A mechanistic study of the temperature dependence of the stress corrosion crack growth rate in SUS316 stainless steels exposed to PWR primary water

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Abstract
Complementary analytical transmission electron microscopy (TEM) and transmission Kikuchi diffraction (TKD) were used to study the influence of temperature on the crack growth rate (CGR) in SUS316 stainless steels. An Arrhenius-type temperature dependence of the CGR has been observed between 250°C and 320°C. However, stress corrosion cracking (SCC) CGRs were found to decrease between 320°C and 360°C, which cannot be explained in terms of a single operating mechanism. High-resolution characterization has produced direct evidence that the SCC CGR in SUS316 is subjected to, at least, two rate-controlling processes: thermally activated diffusion and mechanical response to external stress and internal strain. While diffusion of metallic and non-metallic species at the crack flanks are enhanced at higher temperatures (350°C and 360°C), mechanical response-based mechanisms appear to dominate at lower temperatures (320°C and 340°C). Higher strain concentrations and dislocation densities around the crack tip were found at low temperature, potentially leading to accelerated crack growth and a peak in the CGR at ~ 320°C. It is suggested that phenomena occurring near the crack tip can be potentially very different at high and low temperatures.

Keywords: Transmission electron microscopy (TEM), transmission Kikuchi diffraction, Stress-corrosion cracking, Temperature dependence, Crack propagation
1. Introduction

Although generally known for their excellent corrosion resistance, reactor grade stainless steels such as SUS316 are susceptible to environmental degradation when exposed to a corrosive environment under the influence of stress. As a result, after long operation periods, stress corrosion cracking (SCC) manifests itself as microscopic cracks penetrating the material. In the past decades, owing to thorough research and experiments, a considerable number of factors that influence the rate of SCC crack propagation have been identified. These factors include, amongst others, pre-existing cold work level in the material, water chemistry, material composition, electrochemical potential and SCC test temperature [1-10].

This work comprises a study of the influence of the SCC test temperature on the crack growth rate (CGR) in SUS316 stainless steel exposed to pressurized water reactor (PWR) primary water. Previous studies conducted by Arioka and Terachi et al revealed that the CGR in SUS316 increases with increasing SCC test temperature between 250°C and 330°C but declines thereafter towards higher temperatures [11-14]. The same studies concluded that this behavior can also be found in other alloys (e.g. Alloy 690, SUS304) and that the peak temperature (highest observed CGR) depends on the cold work level in the sample. At the same time, the CGR also appeared to be affected by other mechanical quantities such as the material's yield strength and the stress intensity factor.

While an increase of the CGR with temperature in different alloys is expected if thermally activated mechanisms are present, the reasons for the inhibition of the CGR towards higher temperatures remain unknown. In order to better understand the crack tip microstructure of the alloy tested in this study, which may be linked to the temperature dependence in the CGR, a combined analytical transmission electron microscopy (TEM) and transmission Kikuchi
diffraction (TKD) approach was applied. The crack tip regions of 14 crack tips found in 4 different SCC specimens tested at different temperatures (320°C, 340°C, 350°C and 360°C) were characterized. In addition, optical microscopy measurements were conducted for preliminary characterization of the overall SCC crack region in all samples.

2. Material

For this study, four SUS316 stainless steel samples, tested under simulated PWR primary water conditions by INSS (Japan), were used. The specimens selected for this study included those tested at the temperatures where the trend is reversed (320°C, 340°C, 350°C and 360°C). The composition of SUS316 is listed in Table 1.

| Alloy | Fe  | Cr  | Ni  | C   | Si  | Mo  | Mn  | P   | S   |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| SUS316| Bal.| 16.54 | 10.00 | 0.047 | 0.045 | 2.07 | 1.42 | 0.024 | 0.001 |

Table 1. Chemical content of the alloy used in this study (wt.%)

Prior to autoclave testing, the specimens underwent solution treatment followed by water quenching and uni-directional cold-rolling to a thickness reduction of 20% (also referred to as 20% cold work). The SCC tests were performed at the INSS (Japan) laboratories using pre-cracked ½ CT (compact tension) specimen in T-S direction in an autoclave under constant load (30 MPa m\(^{1/2}\)). For specimens tested in T-S direction, the sample is extracted from the bulk in the short transverse direction and the external load is applied perpendicular to the rolling direction as shown in Figure 1b. The samples were exposed to a testing environment of simulated PWR primary water chemistry (hydrogenated water: 500 ppm B + 2 ppm Li, + 30 cm\(^3\)-STP/kg-H\(_2\)O DH\(_2\)) for 720.5
hours at 360°C, 350°C and 340°C. The fourth sample was exposed for 1004 hours at 320°C. All samples exhibited SCC by the time the test was concluded.

Subsequently, the cross-sectioned surface of each sample was ground with SiC paper and polished with 1-micron diamond suspension. Mirror-finish was achieved by final treatment with colloidal silica.

3. Experimental

The cross-sectioned samples were first examined via optical microscopy, revealing the SCC crack path and length. The measurements of the crack length were conducted on the surface of the polished sample cross-section. Instead of using the conventional fracture surface method [11,12] for determining the CGR, the total crack length (comprised of two crack branches due to sample extraction in T-S orientation, Figure 1a) was measured and divided by the test duration. The results are listed in Table 2.

![Figure 1](image)

**Figure 1.** a) Optical micrograph of SCC crack cross-section in SUS316 sample (tested at 360°C); SCC crack branches off into two separate crack paths, branch 1 and branch 2; total crack length comprised of length of both crack branches and CGR determined by dividing the total crack length by the test duration (results listed in Table 2); b) illustration of SCC ½ CT specimen tested in T-S orientation
For further investigation, the volumes containing potentially active crack tips were located and lifted out using a single-beam focused ion beam (FIB) instrument, FEI FIB200, fitted with a static in-situ micromanipulator and a platinum gas injection system (GIS). The lift-outs were conducted in plan-view orientation; for details see [15,16]. A Zeiss NVision 40 (dual-column) FIB was subsequently used for the final TEM lamella thinning process. Initial TEM imaging was performed with a JEOL 2100 LaB₆ TEM operated at 200 kV and analytical TEM (scanning TEM, STEM, and electron energy loss spectroscopy, EELS) was carried out with a JEOL ARM200F (cold-field emission gun, cold-FEG) TEM at 200 kV equipped with a Quantum Gatan image filter (GIF) spectrometer and a Jeol Centurio 100 mm² energy-dispersive X-ray detector (EDX). Gatan Digital Micrograph was used to quantify the EELS spectra and extract individual maps for each selected element. After drift-compensation, the acquired EELS data were corrected for statistical errors or noise via multivariate statistical analysis (MSA) software (Hyperspy 0.8, open source).

In this study, TKD data was acquired using a Zeiss Merlin scanning electron microscope (SEM) and an eFlashHR Bruker electron backscatter detector (EBSD) system. An accelerating voltage of 30 kV and a probe current of 3 nA were used to acquire TKD maps of 11 nm step size. Average misorientation maps were used to qualitatively determine the dislocation density in the samples based on a color temperature spectrum (warmer areas such as red, orange and yellow indicated higher dislocation density than colder areas such as blue and green). In addition, misorientation line profiles were used for the determination of the size and extent of the plastic zone around the crack tip. Finally, the geometrically necessary dislocation (GND) density distribution, based on the TKD raw data, was determined in order to compare the dislocation
densities at high and low temperature. More details on the acquisition of TKD maps for the purpose of SCC research and the methodology used can be found in [17].

4. Results

As a first step, optical micrographs of all four SCC samples were used to determine the total crack length and the CGR at each temperature (T). Figure 2 shows the optical micrographs of the different SCC samples tested at 360°C, 350°C, 340°C and 320°C. In addition, the location and number of all crack tip lift-outs performed in the framework of this study are indicated as well as the direction of cold-rolling and the external load.
Figure 2. Optical micrographs of SCC specimen tested at different temperatures: a) SUS316 - 360°C; b) SUS316 - 350°C; c) SUS316 - 340°C; d) SUS316 - 320°C; cold-rolling direction and external loading direction are indicated (bottom left corner) and location of crack tips (CT) lifted out via FIB in each sample are indicated as well.

It can be observed that the total crack length and number of crack tips increases steadily with decreasing SCC test temperature. The results are listed in Table 2.
| Sample               | Test duration [h] | Total crack length [mm] | CGR [mm/s]e-7 | Total number of crack tips | No. of crack tips lifted out |
|----------------------|-------------------|-------------------------|---------------|---------------------------|----------------------------|
| SUS316 - 360°C       | 720.5             | 0.41                    | 1.58          | 2                         | 2                          |
| SUS316 - 350°C       | 720.5             | 0.8                     | 3.08          | 3                         | 3                          |
| SUS316 - 340°C       | 720.5             | 1.34                    | 5.17          | >5                        | 4                          |
| SUS316 - 320°C       | 1003.9            | 2.23                    | 6.17          | >10                       | 6                          |

Table 2. SUS316 bulk specimen data: test duration; total length of crack path measured via crack length method including both branches; calculated CGR (total crack length divided by test duration); total number of SCC crack tips found in sample; number of SCC crack tips lifted out and prepared as TEM lamella via FIB.

As explained above, the method of determining the CGR used in this paper (the reason of which will be discussed in section 5) is based on the total crack length, including the two main bifurcations, measured from the polished cross-section (Figure 1a) as opposed to the well-established fracture surface method used in [11,12]. The results of both CGR measurements were plotted for comparison, as shown in Figure 3 (green line: CGR via crack length method, blue line: CGR via fracture surface method). The CGR results of both methods match well at higher T (350°C and 360°C), but deviate strongly from each other towards lower T (340°C and 320°C). While the peak in the CGR measured via fracture surface method appears at ~ 340°C (data for this plot was provided by INSS), the total crack length measurements show a further rise in the CGR towards lower T.
4.1 Characterizing diffusion-based mechanisms

Due to the monotonic T-dependence of the CGR at lower T (CGR rising constantly between 250°C and 330°C, [12,13,18]), it was established by Arioka et al. that diffusion-based mechanisms might be one of the rate-controlling factors in the SCC crack propagation process. In order to gain evidence for the impact of the SCC test temperature on the diffusion processes occurring near the crack tip, high-resolution analytical STEM was applied.

The STEM HAADF images and EELS elemental maps of some selected SCC crack tips from all four temperatures are displayed in Figure 4 and Figure 5. It can be observed, that there is significant (up to 50 nm deep) crack flank oxidation and diffusion of metallic and non-metallic
species near the crack tip in all high-T samples (350°C and 360°C, Figure 4). In addition, oxide fingers of ~ 60 nm depth were discovered in some of the high-T samples as shown in Figure 4b. The EELS elemental maps indicate that these oxide fingers are Cr-enriched and Fe-depleted. There is also a substantial Ni enrichment at the oxide-metal interface. A similar behavior is observed in the oxidized crack flanks in the low-T samples (340°C and 320°C), as shown in Figure 5. However, oxide penetration only seems to reach about 5 - 10 nm into the matrix. Crack flank oxidation (and hence diffusion) in all tested low-T samples seems less pronounced, extending over shorter ranges. At the crack tip, a higher Cr enrichment is observed in the low-T samples, which might be caused by a different (higher) stress concentration profile.

![Figure 4. STEM images and EELS elemental maps of crack flank diffusion near the crack tip in high T sample; top: HAADF images, bottom: EELS elemental O K edge and Cr/Fe/Ni L edge maps; a) sample 360-CT2, crack tip oxide contains 42% O, 19% Cr, 33% Fe and 6 % Ni; b) sample 350-CT2, crack tip oxide contains 55% O, 18% Cr, 22% Fe and 2 % Ni](image)
Figure 5. STEM images and EELS elemental maps of crack flank diffusion near the crack tip in low T sample; top: HAADF images, bottom: EELS elemental O K edge and Cr/Fe/Ni L edge maps; a) sample 340-CT1, crack tip oxide contains 18% O, 21% Cr, 50% Fe and 10% Ni; b) sample 320-CT5, crack tip oxide contains 43% O, 28% Cr, 15% Fe and 14% Ni

The chemical composition of crack tip oxide was determined for each TEM sample and is presented in Table 3. The crack tip is defined as the last fractured portion of the intergranular oxide at the crack front, similar to [9]. The "crack tip oxide" is defined as the oxidized region (typically intergranular), not yet fractured, directly ahead of the crack tip. Note that, although the quantitative EELS measurements have relative errors better than 10%, the calculated error has a statistical nature, after averaging the results from all crack tips. Individual crack tip oxide compositions are shown in Figures 4 and 5 for selected crack tips as a reference.

| Sample       | O (at%)  | Cr (at%) | Fe (at%) | Ni (at%) |
|--------------|----------|----------|----------|----------|
| SUS316 - 360°C | 50±6     | 19±5     | 23±7     | 7±2      |
| SUS316 - 350°C | 53±7     | 14±3     | 24±4     | 9±3      |
| SUS316 - 340°C | 52±7     | 19±6     | 20±9     | 8±4      |
| SUS316 - 320°C | 50±12    | 18±5     | 27±11    | 5±3      |
Table 3. Average crack tip oxide composition for the different samples tested. A 10x10nm area ahead of the crack tip was analyzed by EELS. The compositions displayed were calculated and averaged from all crack tips from a given temperature.

Electron diffraction experiments on the crack tip oxides revealed a spinel chromite structure (FeCr$_2$O$_4$) similar to that found in the inner surface oxides [6]. However, the Fe/Cr ratio has a high variability and every crack tip showed a different oxide composition. The observed Ni is likely to be from the higher Ni content (Cr and Fe depleted) oxide-metal interface, which is 3D in nature and was captured by the 10x10nm analysis area. In addition, local compositions closer to Cr$_2$O$_3$ were observed in the crack tip region in some samples, with Fe and Ni also present. This, again, is likely to be a result of the limited 3D resolution due to the projection effect in TEM samples.

4.2 Characterizing mechanical response-based mechanisms

Taking into account Terachi's findings regarding the impact of mechanical properties on the SCC crack growth rate [11], the second rate-controlling mechanism introduced in this paper is the mechanical response of the material to externally applied loads and internal strain. In order to locally measure the response of the material to these forces, the strain concentrations near the crack tip and the general level of plastic deformation in the prepared TEM samples were studied via TKD.

Figure 6 shows the average misorientation (MO) maps and MO line profiles acquired from the crack tip outwards into the matrix for the high-T samples (350°C and 360°C). Misorientation maps represent graphically local crystal rotations (in degrees) with respect to a fixed point and are
qualitative measures of dislocation densities. For details on the procedure please refer to [17]. The color temperature spectrum indicates that the general level of deformation in these samples is rather low (mainly blue and green; for color images please refer to the online version of this publication). However, sample 360-CT1 (Figure 6a) shows higher levels of deformation ~ 2 μm ahead of the crack tip (where slip transfer has occurred) and there seems to be elevated strain concentration around the crack tip in sample 350-CT2 (Figure 6d).

In order to quantify the size and extent of the plastic zone (PZ) around the crack tip in both samples, MO line profiles (Figure 6b and c for 360-CT1 and Figure 6e and f for 350-CT2) were extracted from the crack tip outwards into the matrix. The PZ size for sample 360-CT1 was determined as 100 nm (top grain) by 150 nm (bottom grain) and the extent of the PZ was between 1.7° and 2.5° (error ~ 1.2°) in both grains. Similarly, the PZ size in sample 350-CT2 was determined as 50 nm by 200 nm (a second plateau was present at 600 nm) and the extent of the PZ was between 2.0° and 3.1° (error ~ 1.2°). The low misorientation values at high T lead to significant fluctuations in the data which resulted in an error of ~ 1.2° for both measurements. However, the errors are relatively small and should not have a significant impact on the general trends discovered in this study.
Figure 6. Average misorientation maps and misorientation line profiles of high T samples: a) average MO map of 360-CT1; b) MO profile 1, 360-CT1: plastic zone (PZ) size ~ 100 nm, PZ extent ~ 1.7 ± 1.0°; c) MO profile 2, 360-CT1: PZ size ~ 150 nm, PZ extent ~ 2.5 ± 1.5°; d) average MO map of 350-CT2; e) MO profile 1, 350-CT2: PZ size ~ 50 nm, PZ extent ~ 2.8 ± 1.2°; f) MO profile 2, 350-CT2: PZ size ~ 200 nm/600 nm, PZ extent ~ 2.0 ± 1.0°/3.1 ± 1.2°.

In contrast to the high-T measurements, the data acquired from the low-T samples shows higher levels of deformation (Figure 7). Both samples 340-CT1 and 320-CT1 exhibit high levels of deformation near the crack tip (on the color temperature spectrum shown in yellow, orange and red). For instance, the average MO map of sample 340-CT1 (Figure 7a) indicates that these areas of high local deformation correspond to the pile-up of a number of slip- or deformation bands. Furthermore, the strain concentration around the crack tip in sample 320-CT1 (Figure 7d) appears to be particularly high. The extent of the PZ in most low-T samples studied is significantly higher...
than in the high-T samples. While sample 340-CT1 reaches MO plateaus of 6.0° and 9.1° (error ~ 1.6°), the extent of the PZ in sample 320-CT1 is even higher in the bottom grain (10 ± 1.7°). Figure 7d also shows the STEM HAADF image of the crack tip regions and indicates which areas in the sample exhibit particularly high stress levels.

Figure 7. Average misorientation maps and misorientation line profiles of low T samples: a) average MO map of 340-CT1; b) MO profile 1, 340-CT1: PZ size ~ 320 nm, PZ extent ~ 9.1 ± 1.5°; c) MO profile 2, 340-CT1: PZ size ~ 450 nm, PZ extent ~ 6.0 ± 1.7°; d) average MO map of 320-CT1; e) MO profile 1, 320-CT1: PZ size ~ 500 nm, PZ extent ~ 4.8 ± 1.0°; f) MO profile 2, 320-CT1: PZ size ~ 450 nm, PZ extent ~ 10.0 ± 1.7°

The MO line profile results were compared to data from high-resolution Kernel average misorientation (HR_KAM) maps that were created using the cross-correlation-based analysis of
the TKD patterns at the exact same location (Figure 8). Cross-correlation analysis of the pattern was conducted off-line using the methods described in [19,20]. Note that all the previous average MO maps were generated by the Hough based analysis of the patterns (see Figure 6a, Figure 6d, Figure 7a, Figure 7d). In Figure 8, the black line represents an MO line profile extracted from 340-CT1 in the top grain from the location of the crack tip outwards, similar to the MO line profile in Figure 7b. The red line, exhibiting a line plot of the HR-KAM acquired at exactly the same location in 340-CT1, corresponds very well with the MO line profile acquired via TKD. These results suggest that the use of TKD MO line profiles for the study of strain distributions near SCC crack tips is comparable with the misorientation from the cross correlation analysis.

![Graph](image)

Figure 8. Comparison of TKD relative MO profile (black line), similar to Figure 7b, and a line profile extracted from the high resolution Kernel average (HR-KAM) MO data (red line). Both profiles were extracted from the exact same region in sample 340-CT1 (top grain, from crack tip outwards).
In addition to the misorientation measurements, Figure 9 illustrates the geometrically necessary dislocation (GND) density distribution in samples 360-CT1 and 340-CT1. This method uses high-resolution, cross-correlation-based [19] data for the evaluation of the lattice curvature, which is linked to the dislocation content using the Nye’s tensor [21], and to calculate GND densities [22].

Figure 9. Maps of GND density distribution: a) in sample 360-CT1; b) in sample 340-CT1; color temperature scale on left hand side of each figure in logarithmic scale [log (GND density in lines/m²)]; c) GND density histograms showing the distribution of the GND density for both samples (red line: 360-CT1, blue line: 340-CT1)
Figure 9a and b show the total GND distribution around the crack tip in the high-T sample (360°C) and the low-T sample (340°C), respectively. Based on both average misorientation maps (Figure 6a and Figure 7a) and the GND distribution (Figure 9a and b), it is noticeable that the misorientation tends to be higher with the lower temperature, indicating that more dislocations are contained around the crack tip. In addition, quantitative assessment of the GND density via frequency histograms, constructed using all valid measurements points within each map (Figure 9c), also indicates a slight increase in the GND density as the temperature decreases.

Finally, the extent of the plastic zone (and therefore level of deformation) was averaged for each temperature, considering all misorientation measurements in both top and bottom grains of all samples, and plotted against the SCC test temperature (Figure 10, red line). This curve shows a similar progression as the CGR-T graph (green dashed line), although the trend in the deformation slows down for the higher temperatures.
Figure 10. Illustration of plastic deformation around the SCC crack tips at different temperatures; Red line: extent of PZ measured at each T (averaged over all crack tips and both grains) in units of misorientation °; Green dashed line: T-dependence of CGR (previously measured) for comparison

5. Discussion

The total SCC crack length has been shown to decrease with increasing operating temperature between 320°C and 360°C (Figure 3, green line). The optical micrograph images in Figure 2 and the resulting data in Table 2 indicate that both the CGR and the total number of crack tips are ~ 5 times higher at 320°C than at 360°C. This trend suggests that there are mechanisms involved in the crack propagation process that enable significantly higher CGRs at lower temperature (within this temperature range). In contrast, independent CGR studies of Arioka et al suggest an Arrhenius-type temperature dependence of the CGR, increasing steadily between 250°C and ~
330°C [13]. However, that study and the one presented in this manuscript were carried out on the same alloy, 316 stainless steel, tested in simulated PWR primary water conditions at the INSS laboratories, and it was therefore concluded that the peak CGR occurs at roughly 320°C (the lowest temperature in this study).

Historically, CGR measurements are conducted by determining the depth of the SCC crack on the fracture surface after intentional fracture [11,18]. However, while this measurement is adequate from an engineering point of view, where global crack depth is crucial, it does not take crack bifurcations into account (which is relevant for the T-S specimens in this study). Therefore, for the purpose of this work, which focuses on understanding the operating SCC mechanisms, the crack lengths were obtained from the prepared cross-sections by adding up the lengths of both branches of the SCC crack (Figure 1a). This method is preferred because it takes into account the effect of applied stresses during SCC testing at each crack tip. In samples with multiple crack tips, the load is effectively shared between the various active cracks. It should be noted that the results from the fracture surface method were averaged over the entire depth of the sample, whereas the crack length method is based on one single cross-section within the sample. However, the length of the SCC crack varies throughout the depth of the sample, being larger in the center than closer to the surface (the shown cross-sections were located close to the surface of the sample). Therefore, the shown CGR measurements via the crack length method might slightly underestimate the CGR.

5.1 Mechanistic study of the T-dependence on the SCC CGR

It was shown in section 4.1 that the crack flank oxidation near the crack front is more pronounced at higher T. For samples tested at 350°C and 360°C, oxide penetration depths of up to 60 nm were found. In addition, extensive diffusion of Fe and Ni was detected at the crack flanks near the crack
tip (Figure 4). In contrast, the oxidation of the crack flanks at lower T (340°C and 320°C) only reached a width of up to 10 nm and very thin Ni enrichment (of ~ 5 nm width) was found at the metal-oxide interface. Therefore, it is suggested that the diffusion of metallic and non-metallic species is, as expected, more pronounced at higher T, possibly leading to enhanced oxidation rates. Nevertheless, it should be noted that due to the lower CGR at higher T, the crack inherently propagates slower and the crack tip as well as the crack flanks have more time to oxidize than the fast propagating crack tips at lower T, preventing a “true” direct comparison.

Enhanced oxidation rates with increasing T could explain the trend discovered by Arioka et al., which describes a proportional relationship between CGR and T between 250°C and 330°C [12,13,18]. Furthermore, it is possible that higher diffusion rates at higher T accelerate the formation of a protective oxide layer in the crack tip region, e.g. due to the higher availability of Cr. For instance, traces of chromia were observed directly ahead of the crack tip via atom probe tomography characterization of a SCC crack tip (for details see [23]). In conclusion, although it is likely that passivation might be more efficient at high T due to enhanced thermally activated diffusion, oxidation rates are also higher and the differences on the intergranular oxidation ahead of the crack tip cannot explain on their own the slower CGR observed at higher T.

Nevertheless, despite the stronger diffusion at higher T, the CGR exhibits a peak at ~ 320°C, which suggests that another rate-controlling mechanism must be involved in the crack propagation process. Based on the results in Terachi's study [11] on the impact of mechanical properties on the CGR, the second mechanism suggested in this work is the mechanical response to externally applied forces and internal strain. The foundation of this proposal is the impact of the pre-existing cold work level and the material's yield strength on the CGR. It was shown that increasing yield strength promotes accelerated SCC crack growth and that the yield strength is
higher for lower T in SUS316 (575 N/mm$^2$ for 320°C and 570 N/mm$^2$ for 360°C). The reason for this is that at higher T, dislocations move more easily through the crystal lattice and plastic deformation such as slip compensates for most of the applied stresses. At lower T, however, the dislocation mobility is restricted and the material does not deform as easily. This can result in dislocation pile-up and brittle-like fracture at SCC crack tips for low-T samples, although SUS316 is considered a highly ductile material.

The results in this study (section 4.2) show that the dislocation density around the crack tip and overall level of plastic deformation in the samples tested at 320°C and 340°C (Figure 7) is indeed higher than at higher T (350°C and 360°C, Figure 6). For instance, Figure 7a shows a number of slip and deformation bands that have piled up near the SCC crack. In addition, the level of deformation around the crack tip was measured using misorientation profiles and GND-density measurements and showed much higher strain concentrations around the crack tips in the low-T samples. It should be mentioned that the average MO maps shown in Figure 6 and Figure 7 are not directly comparable. The range of the color temperature spectrum is specific for each individual map and not universally valid. Therefore, MO line profiles had to be conducted in order to effectively compare the strain concentrations and defect density in the crack tip area and relate the results from different maps to each other. However, these MO line profiles extracted from the TKD data (shown in Figure 6 and Figure 7) are only qualitative and do not reveal any quantitative information. Therefore, the GND density distribution was calculated and plotted (Figure 9) for two crack tips, indicating quantitative values for the strain concentration near the crack tip. This data confirms that the strain concentration near the crack tip is higher for lower temperatures. In addition, Figure 9c compares the MO line profile data generated from the TKD software to the
MO Kernel data generated from the GND density distribution in the same sample and at the same location, with good correlation of both plots.

Within the studied temperature range, it appears that the effects of mechanical response-based mechanisms are more dominant than thermally activated diffusion mechanisms. The reason for this is that the peak CGR was found at ~320°C, a temperature where crack flank diffusion was observed to be low and local strain concentrations high. Therefore, the interaction of the two discovered trends of rising diffusion/oxidation rates with increasing T and the higher likelihood of brittle-like fracture towards decreasing T might lead to maximization of the CGR around 320°C (Figure 11c).

5.2 Novel insights regarding the ongoing processes near the crack tip
In recent SCC literature, a possible connection between the formation and mobility of vacancies in the crack tip region and the SCC crack propagation process has been suggested [24-26]. This study provides potential evidence of higher diffusion rates at higher T which, being of substitutional type, have to be a result of an increased vacancy generation and mobility. However, higher strain gradients at the crack tip due to locally higher concentration of defects at lower T can have the same or maybe an even more pronounced effect on enhancing intergranular oxidation [27]. In the framework of this study, novel insights into the mechanisms occurring at the SCC crack tip were obtained, which may suggest the involvement of additional processes in SCC crack propagation.

For this purpose, an explanation of how mechanical response-based mechanisms and diffusion-based mechanisms interact and influence the ongoing processes near the crack tip, leading to the CGRs observed at low T (340°C and 320°C) and high T (350°C and 360°C), is
presented in Figure 11. This explanation is based on the experimental evidence found throughout this study.

For SCC crack tips at low T, an increased flux of dislocations towards the crack tip (mainly through the GB, but potentially also from other regions in the sample) is suggested as shown in Figure 11a. The higher local dislocation density in the plastic zone, due to lower ductility at lower T, results in a higher strain gradient that attracts more dislocations towards the crack tip, further increasing the dislocation density in the PZ. In addition, the flux of vacancies into the PZ may lead to the formation of voids inside the GB oxide directly ahead of the crack tip, making this region even more brittle and prone to fracture. In contrast, the SCC samples tested at higher T deform more easily via slip due to enhanced dislocation movement through the crystal (Figure 11c). Therefore, the dislocation density is lower near the crack tip and fewer vacancies accumulate to form voids due to the smaller strain gradient. In general, it is assumed that the material as well as the crack tip region is more ductile and less prone to fracture at higher T. In addition, the formation of a protective Cr-oxide spinel at the crack tip and along the crack flanks may be facilitated by the higher diffusion rates at higher T. It is commonly known that the availability of Cr has a significant impact on the quality of the protective oxide layer. Chromia (Cr$_2$O$_3$) is known as the most protective type of oxide for stainless steels, followed by the stoichiometric spinel oxide (FeCr$_2$)O$_4$, also known as chromite [28], which was found at the crack tip of sample 320-CT5. Despite the belief that the formation of chromia in SUS316 is generally impeded due to the lack of available Cr, a region containing stoichiometric Cr$_2$O$_3$ was recently found in the PZ ahead of a SCC crack tip via atom probe tomography [23]. It is therefore possible that due to the high strain gradients and the abundance of vacancies for substitutional diffusion, such as in the samples tested at low T (Figure 11a), enough Cr may accumulate in the crack tip region, locally forming chromia or a
protective Cr-oxide spinel such as chromite. Despite the potential formation of this oxide layer, brittle-like fracture due to vacancy-induced porosity at lower T might still be accelerated in comparison to the more ductile crack tip area at higher T. As a result, the CGR is higher at lower temperatures.

A degree of porosity in the crack tip oxides was observed in most crack tips. However, since the microscope was always used in STEM mode in this study, better suited Fresnel contrast experiments could not be performed. Therefore, although void formation could have happened in the plastic zone around the crack tip, we cannot present enough evidence. However, the evidence presented in this paper substantiates the claims regarding the influence of mechanical deformation in the sample on the temperature dependence of the CGR in SUS316 stainless steel.
a) **Mechanical Response**

- **Low T**
  - Material less ductile
  - Higher dislocation density in PZ
  - Lower diffusion rate
  - Moderate oxidation at crack flanks

- **High T**
  - Higher ductility
  - Lower dislocation density in PZ
  - Higher diffusion rate
  - Strong, long-range oxidation at crack flanks

b) **Diffusion-Based**

- **Low T**
  - Ni enrichment
  - Accelerated diffusion in PZ
  - Cr-rich protective crack tip oxide
  - Porosity due to voids near crack tip
  - Brittle-like fracture

- **High T**
  - Fe precipitation
  - Long-range matrix diffusion at crack flanks: up to 60 nm
  - Fast establishment of protective oxide that is less brittle than at low T
  - Higher strain needed for fracture
  - Lower CGR

c) **CGR vs. T [°C]**

- **Thermally Activated Response**
- **Maximum CGR**
- **Mechanical Response**

*Graph shows CGR (Crack Growth Rate) as a function of temperature (T) [°C].*
Figure 11. Illustration of possible mechanisms occurring at the crack tip: a) low T: high dislocation density near crack tip creates larger strain gradient; dislocations move towards crack tip; crack tip regions becomes more brittle due to void generation; b) high T: easier compensation of stresses via slip due to enhanced dislocation movement through the crystal; lower dislocation density in PZ; c) phenomenological diagram illustrating the combined effects of thermally activated diffusion and mechanical response-based mechanisms on the temperature dependence of the SCC CGR in SUS316: the maximum CGR was identified at ~ 320°C

6. Conclusions

The temperature dependence of the SCC CGR in SUS316 stainless steel exposed to PWR primary water was investigated. Based on previous findings from Arioka et al and the results of this study, it was found that the SCC CGR increases with rising temperature between 250°C and ~ 320°C but exhibits sudden recession towards higher temperatures up to 360°C. The highest CGR is observed at around 320°C.

The experimental results obtained in this work lead to the conclusion that both thermally activated diffusion and mechanical response-based mechanisms are involved in the crack propagation process. Diffusion processes were found to be more pronounced at higher temperatures and higher strain concentrations around the crack tip were found to be more prominent in the low-temperature samples. However, in the temperature range studied (320°C to 360°C), it seems that mechanical response to externally applied forces and internal strains dominate, maximizing the CGR at around 320°C.

Finally, additional mechanisms (based on different mechanical properties at different temperatures) potentially occurring in the crack tip region were discussed. The accumulation of vacancies near the crack tip, also known as voids, has often been thought of as a precursor for SCC crack propagation. High strain concentrations resulting from dislocation pile-up in the less ductile
low-T material may result in the accumulation of vacancies and therefore potential formation of voids. In addition, the overall dislocation density increases in the highly strained crack tip region. A higher number of voids ahead of the crack tip combined with the more brittle-like behaviour of the material at low T may be the reason for the enhanced CGRs compared to high T. Although the peak CGR in this study was found around 320°C, it is known that this peak varies depending on the cold-work level of the material, the material composition as well as the water chemistry.

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