The effect of prior cold work on the chloride stress corrosion cracking of 304L austenitic stainless steel under atmospheric conditions

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Abstract

A systematic study of the effect of cold work (CW) on chloride-induced stress corrosion cracking (SCC) in 304L stainless steel was made. CW between 0 and 40% was applied prior to corrosion of specimens at 75°C and 70% relative humidity, for 500 hours, using MgCl₂ (at atmospheric pressure). Samples cracked most readily between 0.5-5% CW; at 20% and above no cracks were present. Additionally, above 5 % CW, some specific orientation relationships become evident, with cracks primarily aligned along <111> parallel to the transverse direction. The results suggest that at levels of CW >20%, the synergistic effect of micro-mechanisms may hinder SCC in this system.

1. Introduction

Stress corrosion cracking (SCC) is a common, often dramatic failure mode for many different alloy systems [1]. SCC occurs *via* a combination of three critical factors: a tensile stress (which can be applied and/or residual), a specific corrosive environment and a susceptible material [2,3]. SCC cracks are typically very sharp (1-100 nm at the crack tip), and can cause catastrophic pseudo-brittle failure of an otherwise ductile metal [4]. In the case of 304L austenitic stainless steel (ASS) one of the most aggressive chemical species is the chloride ion, Cl⁻, and cracks propagate most often by a transgranular path (TGSCC), rather than an intergranular path (IGSCC), which is more common in ASS with higher C content (~0.08 wt%) [5,6]. Cl-induced SCC is problematic as 304L ASS is widely used as piping material for the primary cooling circuit within a nuclear power plant (NPP), as well as material for canisters used for dry cask storage of spent nuclear fuel ('interim storage') [5,7,8]. Furthermore, both the storage and plant sites are often located close to marine environments, exposing them to a mixture of chloride and sulphate salts. Considering that NPP and canisters for spent fuel storage must survive for an extended period of time (at least 40 years), in potentially aggressive atmospheric conditions ([5], it is critical to fully understand the SCC resistance of these materials. It is worth noting that dry storage containers, for nuclear fuel, are usually in contact with the atmosphere, without any filtering of the sea air [8–11]. The temperatures will also slowly change during their design lives as the decay heat from the fuel exponentially decays [9,12]. The containers surfaces will be reasonably hot at the start of life (~100 °C) [10,12], and, considering the typical burn-up of a LWR and its decay heat, transition through all temperatures until reaching temperatures of ~40°C at 100 years [13]. As the temperature decreases below 100 °C, progressively more salt will be able to deposit on the cask surface and the potential for SCC will arise [14].

Until the late 1990s it was commonly assumed that the applied stress, in addition to the residual stresses, required for SCC to take place had to be relatively high, around the alloy yield stress [3,15]. However, more recent work has shown that the level of applied tensile stress required for crack initiation and propagation was far lower than what was originally believed - requiring only about half of the yield stress [5]. Furthermore, it was suggested by Spencer *et al.* that an applied tensile stress threshold may actually be even lower than previously envisaged, as low as 10 MPa in the presence of

cold work (CW) [16]. This could be due to the heterogeneous distribution of stresses at a micro level, created when the material is plastically deformed [17,18].

It has also been suggested in many studies that very high levels of applied tensile stress (i.e. > yield stress) may decrease the crack initiation time and increase the number of cracks [3,19]. There is good evidence that between K_{IAEC} (crack initiation threshold) and K_{IC} (final fracture) the crack growth rate is practically constant [20], as shown schematically in Fig. 1. The presence of cracks changes the stress field locally, reducing the stress either side of the crack [21]. This means that a minimum distance must be present between cracks, before the stress again reaches a level where cracking is possible, and therefore high levels of applied tensile stress won't necessarily cause higher crack density. In fact it is questionable if tensile stress alone, once an electrochemical attack is established, is the driving force for SCC or whether it is the crack tip stress intensity that is the most important parameter. Furthermore, Jivkov *et al.* questioned the *existence* of a true threshold stress intensity value, and suggested that *any* level of stress intensity can cause SCC. The phenomenon will simply occur over a longer period of time, provided the crack growth rate is higher than general corrosion [22]. In other words, once the three conditions for SCC are met cracking will occur, although the kinetics may be very slow and time to rupture might be 30 or more years [5].

1

Fig. 1. The three stages of environment assisted crack growth under sustained loading with increasing stress intensity [20].

Understanding SCC is challenging because of the many factors affecting it: chemistry, applied stress and alloy microstructure. Within the microstructure it is likely that a prominent role is played by micro residual stresses caused by prior CW [23–26]. There is evidence that CW alone could be enough to cause SCC, even without applied tensile stress, as some form of CW has been observed in all SCC studies, for both IGSCC and TGSCC in ASS [5]. It has also been observed that pipes in the cooling system of reactors only fail in the presence of CW [3,5,15]. CW has always been deemed detrimental, and increasingly so as more CW is introduced into the sample [27]. However, early reports were not necessarily in agreement with this hypothesis. When it was found that samples subjected to very high levels of CW (>40% CW) did not crack, further investigation was suggested but, to our knowledge, rarely carried out [28]. One of the factors that could affect crack resistance could be the presence of coincident site lattice (CSL) boundaries, in particular $\Sigma 3$ [29,30]. CSL boundaries have been proven to have a beneficial effect when it comes to SCC, especially in the case

of IGSCC. These boundaries could have a beneficial effect for TGSCC too, as they can be energetically unfavourable for crack propagation [3,31]. Another important role of microstructures of ASS is played by martensite in SCC. Martensite (ϵ or α') because they are hard and brittle phases have been considered detrimental factors in SCC as hard/brittle phases normally reduce the resistance of material to crack propagation [32,33]. On the other hand, it has been suggested by some authors that the deformation induced α' martensite phase may increase the resistance to SCC [6]. They propose that when enough deformation induced martensite is created, through CW, that α' may cathodically protect the austenitic phase [6]. In this work the role of CW in SCC has been studied along with the microstructural factors that may impede or enhance SCC, such as CSL boundaries or α' martensite.

CW is usually introduced as part of the manufacturing process, but also during the fitting, through processes such as: welding; geometrical constraints and surface finish (grinding and machining) [23,26,34]. Furthermore, CW affects all stages of cracking, from pitting and crack initiation, to crack propagation [2,3,5,26,35–37]. However, despite efforts, there is still paucity of data on the role of CW, and often in published studies only a few CW levels are chosen and conclusions are drawn without enough data to determine a relationship. Therefore, the aim of this work is to systematically assess the role of CW, from 0% CW samples, to a high level of CW of 40%, which is quite close to the UTS of the material used (55%), paying particular attention to the role of microstructure. The CW was applied by placing the samples in uniaxial tension before unloading them. A bend geometry, mimicking a 4-point-beam-bending, was subsequently used to apply a tensile stress to the samples top surface [38,39]. Tests were performed in a controlled environment, at a constant temperature (75 °C) and a controlled relative humidity (RH) of 70%, for 500 hours. An applied stress level of 60 MPa, well above the threshold values suggested by Spencer *et al.*, was chosen in order to ensure cracking and to enable feasible testing time [16]. Factors investigated were: crack density; favoured crack orientation; role of special grain boundaries; crack deviations per crack length and *bcc* phase content. Secondly, the role of applied stress (from 60-180 MPa), on SCC susceptibility was investigated for a fixed level of CW (chosen at 10% CW following the preliminary experiments) using indicators such as crack density.

2. Experimental

The material used in this work was standard 304L ASS, complying with BS EN 10008-2-2005 requirements for grade 1.4307 (304L), provided in 1 mm thick sheets. The material was provided in the hot rolled condition. In the as-received condition the steel had a room temperature 0.2% proof stress of 344 MPa, a tensile strength of 663 MPa, an elongation to failure of 55% [16]. The composition used is provided in Table1.

Table 1. 304L steel composition (wt%).

	C	Cr	Mn	Ni	P	S	Si	Co	Cu	Fe
304L	0.022	18.19	1.23	8.35	0.034	0.004	0.25	0.152	0.078	Bal.

All samples were machined into rectangular section dog-bone samples by electro-discharge machining (EDM). A schematic of the dog-bone samples is shown in Fig. 2. The samples were stress-relieved at 900 °C for 30 minutes under a nitrogen or argon atmosphere and quenched in water in order to relieve manufacturing stresses, as well as any stresses introduced by EDM that may affect the results [16]. This stress relief heat treatment was carefully chosen in order to avoid the creation of intermetallic phases (specifically sigma phase), and abnormal grain growth in the austenitic phase

[40,41] and therefore preserve the rolled sheet grain microstructure. The yield stress, after stress relief, was measured to be 210 MPa. The Vickers micro-hardness of the as-received material was also measured before and after stress relief was applied to the specimens. Hardness was measured on a total of 12 samples, (10 N load was applied for 10 s) and each sample was indented five times (pre and post stress relief) and the mean and standard deviation were calculated. Post stress-relief the 12 samples were then uniaxially prestrained in a tensile machine, at room temperature, to seven different levels of CW of 0.5%, 1%, 2%, 5%, 10%, 20% and 40%. The pre-strained samples were then subjected to the equivalent of 4-point-beam bending test, to produce an applied stress on the top surface of the samples. For the majority of the samples tested this was 60 MPa. The bend jigs were then placed in a controlled environment at $75^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$ at $70\% \text{ RH} \pm 2\%$, for 500 hours [16]. A Perspex box in a furnace was used for the test. The RH inside the chamber was ensured using a beaker with a super-saturated solution of NaCl in water [16]. The temperature and RH inside the chamber were monitored using a data logger.

Fig. 2. Schematic representation of the dog-bone specimens employed in this work; all dimensions in mm.

The samples were inspected once every 3 to 5 days. Once the test was terminated the samples were cut using a diamond saw at the lowest feed rate of 0.05 mm/min to avoid the introduction of further residual stresses. The samples were subjected to standard metallographic preparation using SiC up to 4000 grit paper. A colloidal silica suspension, oxidised porous silicon (OPS) finish was applied for the polishing. A final polishing step was introduced using a VibroMet2 machine, for an average of 8 hours, once again using OPS. This is a very gentle polish that provides a finish that ensures the removal of additional stresses induced during the cutting and grinding process. This level of surface finish was required to achieve a high level of indexing when using electron back scattered diffraction (EBSD) analysis.

Optical characterisation of the samples surfaces was carried out on a total of 25 samples using an Olympus – BXS1 optical microscope. A range of magnifications available were used, namely 25x, 100x, 200x, 500x, and 1000x. The lowest magnification set-up was used to record and reconstruct the morphology of the main cracks. All cracks, on all samples, were recorded and analysed. It is worth noting that an average of three samples per CW level was used. Once the number of crack deviations was established, for each crack, it was then normalised by the crack length. All samples were analysed with the same magnification in order to have the same reference frame of analysis. Several pictures per sample were taken and later stitched together using image editing software (ImageJ).

The same analysis on changes in crack patterns was carried out using EBSD by a system attached to a field emission gun scanning electron microscope (FEGSEM). The EBSD analysis was designed to capture as much information and detail as possible, including measurements of phase fractions, grain size, grain orientation compared to cracks and to study crack tips. The number of *bcc* phase grains intersected by cracks, in the range of CW from 0.5% to 10%, was recorded. As was the number of times a crack changed its trajectory. Local orientations for all CW levels were then measured by

EBSD and maps were specifically collected from regions with cracks for comparison to those, on the same specimen, that were without cracks. All of these results were collected from the transverse direction (TD) – rolling direction (RD) plane of the rolled sheet, as illustrated in Fig. 3. An Auriga Zeiss FEGSEM was used for analysis. The acceleration voltage used ranged from 1.5 keV to 20 keV, with 20 keV used for EBSD characterisation. The software used for EBSD data analysis was Bruker Esprit 1.9, which was used for phase identification and grain size measurements. The phases observed were mainly the *fcc* austenitic phase, and lower percentage of *bcc* phases. Step size and map size were kept fixed, for ease of comparison, at 0.2 μm and 700 x 500 pixels respectively. The indexing average for all the 83 maps collected across all samples was kept over 85%.

Fig. 3. RD is parallel to the X sample direction, while TD), along which cracks propagate on the top surface, is parallel to the Y sample direction. The Z sample direction goes through the sample thickness. The MgCl₂ was applied to the TD-RD plane.

3. Results & Discussion

3.1 Effect of CW and applied stress levels

Fig. 4a) shows the average crack density as a function of CW level at a fixed value of applied stress of 60 MPa. From the data it can be seen that the number of cracks increases markedly with CW with a peak at 0.5% it then decreases steadily with additional CW. However, interestingly, there are no cracks observed for samples that have been exposed to $\geq 20\%$ CW. This shows that CW has a significant effect on cracking at low to medium amounts of CW, clearly accelerating the process, whilst from the 20% and above it appears, in these experiments, to completely suppress the process, at least within the time of testing of 500 h. This does not agree with the majority of the literature that has proposed a direct correlation between increase in CW level and increased crack density [5,27,29,42].

The effect of applied tensile stress is shown in Fig. 4b) where the amount of CW was kept constant at 10%. In comparison with CW, the effect of applied tensile stress appears to show very little relation to crack density. This means that even for quite low applied tensile stress values, SCC can be observed in the presence of CW, this is in agreement with some previous work [5,16]. However, it does not explain the difference between the effect of CW and applied tensile stress. This might arise due to the applied tensile stress producing a more homogeneous stress state across the sample, while the CW produces plastic deformations and local residual stresses, which will not necessarily be homogeneous, and in the case of the early stages of plasticity are likely to be concentrated on particular grains and thus in specific local regions [18,43,44]. However, as CW increases, the plasticity is likely to become more homogenous reducing the magnitude of stress variations from grain to grain. As far as we know these plasticity concentrations, followed by saturation, have not been previously investigated in 304L ASS but they have been observed in copper by HR-EBS

[18,43–45] and in that case resulted in local stresses as high as 100 MPa, prior to saturation [18]. The heterogeneous stress state is due to the plastic deformation process that materials with low stacking fault energy, such as ASS [46], undergo. As plastic deformation is introduced into ASS, the planar dislocation structure evolves into stacking faults [6,47–49]. As more deformation is induced, the stacking faults form a cell structure.

Fig. 4. a) Plot of crack density against CW. Number of cracks has been normalised by the surface areas of the samples and shown with error bars of standard deviation. Crack density is a maximum at 0.5% CW and highest in the range 0.5 to 5%. No cracks were observed at more than 20% CW. (b) Crack density was measured with respect to applied tensile stress and shown with standard deviation error bars. No significant change in the crack density was observed with increasing applied stress. The CW level for all the applied stresses was 10%.

Cell walls differ from grain boundaries as they exhibit lower misorientation and a different morphology [50]. At low strain, these cell structures are rather heterogeneous, but as further deformation is introduced into the material, a much more uniform distribution of dislocations is observed [6,47–49]. It has also been reported that in low stacking fault energy materials, the deformation process/formation of cell structure, is accompanied by the formation of deformation induced martensite, first as ϵ martensite and then as α' martensite [6,47].

In summary it is suggested that it is the *heterogeneous* stress state, created by low levels of plastic strain, not the globally applied stress, which is critical to the increase in the crack density observed.

3.2 *bcc* phases

One of the features studied with EBSD was the presence of *bcc* phases. It is hard to distinguish between the different *bcc* phases, such as δ ferrite, α ferrite and α' martensite phase by EBSD. The manufacturing history and chemical composition of the samples normally produces a very small percentage of δ ferrite [40,51]. Whilst it is difficult to assess which *bcc* phase is present in the 0% CW samples, it can be assumed that any increases in *bcc* phase, that are measured in samples with higher CW levels, cannot be α or δ ferrite and will most likely be due to increases in stress induced α' martensite [6,47,51]. We note that, it has been suggested in the literature that large volumes of martensite may cathodically protect the austenitic phase [6] inhibiting SCC.

Fig. 6 shows phase maps of three different CW levels, with the austenite phase shown in green, while the *bcc* phase is shown in red. Fig. 6a) and Fig. 6b) show examples of cracked areas of 0.5% and 5% CW samples respectively. Fig. 6c) shows an example of a 40% CW sample. In the 5% CW sample, shown in Fig. 6b), some of the *bcc* grains seem to be aligned along the rolling direction, which suggests they are δ ferrite grains due to the manufacturing process (hot rolling). This is further confirmed by Fig. 6c). Fig. 6c), the 40% CW sample, exhibits a large fraction of *bcc* grains, the majority of which are not aligned along the rolling direction but along the transverse direction. Samples subjected to 40% CW didn't exhibit cracking, and therefore the formation of *bcc* grains, cannot be linked with crack growth. These observations suggest that α' martensite was produced by the uniaxially applied plastic strain, rather than as a result of crack growth or manufacturing history. The *bcc* phase fraction present was measured over the whole CW range of 0 to 40% CW. It is noted, that the remaining majority phase found was austenite (very little *hcp* ϵ martensite could be detected on any of the samples, typically <1%). We also did not detect any MnS particles in the maps collected. Fig. 5 shows the results from bulk areas on the TD-RD plane, which have no cracks, compared to mapped regions that contained cracks. The *bcc* phase percentage measured on the crack-free areas was below 10%, for up to 20% CW, before increasing markedly at 40% CW. The *bcc* phase measured on the cracked areas was much higher, ranging from 10% at 0.5% CW to 33% at 10% CW.

It can be assumed that the large increases in *bcc* phase measured in highly CW samples, over the 0% CW, sample were due to formation of α' martensite [40,51]. Furthermore, this would suggest that either the cracks preferentially propagate into areas containing α' martensite [52,53], or that the crack initiates first and then the transformation due to the local stress follows.

The role of martensite in the Cl-induced SCC is only a marginal influence and not crucial in crack propagation. If the martensite were playing a key role in Cl-induced SCC, of ASS, the crack density might be expected to continue to increase for high levels of CW where the highest martensite content was observed. This is clearly not observed (see Fig. 4a)).

In summary it appears that α' martensite plays little or no role in exacerbating SCC in cold worked 304L stainless steels in a chloride containing environment.

Fig. 5. The percentage of bcc phase and austenite as measured over the whole CW range of 0% to 40%. Error bars show standard deviation. Note the standard deviation is smaller than the data points shown.

3.3 Effect of grain size

Fig. 7 shows that the average grain size decreases with increasing percentage of CW. There was some scatter at the lower range of the CW, namely between 0 and 5% CW. Between 0 and 5% CW the measured average grain size was in the range of 9.3 to 14.9 μm . However, the standard error of these data was only $\pm 1 \mu\text{m}$. From 5% to 40% CW the average grain size decreases to 6.1 μm . It must be noted that the grain size was measured using EBSD. As a consequence the diminished grain size with increased CW may be due to the increased presence of twins and martensite. From the hardness tests carried out, before and after stress relief, average H_V values have been obtained. The mean H_V decreases by 113 H_V . The average pre-stress relief hardness was 285.7 H_V (standard deviation of 6.1 H_V) and the average post-stress relief hardness was 172.7 H_V (standard deviation of 2.7 H_V). This shows that the heat-treatment has removed the internal stress and is unlikely to have induced any hard intermetallic phases [40]. The difference observed in hardness, and thus in yield stress, shows that the material is not in an annealed state when-supplied, but contains residual stress from the manufacturing process. However, such a marked decrease in hardness is probably due to the combination of relief of residual stress and recovery of the material.

Fig. 6. Maps obtained with EBSD, with red as bcc phase and green as austenite. (a) shows a crack running through an area investigated in a 0.5% CW sample. (b) shows a thin bifurcating crack (indicated by arrows) running through the investigated area in a 5% CW sample. The black arrows indicate bcc grains aligned along RD. (c) shows a 40% CW sample map exhibiting a large number of bcc grains, which are mostly aligned along TD.

3.4 Crack path analysis

Fig. 8 shows the number of times a crack changes trajectory, as measured from optical micrographs. The number of crack deviations was established for each crack observed and normalised by the crack length. An increase in number of deviations from the main path with CW was observed, but only for low levels of CW below 5%, followed by a plateau after 5% CW. The number of changes in trajectory of the cracks is linked to the energy associated to the crack propagation process. Cracks paths are conditioned by the lowest energy path available. A deviation from the original trajectory usually corresponds to the presence of either an obstacle or conversely a more energetically favourable path. Fig. 9 shows the average number of changes in direction from the main path, per CW level at higher magnification, as observed using a FEGSEM. Note that Fig. 9 has a smaller length scale than the data presented in Fig. 8 (mm and μm respectively). Fig. 8 and Fig. 9 show that even at different magnifications, the cracks exhibit a similar behaviour, although standard deviations in Fig. 9 overlap more making it more difficult to see a conclusive trend. The values for the 2% CW data are slightly lower than 1, 5 and 10% CW values, but still in line with the errors observed. The increase in crack path deviations at higher levels of CW could be linked to the more homogeneous stress distribution. The dominant effect of martensite seems to depend on the concentration: at low percentage, martensite presents its role as a hard phase and therefore a path for crack propagation dominates; as more stress induced martensite is created [47], the cathodic protection of the austenitic phase dominates. At a microstructural level, it becomes less probable to encounter areas with so-called soft and hard grains next to each other [18,43,44], i.e. areas of potentially high micro-residual stresses and therefore areas that are typically prone to easier crack propagation. This possibly explains why cracks

are more likely to deviate as CW increases, eventually plateauing when the deformation within the grains is closer to homogeneous. (Note: Soft and hard grains are defined here as grains that were favourable (soft) and unfavourable (hard), for slip under the applied uniaxial plastic pre-strain.)

Fig. 7. Average grain size versus CW showing decrease in grain size with increasing CW. The typical standard deviation is within $\pm 1\mu\text{m}$.

3.5 Role of special grain boundaries

CSL boundaries, in particularly $\Sigma 3$ boundaries, are well known for their corrosion resistance, especially for IGSCC [31,54–56]. $\Sigma 3$ grain boundaries are generated upon deformation, such as uniaxial straining. Their beneficial presence can be maximised through grain boundary engineering, by following a well-defined thermomechanical route [57]. It has been reported that CSL boundaries can inhibit crack nucleation [54], and further crack propagation through crack bridging [22,58]. It is possible that CSL could play a role in obstructing the SCC process for TG cracks too [24,29]. Aside from impeding crack nucleation, as a crack is crossing a grain boundary, a more corrosion resistant grain boundary, such as $\Sigma 3$, may require more energy to be crossed, and therefore retard crack propagation. In this work it was observed that crack density diminishes with increasing CW. The role of CSL boundaries was investigated in relationship to CW and compared to crack density. If the decrease in crack density was linked to $\Sigma 3$ boundaries, their fraction should increase with increasing CW. Fig. 10 shows the distribution of $\Sigma 3$ boundaries with respect to CW level. A bi-modal behaviour emerges whereby the fraction of $\Sigma 3$ boundaries was higher for low levels of CW decreasing to a constant value, within error, for 10% CW or greater. The decrease in fraction of $\Sigma 3$ boundaries with increasing CW indicated that these special boundaries, at least within the conditions of this experimental work, do not improve the resistance to SCC of 304L.

In summary, Fig. 10 shows that CSL are either not relevant, or that CW plays a more prominent role.

Fig. 8. Number of cracks deviations along crack paths, as recorded for all samples and CW levels between 0.5% and 10% CW, normalised by crack length and shown with standard deviation error bars. Measurements were taken from optical micrographs.

Fig. 9. Number of crack deviations along crack paths, normalised by crack length, measured for all samples and CW levels between 0.5% and 10% CW, shown with standard deviation error bars. Measurements were taken from FEG-SEM images.

Fig. 10. The length of $\Sigma 3$ boundaries was measured by analysing EBSD maps. Their fraction was compared for each CW level, shown with standard deviation error bars.

3.6 Role of texture and alignment of grains to crack paths

Fig. 11 shows an example of the evolution of the texture strength, i.e. preferential orientation, using pole figure analysis. Fig. 11a) shows the texture strength of 0.5% CW sample, whilst Fig. 11b) shows the texture strength of a 40% CW sample. The comparison shows a higher degree of preferred orientation in the more heavily CW sample. More detailed analysis using EBSD, of the orientations of all the grains intersected by a crack, or adjacent to a crack, have been recorded for both primary cracks and branches of cracks, and compared to the orientation observed in bulk (uncracked) areas. Fig.12 shows a slight increase in preferred direction with CW in bulk (uncracked) areas, as would be expected due to the increased texture from increasing uniaxial strain. However, for cracked areas, whilst a large scatter was observed, a trend was visible. For well-established cracks, Fig. 13a) shows the three main crystal directions parallel to the TD sample direction. TD was chosen as sample direction, because this was parallel to the surface crack growth direction, due to the applied stress (see Fig. 3). Fig. 13a) shows that at the higher end of the CW range there was a clear difference between the favoured directions. The $\langle 111 \rangle$ direction shows a clear separation from the $\langle 110 \rangle$ and $\langle 100 \rangle$, which both show a similar likelihood of occurring. As CW decreases this preference for $\langle 111 \rangle$ diminishes. The $\langle 100 \rangle$ on the contrary decreases with increasing CW while $\langle 110 \rangle$ remains more or less constant as the least probable direction (see Fig. 13b).

Fig. 11. Pole figures show the texture strength of different levels of applied CW. (a) shows the texture strength of a 0.5% CW sample, while (b) shows the texture strength of a 40% CW sample. Red colour indicates very common orientation while dark blue indicates lack of orientation.

Fig. 12. EBSD texture measurements made on bulk material on the TD-RD plane for increasing levels of CW. Error bars show standard deviation.

Fig. 13. EBSD texture measurements made on regions containing cracks, from the TD-RD top surface plane, for increasing levels of CW. Error bars show standard deviation. (a) The crystal directions parallel to the crack are shown for well-established (primary) cracks. (b) The crystal directions parallel to the crack are shown for crack branches.

Crack branching was also a commonly observed feature and different morphologies of branching have been observed. Some were characterised by branches with alternating patterns while keeping an overall straight propagation direction (zig-zagged pattern), whilst some branches were very straight, depending on the stage of the crack propagation, *i.e.* early onset or more mature branching. The crack branches have been associated with a specific form of crack propagation, characterised by oxidised deformation bands, also called oxide fingers [3,59,60].

They were therefore extensively recorded and analysed in this work. Fig. 14a) shows an example of these branching cracks along with an inverse pole figure (IPF) map of the area analysed. Fig. 14b) presents an IPF map of the preferred crack growth directions, parallel to the sample TD direction, obtained by indexing individual grains around the crack branches. It was found that straight branches have a slightly higher preference to grow along $\langle 111 \rangle$, unlike zig-zag patterned branching cracks, and also slightly more than well-established cracks. Fig. 13b) shows that at least 40% of total grains intersected by, and/or neighbouring a crack branch, are aligned along the $\langle 111 \rangle$ as similarly seen by Lozano-Perez *et al.* [60]. For this straight crack branch, the percentage of $\langle 111 \rangle$ increases with CW to over 60% at 10% CW, with a mean value slightly higher than in Fig. 13a), although with a larger standard deviation. The pattern for the $\langle 110 \rangle$ direction was less clear but $\langle 100 \rangle$ decreases with increasing CW to a mean value of only 8%.

Fig. 14. a) Secondary electron image of a 0.5% CW sample, showing straight crack branch morphology. (b) Inverse pole figure map of crystal directions parallel the TD sample direction for individual grains around the crack branches.

In summary, this suggests that Cl-induced SCC of 304L ASS may be related to CW through the $\langle 111 \rangle$ slip direction, which becomes more prominent with increasing amount of CW, but further work is required to fully validate this.

3.7 Summary discussion

The work presented here has shown that the level of CW is the most important feature in determining the overall Cl-induced SCC response of 304L ASS and that the worst case scenario is at a level of around 0.5 to 2% CW. The applied stress appears to be almost inconsequential from 60 to 180 MPa on crack densities. α' martensite was strongly linked to the presence of the cracks for all CW levels above $\geq 1\%$ CW, unlike the bulk areas. However, it was observed that, as α' martensite content increased the level of cracking decreased. Therefore the presence of α' martensite does not appear to

be a dominant factor in the appearance of SCC. Similarly, CSL don't appear to play a role in shielding the crack tip and preventing further propagation of the crack. Fig. 10 shows how there is a higher fraction of $\Sigma 3$ boundaries between 0% CW and 5% CW, i.e. the CW range that exhibits the highest crack density. Between 10% and 40% the fraction of CSL decreases sharply along with the number of cracks, therefore the phenomena don't seem to be related. It can be concluded that under the conditions studied here, the CW is the most important factor in the initiation and propagation of SCC, along with the micromechanical effects associated with it, such as dislocation entanglement.

4. Conclusions

1. SCC was most aggressive in the range of 0.5% - 5% CW with a strong decrease in crack density measured for 10% CW.
2. A total absence of cracking was observed for all samples with 20% CW or more. This was observed along with an increasing fraction of *bcc* phase, considered to be α' martensite, at 10% CW and greater.
3. The $\Sigma 3$ CSL boundaries were measured and normalised by the total grain boundary length; their fraction does not increase steadily with CW, which indicates it is not a primary cause for the lack of cracking at more than 10% CW. However, the results show a decrease in $\Sigma 3$ boundary fraction at 10% CW, suggesting a bi-modal behaviour.
4. An increase in applied stress does not change the SCC behaviour, as the crack density does not exhibit a notable trend with applied stresses ranging from 60-180 MPa and does not increase even at high levels of applied tensile stress for a fixed level of CW of 10%.
5. The crack morphologies measured showed a preferred alignment to the $\langle 111 \rangle // \text{TD}$.

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