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Insights into the stress corrosion cracking of solution annealed alloy 690 in simulated pressurized water reactor primary water under dynamic straining

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Abstract

The intergranular attack near both stagnant and active stress corrosion crack (SCC) tips of solution annealed alloy 690 were characterized after constant extension rate tensile tests in simulated pressurized water reactor (PWR) primary water containing 18 cc H2/kg H2O. In both cracks, an intergranular oxide, composed of NiO and Cr2O3, was observed beyond the crack tip with an adjacent Cr depleted grain boundary migration zone. The stagnant crack has a compact Cr2O3 covering the crack tip and the adjacent grain boundary migration zone is deep and free of oxidation, while the active crack has porous penetrative oxide extending into the migration zone. The ability to form a compact Cr2O3 film at the crack tip is important to the IGSCC resistance and may be dictated by the efficiency of Cr diffusion up the migrated grain boundary. When a compact Cr2O3 film does not form at the crack tip, the Cr depleted grain boundary migration zone is subject to penetrative oxidation via the inward diffusion of oxygen, making the zone susceptible to crack propagation. Thus, even a high Cr content cannot guarantee the immunity of a Ni base alloy to SCC during dynamic straining.

1. Introduction

Nickel base alloy 690 is widely used as structural material for components such as steam generator tubes, control rod drive mechanism nozzles and pressurizer heater sleeves in pressurized water reactors (PWR) because of its higher stress corrosion cracking (SCC) resistance than alloy 600 [1–3]. Although no incidence of SCC has been reported on alloy 690 (normally thermally treated (TT)) in PWR (either primary or secondary side) since its application in the 1980s, the alloy is not immune to SCC as the lab tests show that it is susceptible to both crack initiation [4–6] and propagation [7–10]. Both the solution annealed (SA) + 20% cold rolled [4] and mill annealed + 20% prestrained alloy 690 [6] initiated SCC cracks (average crack length of 3–8 μm) after constant extension rate tensile (CERT) test (total test time ranged from 130 to 700 h) in hydrogenated high temperature water between 320 and 450 °C. Extensive work has been done to study the SCC crack growth of alloy 690 and the results show that although the crack growth rates of this alloy (TT condition) are generally low in 325–360 °C simulated PWR primary water (≤5 × 10−9 mm/s at K of 30–40 MPa m1/2) [11,12], cold work and microstructure inhomogeneity can increase the growth rate significantly [7,10]. Research work on the crack initiation of alloy 690 is still very limited mainly due to the difficulty to initiate crack on this alloy. As reviewed by Moss et al. [13], only dynamic straining can consistently initiate cracks on alloy 690 and a SCC initiation model was proposed based on the results from CERT test. In this model [13], the SCC initiation of alloy 690 includes three stages: 1) an oxidation stage in which a protective film of Cr2O3 is formed on the surface over the grain boundaries, 2) an incubation stage in which successive cycles of oxide film rupture and repair depletes the grain boundary of chromium (down to 10–20 at.%), and 3) a nucleation stage in which the chromium depleted grain boundary is no longer able to support formation of a protective chromium oxide layer, exposing the grain boundary to the water environment and subsequent formation and rupture of oxides down the grain boundary. To manage the integrity of alloy 690 in the long term, a mechanistic understanding of how the short crack propagates after initiation is needed.

The microstructure near the SCC crack tip reveals the degradation process at the crack front and can provide valuable evidence...
for a mechanistic study. Although alloy 600 (with typically 16 wt.% Cr) contains lower Cr content and shows higher SCC susceptibility than alloy 690 (with typically 30 wt.% Cr), the SCC process of these two alloys is similar in some respects and can be gleaned from previous work on alloy 600. Thomas and Brummer [14] investigated the SCC crack tips of alloy 600 formed in simulated PWR primary water and found that Cr2O3 forms at the crack tip, and the attacked grain boundary (GB) was filled with porous NiO, minor Cr2O3 and Ni-rich metal, suggesting that the SCC process is driven by active dissolution or oxidation. They [15] also reported that there was a segment of GB enriched in Ni and depleted in Cr beyond the crack tip. Consistent results have also been reported by Sennour et al. [16] and Lim et al. [17] except that their work showed that the oxide within the oxidized GB also contained spinel in addition to NiO.

Characterization of crack tips in alloy 690 is relatively scarce. Arioka et al. [5,8] studied the crack initiation and crack growth behavior of cold-worked alloy 690 in 320–360 °C simulated PWR primary water at an initial K of 20–30 MPa m1/2 and observed creep cavities at GBs near tips of cracks which were thought to be involved in crack initiation and growth processes as crack embryos. Zhai et al. [18] also reported that extensive creep cavities formed at GBs in cold worked alloy 690 with intergranular carbides from both smooth tensile and blunt notched compact tension samples. Whether creep cavitation is a generic mechanism of SCC of alloy 690 is questionable as it has been only reported in cold worked alloy 690, this work is focused on the analysis of intergranular behavior of twin boundary and found that the twin boundary was composed of epitaxial spinel and chromia. They [20] also studied the effects of cold rolling on the structure and SCC susceptibility of twin boundary and found that the twin boundary was susceptible to cracking after cold rolling and the crack was preceded by intergranular oxide and a Cr-depleted GB migration zone.

To advance the current understanding of the SCC process in alloy 690, this work is focused on the analysis of intergranular attack near the SCC crack tip of SA alloy 690 following a CERT test in 360 °C hydrogenated water. The microstructure and elemental compositions of intergranular oxides and the GB migration zone were examined. The results are discussed in relation to the SCC process.

2. Experimental

2.1. Material

The chemical composition of alloy 690 used in this work is 57.6 wt.% Ni, 32.7% Cr, 8.64% Fe, 0.25% Mn, 0.315% Al, 0.08% Si and 0.02% C. The alloy was in the form of a forged bar with a diameter of 185 mm, hot rolled to an 8 mm thick sheet at around 1100 °C, solution annealed at 1100 °C for 1 h and water quenched. Round tensile bars were machined with their axes in the cold rolled direction, similar to a previous study [14]. The tensile bar measured 20 mm in gauge length and 2 mm in diameter. The gauge section of the tensile bar was mechanically abraded up to 4000 grit and electropolished for 30 s at 30 V in a solution of 10% (volume fraction) perchloric acid in methanol which was cooled to ~30 °C. All the samples were cleaned three times alternately with methanol and acetone immediately after electropolishing. Fig. 1 shows scanning electron microscopy (SEM) images of the sample surface after electropolishing. No intergranular surface cracks due to electropolishing were observed on the samples. There were some small, sparse carbides (Fig. 1b) on the grain boundaries but the boundaries showed no sign of migration.

2.2. Apparatus and methodology

SCC tests were conducted in a refreshed stainless steel autoclave using the CERT test technique. The test was performed in 360 °C high purity water containing 18 cm3 (STP) H2/kg H2O which resulted in an electrochemical potential near the Ni/NiO boundary. As described in our previous work [4,21], once the environment parameters were stable, the samples were loaded to just below the yield point at a rate of 1.24 × 10−5/s and then strained at 5 × 10−3/s. Fig. 2 shows the stress–strain curve during the CERT test. The tensile bar was uniformly strained to 7% plastic strain and reached a stress of 300 MPa after an active straining time of 408 h. The total time at temperature was 502 h. The sample shows dynamic strain aging (DSA) which is evident from serrations on the curve. The behavior has been consistently observed in previous work [4,20] and studied in Ref. [21].

The cracks were first examined using SEM. Cross sections of two intergranular cracks were made using focused ion beam (FIB) milling with a final beam current of 80 pA on a FEI Helios Nanolab 650. The oxides on the crack wall and near the crack tip were analyzed with transmission electron microscopy (TEM) on a JEOL 3011 microscope. Selected area electron diffraction (SAED) along with dark field imaging were conducted. The element distribution was analyzed with FEI Talos F200X equipped with a “SuperX” energy dispersive spectroscopy (EDS) X-ray detector system consisting of four silicon-drift detector (SSD) units. High resolution images of oxides and the GB migration zone were taken in a scanning transmission electron microscope (STEM) JEOL 3100R05 which is equipped with high angle annular dark-field (HAADF) detector. Fast Fourier Transformation (FFT) was used to analyze the high resolution images.

3. Results

Approximately 20 grain boundaries at different stages of SCC have been sampled from different tensile bars. In this work, two of those sampled grain boundaries were selected from a single sample to show the typical microstructure features of crack. One crack was shallow. The propagation of this crack was very limited and it was assumed that this crack was stagnant. The preliminary analytical results of this shallow crack have been published in a previous work [22]. More detailed results will be presented here. The other crack is much deeper and wider and was likely an active crack when the SCC test was stopped.

3.1. Shallow (assumed stagnant) crack

Fig. 3a shows the SEM plane view image of the shallow crack. Fig. 3b shows the STEM-HAADF image of the cross section and Fig. 3c is the enlarged image from the selected area of Fig. 3b. In this work, the plan view images of the grain boundaries were taken after the horizontal direction was aligned with the loading axis and the FIB lamellas were cut along the loading axis. A non-compact internal oxide layer formed on the sample surface which appears as a dark region in Fig. 3b. The crack is filled with (bright) Pt particles which are from the Pt deposition during FIB milling and surrounded by a layer of (dark) intergranular oxide (Fig. 3b and c). The internal oxide in the right grain was a little deeper than the
intergranular oxide (Fig. 3b). The center of the crack (outlined with a dashed line) appears darker than the oxide on the HAADF image in Fig. 3c due to the lower mass. The crack tip is at the end of the darker area in the middle of the intergranular oxide in Fig. 3c. The intergranular oxidation penetration is around 130 nm deep and the crack is around 80 nm deep (Fig. 3c). The GB migration zone starts at the tip of the intergranular oxide and extends for some 320 nm (Fig. 3b). This zone is marked by a straight boundary (right) and a curved boundary (left). The curved boundary is the new GB and the straight boundary is the original GB. GB migration in alloy 690 has also been reported to occur under similar environments [23,24].

The phase structure of intergranular oxide was analyzed with TEM. Fig. 4a shows the STEM-HAADF image of the crack. The images in Fig. 4 are flipped left-to-right compared to those in Fig. 3 as the lift-out was examined from the reverse side. The straight orange line marks the top of the surface oxide layer and the white solid line delineates the intergranular oxidation front. The yellow solid curve marks the migrated GB, and the white broken line represents the original GB position. The SAED in Fig. 4b taken from the circled area of Fig. 4a shows that the region consists of a mixture of corundum grains that have a rigid orientation relationship with the substrate: corundum (006)//substrate (111), corundum <210>//substrate <110>. A similar orientation relationship has been reported before [19,25]. The dark field images of corundum from grains on either side of the penetration region (Fig. 4c and d) reveal that this oxide not only exists in the internal oxide layer on the surface, but also forms around the crack tip and against the metal walls of the penetration.

Fig. 5 shows the EDS maps of O, Fe, Cr and Ni in and around the crack. From the oxygen map, the crack appeared darker than the surrounding oxide as it was an open area (Fig. 5a), which provided another approach to identify the crack profile in addition to the approach based on contrast difference in the dark field image. From Fig. 5a, c and d, most of the internal oxide on the grain surface is enriched in Cr. Given that such oxide has a structure of corundum (Fig. 4b), it is confirmed that this oxide is Cr2O3. The oxide in the crack and against the metal substrate (crack inner oxide) is depleted in Fe and Ni (Fig. 5b and d), enriched in Cr (Fig. 5c) and has a corundum structure (Fig. 4), indicating it is also Cr2O3. The central part of the intergranular oxide (crack center oxide) is slightly enriched in Fe and Ni (Fig. 5b and d). The GB migration zone beyond the intergranular oxide is enriched in Ni and depleted in Cr and Fe, as indicated in Fig. 5b, c and d. In order to trace the change of those element contents across the attacked GB, several line scans were taken as shown in Fig. 5a. The scan width was 15 nm and the depth was the thickness of the sample (around 100 nm). The scans along lines a and b confirm that the crack inner oxide is Cr enriched and the crack center oxide contains higher contents of Ni and Fe (Fig. 6a and b). Comparing Fig. 6b with Fig. 6a, it is observed that the Cr content in the crack center oxide increases, while the Ni and Fe contents decrease. Lines c and d scan across the GB migration zone (Fig. 5a). The line profiles (Fig. 6c and d) indicate that the GB migration zone is significantly enriched in Ni and depleted in Cr. Fig. 6d shows lower Ni content and higher Cr content compared to Fig. 6c, indicating that the degree of Cr depletion decreases with depth into the migration zone. It should be noted that the element profile is fairly constant across the migration zone width and the transition from matrix to GB migration zone is very sharp with no enrichment or depletion of element on either side (Fig. 6c and d).

High resolution images were taken along the intergranular oxide from the mouth to the tip of the crack. Fig. 7a shows the overall intergranular oxide and Fig. 7b-d show the high resolution images from the framed areas b-d on Fig. 7a, respectively. On Fig. 7b and c, the white line delineates the outline of the crack and the black line marks the previous GB position. As shown in Fig. 7b, the crack is filled with Pt particles that were deposited onto the sample during the FIB process. The intergranular oxide extends beyond the crack tip (Fig. 7c). The oxide on the left crack wall was analyzed with the matrix tilted to <110> zone axis. The FFT from the left grain and oxide (Fig. 7e) shows that the oxide contains both corundum and NiO structures. The lattice arrangements of oxides from different areas were further analyzed with selected area FFT. The crack center oxide (Fig. 7b–d) has a crystal structure of NiO. Corundum forms in the crack inner oxide which is between the NiO and the matrix (Fig. 7b–d) with an unoxidized island of matrix embedded in it (Fig. 7b). The corundum oxide should be Cr2O3 based on the

![Fig. 1. Scanning electron microscopy (SEM) images of the sample surface after electropolishing.](image-url)
previous TEM analysis (Fig. 4) and the high Cr content from EDS analysis (Figs. 5 and 6). Cr$_2$O$_3$ extends further down the GB than NiO (Fig. 7d). The FFT also shows that the NiO has a cube-on cube orientation relationship with the matrix (Fig. 7e) and Cr$_2$O$_3$, in several variants, maintains a rigid orientation relationship with the matrix as mentioned before: Cr$_2$O$_3$ {006}//substrate {111}, Cr$_2$O$_3$ <210>/>substrate <110>. The intergranular oxide tip was further analyzed with the GB titled to edge on. Fig. 8a shows that a segment of oxide forms preferentially along the migrated GB. The high resolution bright field image indicates the oxide at the tip is amorphous as it lacks crystalline periodicity (Fig. 8b).

3.2. Deep (active) crack

Fig. 9a shows an SEM image of the deep crack sampled for analysis. Some shallow transgranular cracks also initiated due to the severe plastic deformation in the matrix. The intergranular crack is deeper and wider than the shallow one. From the STEM-HAADF image of cross section (Fig. 9b), the crack wall is covered with a thin layer of Pt (bright) from Pt deposition during FIB cutting. The center of crack appears darker than the surrounding oxide and the crack front is outlined by the yellow broken line in the inset of Fig. 9b. The crack contains oxide particles, two of which are circled in Fig. 9b and were selected for TEM analysis. The diffraction patterns (Fig. 9c and d) show that the oxide particles have NiO structure and cube-on-cube orientation relationship with the two neighboring grains.

The chemical composition of the cross section was analyzed with EDS and the maps are shown in Fig. 10. The upper part of the left wall was damaged during FIB cleaning while the rest of the crack is intact. From Fig. 10a and c, the crack wall is covered with a thin oxide layer which is enriched in Cr. The oxide particles in the crack are Ni enriched (Fig. 10d), confirming that these particles are NiO. The oxide beyond the crack tip is non-compact and enriched in Cr (Fig. 10a and c). There is a Ni enriched region beyond the intergranular oxide which is the start of the GB migration zone (Fig. 10d).

The intergranular oxide beyond the crack was further analyzed with high resolution imaging. Fig. 11a shows that the oxide penetrating the GB migration zone is non-compact. The image is flipped left-to-right compared to those in Figs. 9 and 10 as the lift-out was examined from the reverse side. The original GB is delineated with a black broken line and the migrated GB is marked with a yellow line (Fig. 11a). The intergranular oxide is intermixed with the matrix in the GB migration zone. Fig. 11b shows the whole GB migration zone beyond the oxidation front which gradually narrows down with a length of approximately 275 nm. The high resolution images from the three framed areas in Fig. 11a are shown in Fig. 11c-e with the left grain titled to <110> zone axis. The oxide structure was analyzed from the lattice arrangement using FFT. The oxide, mainly composed of NiO and Cr$_2$O$_3$, is mixed with the left grain (Fig. 11c and d). The FFT from this region (Fig. 11f) also shows that NiO is epitaxial with the grain on the left, and Cr$_2$O$_3$, in several variants, maintains the rigid orientation relationship with the left grain as mentioned before. The oxide tip at the migrated GB is amorphous.

Fig. 3. (a) Scanning electron microscopy (SEM) image of a crack from solution annealed alloy 690, strained to 7% at $5 \times 10^{-4}$s in 360°C high purity water containing 18 cm$^3$ (STP) Hz/kg HzO during 502 h exposure, (b) STEM-HAADF image of the cross section at the same location and (c) enlarged image of selected area from (b) (from Ref. [22] with permission of Springer).
4. Discussion

The shallow crack had a compact chromia oxide beyond the crack tip that could have served as an effective oxygen diffusion barrier layer, suggesting that the intergranular oxidation was impeded and the crack was stagnant. The deep crack contains a non-compact oxide and should be still active. Both cracks show GB migration and intergranular oxidation beyond the crack tip, indicating that they are important precursors for crack propagation. GB migration and intergranular oxidation will be discussed separately. Afterwards, the SCC propagation mechanism of alloy 690 in PWR primary water environment will be discussed.

4.1. GB migration

Both cracks exhibit a GB migration zone beyond the intergranular oxidation. The GB migration zone is highly enriched in Ni and depleted in Cr (Figs. 5, 6 and 10). The migration process is diffusion-induced GB migration (DIGM) as it is related to the diffusion of solute [26]. Similar phenomenon has also been observed on alloy 690 strained in hydrogenated subcritical and supercritical water [6]. Mechanical loading is not needed for the occurrence of GB migration as this phenomenon has also been reported to occur on unstressed alloy 690 coupons after exposure to simulated PWR primary water [23,27]. In addition, other Ni base alloys like alloy 600 [28–30] and Ni-5Cr [31] show similar GB migration after exposure to high-temperature hydrogenated water or steam and the GB migration zone is also enriched in Ni and depleted in Cr.

For Ni base alloys containing Cr, GB migration is induced by the diffusion of Cr. It has been reported [23,27] that Cr diffuses toward the surface via the GB to support the formation of a compact chromia film over the GB, thus leaving a Cr depleted GB. The migration of the grain boundary is believed to occur by diffusion induced grain boundary migration, DIGM, on random high angle boundaries (RHABs) of alloy 690, but not on coherent twin boundaries [20]. Figs. 5 and 10 show that in the presence of a crack, DIGM still occurs on RHABs beyond the crack tip and the intergranular oxide. In this case, Cr diffuses out along the migrated GB and supports the formation of a compact chromia film beyond the stagnant crack (Fig. 7), or non-compact chromia region beyond the active crack (Fig. 11).

For the stagnant crack, it is interesting to note that the composition profiles at both the original and migrated GBs are very steep and there is no enrichment or depletion of elements (Fig. 6c).
and d), indicating that the diffusion across these two GBs is very limited. Given that there was no longer lattice discontinuity at the original GB after boundary migration, it was deduced that the lattice diffusion of metallic elements in alloy 690 was very limited at the test temperature. Extrapolation of the volume diffusion coefficient of Cr in alloy 600 with 0.015 wt.% carbon, measured by Chen et al. [32], to 360 °C yields a value of $1.7 \times 10^{-28}$ m$^2$/s and a diffusion distance of approximately 0.035 nm after 502 h, which is insignificant compared to the dimension of the GB migration zone. Therefore, the outward diffusion of Cr must be along the migrated GB, not by lattice diffusion in the GB migration zone. As to the vacancies created by outward diffusion of Cr, it is likely that they are annihilated during the climb of GB dislocations which directly results in GB migration [26]. In addition, the curved shape of the migrated GB means that it can accommodate more defects than the original GB.

Ni enrichment beyond the intergranular oxidation and the crack tip has been widely reported in alloy 600 [15–17] and stainless steel [33–35] in PWR primary water environment. It was suggested [33–35] that such Ni enrichment in stainless steel is enabled by the excess nickel created by the advancing intergranular Cr-rich oxide. It is unlikely that such a mechanism applies to alloy 690 for the following reasons: 1) there is still a Ni-enriched GB migration zone in the un-cracked GB where there is little intergranular oxide but just a thin Cr-rich oxide film over the GB [23,27], and 2) there is no excess of nickel from the intergranular oxidation as Ni is also oxidized into NiO (Figs. 7, 9 and 11). Therefore, Ni enrichment in the GB migration zone likely results from the outward diffusion of Cr.

The GB migration zone needs to be further oxidized before the crack can propagate through it. For the stagnant crack, the GB migration zone shows no sign of oxidation. That is probably because the chromia beyond the crack tip is still compact and can act as a barrier layer to oxygen diffusion. As for the active crack, no protective oxide is found before the migration zone, so oxygen can penetrate into the GB migration zone (Fig. 10). The formed oxide, composed of Cr$_2$O$_3$ and NiO and intermixed with the matrix, is not protective (Fig. 11) as the migration zone has a chemical composition similar to that of alloy 600, which only contains around 15 wt.% Cr (Fig. 6). Such a low Cr content cannot support the formation of a protective film, as evidenced by the formation of a non-compact internal oxide on alloy 600 in high temperature hydrogenated steam [36,37]. Therefore, the GB migration resulting from the outward diffusion of Cr is an important process that impacts the nucleation and growth of IGSCC crack in alloy 690 in PWR primary water. The Cr-depleted GB migration zone is susceptible to penetrative oxidation if a compact Cr$_2$O$_3$ layer cannot form before it.

4.2. Intergranular oxidation

Intergranular oxidation is observed beyond both the stagnant crack (Fig. 5) and the active crack (Fig. 10). For the stagnant crack, NiO forms the crack center oxide (Fig. 7). This oxide possesses a
crystal structure of NiO but also contains Fe (Fig. 5b), suggesting it is an oxide with mixed cation composition, consistent with previous works [23,25,38]. The NiO structure maintains epitaxy with the matrix, indicating that it nucleates through solid reaction of matrix with the inward-diffusing oxygen. Such a process has also been proposed to occur during the formation of surface oxide on stainless steel [39–41] and alloy 690 [19,42]. NiO is also observed on the crack wall and beyond the tip in the active crack (Figs. 10 and 11). Consistently, it has been reported that NiO forms in the SCC cracks of alloy 600 [14,16,17,43] and alloy 690 [6] in PWR primary water environment. The NiO particles on the crack wall still maintain epitaxy with the neighboring grains (Fig. 9). Those particles probably develop from the NiO nuclei previously formed beyond the crack tip as the crack propagates. Fig. 11 clearly shows NiO nucleates in the GB migration zone beyond the crack. After the crack propagates, the NiO previously formed beyond the crack tip would be exposed to the solution and grow by precipitation which is a prevalent mechanism for the growth of surface oxide particles in high temperature water [39–42,44,45]. However, for the oxide formed on the surface, NiO was rarely found in the internal oxide layer of alloy 690 when exposed to hydrogenated high temperature water [19,46,47] although it forms in the inner oxide layer in oxygenated high temperature water [42,48]. So the formation of NiO beyond the crack tip should be due to the high Ni content in the GB migration zone which formed prior to the intergranular oxidation.

In addition to NiO, Cr₂O₃ is also found in both cracks. The Cr₂O₃ has a rigid orientation relationship with the substrate: Cr₂O₃ [006]/substrate [111], Cr₂O₃ [210]/substrate [110]. Such a relationship also exists between the Cr₂O₃ with the matrix in the internal oxides formed on the crack wall [19,25] and surface [19] of alloy 690 in simulated PWR primary water. The Cr₂O₃ layer in the stagnant crack is compact and covers both the crack walls and crack tip (Figs. 5 and 7). It forms in close proximity to the matrix as it is stable at the oxidation front where the oxygen partial pressure is low [19,49]. To support the formation of compact Cr₂O₃, Cr needs to diffuse outwards along the GB, resulting in a GB migration zone. A similar scenario also occurs during the formation of compact Cr₂O₃ over the GB on unstressed alloy 690 coupons [23,27]. The compact Cr₂O₃ in the stagnant crack is believed to be a barrier layer for oxygen diffusion and protect the GB migration zone from being oxidized. That is probably why the crack stops growing.

As for the active crack, the Cr₂O₃ beyond the crack tip is non-compact and is intermixed with NiO and the matrix (Fig. 11). Such an oxide is not protective and oxygen can easily diffuse in. The oxide penetrates deeper into the GB migration zone than along the migrated GB (Fig. 11) which is probably due to the Cr depletion in the migration zone. The Cr-depleted migration zone would be the route for crack propagation. Consistently, it has been reported [20] that the crack on a transformed twin boundary follows the Cr depleted zone and the crack tip is preceded by a mixture of Cr rich oxide and Ni rich metal. There is also a section of unoxidized migration zone beyond the intergranular oxide (Figs. 10 and 11), indicating that outward diffusion of Cr still occurs and the crack would propagate continuously following the GB migration.

It is interesting to note that one crack stagnates while the other one is still active after initiation. It has been reported that the local grain boundary normal stress, determined by the applied stress and orientation of the grain boundary plane with respect to the loading axis, has significant effect on the boundary cracking resistance of stainless steel [50]. The trace angles with respect to the loading axis from plan view and cross section are large for both grain boundaries (Figs. 3 and 9), indicating that both boundary planes are nearly perpendicular to the loading axis. So the difference in cracking susceptibility between these two boundaries should not stem from the difference in the local normal stress. The difference is closely related to the structure of the intergranular oxide beyond the crack tip. A compact intergranular oxide can effectively suppress the
oxygen diffusion and stagnate the crack, while a non-compact oxide can form extensively into the GB migration zone and degrade the boundary. The controlling factor behind the difference in the oxide structure may lie in the efficiency of Cr diffusion. He et al. [51] found that the cracking susceptibility is not uniform even on a single GB and related to the local chemical composition. They suggested that the efficiency of Cr transport along GBs and the protectiveness of inner oxides are critical to the local SCC susceptibility. The grain boundary structure has a significant effect on the diffusivity of Cr. Our previous work [20] reported that coherent twin boundaries in alloy 690 showed no Cr depletion or boundary migration and that it only became susceptible to migration after being transformed into RHAB by cold rolling. Both grain boundaries presented here show grain boundary migration, suggesting that they are very likely RHABs. The grain boundary containing the stagnant crack was confirmed to be a RHAB by transmission electron back scattering diffraction (EBSD) while the boundary containing the active crack was damaged accidently during transportation. Nevertheless, it is believed that the difference in Cr diffusivity between these two boundaries should result from factors other than grain boundary structure. In this work, the diffusion of Cr is much faster along the grain boundary than in the boundary migration zone. When oxidation occurs along the grain boundary, outward diffusion of Cr can promote the formation of compact Cr$_2$O$_3$ beyond the crack front and impede further oxygen diffusion, as evidenced by the stagnant crack. While during the oxidation of

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Fig. 7. (a) STEM-HAADF image of the stagnant crack with the left grain titled to [110] axis, (b–d) high resolution bright field images taken from selected areas on (a), and (e) Fast Fourier Transformation (FFT) of left grain with oxide.
grain boundary migration zone, due to the Cr depletion and very limited lattice diffusion of Cr, a barrier layer cannot form and crack propagation becomes easier, as evidenced by the active crack. While it is beyond the scope of this work, it would be interesting to investigate on how to stagnate an active crack or avoid the formation of active cracks.

Fig. 8. STEM-HAADF image of the stagnant crack with the grain boundary edge on and (b) high resolution bright field image from the tip area in (a).

Fig. 9. (a) SEM image of an active crack on solution annealed alloy 690, strained to 7% at $5 \times 10^{-8}$/s in 360 °C high purity water containing 18 cm$^3$ (STP) H$_2$kg H$_2$O during 502 h exposure, (b) STEM-HAADF image of the cross section at the same location (inset shows the crack front) and selected area electron diffractions (SAED) of (c) area around particle 1 and (d) area around particle 2 in (b).
The structures of stagnant SCC and active cracks on alloy 690 in simulated PWR water are schematically summarized in Fig. 12. The oxide formed on the sample surface is composed of spinel and Cr2O3. For the stagnant crack (Fig. 12a), a layer of NiO structure oxide forms the crack center oxide. The crack inner oxide, a compact layer of Cr2O3, forms between the matrix and the NiO structure oxide. Beyond the intergranular oxide, a deep Ni enriched grain boundary migration zone forms due to the outward diffusion of Cr. For the active crack (Fig. 12b), the crack wall is covered by a layer of mixed oxide with some epitaxial NiO particles on top. Beyond the crack tip, the oxide mixture, composed of NiO and Cr2O3, penetrates the Cr depleted GB migration zone.

4.3. SCC mechanism

So far there is no consensus on the SCC mechanism of alloy 690 in PWR primary water. Intergranular oxidation has been proposed as a SCC mechanism of alloy 600 in PWR primary water [52–54]. Intergranular oxidation has consistently been reported to occur on unstressed alloy 600 coupon [55,56] as well as beyond the crack tip [14,16,17,43] after exposure in primary water. However, intergranular oxidation has not been observed on unstressed alloy 690, likely due to formation of a protective Cr2O3 layer over the GB by virtue of the higher Cr content [23,27,57]. Nevertheless, a high Cr content cannot guarantee the immunity of this alloy to SCC during dynamic straining. Intergranular oxidation still occurred in alloy 690 SA after the protective Cr2O3 layer over the GB was breached [13]. Here we show that when there is no protective Cr2O3 layer beyond the crack tip after initiation, the crack propagates as oxidation occurs in the GB migration zone (Figs. 10 and 11). Arioka et al. [5,8] and Zhai et al. [18] observed cavities at intergranular locations in cold worked 690 TT with intergranular carbides after constant load tests in 320–360 °C simulated PWR primary water and proposed that the creep cavitation may play an important role in the SCC process. However, those works all used thermally treated and cold worked alloy 690 for the tests and the cavities normally nucleated around the carbides. The constant load test on thermally treated alloy 690 without cold working in 360 °C simulated PWR primary water by Maeguchi [58] shows that no rupture was observed after 123,000 h although the complete absence of incipient cracks was not confirmed. It should also be noted that cavities were not observed near the crack tips of solution annealed alloy 690 in this work. So the creep cavitation induced cracking may only be applicable to cold worked alloy 690 with intergranular carbides. Moreover, the cavities were found not just near the crack tip, but also subsurface [5,8,59] that is not affected by the environment. Considering that corrosion is an inevitable part of the SCC process, it is believed that the creep cavitation induced cracking is not a generic SCC mechanism for this alloy in high temperature water.

The cracks on alloy 690 after CERT test in high temperature water should result from SCC process as the same tests in inert environment do not produce cracking [6,60]. Furthermore, the SCC
susceptibility of alloy 690 evaluated by CERT is reasonably correlated with the microstructure features (such as cold work level, intergranular carbide density) [4,61,62]. Moss et al. [13] proposed that dynamic straining could impair the Cr$_2$O$_3$ layer that originally forms over the GB allowing oxygen to diffuse in when the outward diffusion of Cr is not fast enough to replenish the impaired Cr$_2$O$_3$ layer. From this work, the crack propagation resistance is also dependent on the diffusivity of Cr after the crack initiates. The GB migration zone beyond the crack tip becomes oxidized when there is not enough Cr diffusion to maintain a compact Cr$_2$O$_3$ layer above it (Figs. 10 and 11). Due to Cr depletion, the migration zone tends to form non-protective oxide with the inward diffusion of oxygen. The oxidation through the migration zone is faster than along the migrated GB. Therefore, the degraded GB migration zone becomes a preferential route for cracking. The inward diffusion of oxygen into the GB migration zone would be the controlling process for cracking as GB migration is faster than the penetrative oxidation. The kinetic study on SCC process of this alloy based on this

![Fig. 11. (a) and (b) HADDF micrographs of the active crack, (c–e) high resolution bright field images from selected areas in (a) and (f) Fast Fourier Transformation (FFT) of (d).](image-url)
understanding will be carried out in the future.

5. Conclusions

The microstructures of intergranular attack near both stagnant and active stress corrosion crack (SCC) tips of alloy 690 SA were characterized in detail after constant extension rate tensile tests in hydrogenated high temperature water. For both cracks, the intergranular oxide, composed of NiO and Cr2O3, was observed beyond the crack tip with an adjacent grain boundary migration zone which is enriched in Ni and depleted in Cr. No cavities were observed near the crack tips. For the stagnant crack, NiO forms in the crack center oxide and has a cube-on-cube relationship with the neighboring grain, the crack inner oxide consists of a compact layer of Cr2O3 covering both the matrix and the crack tip and the adjacent grain boundary migration zone is deep and free of oxidation. For the active crack, NiO particles maintain epitaxy with the neighboring grains on both crack walls, while non-compact oxide composed of NiO and Cr2O3 forms in the grain boundary migration zone.

Grain boundary migration and intergranular oxidation are two important precursors in the SCC process of this alloy. Grain boundaries migrate due to the diffusion of Cr along the grain boundary toward the surface. The ability to form a compact Cr2O3 film at the crack tip is important to the IGSCC resistance and may be dictated by the efficiency of Cr diffusion up the migrated grain boundary. When a compact Cr2O3 film does not exist at the crack tip, the Cr depleted grain boundary migration zone is subject to penetrative oxidation via the inward diffusion of oxygen, making this zone susceptible to crack propagation. Thus, even a high Cr content cannot guarantee the immunity of alloy 690 SA to SCC during dynamic straining in hydrogenated high temperature water.

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