disregarded for grain size analysis. High-angle grain boundaries (HAGB's) were defined with misorientation $\geq 15^\circ$ and low-angle grain boundaries (LAGB's) between $>1^\circ$ and $<15^\circ$. Local misorientation (LMO) maps were generated by using a 3x3 binning and a 5° sub-grain angle threshold. This analysis gives the average LMO for a misorientation below the pre-determined sub-grain angle threshold, and can be used to locate regions with higher concentrations of misorientation in microstructures. The latter is typically associated with local micro-deformation in the form of elastic and plastic strain, due to the presence of dislocations.⁴⁸

2.2. Atmospheric Chloride-induced Stress Corrosion Cracking Testing

Miniature-tensile specimens with a gauge length of 20 mm, a gauge width of 3 mm, a thickness of 2 mm, and a total length of 69 mm were machined from a 13 mm thick plate material and mechanically ground down to 2500-grit using SiC sandpaper. A strain gauge was attached to the back side of the gauge area. Self-made tensile rigs, as shown in Figure 1, were used to apply a constant load. Two samples were strained; one to 0.1% and another to 0.2% strain with $\pm 0.006\%$ precision, with the actual strain readout recorded from the strain gauge using a *LabVIEW* program.

Six salt-laden water droplets containing chlorides, as specified in Table 2, were deposited onto the sample surface using an *Eppendorf* pipette (all droplets to the same sample). Magnesium chloride and a mixture of magnesium chloride and ferric chloride (0.68 mol FeCl_3 :1 mol MgCl_2 ratio) was used for AISCC testing. The FeCl_3 : MgCl_2 ratio was chosen to balance the chloride molarity of both salts. The entire setup was then placed into a *KBF Binder* humidity cabinet in which the temperature and humidity was controlled to 50°C and 30% RH and exposed for 6 months. The deliquescence point of MgCl_2 at 50°C is $\approx 30\%$ RH, and at this condition the droplet had a chloride concentration of 12-15 M.^{4, 7, 17, 31, 49}

After the test, samples were examined in a *Zeiss* stereomicroscope at 25x magnification. The samples were rinsed in tap water to remove salt remnants, and corrosion products were removed by immersion in a hot ($\approx 80^\circ\text{C}$) citric acid solution for 2-4 hours. This procedure removed the corrosion products without attacking the un-corroded matrix material. The samples were given a final rinse in distilled water and dried using hot air. The extent of corrosion and/or SCC was examined in an *FEI Magellan* SEM. Then, both samples were ground and polished to $\frac{1}{4}$ μm finish, followed by an OP-S end-polishing treatment for 30 minutes. The samples were then cleaned with water and dried for SEM/EBSD analysis. EBSD

was carried out on selected areas with cracks, and grain orientation and local misorientation (LMO) maps were obtained using step sizes between 0.75-5 μm . The lengths of AISCC cracks were measured using optical microscopy and/or SEM. The longest crack is reported only. This procedure considers superficial cracks only, and no post-mortem cross sectioning was done. The crack growth rates were estimated assuming the same incubation time (crack length divided by exposure time).

3. Results

3.1. Microstructure

The as-received microstructure of the type 304 plate is shown by the EBSD inverse pole figure (IPF) color map in Figure 2, giving a general overview of the microstructure, morphology and orientation of grains. The grain size was $45 \mu\text{m} \pm 10 \mu\text{m}$ with a length fraction of twin boundaries of $\approx 44\%$. EBSD analysis also revealed an indexed area fraction of up to 5% ferrite in the microstructure, with a minor presence of 0.01% manganese sulfide inclusions and some M_{23}C_6 carbides. It is very likely that more MnS and carbides were present, but were not indexed by EBSD due to their small dimensions and non-optimized sample preparation produces. Overall, the microstructure was texture-free but with some minor strain heterogeneities at few twin boundaries and HAGBs, shown by the color map in Figure 2c. The microstructure is representative of a typical solution-annealed austenitic stainless steel.

3.2. Atmospheric Corrosion and AISCC Behavior

3.2.1. Elastic Strain (0.1%)

Figure 3 summarizes stereo-microscopic images taken at the end of the AISCC tests before the samples were cleaned. No corrosion attack was observed under the deposit with 1.5 $\mu\text{g}/\text{cm}^2$ of chloride (droplet 1), as shown in Figure 3a. Figure 3b-f show the regions with 14.5 $\mu\text{g}/\text{cm}^2$, 50.7 $\mu\text{g}/\text{cm}^2$, 145 $\mu\text{g}/\text{cm}^2$, 1449.8 $\mu\text{g}/\text{cm}^2$, 434.9 $\mu\text{g}/\text{cm}^2$ of chloride, respectively. Corrosion attack, visible from the apparent rust spots, was observed. Furthermore, SCC was seen under all droplets, except the mixed $\text{FeCl}_3\text{:MgCl}_2$ droplet 6 (434.9 $\mu\text{g}/\text{cm}^2$ Cl^-). However, cracks were also observed under droplet 6 after removing corrosion products, which are discussed later in the manuscript. One major crack was discernible by eye under droplets 2-5, extending beyond the chloride covered area. The cracks seemed to have initiated at the periphery (edge) of the droplet from where they extended towards circa zero and six o'clock, being perpendicular to the horizontal (loading direction). The maximum measured crack length under droplet 2 (14.5 $\mu\text{g}/\text{cm}^2$ of chloride) was $\approx 400 \mu\text{m}$, with longer crack lengths formed with increasing deposition density. The longest crack observed was under droplet 5 (1449.8 $\mu\text{g}/\text{cm}^2$ Cl^-), showing a crack length $\geq 2800 \mu\text{m}$, passing almost through the entire gauge width.

Secondary droplet spreading, which is the radial spreading of the deposited salt, has been observed to occur for all deposits except from the one with 1.5 $\mu\text{g}/\text{cm}^2$ of chloride. Secondary spreading is a well-known phenomenon in atmospheric corrosion and is typical for alloys which exhibit active corrosion under humid conditions.^{27, 50, 51} The size of secondary spreading became larger with the increasing deposition density of chloride, with most spreading observed under 1449.8 $\mu\text{g}/\text{cm}^2$ of chloride, which seemed to spread preferentially along the major crack direction, as shown in Figure 3d,e. Most rust products were seen on the droplet with 1449.8 $\mu\text{g}/\text{cm}^2$ of chloride, with rusted sites in general located at the periphery of the deposited droplet area.

The corrosion products were removed using hot citric acid and the sample was further analyzed in an SEM. All corrosion morphologies were analyzed but only a summary of the most important observations are provided in this work. The area of corrosion attack increased with increasing chloride deposition density, and most corrosion attack was seen under droplet 5 and 6. The main crack in droplet 5 is shown in Figure 4a. This crack was 10's of μm wide, and advanced in a zigzag-like manner, clearly indicating chloride-induced SCC. This behavior is typically related to changes in the crystallographic orientation of grains, with the advancing cracks trying to accommodate changes in grain orientation with respect to the applied load.⁵²⁻⁵⁴ Moreover, some corroded regions, most of them being shallow, were observed on regions adjacent to this large crack, indicative of crevice corrosion. Numerous parallel-arrayed tiny cracks, which were oriented perpendicular to the stress direction and populated in a relatively high density, were seen in almost all of these shallow regions adjacent to the main SCC crack, shown in Figure 4b,e,f,g. These cracks were transgranular and discrete and were seemingly not branched, not typical for chloride-induced SCC. Furthermore, some of the shallow corrosion regions further away from the main crack showed no cracks at all, but preferential attack on slip planes was observed (Figure 4c). In contrast, a crack was observed in a region with deeper, localized corrosion attack, shown in Figure 4d, suggesting a critical pit/crevice depth relationship to trigger environment-assisted cracking (EAC).

The sample with $434.9 \mu\text{g}/\text{cm}^2$ mixed chloride (droplet 6) showed different corrosion and crack morphologies than those deposited with magnesium chloride only. Numerous nano- and micrometer-sized corrosion pits were seen decorating the entire area covered by the droplet, with micro pits preferentially nucleated at the periphery (Figure 5a-e). These pits had an idiosyncratic appearance (whirlpool shape), with the pit depth increasing from the periphery towards the center, highlighted in Figure 5b,c,d. Some cracks could be seen here, which had initiated at the bottom of the pit, oriented both perpendicular and parallel to the loading direction (Figure 5d,e). Moreover, in the center of the whirlpool pit, which was the deepest corrosion site, surface perforation resembling de-alloying was seen (Figure 5e). Further cracks were seen to have developed close to the mouth of the pit, showing both inter- and transgranular nature (Figure 5f). These cracks were short, typically up to 1-2 grains long.

3.2.2. Elastic/Plastic Strain (0.2%)

An overview of all corrosion attack observed after exposure with 0.2% constant strain is summarized in the stereo-micrographic images in Figure 6. No corrosion was observed under droplet 1 with $1.5 \mu\text{g}/\text{cm}^2$ chloride (Figure 6a). Corrosion occurred at the periphery of droplet 2 with $14.5 \mu\text{g}/\text{cm}^2$ chloride (Figure 6b); however, no SCC was observed here. Cracks were found under droplet 3, with one champion crack passing through the entire droplet area, slightly inclined (ca. 70°) to the loading direction (Figure 6c). The longest crack was observed under deposit 4 with $145 \mu\text{g}/\text{cm}^2$ chloride, which was also inclined (ca. 80°) to the loading direction (Figure 6d,left). Most corrosion attack seemed to be concentrated around the edge of the droplet where also all cracks were located. The main crack was ca. $100 \mu\text{m}$ wide and advanced through the entire gauge width; however, not yet leading to failure of the specimen. Next to the crack walls, chloride deposits were found indicating secondary droplet spreading. Most spreading as well as corrosion was observed under deposit 5 with $1449.8 \mu\text{g}/\text{cm}^2$ chloride (Figure 6d,right). Corrosion was also confined to the periphery of the droplet; however, secondary spreading was observed which caused linkage with droplet 4 on the left side. This may have led to minor changes in the overall deposition density of those two droplets, and results of those are therefore discussed together. A number of heterogeneous corrosion sites, seemingly concentrated around the center of the deposited area under droplet 6 with mixed chloride was observed, shown in

Figure 6e. Secondary spreading was also present under this droplet, with chloride-covered areas spreading towards the loading direction.

Further, higher resolution SEM analysis of droplet 3 with $50.7 \mu\text{g}/\text{cm}^2$ chloride also revealed a zigzag-like crack shape perpendicular to the loading direction (Figure 7). Regions with slip bands, indicating local plastic deformation, were observed in the vicinity to the crack, with the crack tip showing a higher density of slip bands indicative of larger plastic deformation. Numerous small cracks along slip bands were also observed, following the path of the main crack. Plastic deformation next to the crack tip, which seemed to have been blunted, caused local grain protrusion sites, resulting in a complex, convoluted surface appearance. Small but deep pits with diameters $< 2 \mu\text{m}$ were also present in the wake of the crack path (see the image insert in Figure 7a).

More severe cracks were observed under deposit 5 with $1449.8 \mu\text{g}/\text{cm}^2$ chloride (Figure 8). The crack path along the surface was discontinuous, with also a zigzag-like crystallographic appearance (Figure 8a). Deformation bands were present at these discontinuous sites, indicating 3D crack diversion towards the interior (Figure 8e), resulting in a crack bridge. The crack traversed through the entire gauge width, but without leading to failure of the specimen (Figure 8b). Highly plastically-deformed regions, adjacent to the walls of the main crack were seen, where numerous smaller cracks had formed (Figure 8c). These cracks were of different nature than the main crack (Figure 8d). Many small, sub-micrometer-sized crack nuclei, with sizes down to 10^2 's of nm in a high population density, were observed (Figure 8d). Moreover, some shallow corrosion sites with sizes of a few 10^2 's of micrometers with discrete, crevice-like appearance were observed (Figure 8f), indicating preferential attack along slip bands, perpendicular to the loading direction.

Analysis under deposit 6 with mixed $434.9 \mu\text{g}/\text{cm}^2$ chloride revealed nm-sized pit nuclei, concentrated on the periphery of the droplet (Figure 9a). In the interior of the deposited area, numerous larger corrosion pits with SCC emanating from pit mouth regions were observed. The cracks were oriented $30\text{-}45^\circ$ to the loading direction (Figure 9b,c). The grain boundaries became visible, and preferential localized attack occurring on slip bands (Figure 9b,d,e) was also observed. Numerous nano-sized cracks, with a very high population density had developed within these localized corrosion sites, with the cracks being oriented parallel to the loading direction, indicating HE or hydrogen-related cracking.^{6, 55, 56}

The maximum crack length measured in each droplet as a function of strain is summarized in Figure 10 and Table 3. The chloride deposition density seemed to have a large effect on the maximum crack lengths and the estimated crack growth rates. Below a density of $50.7 \mu\text{g}/\text{cm}^2$ chloride, crack formation and propagation became increasingly disfavored, with no AISCC observed after 6 months for $1.5 \mu\text{g}/\text{cm}^2$ chloride exposure. The presence of ferric ions seemed to cause more localized and general corrosion, thereby reducing the AISCC susceptibility. The applied strain seemed to accelerate AISCC. The crack length increased with increasing chloride deposition density, and this observation was clearer for elastically-loaded samples (0.1%).

3.3 Topography Characterization

The AISCC tested samples were then re-polished to $\frac{1}{4} \mu\text{m}$ diamond paste finish, followed by OPS end-polishing for confocal microscopy (topography) and SEM/EBSD analyses. This was carried out to obtain information about crack crystallography and penetration depth. The largest cracks were analyzed only, with the corresponding crystallographic orientation and LMO

information for the specimens strained to elastic and elastic/plastic loads summarized in Figure 11 and Figure 12, respectively.

All cracks in the specimen loaded to 0.1% strain were branched and had transgranular pathways, with bifurcations observed. The cracks in the specimen loaded with 0.2% strain, in contrast, were less branched and seemed to have straighter crack growth paths, with the cracks being all transgranular in nature. The cracks were, furthermore, wider and seemed to have higher propensity to make vertical zigzag movements towards the bulk (higher crack penetration), in particular the crack developed under droplet 4. Large strains were localized adjacent to crack walls for both loading conditions, with finer cracks indicating more intense strain. None of the cracks could be associated with the presence of delta ferrite.

4 Discussion

Atmospheric corrosion beneath droplet deposits is typically associated with the formation of an aeration cell across the entire deposited area, due to varying electrolyte thickness and, hence, differential oxygen concentrations, leading to confined anodic regions surrounded by cathodic sites, with the latter often formed around the droplet edges.^{25-27, 51, 57-60} Only a small number of corrosion pits are formed under droplets, typically far fewer compared to pits formed under fully immersed conditions, often resulting in a ‘chicken’s eye’ appearance.^{26, 61, 62} However, numerous corrosion sites can be formed if the droplet is discontinuous, especially if secondary spreading in the form of lateral volume expansion of the droplet occurs, or when highly susceptible sites exist in the microstructure.^{6, 27, 63-66}

The droplet height is controlled by the humidity as well as the amount of salt deposited onto the surface.^{25-28, 62, 67, 68} The height further depends on the size of the droplet, and typically decreases with increasing droplet diameters.^{25, 26, 69} The humidity controls the chloride concentration independent of the amount of salt deposited, and the most aggressive electrolytes are formed at the DRH of the salt.^{25-28, 62, 67, 68} Solid salt fragments may remain undissolved near the DRH under which crevices can be formed, which can further exacerbate local attack.^{35, 36, 70} Similar effects may also be caused by corrosion products (rust layer) which can be deposited onto the surface.⁷⁰ Moisture retention beneath solid salt fragments may occur due to capillary forces resulting in rapid crevice-like corrosion attack.^{35, 36, 41} All these aspects have importance in triggering AISCC since the number and size of localized corrosion sites (not necessarily pits but also crevices) as well as the morphology and local environmental conditions determine whether cracks can nucleate or not.

4.1 Corrosion Topography and Secondary Spreading

Most of the observed corrosion attack was shallow, seemingly associated with crevice formation, possibly beneath solid MgCl_2 salt fragments. MgCl_2 has been argued to have poor wetting properties, and insoluble MgOH_2 compounds, typically formed on the edge of the droplet, have been reported to retard the effect to secondary spreading.⁶² Crevice corrosion was far less prominent under droplets containing mixed $\text{FeCl}_3\text{:MgCl}_2$ droplets, which seemingly favored pitting corrosion. The DRH of FeCl_3 is 11% RH⁷¹ at room temperature and potentially further reduces at 50°C; hence, it seems that the ferric ions could keep the entire deposit wet, reducing the probability of crevice formation. The local depth of corrosion attack was significantly deeper under droplets containing mixed $\text{FeCl}_3\text{:MgCl}_2$, compared to MgCl_2 only. Ferric ions have an acidic and oxidizing character, and are therefore believed to promote local, accelerated corrosion attack. There is also the possibility to form mixed MgFe_2Cl_8 compounds

in highly concentrated $\text{FeCl}_3\text{:MgCl}_2$ solution, which would possibly act in a similar manner as the presence of carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$) in promoting AISCC.¹⁹

Interestingly, in the presence of ferric ions most pits have distinctively stepped structures, with steps as small as $\leq 1 \mu\text{m}$, which is by far less than the grain size of the material ($\sim 45 \mu\text{m}$). These steps are possibly related to the crystallographic orientation of grains, which can have different dissolution characteristics.⁷² The bottom of these deep, stepped pits (Whirlpool appearance) had often a perforated appearance, which may be associated to de-alloying or preferential element dissolution. Iron in stainless steels typically dissolves faster than nickel, chromium, and molybdenum, and therefore, it is likely that at the bottom of the pit, where larger over-potentials exist, preferential dissolution of iron may have taken place, resulting in this perforated appearance.^{54, 73} Fe was earlier demonstrated to selectively dissolve in a duplex stainless steel (in both ferrite and austenite phases) under anodic polarisation.⁷³

Deep, funnel shaped pit shapes were also reported by Davenport et al. on type 304 under MgCl_2 deposits, which were related to microstructure processing orientation.⁶⁷ Pits formed on the surface transverse to the rolling plane appeared in their study as circular layered pits, whereas those initiated on the rolling plane had a deep layered structure. Such pits, however, were formed without the presence of ferric ions. Street et al. also reported similar pit morphologies and called them 'spiral' or 'satellite' pits, which were also related to the microstructure processing orientation (preferential growth along the rolling direction).⁷⁴ In a more recent work, Mohammed-Ali et al. reported atmospheric corrosion pits having a layered morphology, being related to the microstructure processing orientation (favored dissolution ferrite along the rolling direction) as well as ferritic grains, which were band-wise arrayed along the rolling direction and corroded selectively promoting anisotropic dissolution.⁷⁵ The pits we observed in the presence of ferric ions, however, cannot be related to the microstructure (only) since the step marks (that which gives the whirlpool appearance) within the pit are as small as $\leq 1 \mu\text{m}$ which is by far less than the grain size of the material ($\sim 45 \mu\text{m}$). It may, however, be related to slip bands which can have different dissolution characteristics.⁷²

Another idiosyncratic corrosion form was the occurrence of a high density of sub-micrometer-pits initiated next to each other (Figure 9a) under droplets containing mixed $\text{FeCl}_3\text{:MgCl}_2$. Such an appearance resembles transpassive corrosion which occurs when the material is polarized to anodic potentials where the passive film is non-protective and highly conductive.⁷³ Ferric ions can push the oxidation potential to high anodic potentials, and it is likely that the transpassive corrosion regime was reached at this location. Slip band attack, revealing the grain orientation in Figure 8f and Figure 9d,e has often been associated with crack nucleation, typically observed under fully immersed conditions.^{54, 72} However, slip band attack at sites believed to be caused by crevice corrosion with atmospheric exposures, has not been reported, and it remained unclear whether the crevice corrosion attack shown in Figure 8f then develop into AISCC.

The occurrence of secondary spreading was also observed and typically occurs with the onset of corrosion.^{51, 69} The corrosion chemistry of the spread droplets can largely vary, due to selective ion migration.^{51, 69, 76} The spreading mechanism, which involves three different stages, has been described by Zhang et al.⁵¹ and Tsuru et al.²⁷ as follows: (i) wetting of the peripheral area beyond the salt-laden thin-film electrolyte (droplet) due to hydroxylation by cathodic oxygen reduction, and the adsorption of water from air, (ii) formation of micro-droplets at the edge of the primary droplet (cathodic sites) and growth, (iii) coalescence of the micro-droplets and eventual link to the main droplet. The extent of spreading is a sign for the extent of

corrosion. More spreading as well as corrosion was observed with increasing chloride deposition density (Figure 3 and Figure 6).

Spreading is also a matter of time, since short-time exposure tests (one day) did not show considerable droplet extension although corrosion pits were observed. These observations suggest that cathodic oxygen reduction reactions and, hence, the local pH are primarily responsible for secondary spreading and not the anodic dissolution reactions only since more spreading usually occurs for larger droplets and/or droplets with higher chloride deposition densities due to higher supplied cathodic currents.⁶² It is further interesting to note that under droplets containing mixed $\text{FeCl}_3\text{:MgCl}_2$, no remarkable spreading was observed. The Mg^{2+} ions spread preferentially (visible from the bright contrast near the edge of the primary deposited area shown in Figure 3f and Figure 6e), which then also changes the corrosion chemistry across the boundary layer (ferric ions have a brownish color).

Secondary spreading apparently changed the size and geometry of the deposition area of the salt. This most-likely led to a change of the droplet thickness which is an important parameter determining the anode-to-cathode ratio and the rate of oxygen supply and other mass transports.^{27-29, 69, 77} The droplet thickness may have further been changed due to the formation of new salt compounds of the dissolved metal ions from the alloy.

4.2 Propensity to Atmospheric Corrosion

The area of corrosion, and possibly the volume as well, increased with increasing chloride deposition density, in line with previous works.^{2, 3, 6, 17, 18, 20, 23, 62, 67, 78} Ferric ions further accelerated the corrosion, resulting in deeper corrosion attack. The chloride deposition density influenced the continuity of the droplet during atmospheric exposure, with low deposition densities leading to discontinuous, discrete droplet sites. The salt under droplet 2 with $14.5 \mu\text{g}/\text{cm}^2$ seemed to concentrate around the edge of the deposited area, possibly resulting in chloride deposition densities far larger than the calculated density, which assumes homogeneous salt distribution over the entire deposited area. Moisture discontinuity has been reported to be associated with the humidity, amount of salt per unit area (deposition density), and size of the droplet.⁶² A systematic work about the moisture continuity, however, has not been reported, but the deposited areas were seen to be more circular for droplets with deposition densities higher than $70 \mu\text{g}/\text{cm}^2$.⁶² Droplet discontinuity was further reported to occur with decreasing salt deposition density, indicating that moisture is sustained primarily by the amount of salt per unit area providing internal coherency of the droplet.⁶² These observations may question the homogeneity of the chloride within the droplet. The deposition density may alternate or change over time, especially if secondary spreading occurs. The droplet continuity determines the oxidation power of the droplet to the metal. Typically, more aggressive electrolytes are formed with increasing cathode to anode ratios, increasing with the diameter of the droplet.⁶⁹ Droplets as small as $\sim 45 \mu\text{m}$ in diameter have been reported to prevent corrosion to occur due to the reason that the anode and cathode cannot be separated.⁶⁹ A minimum separation distance between anodic vs. cathodic reaction is required for corrosion to occur.⁶⁹

Pits, crevices, and cracks were found for chloride deposition densities as low as $14.5 \mu\text{g}/\text{cm}^2$, but below this concentration, neither corrosion nor cracking was observed. Mi et al.⁶² also reported atmospheric pitting corrosion of inkjet-printed deposits with $\sim 18 \mu\text{g}/\text{cm}^2$ of chloride (22°C / 45-55% RH), with no corrosion observed under deposits with $7 \mu\text{g}/\text{cm}^2$. The number of pits were seen to increase with decreasing RH and increasing deposition density.⁶² This may support the statement that there is a threshold chloride deposition density below which the

material is safe against AISCC and possibly also against corrosion, or it may suggest that the initiation time is longer than the testing times.^{2, 20, 23, 78}

Cracks formed during atmospheric corrosion have been typically ascribed to SCC, and therefore the term AISCC has been commonly used.^{1-3, 5-7, 9, 17-21, 23, 41, 49, 64-66, 79-84} However, the data shown in this report revealed cracks that may also be related to HE, which has earlier been reported to occur in duplex stainless steel.^{6, 64} The cathodic reaction in chloride solutions at near-neutral pH is typically dominated by water reduction, producing hydroxide ions. However, the pH at localized corrosion sites can drop to pH 2-3, where cathodic hydrogen evolution may become possible, with the atomic hydrogen rapidly penetrating the material.⁶ The main cracks observed in this work were related to chloride SCC; however, local hydrogen-related cracks may have been supporting the cracking process in situations where the crack growth kinetics are slower (lower temperatures) at which diffusion of hydrogen towards the crack tip may play a key role, where the hydrogen can lower the stress intensity factor for crack propagation or re-initiation of a stopped or an arrested crack.⁸⁵ Some ppm fractions of hydrogen are sufficient to cause cracking which may support the reversion to martensite, further enhancing the SCC amenability.⁸⁶

The salt concentration is controlled by the humidity, and the droplet thickness has been argued to have two possible effects^{62, 68}: (i) if the cathodic oxygen reduction rate is under diffusion control, then a thicker droplet should decrease the rate of the cathodic reaction, leading to smaller pits. (ii) When, however, Ohmic effects dominate, then a thicker droplet should lead to more aggressive pits.⁶² Mi et al. reported increasing pit size with chloride deposition density indicating predominant Ohmic effects as the driving course for atmospheric pitting corrosion.⁶² However, the more recent work by Kelly et al. who did a more comprehensive study of the electrolyte film thickness stated that Ohmic and mass transport effects are competing in providing the cathodic currents.⁸⁷ Our opinion on droplet corrosion at or close to the DRH of a salt is that it is less appropriate to consider oxygen reduction reactions as the prime cathodic reaction. Hydrogen evolution reactions are predominant, possibly making oxygen reduction reactions negligible, in particular when SCC propagates. The hydrogen effect is more dominant in the presence of ferric ions, which reduces further the pH and increase cathodic reductions due to the redox couple $\text{Fe}^{2+}/\text{Fe}^{3+}$.

4.3 Propensity to SCC and Factors Controlling Cracking and Corrosion

SCC typically develops from corrosion pits, with pits being formed stochastically in single-phase austenitic stainless steels.^{21, 54, 88} Pit initiation, however, can be favored on inclusions or carbide precipitates, and delta ferrite has been reported to dissolve selectively under atmospheric corrosion conditions.^{54, 67, 75, 88} Pits can further nucleate preferentially on regions containing high strain and facilitate early breakdown of passive film.^{6, 63-65, 89-91} Hydrogen, formed during corrosion reactions, can enhance the pitting susceptibility by lowering the electrochemical nobility in local scale due to trapped hydrogen and perturbed the passive surface oxide film, facilitating early breakdown.^{6, 63-65, 89-91} Pit initiation in commercial austenitic stainless steels, hence, is rather deterministic due to multiple sites present in the microstructures. Some of the pits were seen to grow faster in depth than laterally, possibly suggesting rapid strain localization at the pit bottom, favoring crack initiation. Crevice corrosion has also been reported to favor cracking, and since crevices are under some circumstances more favored than pitting, as in the testing conditions used in this work, crevice-to-crack transition is more likely to occur since crevices usually develop faster than corrosion pits.^{13, 47, 54, 92, 93}

Pit-to-crack transition has been further shown to be associated with plastic strain development either at the shoulder or bottom of the pits, depending on the magnitude of the applied load, a phenomenon noted as pit growth-induced dynamic plastic strain, determining the transition from pitting to cracking.⁹⁴⁻⁹⁷ The strain and stress distribution on crevice walls is not known. Cracks typically follow a defect profile along the volume or surface of the materials, with strain localization determining the crack path.⁹⁴⁻⁹⁷ The cracks formed in the specimen loaded to 0.2% strain were far straighter and showed fewer zigzags than those formed at 0.1% strain, suggesting different strain and stress distribution within the microstructure.

The onset of cracks was not monitored, but is likely that cracks developed already during the initial stage exposure, possibly from crevices. Masuda⁷⁷ reported atmospheric SCC within 14 hours of exposure to MgCl₂ thin-film electrolytes, supporting this hypothesis. Masuda, however, used U-bend specimens for SCC testing and showed SCC cracks initiating from corrosion pits.⁷⁷ The apex of U-bend specimens is usually highly deformed (more than 5% strain).⁶⁶ U-bends do not provide good control over applied stress, and typically result in an uneven stress distribution around the apex.^{41, 66} The propensity to chloride-induced SCC of 304 is high and, therefore, it is more appropriate to use lower loads, mimicking uniaxial stresses, best achieved by using strained tensile specimens.^{41, 66} The occurrence of SCC indicates that the crack growth rates exceeded by far the corrosion rates under all conditions. Mean crack growth rates of 10⁻¹⁰ to 10⁻¹² m/s for all droplets were obtained (Table 3).

Nakayama et al.⁹⁸ reported SCC growth rates of 1.7·10⁻¹⁰ m/s in a highly sensitized stainless steel (weld joints) under NaCl deposits with a deposition density of 10 µg/cm², similar to those observed in this work (Table 3). The chloride concentration at 50°C and 30% RH in MgCl₂ droplets can reach up to 15 M^{6, 17}, with the formation of pits or crevices then becoming only a matter of time. Masuda reported corrosion pits of ~60 µm diameter, which formed within 14 hours of exposure to MgCl₂ droplets at 30°C and 28% RH, using type 304 U-bends samples.⁷⁷ SCC cracks of length up to 100 µm were seen at such a short time, clearly showing the high susceptibility of type 304 stainless steel to AISCC. Masuda, furthermore, reported hydrogen bubbles forming above the crack positions and noted a hydrogen-assisted SCC mechanism.⁷⁷ The cracks showed Volta potential differences of up to 300 mV with respect to neighboring regions, with the crack being anodic relative to the matrix.⁷⁷ SCC propagation could be monitored, in-situ, and crack propagation was demonstrated to follow paths of anodic Volta potentials, which developed by time at some distance ahead of the crack tip.⁷⁷ Masuda pointed out that the SCC growth rate is related to hydrogen, without, however, providing further explanation or details to the mechanism.

The oxygen concentration in bulk solutions is typically in the order of 7-8 ppm (2.1 - 2.5·10⁻⁴ M) and decreases with temperature and chloride concentration, with the oxygen concentration reducing to ~10⁻⁶ M at 10 M of chloride at room temperature.³⁷ The oxygen content at 50°C and 15 M of chloride would be far lower and, hence, oxygen reduction kinetics in atmospheric corrosion processes of stainless steel are, therefore, rate-determining. The pH within droplets near the metal/electrolyte interface can rapidly reduce to acidic values due to dissolved CO₂ and hydrolysis reactions, favoring cathodic hydrogen evolution reactions.^{25, 26, 85} Moreover, the crack chemistry can be far more acidic and reach pH down to 2-3 where hydrogen evolution reactions then dominate.⁹⁹ The oxygen concentration at the crack tip usually depletes quite rapidly which promotes anodic activities, with the crack wall and crack mouth becoming cathodic sites.⁹⁹ When the crack gets sufficiently long, the IR drop between the crack tip and the free surface where more electrolyte is available, can reach high values, so that the crack tip is practically disconnected from the electrolyte volume.⁹⁹ A site-specific corrosion cell, with

the crack tip forming the anode and the crack walls at some distance behind the crack tip forming the cathode, is established, both favoring metal dissolution at the crack tip and also producing atomic hydrogen near the crack tip at some distance to it at the crack walls.⁹⁹ Regions adjacent to the crack walls, in particular the crack tip, are highly strained (as shown in the EBSD results in Figure 11 and Figure 12), and some of the hydrogen formed can be absorbed into the material and diffuse to the sites with high strain. Most strain is located ahead of the crack tip, often plastic, being attractive sites for trapped hydrogen.

Hydrogen absorption in austenitic structures is very high and is further enhanced in the presence of tensile strains.^{89, 100-103} The velocity of hydrogen diffusion was estimated using Fick's second law, with diffusion coefficients of $2.86 \times 10^{-13} \frac{m^2}{s}$ (at room temperature¹), yielding a diffusion rate of 1 $\mu m/s$.¹⁰⁵ Thus, hydrogen migration through the microstructure is 4-6 orders of magnitude faster than the obtained SCC crack growth rate, indicating that there was time for the hydrogen to reach the crack tip before the crack further advanced. Hydrogen typically reduces the ability to passivate^{90, 91, 106, 107} and also leads to embrittlement⁸⁶, favoring both anodic metal dissolution and mechanical rupture of both the passive film and the bulk material at and ahead of the crack tip.^{89-91, 106, 107} The cracking mechanism, therefore, must have been associated with the support of hydrogen, accelerating SCC propagation. This effect was more apparent for the higher strained condition in our work (0.2% strain), since the crack path was more straight and longer (Figure 6-8, Figure 12).

Hydrogen was also seen to lead to individual cracks, suggesting hydrogen embrittlement acting in parallel to SCC at different sites (Figure 4b,d-g, Figure 8c,d,f, and Figure 9d-f). Numerous parallel-arrayed micro-cracks were seen in the vicinity of the main crack, indicating a HE-related mechanism. These cracks were seen next to the main crack, suggesting that the cracks were formed when the crack propagated to such extent where crack tip and the end of the crack established a corrosion cell, in which the crack walls formed the cathode, producing atomic hydrogen. The corrosion cell is then moving with the crack as the crack propagates. Masuda reported SCC crack growth of washed U-bends which were subjected to atmospheric corrosion under $MgCl_2$ droplets.⁷⁷ The crack was monitored to grow without the presence of residual chloride above the outer surface (surface was washed off), indicating corrosive residues within the cracks which could lead to a continuation of the crack, self-driven and perhaps in an autocatalytic way.⁷⁷ It is therefore very likely that the cracking process was also in our case autocatalytic, which may also explain the similar SCC crack growth rates observed for the different chloride exposure conditions. The chloride deposition density reduces the initiation time for cracking, but should not influence the SCC crack growth rate.⁴⁷ This might explain the similar SCC growth rates observed by Nakayama et al. who used NaCl droplets.⁹⁸

The initial concentration of ferric ions in the droplet was 0.2 M (Table 2), being able to lower the pH to 1 via water hydrolysis reactions, suggesting hydrogen evolution as the prime cathodic reaction under the droplet containing mixed $MgCl_2:FeCl_3$ salt. The corrosion rates can exceed the crack growth rate, and therefore, cracks with shorter lengths were observed on the droplets containing ferric ions. This may further suggest that the cracks observed under the droplet mixed $MgCl_2:FeCl_3$ salt were predominantly superficial and most-likely due to HE or a parallel/synergy act of HE with SCC. SEM and confocal microscopy analysis of the tested specimens after grinding and polishing of the surface did not reveal any deep cracks, clearly supporting this statement (Figure 11 and Figure 12).

¹Diffusion at 50°C is slightly higher¹⁰⁴ (only in decimals higher) and can be considered as practically the same in this context due to the approximated approach.

EAC/SCC is the initiation and subcritical growth of cracks under the simultaneous and synergistic interaction of mechanical stress and an 'electrochemically active' environment.¹⁰⁸ The amount of minimum strain/stress to cause SCC has long been discussed, and applied loads of even 5% of yield were shown to be sufficient to enable SCC, with the temperature rapidly increasing the susceptibility.^{54, 109, 110} Austenitic stainless steels are susceptible to chloride-induced SCC already at low stress, and therefore, a mitigating scheme for SCC would be to control the environment temperature or to inhibit corrosion reactions.^{17, 18, 23, 45} SCC is further facilitated by the magnitude of applied constant load and is basically a matter of time due to creep effects.¹⁰⁸ Sufficiently high crack-tip strain rates can occur also under global static loading conditions that can lead to rapid failure.¹⁰⁸

In this work, it was shown that 0.1% global-static elastic strain is sufficient to promote SCC under atmospheric corrosion exposure conditions with 14.5 $\mu\text{g}/\text{cm}^2$ of chloride. However, neither cracking nor corrosion was observed under the deposit with 1.5 $\mu\text{g}/\text{cm}^2$ of chloride for both loading conditions (0.1% and 0.2% constant loads), clearly demonstrating the effect of corrosion chemistry on the SCC. SCC requires the simultaneous action of corrosion reactions to enable stable crack growth, which apparently can be mitigated if pitting or crevice corrosion can be inhibited or retarded.¹⁰⁸ So, the amenability of 304L austenitic stainless steel to corrosion is decisive whether SCC can be initiated. Strain can accelerate both corrosion and the initiation time to SCC.^{45, 108} Therefore, more harsh cracks were observed under 0.2% applied load. SCC further requires local plastic deformation which explains the strain/stress threshold under which SCC has been argued as practically not to occur. However, the threshold strain/stress may be very low, and it can be reached when corrosion has propagated to such extent where the effective stress increases due to reduction of load bearing area.^{94, 111-113} The microstructure under static-elastic strain is globally elastic but the geometry and morphology of localized corrosion sites typically act as stress concentrator which can cause micro-plastic deformation, facilitating SCC. Above the threshold stress and temperature for SCC, cracking becomes a matter of time irrespective of the magnitude of stress acting on the material. However, more stress will facilitate and accelerate the initiation time for SCC events (cracks can stop and arrest for a while and then be re-activated which all may not occur if the applied stress is very high).¹⁰⁸ Therefore, accelerated and more severe SCC was observed on the sample loaded to 0.2% strain.

Summary and implications

The test results have shown that the crack growth kinetics can by far exceed pit growth kinetics, and that SCC is the life-determining factor for type 304 austenitic stainless steel, with strains as low as 0.1% sufficient to cause service life-threatening cracking. SCC was shown to form with chloride deposition densities as low as 14.5 $\mu\text{g}/\text{cm}^2$ at low uniaxial loads, which has not been reported before. Moreover, hydrogen was also shown to play a key role in the SCC process, accelerating SCC, leading to HE, and also favoring localized corrosion reactions. SCC kinetics at room temperature are generally slower than at 50°C. The work has shown that it has utmost importance to prioritize schemes to mitigate SCC and to consider hydrogen when modelling work is carried out. Furthermore, the predictive models using pits as the precursor of SCC/HE need to be revisited and should regard crevice corrosion. There is also need for a thorough investigation with improved control over stress distribution on the susceptibility to AISCC.

The work has also shown the complexity of atmospheric corrosion processes occurring under magnesium chloride deposits which can largely differ when the initial droplet chemistry is

different (such as containing ferric ions). The droplet chemistry will be changing during corrosion of alloys due to different dissolution kinetics of alloying elements, and new compounds with varying solubility are likely to be formed. The experiments may have resulted in different corrosion scenarios when seawater had been used. The compounds in the electrolyte of sweater (strictly speaking also in the droplets used in this work due to dissolved elements during corrosion) have different DRH, and dry compounds, such as NaCl at low RH (<72 % RH)²⁹, can act as crevice formers which can accelerate corrosion and possibly also cracking events. The droplet size, cycling humidity and/or temperature effects, and micro-organisms can further complicate the matter.^{29, 61, 62, 67, 114, 115} Atmospheric corrosion requires careful consideration of all factors contributing to corrosion/cracking events which should be kept in mind for simulative models for long-term life-time predictions of structural components such as ILW container canisters.

Conclusions

1. AISCC occurred at chloride deposition densities as low as 14.5 µg/cm² under elastic (0.1%) and elastic/plastic (0.2%) strain.
2. AISCC growth rates were in the order of 10⁻¹⁰-10⁻¹² m/s for all conditions.
3. The chloride deposition density accelerated corrosion and SCC.
4. Hydrogen is believed to support the SCC process, and led to superficial, parallel-arrayed cracks due to hydrogen embrittlement.
5. Ferric ions can accelerate corrosion but seemingly reduce the amenability to SCC.
6. Strain increased the contribution effect of hydrogen to SCC.

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Tables

Table 1: Chemical composition of the used type 304 (UNS S30400) austenitic stainless steel (in weight-%).

Cr	Ni	Mn	Si	C	N	P	S
18.15	8.6	1.38	0.45	0.055	0.038	0.032	0.005

Table 2: Droplets used for corrosion tests.

No.	Concentration [mol]	Salt	Droplet Volume [μ l]	Droplet Diameter [mm]	Deposition Density of Cl^- [$\mu\text{g}/\text{cm}^2$]
1	0.001	MgCl_2	0.5	1.76	1.5
2	0.01	MgCl_2	0.5	1.76	14.5
3	0.035	MgCl_2	0.5	1.76	50.7
4	0.1	MgCl_2	0.5	1.76	145
5	1	MgCl_2	0.5	1.76	1449.8
6	0.2	1 MgCl_2 : 0.68 FeCl_3	0.5	1.76	434.9

Table 3: Observed maximum crack length and calculated crack growth kinetics.

No.	Deposition Density of Cl^- [$\mu\text{g}/\text{cm}^2$]	Low strain (0.1%)		Low strain (0.2%)	
		Longest SCC Crack Observed [μm]	Calculated Crack Growth Rate* [m/s]	Longest SCC Crack Observed [μm]	Calculated Crack Growth Rate [m/s]*
1	1.5	-	-	-	-
2	14.5	400	$2.6 \cdot 10^{-11}$	-	-
3	50.7	2341	$1.5 \cdot 10^{-10}$	3000	$1.9 \cdot 10^{-10}$
4	145	2597	$1.7 \cdot 10^{-10}$	3000	$1.9 \cdot 10^{-10}$
5	1449.8	2800	$1.8 \cdot 10^{-10}$	3000	$1.9 \cdot 10^{-10}$
6	434.9	50	$3.2 \cdot 10^{-12}$	500	$3.2 \cdot 10^{-11}$

*only surface cracks were considered

Figures

Figure 1: Photograph of the tensile rig used for the AISCC tests.

Figure 2: EBSD analysis of the as-received microstructure: (a) IPF Z color map, (b) boundary map showing twins (thick red lines) and high angle grain boundaries (thin black), (c) LMO map.

Figure 3: Stereoscopic images of the deposited areas with salt-laden droplets on the steel, being strained to 0.1% constant load, with chloride deposition densities of: (a) $1.5 \mu\text{g}/\text{cm}^2$, (b) $14.5 \mu\text{g}/\text{cm}^2$, (c) $50.7 \mu\text{g}/\text{cm}^2$, (d) $145 \mu\text{g}/\text{cm}^2$, (e) $1449.8 \mu\text{g}/\text{cm}^2$, (f) $434.9 \mu\text{g}/\text{cm}^2$. Note the cracks which advanced beyond the deposited area. Loading direction was to the horizontal of the images.

Figure 4: SEM analysis of sample exposed to 1449.8 $\mu\text{g}/\text{cm}^2$ chloride (droplet 5) and strained to 0.1% constant load: (a) macroscopic view of a longest SCC crack, (b) numerous parallel-arrayed cracks formed on crevice corrosion sites located adjacent to the main crack shown in (a), (c) crevice-like localized corrosion region showing slip plane facets but not SCC, (d) a corrosion pit with an SCC crack at the center of the pit bottom and some cracks situating next to each other, (e) several cracks, (f) numerous parallel-arrayed cracks with high density, (g) numerous parallel-arrayed cracks formed adjacent to the (blunt) crack tip. Loading direction was to the horizontal of the images.

Figure 5: SEM analysis of the sample exposed to 434.9 $\mu\text{g}/\text{cm}^2$ chloride with ferric ions (droplet 6) and loaded to a constant load of 0.1%: (a) showing some localized corrosion sites at the periphery at the deposited area, (b-d) showing pits with a whirlpool shape, (e) showing perforation/de-alloying morphology at the pit bottom (center of the whirlpool) with a crack formed on the pit mouth, (f) inter- and transgranular SCC cracks on a crevice corrosion site. The loading direction was to the horizontal of the images.

Figure 6: Stereoscopic images of the deposited areas with salt-laden droplets on the steel, being strained to 0.2% constant load, with chloride deposition densities of: (a) $1.5 \mu\text{g}/\text{cm}^2$, (b) $14.5 \mu\text{g}/\text{cm}^2$, (c) $50.7 \mu\text{g}/\text{cm}^2$, (d) $145 \mu\text{g}/\text{cm}^2$ (left) and $1449.8 \mu\text{g}/\text{cm}^2$ (right), (e) $434.9 \mu\text{g}/\text{cm}^2$ with ferric chloride. Note the cracks advancing beyond the deposited area. The loading direction was to the horizontal of the images.

Figure 7: SEM analysis of the sample exposed to $50.7 \mu\text{g}/\text{cm}^2$ chloride (droplet 3) and loaded with 0.2% of constant strain: (a) Large deformation sites around a stopped/blunt crack, (b) crack walls of the longest crack showing diverted cracks being parallel to the loading direction, (c,d) slip lines jutting out the surface next to the crack tip. The loading direction was to the horizontal of the images.

Figure 8: SEM images of the sample exposed to 1449.8 $\mu\text{g}/\text{cm}^2$ chloride (droplet 5) and loaded with 0.2% of constant strain: (a) a crack connected underneath the surface, (b) a crack region showing crack opening of up 100 μm showing also displacement of the disconnected surfaces in z direction, (c,d) multiple cracks formed next to each other, (e) magnified view of the center of the image in (a), (f) a crevice-like corrosion pit showing attack along slip lines. The loading direction was to the horizontal of the images.

Figure 9: SEM images of the sample exposed to 434.9 $\mu\text{g}/\text{cm}^2$ chloride with ferric ions (droplet 6) and loaded with 0.2% of constant strain: (a) numerous nano-pits formed in closest vicinity, (c, b) corrosion pits where cracks initiated from which were oriented 30-45° degree to the loading direction, (d,e) preferential attack on slip lines, (f) numerous nano-crack formed with high density in a localized corrosion site. The loading direction was to the horizontal of the images.

Figure 10: Summary of AISCC measurements showing the observed maximum crack length as a function of chloride deposition density and strain.

Figure 11: Confocal (topography) microscopy and EBSD analysis performed on the cracks observed under droplet 3 with 50.7 μg/cm² of chloride after grinding and polishing of the surface down to OPS finish. The cracks were seen to have bifurcated nature. Strain localization on the crack walls were detected to be associated with high density of LAGB's and large LMO variation. The phase map shows both LAGB's and HAGB's (black lines).

Figure 12: Confocal (topography) microscopy and EBSD analysis performed on the cracks observed under droplet 4 with $145 \mu\text{g}/\text{cm}^2$ of chloride after grinding and polishing of the surface down to OPS finish. The cracks were seen to have bifurcated nature. Strain localization on the crack walls were detected to be associated with high density of LAGB's and large LMO variation. The phase map shows HAGB's (black lines) and delta ferrite (red).