# Light Water Reactor Sustainability Program

The role of grain boundary oxides in the susceptibility to irradiation assisted stress corrosion cracking for high dose 304 stainless steel under pressurized water reactor relevant conditions



September 2022

U.S. Department of Energy Office of Nuclear Energy

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# The role of grain boundary oxides in the susceptibility to irradiation assisted stress corrosion cracking for high dose 304 stainless steel under pressurized water reactor relevant conditions

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September 2022

Prepared for the U.S. Department of Energy Office of Nuclear Energy

## SUMMARY

The objective of this LWRS project is to pin down the mechanism of irradiation-assisted stress corrosion cracking (IASCC) in high dose (neutron-irradiated) solution-annealed 304 stainless steel in PWR primary water environment and to propose mitigation strategies. A novel miniaturized four-point bend test was used to determine the crack initiation stress and to relate it to the microstructure features responsible for crack initiation. In this current work, our efforts were devoted to identifying the role of grain boundary (GB) oxidation in IASCC. For this purpose, specimens from SA304 SS (dose levels: 5.4 and 69 dpa) irradiated in BOR-60 reactor at RIAR, were selected for investigation in the Irradiated Materials Testing Lab (IMTL) at the University of Michigan. An approach to separate the corrosion and stress was developed to determine the exact role of GB oxidation on IASCC. To accomplish that, pre-oxidation in simulated PWR primary water with subsequent straining in high temperature argon gas was carried out individually.

#### **KEY FINDINGS**

- Separation of oxidation and straining approach confirms that GB oxidation is both a necessary and sufficient condition to initiate IASCC. Pre-oxidation without application of load in simulated PWR primary water followed by straining in high temperature Ar clearly showed the effect of exposure time on GB oxidation and the impact on lowering the stress to initiate crack. Exposure of SA304 SS (5.4 dpa) for 210 h in high temperature water initiated the cracks at 0.6YS in Ar whereas the companion sample of same dose level exposed to 1010 h in primary water cracked at low stress level of 0.5YS in Ar. The long-term exposure in water leads to oxidation of the grain boundary that ultimately lowering the crack initiation stress. The decrease in stress to initiate crack with long-term exposure substantiates the role of GB oxidation on IASCC.
- Increased exposure time in water results in more severe GB oxidation and a lowering of the stress to crack the grain boundary. A factor of 5 increase in exposure time from 200 to 1000 h produced a lower failure stress, and for the same stress level, a greater number of cracks, greater crack length and higher crack length per unit area.
- While pre-exposure experiments followed by straining in high purity Ar has shown that grain boundary oxidation is a necessary and sufficient condition to initiate IASCC, the application of stress during exposure results in more and longer cracks. As shown, both the surface crack length and the crack length per unit area are much greater than that in the pre-exposed and subsequently tested samples in Ar. Stress accelerated oxidation and subsequent cracking is probably the main reason for larger average crack length, which also likely results in greater crack depths. The depth of cracks in the samples stressed during oxidation can exceed 10,000 nm while of those tested in the pre-exposed + straining in Ar had a maximum depth of 460 nm.
- There was no evidence of cracking upon straining of an unoxidized SA304 SS (69 dpa) sample to 0.8YS in high temperature Ar whereas the same dose level sample pre-oxidized in water for 210 h followed by straining in Ar cracked at much lower stress level of 0.6YS. These findings confirm that the samples are not inherently susceptible to IG cracking and that oxidized GBs serve as initiation sites for IG cracking. The DC-GB intersections and/or triple junction sites can promote cracking only when the GB is oxidized.

# ACKNOWLEDGEMENT

This project was co-founded by DOE under the Light Water Reactor Sustainability (LWRS) program Materials Research Pathway (Contract 4000136608) and EPRI (Contract 10010367). The authors would like to thank Connor Shamberger for assistance in the Irradiated Materials Testing Laboratory at the University of Michigan. Gratitude is also extended to Dr. Maxim Gussev, Patricia Tedder, Jesse Werden and other technical support staff at Oak Ridge National Laboratory (ORNL) for assistance with specimen handling and preparation.

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# ACRONYMS

| American Society of Testing and Materials         |
|---|
| boiling water reactor                             |
| backscattered electron                            |
| constant extension rate tensile                   |
| cold-work   |
| dislocation channel                               |
| dissolved oxygen                                  |
| electron back-scattered diffraction               |
| energy-dispersive X-ray spectroscopy              |
| electron discharge machining                      |
| electron energy loss spectroscopy                 |
| Electric Power Research Institute                 |
| full width at half maximum                        |
| High angle annular dark field                     |
| High angle grain boundary                         |
| high resolution                                   |
| grain boundary                                    |
| irradiation assisted stress corrosion cracking    |
| intergranular                                     |
| Irradiated Materials Testing Laboratory           |
| Low Activation Materials Development and Analysis |
| localized deformation                             |
| linear variable differential transformer          |
| light water reactors                              |
| Nano beam electron diffraction                    |
| Oak Ridge National Laboratory                     |
| pressurized water reactor                         |
| primary water                                     |
| Real-rod Dark-field                               |
| radiation induced segregation                     |
| solution anneal                                   |
| Selected area electron diffraction                |
| scanning electron microscope                      |
|   |

| SS           | stainless steel                           |
|--------------|---|
| STEM         | scanning transmission electron microscopy |
| STEM-SI EDS  | STEM spectrum imaging using EDS signals   |
| STEM-SI EELS | STEM spectrum imaging using EELS signals  |
| TEM          | transmission electron microscope          |
| TJ           | triple junction                           |
| UM           | University of Michigan                    |
| YS           | yield strength                            |
|              |   |

# The role of grain boundary oxides in the susceptibility to irradiation assisted stress corrosion cracking for high dose 304 stainless steel under pressurized water reactor relevant conditions

#### 1. INTRODUCTION

The overall objective of this LWRS project is the determination of IASCC susceptibility of highly irradiated SA304 SS and CW316 SS in simulated PWR primary water with various damage levels (5.4 to 125.4 dpa), in particular, the determination of the stress to cause crack initiation, the correlation to microstructural features, and identification of any precursor state and potential mitigation strategies. The focus is on the dose dependence of crack initiation to very high dpa, the nature of the initiation site, the role of localized deformation, and the role of grain boundary oxidation in crack initiation of highly irradiated austenitic stainless steel [1, 2]. The outcome of this LWRS program will provide a firmer understanding of parameters and microstructures governing IASCC and key elements that need to be included in a predictive model of the initiation of intergranular cracks that can be used to develop mitigation strategies. IASCC continues to cause major degradation to core structural materials of both PWRs and BWRs in the US and international reactor fleets. This is of most concern for the existing reactor fleet with a life extension of 60 to 80 years, but also for the introduction of advanced reactors that will be subjected to the similar environments. Hence, understanding the mechanisms responsible for IASCC and establishing mitigation strategies are of high priority.

During the years 2000 to 2010, tensile and compact tension specimens, and transmission electron microscopy (TEM) discs of multiple alloys were subjected to irradiation in the BOR-60 fast reactor in RIAR, Russia as part of the framework of BORIS (BOR-60 Internal Study) irradiation experiments [3, 4]. The typical dose range was 5–20 dpa, but several capsules reached or exceeded 100 dpa. Irradiated specimens were involved in multiple programs including the Cooperative IASCC Research program [3]. Under certain circumstances, irradiated materials and untested specimens (308, 304, and 316 stainless steel specimens with various dpa levels) were made available to research teams working in the radiation materials field. During FY2016–2017, a collaborative effort was launched to transport several high- and very-highdose specimens (up to 125 dpa) from Dimitrovgrad, Russia, to Halden, Norway, and after that to Oak Ridge National Laboratory (ORNL) in Oak Ridge, Tennessee. Much of the effort involved acquiring the proper license(s) and documenting that irradiated materials were appropriately prepared for shipment. The irradiated materials arrived in Halden, Norway, on August 23, 2016. After that, new activity calculations, inventory, additional packaging, documentation, and licensing efforts were pursued. The materials were shipped from the Halden reactor to ORNL in early 2018. In March 2018, 13 tensile specimens were delivered to the Irradiated Materials Examination and Testing hot cell facility at ORNL. The internal holder with specimens was extracted and examined, revealing no transportation-related issues. Finally, specimens were unloaded and underwent individual examination and inventory and were made available to this project. This study utilizes several stainless-steel specimens (solution-annealed 304 SS and cold-worked 316 SS) that were irradiated in the BOR-60 liquid sodium fast reactor to doses ranging from 5.4 to 125.4 dpa. It is important to learn whether IASCC susceptibility increases with dose to very high dpa corresponding to a service lifetime of 60 to 80 years.

IASCC occurs under the combination of applied stress and corrosive environment in irradiated materials. Within the framework of LWRS-program much progress has been made in understanding IASCC susceptibility, though a clear cause-and-effect has yet to be established on the mechanism of intergranular cracking in highly neutron irradiated stainless steels in the PWR environment. As documented, to evaluate the IASCC susceptibility of these materials, a constant extension rate tensile test technique was used to reveal the change of fracture behavior and mechanical property with various dose levels [2, 5]. Also, novel miniaturized four-point bend tests were conducted to identify the critical stress to induce crack initiation and the microstructure features that correlate with crack initiation [1, 2]. An advantage of the bend test is that it creates a stress gradient through the sample thickness such that cracks grow into a progressively decreasing tensile stress, slowing crack propagation and preserving the sample beyond formation of the first crack [6]. Furthermore, this test creates an area at the surface of nearly constant strain, enhancing the possibility of observing multiple crack initiation sites on a single specimen.

IASCC is a well-studied phenomenon, however, irradiation dramatically increases susceptibility as cracking occurs well below the yield strength [7, 8]. The present objective is to identify the role of grain boundary (GB) oxidation on intergranular cracking of neutron irradiated SA304 stainless steel. This was achieved by separation of oxidation and straining approach, i.e. pre-oxidation without application of load in primary water (PW) followed by straining in an inert Ar gas environment at the same temperature. In order to provide a much clearer view of factors affecting the IG cracking, the quantitative results of the dynamic straining in PW of SA304 SS have been considered for the discussion.

#### 2. EXPERIMENT

#### 2.1 Materials and Specimens

#### 2.1.1 Materials

The alloy investigated in this study is solution annealed (SA) 304 stainless steel. The chemical composition of the SA304 SS (in wt.%) heat is given in Table 1. The irradiations were performed in BOR-60 fast reactor at a temperature of 320°C with a neutron flux of  $\sim 1.8 \times 10^{15}$  n/cm<sup>2</sup>s (E>0.1 MeV), which corresponds to a damage rate of 9.4x10<sup>-7</sup> dpa/s using the NRT model [3]. In the table, the suffix H represents the traditional solution annealed condition.

Table 1. Chemical compositions (wt.%) of the SA304 stainless steel.

| Alloy/heat                | С     | S      | Р     | Si   | Mn   | Ni   | Cr    | Мо | Cu   | Co    | Nb-<br>Ta | B<br>(ppm) | O<br>(ppm) | N<br>(ppm) |
|---------------------------|-------|--------|-------|------|------|------|-------|----|------|-------|-----------|------------|------------|------------|
| 304-1 H/Creusot-<br>Loire | 0.022 | 0.0007 | 0.032 | 0.38 | 1.79 | 9.88 | 18.61 | -  | 0.25 | 0.064 | -         | 9          | -          | 610        |

#### 2.1.2 Specimen Preparation

Two pieces of material sliced from a tensile bar head using Electron Discharge Machining (EDM) were used to prepare four-point bend specimens. The position where the slices were made and the dimensions of the four-point bend specimen are shown in Figure 1. The remaining material was used to prepare transmission electron microscopy (TEM) specimens, to study the microstructure in the as-received irradiated condition. Rectangular samples with 1 mm thickness were made after EDM cutting. A Buehler Mini-met 1000<sup>TM</sup> sample grinding and polishing tool performed sample thinning to a target thickness of 800 µm using 120, 180, and 340 grit SiC grinding paper on each side to achieve a uniform thickness (final thickness variations were less than 10 µm). One side of the sample was then polished with a nylon pad containing 3 µm polishing media in the Mini-met<sup>TM</sup> and subsequently electrochemically polished in a Struers LectroPol-5<sup>TM</sup> system in four steps. One electrochemical polishing step was applied for 15 s at a potential of 30 V at 20 °C in a commercially available Struers A2 solution (60% perchloric acid). The final dimensions of the four-point bend sample are shown in Figure 1b. The ID, dose, and thickness of all samples used for this research project are given in Table 2.



Figure 1. Schematic showing (a) tensile bar head dimensions and location of the cut (the marked area), and (b) bend test sample dimensions (unit: mm).

| Alloy/heat | Parent tensile sample<br>ID | Four-point bend sample ID | Dose<br>(dpa) | Thickness<br>(µm) |
|------------|-----------------------------|---------------------------|---------------|-------------------|
| 304-1 H    | A84                         | A84-1-1                   | 5.4           | 800               |
| 304-1 H    | A84                         | A84-1-2                   | 5.4           | 900               |
| 304-1 H    | A84                         | A84-3                     | 5.4           | 849               |
| 304-1 H    | A84                         | A84-4                     | 5.4           | 838               |
| 304-1 H    | A98                         | A98-1-1*                  | 69            | 813               |
| 304-1 H    | A98                         | A98-1-2*                  | 69            | 935               |
| 304-1 H    | A98                         | A98-3                     | 69            | 844               |

Table 2. Details of neutron-irradiated four-point bend specimens used for this study.

\* FIB lift-outs were prepared from the tested bend samples for TEM analysis.

# 2.2 Test Systems and Experimental Procedures

#### 2.2.1 Autoclave System

The four-point bend testing systems IM2 and IM3 are located in an irradiated material testing lab (IMTL) at UM. The water loop schematic diagram is shown in Figure 2. The water loop consists of two sub loops, loop 1 for conditioning the water at room temperature and low pressure, and loop 2 for simulating light water reactor environment at high temperature and high pressure. The environmental parameters such as conductivity and dissolved gas concentration are controlled in loop 1. The water is then pressurized and heated in loop 2, reaching the desired temperature and pressure in the autoclave and recirculated to the primary water column. The conductivity and dissolved oxygen (DO) are monitored at both inlet and outlet of loop 2.



Figure 2. Schematic of the water loop used in the autoclaves at the Irradiated Materials Testing Laboratory.

Both the IM2 and IM3 loading systems have one pull rod located in the center of the autoclave head, which was used to meet the requirement of fine control of the deflection of the four-point bend specimen (see Figure 3). Load is applied with a 50 kN servo motor. A linear variable differential transformer (LVDT) is mounted on the pull rod to measure displacement. A load cell was connected with the pull rod, which was used to measure the load applied to the sample. The pull rod is sealed at the feed-through into the autoclave with a self-energizing graphite seal with an internal spring that expands under pressure. The pull rod inside of the autoclave is connected to an Inconel 718 sample loading fixture. Electrical insulation is provided by zirconia washers located in the loading fixtures. After loading the specimens, the autoclave body is sealed to the autoclave head, thus preventing any leakage during the experiment.



Figure 3. Photographs of the IM autoclave system and water loop. (a) Control panel front, (b) control panel back with plumbing and sensors, and (c) load frame, motor, and autoclave covered with insulating jacket.

### 2.2.2 Pre-Oxidation and Four-Point Bend Testing Conditions

#### **Exposure test environment**

The exposure tests were conducted individually in simulated PWR water environment in IM2 autoclave system to pre-oxidize the samples without application of load. The PWR primary water chemistry parameters listed in Table 3.

| Parameter                                     | PWR primary water |
|---|-------------------|
| Temperature (°C)                              | 320               |
| Pressure (MPa)                                | 13.7 (2000 psi)   |
| Inlet conductivity (µS/cm)                    | 21.53             |
| H <sub>2</sub> concentration (cc/kg)          | 35                |
| O <sub>2</sub> concentration (ppb)            | <5                |
| Boron as H <sub>3</sub> BO <sub>3</sub> (ppm) | 1000              |
| lithium LiOH (ppm)                            | 2                 |
| pH at 25°C                                    | 6.5               |

Table 3. Simulated PWR primary water chemistry parameters in IMTL autoclaves.

#### Four-point bend test environment and straining modes

Four-point bend tests were conducted in various conditions such as single and/or interrupted constant strain rate test in Ar as well as in PWR primary water, and constant load test. Bend testing of pre-oxidized

samples was conducted in an inert Ar atmosphere to separate the oxidation and straining processes. The single and/or interrupted bend tests in Ar or water were conducted at constant strain of  $4.3 \times 10^{-8}$  s<sup>-1</sup> while samples undergoing constant load bend tests were ramped to the target load at a strain rate of  $4.3 \times 10^{-7}$  s<sup>-1</sup>. Though pre-oxidation in water followed by straining in Ar was the major focus of activity in the current year, a brief description of dynamic straining in water and the constant load bend test in water are also given here as those test results are referred to and discussed in this report.

#### Fixture for the four-point bend sample

The four-point bend test method was developed by Stephenson at al. [4] and a detailed description of this method can be found in reference [5]. The four-point bend sample has a constant strain area of 0.5 mm  $\times$  3.5 mm, which makes it possible to locate the crack initiation site in a reasonable time. The four-point bend test fixture used for this study was fabricated from Inconel 718 alloy in accordance with the schematic shown in Figure 4. Heat treatment of post-fabricated fixture parts created a hardened state to prevent deformation during bend testing. Four round posts called centering pins, elevated from the bottom support surface by 0.4 mm, surrounded the sample to prevent rotational misalignment. Set screws to the left and right of the sample and centered the sample laterally and were retracted after pre-loading the sample to prevent constraint during bending.



Figure 4. (a) Schematic of the four-point bend loading fixture, and (b) the real fixture including a bend sample with side and top view.

### 2.2.3 **Pre-Oxidation in High Temperature Water**

To determine whether initiation of an intergranular crack is possible after the oxidation of grain boundaries in high temperature water and with application of load, pre-oxidation steps were conducted for 210 h and 1010 h at 320°C, in simulated PWR primary water. The bend samples of dose level 5.4 dpa (A84-3) and 69 dpa (A98-1-1) were exposed in PW for 210 h and the sample A84-4 (5.4 dpa) was exposed in PW for 1010 h. The primary water parameters were listed in Table 3. Upon completion of the SEM examination of the pre-oxidized surface, samples were strained in an inert argon gas atmosphere to assess the propensity for crack nucleation, i.e. rupturing of the oxidized grain boundary during straining in argon. Success in causing grain boundary fracture would establish that it is the oxidation of the grain boundary that is responsible for IG crack initiation.

#### 2.2.4 Four-Point Bend Test in High Temperature Argon

#### Constant strain rate & target stress

The four-point bend tests were carried out using the IM2 and IM3 autoclave systems in IMTL. Bend samples were loaded on the fixture with a tailor-made tweezers, centered by tightening the set screws on either side uniformly and held in place by bringing the loading points into contact with the sample and lightly tightening the connection of the pull rod at the system crosshead. Sample bending was performed by displacing the crosshead at a constant rate of  $1.714 \times 10^{-8}$  in/s, generating a constant strain rate of  $4.3 \times 10^{-8}$  s<sup>-1</sup> on the polished surface, until achieving the desired amount of load. The target stress in the constant strain region was achieved by applying a corresponding load based on the linear relationship between stress with load, as shown in Figure 5. The relationship between the bend yield load in four-point bend and the tensile yield stress was formed utilizing previous experimental data on neutron-irradiated 304 stainless steel specimens by Stephenson et al. [6, 9] and benchmarking experiments utilizing a heat of 316 SS cold-worked to varying degrees. While there is some variability, this comparison allowed a prediction of the bend yield load based on previous measurements of the tensile yield stress. Due to the linear relationship, it was assumed that loading to a percentage of the bending yield load in a four-point experiment is directly comparable to loading to that percentage of the yield stress for the specimen.



Figure 5. Comparison between the measured tensile yield stress and four-point bend yield load for several specimens, both irradiated and unirradiated. The linear fit was utilized to predict the bend yield load for conditions previously strained in tensile experiments.

The relationship between bend yield load and tensile yield stress was obtained from specimens with a thickness of ~800  $\mu$ m. In a four-point bend experiment the maximum bend stress,  $\sigma_{max}$ , is directly related to the specimen thickness. The maximum stress in the tensile surface is inversely proportional to the square of the thickness [10], as described by the following equation.

$$\sigma_{max} \propto \frac{1}{h^2}.$$
 (2)

Therefore, the applied load was adjusted based on the thickness of the sample when a certain fraction of yield stress was targeted.

#### Straining in high temperature Ar

To avoid the corrosive environmental effect, i.e. to avoid the influence of simultaneous application of corrosion and stress, four-point bend tests were conducted in an inert argon gas atmosphere. Thus, straining in argon gas environment aimed to clarify the environmental contribution on intergranular cracking. The argon four-point bend tests were performed at  $320^{\circ}$ C to be consistent with tests conducted in water. Though ultra-high purity argon was used, it was further purified to remove any trace amounts of water and oxygen from the system that could potentially oxidize the samples during straining. Both autoclave systems (IM2 and IM3) were installed with the Ar-gas set up to perform straining in high temperature Ar of pre-oxidized (two 5.4 dpa samples and one 69 dpa sample) and as-received (69 dpa) sample. The autoclave test system was thoroughly purged for 12 h with the purified argon gas with a flow rate of 215 ml/min, and in this way, the environmental contribution to cracking was avoided. There is a tare load applied to the bend specimen by the vessel water pressure to mimic the tare load condition (55.4 lb) that the sample experiences in high temperature water at an initial strain rate of  $4.3 \times 10^{-5}$ /s. Once the tare load condition is reached, the strain rate was dropped to the same strain rate as that used in the water tests.

#### 2.2.5 Dynamic Straining in High Temperature Water

The four-point bend tests in simulated PWR primary water were carried out at constant strain rate (4.3  $\times 10^{-8}$ /s) as described in the above section. It is important to note that there is a tare load applied to the bend specimen by the vessel water pressure that is not directly measured by the pull rod load cell. With a 4.76 mm diameter pull rod and the 2000 psi system pressure, a tare load of 55.4 lb (246.5 N) was added to the bend specimen, under simulated PWR conditions. The testing was performed in increments to create crack initiation and limit the amount of crack propagation in the material. Increments are reported as the fraction of irradiated yield stress (YS). This interrupted straining procedure needs to be conducted only when the crack is not initiated at the first desired load. In these constant strain rate mode tests (single as well as multiple, interrupted straining), the unloading was very rapid (~ 1000x higher actuator rate).

#### 2.2.6 Constant Load Bend Test

The constant load test was conducted by keeping the sample at the targeted stress for 200 h after achieving the desired amount of load in a simulated PWR primary water environment. To reach the target stress, a strain rate of  $4.3 \times 10^{-7} \text{ s}^{-1}$  was used. Upon reaching the desired amount of time (i.e. 200 h) by holding the sample in a targeted stress level, the sample was quickly unloaded. In constant load mode, the testing was performed in increments to create crack initiation when there was no cracking at the first desired amount of load itself, i.e. an interrupted constant load four-point bend test.

### 2.3 Crack Characterization

#### 2.3.1 Crack Initiation Detection

The bending experiments were conducted in small increments to more precisely determine the crack initiation stress and study the microstructure responsible for crack initiation. Upon completion of each fourpoint bend test, the uniform strain area (0.5mm×3.5mm) of a tested sample was examined in SEM (JEOL JSM-6480) to determine the surface morphology and cracking susceptibility. As described in earlier sections, bend tests were conducted in either Ar or primary water. After each stress increment, the specimen was removed from the autoclave and examined in SEM. The uniform-strain region was imaged under 1000x magnification in BSE mode to record any sites of crack initiation as well as changes in the localized deformation. The GBs that are darker and wider than the others in BSE mode and oriented perpendicular to the tensile stress were most likely to crack upon subsequent straining. Therefore, GBs with this feature were tracked after each stress increment to record any changes in the GB and its surroundings. The higher magnification SE- and BSE-images (5000 -15000x) were taken when crack initiation was observed. The cracks and microstructure features at the crack initiation sites were characterized and their relationship with the cracks was analyzed.

#### 2.3.2 Cracking Criteria

The width of an IG crack tip can be less than 5 nm, indicating that the opening on the surface could be very small just after initiation occurs [11]. Therefore, defining a criterion for what is a crack depends on the detectability of the system. To detect the crack and determine the correlation of microstructures with crack initiation with our available SEM (JEOL JSM-6480) required a magnification of 5000x to 15000x. In the case of long-term (1010 h) pre-oxidized sample, detecting microstructural features is quite challenging as the surface coverage of Fe-rich oxide crystallites are very significant. So, a simple criterion for a crack considered in this work, is the visibility of a thick bold black line in BSE mode of the SEM. One feature used to define a crack is that it is a region on a boundary bounded by two bright lines representing the edges of the crack, and are created by the effect of the sharp curvature of the edges on the secondary electron (SE) production. These sharp bright lines can easily be seen in SE mode. The cracking criteria documented in the previous reports [1, 2], i.e. the plot of gray value (using ImageJ<sup>®</sup> software) across the crack with the two peaks from the two bright edges is valid only for the obvious cracks. However, as shown in Figure 6, with the appearance of black thick bold line in BSE image and the bright line feature from the sharp edge of a crack in SE mode (especially at 10000x or 15000x magnification), we can differentiate between a crack and an oxidized grain boundary.



(a) BSE

(b) SE



(c) SE

Figure 6. The SEM micrographs show the oxidized as well as the cracked GB in SA304 SS (A84-1-2; 5.4 dpa) bend sample.

### 2.4 Microstructure and Microchemistry Characterizations by TEM

Focused ion beam (FIB) lift-outs for TEM study were prepared from the four-point bend tested samples A98-1-1 (SA304 SS; 5.4 dpa) and A98-1-2 (SA304 SS; 5.4 dpa). The lift-outs were first cut and transferred to FIB grids with thickness of ~1.5 µm at 30 keV at LAMDA facility in ORNL using a FEI Versa FIB-SEM. The lift-outs were further thinned at the Michigan Center for Materials Characterization (MC<sup>2</sup>) at the UM using a Thermo-Fisher Helios 650 Xe Plasma FIB-SEM at 30 keV down to about 150 nm and were finally thinned at 5 keV to reduce FIB damage induced at high beam energy. The Talos is equipped with four 30 mm<sup>2</sup> silicon drift detector (SDD) energy dispersive spectroscopy (EDS) system that can give strong X-ray signals for scanning transmission electron microscopy (STEM) spectrum-imaging (SI) (STEM-SI) using X-ray signals and thus, was used for grain boundary microstructures and microchemistry characterization of attacked/cracked grain boundaries.

#### 3. **RESULTS**

The four-point bend test results of neutron irradiated SA304 SS (with dose level: 5.4 dpa, 69 dpa, 95 dpa and 125.4 dpa) samples have already been documented [1, 2]. In addition to the interrupted straining four-point bend test at constant strain rate, two new approaches such as constant load mode bend tests (dose level: 5.4 dpa and 95 dpa), and the separation of oxidation in high temperature water and straining in high temperature Ar (69 dpa) were introduced and the first test results were presented in Ref. [1]. This novel separation experimental approach, i.e. pre-oxidation in PWR primary water followed by straining in an inert argon gas environment, is applied now on SA304 SS (5.4 dpa) samples and the test results are presented in this current report. For this purpose, two bend samples (A84-3 and A84-4) with a damage level of 5.4 dpa were experimented individually with different exposure times in simulated PWR primary water (PW) at 320°C followed by dynamic straining at constant strain rate in high temperature Ar until crack initiation. At first, the surface of bend samples in as-received condition were characterized using SEM/EDS and then, separation of oxidation and straining tests were carried out individually.

### 3.1 Surface Characterization of As-Received SA304 SS (5.4 dpa)

Two four-point bend samples (A84-3 and A84-4) were prepared from the tensile sample A84 of damage level 5.4 dpa. Firstly, both the bend samples were characterized using SEM/EDS in an as-received condition to determine their microstructure and surface conditions, and then exposure test in PW with a subsequent straining until crack initiation in Ar occurred. The surface characterization of as-received bend sample (5.4 dpa) SA304 SS is presented in this section.



Figure 7. Surface morphology of the as-received four-point bend sample A84-4 (5.4 dpa; SA304 SS), (a) BSE image, and (b-c) SE images showing the microstructure of as-received surface condition and the appearance of inclusions.

The as-received surface of a bend sample A84-4 (5.4 dpa; SA304 SS) was examined using SEM/EDS and the results are presented in Figures 7-9. The BSE images (see Fig. 7a, 9a, 9c and 9e) show that the austenite phase grain boundaries of the as-received bend sample surface were clean, without any visible carbide or any other secondary particles. Also, the BSE images revealed the surface contains equiaxed austenite grains containing several inclusions and elongated band-like features. The EDS analyses such as point spectra, line scan and mapping were made to identify the chemistry of inclusions, and the band-like features. The SE images in figures 7b-c and 8a, and their corresponding EDS mapping analysis (see Fig. 8) shows the surface topography and inclusion chemistry was identified as non-metallic (Ca-Mg-Al)-rich oxides. This appearance of elongated shapes of these inclusions were probably mark the rolling direction of this material.



Figure 8. Surface morphology and EDS mapping of non-metallic oxide inclusion in as-received four-point bend sample A84-4 (5.4 dpa; SA304 SS), (a) SE image, and (b-h) EDS elemental mapping showing the chemistry of the inclusion.



Figure 9. BSE (a, c and e) and the corresponding SE images (b, d and f) with various magnifications showing the elongated band-shaped ferrite phase in the austenite matrix of as-received A84-4 (5.4 dpa; SA304 SS) sample. An An overlay of SE image and the obtained line scan (LS; distance from left to right is 13.1  $\mu$ m) across the ferrite phase is shown in Fig. (d). The quantification results of EDS point spectra collected at spot #1 and #2 in Fig. (f), are listed in Table 4. Yellow box in BSE-image mark the location of respective high magnification BSE-image. The black arrows in SE-mode images (b, d and f) point to ferrite phase.

The microstructure of A84-4 has band-like vertically oriented microfeatures, as shown in the BSE images in Figures 7 and 9. The orientation of the elongated band-like colonies (dark contrast phase, marked in black arrows in Figure 9) represents the rolling direction of the material. EDS line scan analysis was made across the band-like vertically oriented microfeature. The overlay of the line scan and SE image (Fig. 9d) reveal that the band-like microfeature is Cr-rich, but Ni- and Fe-depleted phase. Additionally, EDS point spectral analyses were made and the quantification results (Table 4) clearly indicates that the band-like microfeature is retained ferrite phase in the austenite matrix of this material. The 10000x-high magnification images (Figure 9f) showing that each band-like colony consisted of several small ferrite grains forming a bamboo-like structure. The black arrow in Fig. 9b, 9d and 9f (SE-images) point to ferrite phase. Overall, these surface morphology observations at different magnifications clearly show that surface is free of slip lines and no sign of surface damage/strain-induced plastic deformation.

Table 4. EDS-quantitative analysis of the retained ferrite phase and austenitic matrix of the asreceived bend sample A84-4 (5.4 dpa; SA304 SS).

| Element | EDS spot #1 |       | EDS spot #2 |       |  |
|---------|-------------|-------|-------------|-------|--|
|         | Wt.%        | At.%  | Wt.%        | At.%  |  |
| Cr      | 26.63       | 28.12 | 19.87       | 21.13 |  |
| Fe      | 68.36       | 67.20 | 70.67       | 69.96 |  |
| Ni      | 5.00        | 4.68  | 9.46        | 8.91  |  |

### 3.2 Exposure Tests in High Temperature Water

To separate the role of corrosion on IASCC, the bend samples were exposed in high temperature water without application of load, followed by straining in an inert environment. This new concept of separation of oxidation and straining were introduced at UM and the first preliminary results on bend sample A98-1-1 (69 dpa; SA304 SS) were documented in the 2021-LWRS milestone report [1]. Sample A98-1-1 (69 dpa) was pre-oxidized in simulated PWR primary water (PW) for 210 h at 320°C without load, and then strained in Ar at the same temperature. Interestingly, this sample cracked at 0.5YS in Ar whereas the companion sample A98-1-2 (69 dpa) strained in PW cracked at 0.8YS. On the other hand, we found no evidence of cracking in pristine (no previous exposure in PW) sample A98-3 (69 dpa) strained in Ar 0.8YS, demonstrating that the alloy is not susceptible to IG cracking unless exposed to PW. Therefore, to provide clear insight into the exposure time in PW, as well as to identify the role of grain boundary oxidation on IG cracking, two SA304 SS bend samples with a damage level of 5.4 dpa (A84-3; A84-4) were pre-oxidized in simulated PWR primary water at 320°C without application of stress. Bend sample A84-3 (5.4 dpa) was pre-oxidized in high temperature water for 210 h whereas the sample A84-4 (5.4 dpa) was pre-oxidized in high temperature water for 1010 h. In the following sub-sections, the oxidation characteristics of these two pre-oxidized bend samples (A84-3 and A84-4) are presented to show how the exposure time in PW influenced oxidation.

#### 3.2.1 Pre-Oxidation of A84-3 (5.4 dpa) for 210 h



Figure 10. The thermal profile, pressure, and conductivity of simulated PWR primary water during pre-oxidation of a bend sample A84-3 (5.4 dpa) in high temperature water at 320 °C for 210 h, without application of stress.

The four-point bend sample A84-3 (SA304 SS; 5.4 dpa) was exposed to simulated PWR primary water at 320°C for 210 h, without application of stress. The exposure environment conditions such as pressure stability, and conductivity of water as well as the temperature profile throughout the duration of this pre-oxidation test are shown in Figure 10. Upon completion of the 210 h exposure in PW, the surface was examined in SEM, with the motive of capturing as much as possible oxidized GBs in the area (0.5 mm×3.5mm) where the sample will experience a uniform strain region in four-point bend test in Ar. Figures 11-13 showing the SEM-EDS analyses of pre-oxidized sample A84-3. The high magnification BSE and the corresponding SE images in Figure 11 clearly showing the morphology of pre-oxidized surfaces, in particular, the oxidized grain boundary triple junctions. The outer oxide crystallite particles formed on the surface are dispersed and discontinuous, also inhomogeneous in terms of their size, as shown in Figure 11. The BSE and SE images shown in Figures 11 e and f, show that the severity of oxidation varies from one GB to another and the GB junction was further analyzed with the EDS mapping and point spectra modes (Fig. 12).



(a) BSE

(b) SE



(e) BSE

(f) SE

Figure 11. The plan view BSE images (a, c and e) and the corresponding SE images of a bend sample A84-3 (SA304 SS; 5.4 dpa) after 210 h of oxidation at 320 °C in simulated PWR primary water. The morphology of pre-oxidized surface reveals the various range of oxidation at GBs and grain interiors upon exposure to high temperature water.

The EDS mapping shown in Figure 12 reveals that random-sized outer crystallites are rich in Fe-oxide. The acquired spot spectra as well as their quantification results (from spot #1) listed in Table 5 confirms that the surface crystallites are Fe-rich oxides. Preferential oxidation of the GB can be clearly seen in all cases, though the oxide chemistry at the grain interior and GB cannot be confirmed with these EDS results.



(a) SE



Figure 12. The SEM-EDS analysis of a bend sample A84-3 (SA304 SS; 5.4 dpa) after 210 h of oxidation at 320°C in simulated PWR primary water, (a) plan view SE image, and (b-e) the corresponding EDS-maps.

Table 5. The EDS-quantitative analysis obtained from the spectra acquired at various spots (#1: large crystallite oxide; #2: Oxidized GB; #3: Grain interior) marked on the SE-micrograph (Figure 12a) of 210 h - pre-oxidized sample A84-3 (5.4 dpa).

| Element | EDS spot #1 |       | EDS spot #2 |       | EDS spot #3 |       |
|---------|-------------|-------|-------------|-------|-------------|-------|
|         | Wt.%        | At.%  | Wt.%        | At.%  | Wt.%        | At.%  |
| 0       | 39.95       | 69.74 | 13.64       | 35.29 | 9.35        | 26.29 |
| Cr      | 9.44        | 5.07  | 18.52       | 14.74 | 18.12       | 15.67 |
| Fe      | 45.16       | 22.59 | 59.19       | 43.87 | 63.36       | 51.02 |
| Ni      | 5.45        | 2.59  | 8.66        | 6.11  | 9.17        | 7.02  |

Figure 13 shows an interesting observation on the surface of A84-3 (5.4 dpa) exposed to high temperature water for 210 h. The BSE image (Figure 13a) and SE micrographs (Figure 13b) show that the surface morphology on the retained ferrite differs (the black arrow marks the ferrite phase in Figure 13a) from the austenite matrix. The coverage of more tiny nodules of Fe-rich oxides appears to be greater in the ferrite region. As-received microstructure of SA304 SS contains retained ferrite and inclusions, as presented in Figure 9. Strikingly, the preferential oxidation at the interface of ferrite and austenite can also be seen in Figure 13 and that was also confirmed with the EDS quantification results of spot #1, listed in Table 6.



Figure 13. The SEM-EDS analysis of ferrite phase site in 210 h - pre-oxidized sample A84-3 (SA304 SS; 5.4 dpa) in high temperature water without application of load, (a) plan view BSE image, and (b) the corresponding SE image. The EDS spectra were acquired on the three spots marked in SE image. Ferrite phases were identified with black arrows in BSE image.

Table 6. The EDS-quantitative analysis obtained from the spectra acquired at various spots (#1: Oxidized GB; #2: ferrite phase; #3: Grain interior) marked on the SE-micrograph (Figure 13b) of 210 h - pre-oxidized sample A84-3 (5.4 dpa).

| Element | EDS spot #1 |       | EDS spot #2 |       | EDS spot #3 |       |
|---------|-------------|-------|-------------|-------|-------------|-------|
|         | Wt.%        | At.%  | Wt.%        | At.%  | Wt.%        | At.%  |
| 0       | 11.78       | 31.49 | 3.99        | 12.50 | 5.35        | 16.35 |
| Cr      | 21.81       | 17.94 | 24.70       | 23.79 | 18.32       | 17.22 |
| Fe      | 59.45       | 45.51 | 66.03       | 59.21 | 67.75       | 59.29 |
| Ni      | 6.96        | 5.06  | 5.27        | 4.50  | 8.58        | 7.14  |

#### 3.2.2 Pre-Oxidation of A84-4 (5.4 dpa) for 1010 h



Figure 14. The thermal profile, pressure, and conductivity of simulated PWR primary water during pre-oxidation of a bend sample A84-4 (5.4 dpa) in high temperature water at 320 °C for 1010 h, without application of stress.

For a longer-term exposure bend sample A84-4 (SA304 SS; 5.4 dpa) was pre-oxidized in simulated PWR primary water at 320°C for 1010 h to study the influence of exposure time on pre-oxidation and their consequence on IASCC. The exposure environment conditions such as pressure stability, and conductivity of water as well as the temperature profile throughout the duration of this pre-oxidation test are shown in Figure 14. Similar to the protocol followed for 210 h exposed sample, after completion of 1010 h exposure the pre-oxidized surface was examined in SEM, with the motive of capturing as much as possible oxidized GBs in the constant strain area. Figures 14 and 15 showing the plan view SEM analyses of the pre-oxidized sample A84-4. The representative 5000x magnification BSE and the corresponding SE images as well as the 10000x magnification SE images in Figure 15 show the oxidized grain boundaries, and triple boundary junctions. With the increased exposure time to 1010 h in PW, the Fe-rich oxide micro-crystallites coverage become high and compact despite the inhomogeneity in size. The high magnification SE images (see Figures 15c, 15f and 15i) marked the oxidized grain boundaries and grain interior with numerous polyhedral Fe-rich oxide crystallites. It is important to note that irrespective of exposure time, the degree of oxidation varies from one GB to another, likely due to the misorientation angle between grains.



Figure 15. The plan view BSE images (a, d and g) and the corresponding SE images of a bend sample A84-4 (SA304 SS; 5.4 dpa) after 1010 h of oxidation at 320 °C in simulated PWR primary water. The morphology reveals that long-term exposure leads to increase in surface coverage of Fe-rich oxide crystallites, and various degrees of GB oxidation. Yellow box in 5000x SE-image mark the location of 10000x SE-image.
The 2000x magnification BSE image in Figure 16(a) shows the range of GB oxidation severity in A84-4 (5.4 dpa) upon long-term exposure (1010 h) in PW, and three GBs (#1-3) from this site were marked and further imaged with higher magnifications (i.e. 5000x and 15000x), as shown in Figure 16. As can be seen in Figures 16d, 16g and 16j, GBs #1 and 2 are oxidized to a greater extent than GB #3. Overall, the Fe-rich oxide crystallite coverage is quite high after such a long-term exposure in PW.



(e) BSE

(f) SE

(g) SE



Figure 16. The SEM analyses (BSE and SE micrographs at different magnifications) of 1010 h - pre-oxidized sample A84-4 (SA304 SS; 5.4 dpa) in high temperature water without application of stress, showing the oxidation of grain boundaries with different degrees.

## **3.3** Four-Point Bend Tests in High Temperature Ar

This section presents the results of straining in Ar of the two pre-oxidized SA304 SS bend samples (A84-3 and A84-4) with a dose of 5.4 dpa. As described earlier, sample A84-3 was exposed for 210 h in simulated PWR primary water at 320°C without application of stress whereas the sample A84-4 was exposed for 1010 h in the same PW condition, i.e. both the samples were pre-oxidized without applying load in PW environment. Upon pre-oxidation, the samples were strained in Ar at the same temperature as described in sub-sections 3.3.1 and 3.3.2.

### 3.3.1 Straining of 210 h – Pre-Oxidized A84-3 (5.4 dpa)

An interrupted straining in high temperature Ar (0.4YS, 0.5YS, 0.6YS and 0.7YS) was conducted on the pre-oxidized sample A84-3 (5.4 dpa; SA304 SS), and crack initiation occurred at 0.6YS. It should be noted that the irradiated yield strength of the SA304 SS (obtained from the prior tests) with the various dose level (up to 125.4 dpa) showed very similar values, i.e. 794-826 MPa. The first step was to strain the sample to 0.4YS, which produced no cracks. This process was repeated with increments of 0.1YS. Figure 17 (a) shows the bend tests performed in high temperature Ar, in an interrupted manner starting from 0.4YS until crack initiation found at 0.6YS. The temperature profile, load and LVDT displacement data of the crack initiation stress 0.6YS are given in Figure 17b.





Figure 17. (a) Load versus LVDT displacement curves of 210 h pre-oxidized A84-3 (5.4 dpa; SA304 SS) sample during interrupted straining (0.4YS, 0.5YS and 0.6YS) in Ar at 320 °C, (b) the thermal profile, load and LVDT displacement data during straining of a pre-oxidized sample A84-3 (SA304 SS; 5.4 dpa) to 0.6YS in Ar (0.215 l/min). Initial strain rate was  $4.3 \times 10^{-6}$ /s, then lowered to  $4.3 \times 10^{-8}$ /s.

Since only three very small cracks were observed at 0.6YS, the A84-3 (5.4 dpa) sample was further strained to 0.7YS. The details of temperature profile, load and LVDT displacement data during this last straining step of this sample A84-3 is shown in Figure 18.



Figure 18. The thermal profile, load and LVDT displacement data during straining of a pre-oxidized sample A84-3 (SA304 SS; 5.4 dpa) to 0.7YS in Ar (0.215 l/min).

## 3.3.2 Cracking Characteristics – A84-3

#### 0.6YS-Ar

After each stress increment the entire uniform strain region surface was examined in SEM to identify the minimum stress to initiate a crack. There was no evidence of cracking at 0.4YS and 0.5YS. The cracks were initiated upon straining to 0.6YS. There were only three tiny cracks initiated at location where a dislocation channel (DC) intersects with the oxidized GB. In fact, these cracks were found at a location that is an interface of retained ferrite phase in austenite matrix. Figure 19 shows the BSE and SE image montage of both the cracks initiated after straining to 0.6YS in Ar. It can be clearly seen that the cracking occurred at DC-GB intersection (Figure 19 (a)) where there is also an interface of retained ferrite phase in the austenite matrix. The EDS mapping analysis of DC-GB intersection site where the crack initiated in this sample is shown in Figure 20. The Cr (Figure 20c) and the Ni (Figure 20e) maps clearly reveal the Cr-rich oxide associated with the retained ferrite phase in the austenitic matrix. The O map and Cr map clearly show that larger oxide crystallites at the outer surface is Cr-depleted. The high magnification BSE and SE micrographs of that DC-GB intersection site where the crack initiated shown in Figure 21 mark the crack as well as the retained ferrite phase.





Figure 19. Photomontage of the plan view SEM micrographs showing the initiated cracks at the DC-GB intersection (interface of retained ferrite phase and the boundary adjacent to it) in 210 h - preoxidized A84-3 (SA304 SS; 5.4 dpa) followed by interrupted straining to 0.6YS in high temperature Ar, (a) BSE and (b) SE.



Figure 20. The SEM-EDS mapping of a crack initiated at the DC-GB intersection in 210 h - preoxidized A84-3 (SA304 SS; 5.4 dpa) followed by interrupted straining to 0.6YS in high temperature Ar, (a) BSE, (b-e) EDS mappings of O, Cr, Fe and Ni.



(a) BSE

(b) SE

Figure 21. The high magnification BSE and SE images of an initiated crack at the DC-GB intersection situated in retained ferrite-austenite interface in 210 h - pre-oxidized A84-3 (SA304 SS; 5.4 dpa) followed by interrupted straining to 0.6YS in high temperature Ar.

The SEM micrographs in Figure 22 show the severe oxidation at the phase boundary of retained ferrite. Particularly the BSE image (Figure 22a) reveals two distinct features that confirm the ferrite phase and severe oxidation at its phase boundary and the GB. BSE and SE images (Figure 22b-c) confirm the severe oxidation at the phase boundary of that retained ferrite phase. EDS elemental maps were generated on this area, and the results are given in Figure 23. The Cr and Ni maps confirm the Cr-rich and Ni-depleted features of a ferrite phase. No deformation such as DCs were found at this site.



Figure 22. The BSE and SE micrographs showing the severe oxidation at the retained ferriteaustenite matrix interface in 210 h - pre-oxidized A84-3 (5.4 dpa) sample that was dynamically strained to 0.6YS in Ar.



Figure 23. The BSE image and the corresponding EDS mapping showing the Cr-rich oxide at the retained ferrite and austenite matrix interface in 210 h - pre-oxidized A84-3 (5.4 dpa) sample that was dynamically strained to 0.6YS in Ar.





Figure 24. The BSE and SE image obtained after straining to 0.6YS in Ar showing the uncracked intersection of DC-GB in A84-3 (5.4 dpa).

The BSE and SE image montage in Figure 24 shows an interesting site where the coexistence of DC-GB intersection as well as the triple junction, but no evidence of cracking. At this high magnification SEM micrographs, the coverage of Fe-rich oxide crystallites appears to be less on this triple junction area, and the oxidized grain boundaries in this TJ seems to be narrow as well.

### 0.7YS-Ar

While only three short cracks were found upon straining to 0.6YS in Ar, ten cracks were found upon straining to 0.7YS. Detailed SEM examination was carried out and few representative cracked grain boundaries and uncracked boundaries with interesting microfeatures were presented in Figures 25-27. Figure. 25 shows the BSE and the corresponding SE micrographs of three representative cracks in A84-3 upon straining to 0.7YS in Ar. As can be seen in Figure 25, all of these cracks occurred on grain boundaries where the localized deformation in the form of dislocation channel intersected the oxidized grain boundary. Fig. 25c and 25f clearly reveals a crack that appeared to originate where the DC intersected the triple junction. It is important to note that all these cracks were newly occurred upon straining to 0.7YS.





Figure 26 shows the BSE and the corresponding SE micrographs of a narrow crack where the DC intersects with the grain boundary. As the oxidized grain boundary appears to be very thin, the intersection site of DC-GB appears to be a narrow crack. Though the formation of a DC as well as crack nucleation was found at the DC-GB intersection after straining to 0.6YS in Ar, there was no noticeable change (i.e. crack broadening or lengthening) occurred upon straining to 0.7YS in Ar. The BSE and SE micrographs presented in Figure 27 reveals a site where the DC intersects a boundary near the intersection of three grains, i.e. triple junction DC-GB intersection site as shown in the 5000x and 10000x BSE and the corresponding SE images. While the relative origins of the crack and dislocation channel are not known, they are clearly related. Results of the characterization of cracks upon straining in Ar of a sample 84-3 (5.4 dpa; SA304 SS) that was 210 h pre-oxidized in PW without applying load are summarized in Table 7.



Figure 26. The high magnification BSE and the corresponding SE micrographs showing a narrow crack at the DC-GB intersection after straining 210 h - pre-oxidized A84-3 (5.4 dpa) bend sample to 0.7YS in high temperature Ar.



(a) BSE

(b) SE



(c) BSE

(d) SE

Figure 27. The BSE and SE images obtained after straining to 0.7YS in Ar, showing the slip along the GB where intersection of DC-GB was found in A84-3 (5.4 dpa).

| Table 7. Four-point bend test results of a sample A84-3 (SA304 SS; 5.4 dpa; 210 h of pre-oxidation | n |
|--|---|
| in PW) after straining in Ar.  |   |

| Sample ID<br>/ Dose<br>(dpa) | Fraction of<br>Yield Stress<br>(YS) in Ar | Number of<br>cracks | Average<br>crack length<br>(µm) | Crack<br>number<br>density<br>(#/mm <sup>2</sup> ) | Crack length<br>density<br>(µm/mm²) |
|------------------------------|---|---------------------|---------------------------------|--|-------------------------------------|
|                              | 0.4                                       | 0                   | 0                               | 0  | 0                                   |
| AQA 2 /5 A                   | 0.5                                       | 0                   | 0                               | 0  | 0                                   |
| A64-373.4                    | 0.6                                       | 3                   | 4.6                             | 1.7  | 7.9                                 |
|                              | 0.7                                       | 10                  | 4.7                             | 5.7  | 26.8                                |

### **3.3.3** Straining of 1010 h – Pre-Oxidized A84-4 (5.4 dpa)

Sample A84-4 (5.4 dpa) was exposed to 1010 h in simulated PWR primary water at 320°C followed by straining in Ar at the same temperature. As described earlier, no cracking was found in sample A84-3 (5.4 dpa) after exposure in PW for 210 h and straining in Ar to 0.4YS and 0.5YS, and only three tiny cracks were found after straining to 0.6YS. Upon further straining to 0.7YS ten cracks were found. However, the cracks observed in A84-3 were mostly short cracks. Based on this observation, the companion 5.4 dpa sample was subjected to long-term exposure (1010 h) in PW and strained in high temperature Ar in an interrupted manner, i.e. 0.5YS and 0.6YS. Figure 28a shows the load vs LVDT displacement curves obtained after straining to 0.5YS and 0.6YS in Ar. The straining characteristics with the temperature profile for both the straining steps were given in Figure 28b and c. Strain rate and all other conditions were same as we conducted the bend tests in Ar for A84-3 sample.



Figure 28. (a) Load versus LVDT displacement curves of 1010 h pre-oxidized A84-4 (5.4 dpa; SA304 SS) sample during interrupted straining (0.5YS and 0.6YS) in Ar at 320 °C, (b and c) the thermal profile, load and LVDT displacement data during four-point bend testing at 0.5YS and 0.6YS in flowing Ar (0.215 l/min). Initial strain rate was  $4.3 \times 10^{-6}$ /s, then lowered to  $4.3 \times 10^{-8}$ /s.

### 3.3.4 Cracking Characteristics – A84-4

Upon straining to 0.5YS in high temperature Ar, two lengthy cracks were initiated in 1010 h preoxidized sample A84-4 (5.4 dpa). One crack initiated at the inclusion site whereas the other one at the triple junction. The crack that was initiated at the larger inclusion site is shown in Figure 29. A complete tracking of this site from the beginning to final straining step, i.e. in all stages such as as-received, pre-oxidation, 0.5YS in Ar and 0.6YS in Ar, are shown in Figure 29. The tracked BSE and SE images clearly indicate that cracking initiated at 0.5YS. More details of the chemistry and surface conditions of these inclusions in asreceived SA304 SS are given in section 3.1 of this report. These inclusions are found to be non-metallic oxide inclusions within the austenite matrix in SA304SS.









Figure 29. The SEM micrographs showing the crack initiation at an inclusion site of A84-4 sample pre-oxidized for 1010 h in PW followed by straining in Ar. Crack initiated at 0.5YS in Ar.



Figure 30. The BSE and SE image montage of a lengthy crack initiated in sample A84-4 (SA304 SS; 5.4 dpa) pre-oxidized for 1010 h in PW followed by straining to 0.5YS in high temperature Ar. Crack widening with stress increment is shown in Fig. 32.

The 5000x magnification BSE and SE image montage of a crack that was initiated at 0.5YS in Ar are shown in Fig. 30. This crack length is  $38.3 \mu m$ , further straining to 0.6YS leads to widening as well as slightly lengthening as well.



Figure 31. The SEM micrograph montage of lengthy crack in sample A84-4 (SA304 SS; 5.4 dpa) pre-oxidized for 1010 h in PW followed by interrupted straining until 0.6YS in high temperature Ar. This crack was initiated already in previous straining step (i.e. 0.5YS-Ar), further straining to 0.6YS widened (see, Fig. 32) as well as slightly lengthened the crack.

The SEM photomontage of BSE and SE images showing the status of a crack at 0.6YS that was originally initiated at 0.5YS in a larger inclusion site indicate crack widening with increasing stress increment. The formation of a DC at 0.6YS and its intersection above the TJ can also be seen at the top regime of the crack in Figure 31. The high magnification images in Figure 32 clearly shows the crack widening upon straining to 0.6YS. The high magnification SE images showed in Figure 32 are corresponding locations where yellow boxes were marked in Figure 30b and Figure 31b.



Figure 32. The SE images showing crack widening in A84-4 (5.4 dpa) sample with stress increment from 0.5YS to 0.6YS in Ar at 320  $\circ$ C. The sample A84-4 was pre-oxidized in primary water for 1010 h and then strained in Ar.



Figure 33. The BSE images showing the cracked GB in 1010 h pre-oxidized A84-4 (5.4 dpa) sample subjected to 0.5YS in Ar at 320 °C.

Figures 33 and 34 show the status of the GB before and after straining to 0.5YS and 0.6YS in Ar. The GB that was oxidized in the exposure test cracked at 0.5YS as shown in the BSE images in Figure 33. The high magnification BSE image shows that this crack was initiated at a triple junction where the GB junction intersected with the channel. Upon straining to next level, i.e. 0.6YS in Ar, an extension of this crack was

observed (Figure 34c and d) but this crack did not appear to widen with the stress increment, rather the crack length increased.



Figure 34. (a-c) The SEM images showing the cracked GB at triple junction in A84-4 (5.4 dpa; 1010 h pre-oxidized in PW) followed by straining to 0.5YS in Ar, (d) SE image showing the lengthening of the crack upon straining to 0.6YS in Ar.

Figure 35 shows the site where the extension of a crack that was initiated in previous straining step (0.5YS) and a new crack initiated at 0.6YS, situated very adjacent to ferrite phase. As can be seen in the high magnification images, the cracks are appearing to be very narrow and the coverage of Fe-rich crystallites are more. A break in the larger outer crystallite confirms that this is a cracked GB.

Table 8 provides the cracking summary of A84-4 (5.4 dpa) sample that was 1010 h exposed to PW at 320°C and strained then in Ar at 0.5YS and 0.6YS. Only two long cracks with an average crack length of 23.9 µm were found after straining to 0.5YS in Ar whereas 24 cracks were found after straining to 0.6YS.



(a) BSE - 0.5YS-Ar

(b) BSE - 0.6YS-Ar

Figure 35. The BSE images showing the nucleation of new crack and an extension of a old crack (that initiated at 0.5YS) with stress increment in A84-4 (5.4 dpa; SA304 SS) subjected to 1010 h of pre-oxidation in PW followed by interrupted straining in Ar.



Figure 36. The SEM micrographs showing the cracked GB in 1010 h - pre-oxidized A84-4 (5.4 dpa) bend sample upon straining to 0.6YS in Ar.

| Sample ID<br>/ Dose<br>(dpa) | Fraction of<br>Yield Stress<br>(YS) in Ar | Number of<br>cracks | Average<br>crack length<br>(µm) | Crack<br>number<br>density<br>(#/mm <sup>2</sup> ) | Crack length<br>density<br>(μm/mm²) |
|------------------------------|---|---------------------|---------------------------------|--|-------------------------------------|
| A84-4 /5.4                   | 0.5                                       | 2                   | 23.9                            | 1.1  | 27.4                                |
|                              | 0.6                                       | 24                  | 10.9                            | 13.7   | 149                                 |

Table 8. Four-point bend test results of a sample A84-4 (SA304 SS; 5.4 dpa; 1010 h of pre-oxidation in PW) after straining in Ar.

The separation of oxidation and straining steps was applied to both the 5.4 dpa and 69 dpa samples. In addition to the interrupted straining in PW, a constant load four-point bend testing on another companion 5.4 dpa sample was carried out for 200 h in PW. As a reference experiment, straining in Ar of an as-received (irradiated-only) 69 dpa sample was conducted and the results were also compared. Table 9 summarizes the cracking characteristics of SA304 SS samples (with dose levels of 5.4 dpa and 69 dpa) that underwent four-point bend testing in various conditions.

| Sample<br>ID<br>(dpa) | Cumulative<br>Exposure<br>time in PW<br>at 320°C (h) | Cumulative<br>Exposure<br>time under<br>load in PW at<br>320°C (h) | Stress<br>fraction<br>(YS) | # of<br>cracks | Avg.<br>crack<br>length<br>on<br>surface<br>(μm) | Crack<br>number<br>density<br>(#<br>cracks<br>/mm <sup>2</sup> ) | Crack<br>length per<br>unit area<br>(μm/mm²) |
|-----------------------|--|--|----------------------------|----------------|--|--|--|
| A Q / 1 1             | 51.4   | 40.5   | 0.5                        | 0              | 0  | 0  | 0  |
| A04-1-1<br>(5.4)      | 109.8  | 79   | 0.6                        | 5              | 58.1   | 2.9  | 166  |
| (3.4)                 | 146.4  | 105.7  | 0.7                        | 17             | 62.8   | 9.7  | 610.2  |
| A84-1-2<br>(5.4)      | 200  | 200  | 0.5                        | 4              | 136.9  | 2.3  | 312  |
| A84-3<br>(5.4)        | 210  | 0  | 0.4                        | 0              | 0  | 0  | 0  |
|                       |  |  | 0.5                        | 0              | 0  | 0  | 0  |
|                       |  |  | 0.6                        | 3              | 4.6  | 1.7  | 7.9  |
|                       |  |  | 0.7                        | 10             | 4.7  | 15.7   | 26.8   |
| A84-4                 | 1010 0   | 0  | 0.5                        | 2              | 23.9   | 1.1  | 27.4   |
| (5.4)                 | 1010   | 0  | 0.6                        | 24             | 10.9   | 13.7   | 149  |
|                       | 65.6   | 43.7   | 0.5                        | 0              | 0  | 0  | 0  |
| A98-1-2               | 149.5  | 91.5   | 0.6                        | 0              | 0  | 0  | 0  |
| (69)                  | 243.9  | 165  | 0.7                        | 0              | 0  | 0  | 0  |
|                       | 329.4  | 216.3  | 0.8                        | 7              | 39.2   | 4  | 156  |
| A98-1-1<br>(69)       | 210  | 0  | 0.5                        | 11             | 2.2  | 6.3  | 13.9   |
| A98-3<br>(69)         | 0  | 0  | 0.8                        | 0              | 0  | 0  | 0  |

Table 9. Cracking characteristics of SA304 SS (5.4 dpa and 69 dpa), strained in various conditions in four-point bend mode.

# 3.4 Characterization of Four-Point Bend Samples A98-1-1 and A98-1-2

# 3.4.1 Microstructure and Microchemistry of A98-1-1 (69 dpa) – Pre-Oxidized in Water for 210 h and Strained in Ar

## **Neutron Irradiation Induced Grain Boundary Segregation (RIS)**

Figure 37 shows STEM-SI EDS data collected from an un-attacked GB region which clearly shows RIS has occurred in the neutron irradiated sample, resulting in enriched Si and Ni and depleted Cr and Fe at the GB.



Figure 37. (a) is a STEM-HAADF image taken from the A98-1-1 sample far away from the surface; (b)- (e) are corresponding Fe-, Cr-, Ni- and Si-maps, respectively; (f) shows element profiles along the outlined region in (a).

# Microstructure and Microchemistry of Attacked GBs

Figure 38 displays three attacked grain boundaries (GBs) in the A98-1-1-A, A98-1-1-B and A98-1-1-C samples, respectively. The oxide layer on the surface of the sample is only 35 nm and the HAGBs have been oxidized from the surfaces down to 100nm, 250nm, and 250nm, respectively, along the GBs.



Figure 38. (a), (c), and (e) are STEM-HAADF images taken from the A98-1-1-A, -B and -C samples, respectively, showing three attacked GBs; (b), (d) and (f) are corresponding O-maps, respectively.

Figure 39 displays STEM-SI EDS data (a-e), (f-j) and (k-o) showing the distributions of Cr, Fe, Ni, and O maps of regions centering to the top surfaces of the three attacked GBs in the A98-1-1-A, -B and -C irradiated and strained samples, respectively. The data show that the GBs were oxidized asymmetrically and the surfaces consist of an island-like Fe(Ni)-rich spinel oxide layer and a thin Cr-rich layer followed by a Ni-rich layer. Enrichments of Ni at the attacked tips were seen in the three attacked GBs which can be attributed to grain boundary migration (GBM). This phenomenon is much more profound in the attacked GB shown in (a-e).



Figure 39. (a), (f) and (k) are STEM-HAADF images showing the three attacked GBs in the A98-1-1-A, -B and -C samples shown in Fig. 38; (b-e), (g-j) and (l-o) are corresponding Fe-, Cr-, Ni-, and O-maps, respectively.

Figure 40 displays element profiles data across three lines perpendicular to the attacked GB shown in Fig. 39a in the A98-1-1-A sample with the element contents at the centers of each region.



Figure 40. (a) a mixed element map showing O, Si, Cr, Fe and Ni distributions along the attacked GB in the A98-1-1-A sample. (b), (c) and (d) showing element profiles along the three outlined region marked in (a), respectively; (e), (f) and (g) are tables showing the element contents along the vertical dotted line across (b) to (d).

### Microstructure and Microchemistry of Cracked GBs

Figure 41 shows STEM-SI EDS data collected from two cracked GBs in the A98-1-1-D and -E samples, respectively. The data show that the surfaces of the sample consist of an island-like Fe(Ni)-rich spinel oxide layer and a thin Cr-rich layer followed by a Ni-rich layer. Enrichments of Ni at the attacked tips were also seen in the two cracked GBs. The lengths of the two cracks along their GBs are about 400 nm and 460 nm, respectively.



Figure 41. (a) and (f) are two STEM-HAADF images showing two cracked GBs in the A98-1-1-D and -E samples, respectively; (b)-(e) and (g)-(j) are corresponding Fe-, Cr-, O-, and Ni-maps, respectively, showing the element distributions in the cracked GB regions.

Figure 42 shows the microstructure and microchemistry of the crack-tip region of the cracked GB shown in Fig. 41a. The data clearly shows the enrichment of Ni at the crack-tip due to GBM and the RIS beyond the crack along the GB.

Figure 43 shows the microstructure and microchemistry of the crack-tip region of the cracked GB shown in Fig. 40f. Again, the data clearly shows the enrichment of Ni at the crack-tip due to GBM and the RIS beyond the crack along the GB that is enriched in Si and Ni and depleted in Cr.



Figure 42. (a) and (b) are STEM-HAADF and BF images showing the crack tip region of the cracked GB in the A98-1-1-D sample as also shown in Fig. 41a; (c)-(g) are corresponding Fe-, Cr-, O-, Niand Si maps, respectively; (h) is a mixed element map showing distributions of O, Si and Ni in different colors.



Figure 43. (a) and (b) are STEM-HAADF and BF images showing the crack tip region of the cracked GB in the A98-1-1-E sample as also shown in Fig. 41f; (c)-(g) are corresponding Fe-, Cr-, O-, Niand Si maps, respectively; (h) is a mixed element map showing distributions of Si and Ni in different colors.

# 3.4.2 Microstructure and Microchemistry of A98-1-2 (69 dpa) – Dynamically Strained in Water

### **Neutron Irradiation Induced Grain Boundary Segregation (RIS)**

Figure 44 shows STEM-SI EDS data collected from an un-attacked GB region which clearly shows RIS has occurred in the neutron irradiated sample A98-1-2, resulting in enriched Si and Ni and depleted Cr and Fe at the GB, similar to that for A98-1-1.



Figure 44. (a) is a STEM-HAADF image taken from the A98-1-1 sample far away from the surface; (b)- (e) are corresponding Fe-, Cr-, Ni and Si-maps, respectively; (f) shows element profiles along the outlined region in (a).

### Microstructure and Microchemistry of Attacked GBs

Figure 45 shows an attacked grain boundary in the A98-1-2-A sample. The oxide layer on the surface of the sample is only 30 nm thick and the HAGBs have been oxidized from the surfaces down to 600 nm along the GB. Some TiOx particles were seen on the surface, possibly from contamination.



Figure 45. (a) is a STEM-HAADF image of an attacked GB in the A98-1-2-A sample; (b)-(f) are corresponding Fe-, Cr-, Ti-, Ni-, and O-maps, respectively.

Figure 46 shows STEM-SI EDS data from the region outlined in Figure 45a. The data show that the attacked GB has three layers on each grain face, a Fe-rich spinel oxide layer and a Cr-rich Cr<sub>2</sub>O<sub>3</sub> layer followed by a Ni-rich layer adjacent to the metal. Also, some Cr-rich oxides were seen at the GB.

Figure 47 shows the microstructure and microchemistry of the tip region of the attacked GB shown in Figures 45 and 46. The data clearly shows the enrichment of Ni at the attacked GB-tip due to GBM and the RIS beyond the attacked tip along the GB, i.e., with enriched Si and Ni and depleted Cr and Fe at the GB.



Figure 46. (a) is STEM-HAADF image of the attacked GB in the A98-1-2-A sample as also shown in Figure 45a; (b)-(f) are corresponding Fe-, Cr-, Ni-, O-maps, and Si-maps, respectively; (g) is a mixed element map with O, Cr, Fe and Ni in different colors and (h) shows element profiles along the outlined region in (g).



Figure 47. (a) is a STEM-HAADF image of the attacked tip region of the attacked GB in the A98-1-2-A sample as shown also in Figures 45a and 46a; (b)-(f) are corresponding Fe-, Cr-, Ni-, O- and Si-maps, respectively; (g) is a mixed element map with O, Cr, Fe and Ni in different colors and (h) and (i) display element profiles along the outlined regions, 1 and 2 in (g), respectively.

# **Microstructure and Microchemistry of Cracked GBs**

Figure 48 shows STEM-SI EDS data collected from a short-cracked GB region in sample A98-1-2-B. The crack is about 350 nm long along the GB terminated at a Cr-rich oxide.



Figure 48. (a) and (b) are STEM-HAADF and BF images of a short-cracked GB in the A98-1-2-B sample; (c)-(h) are corresponding Fe-, Cr-, Ni-, O-maps, Si- and Pt-maps, respectively.

Figure 49 shows STEM-SI data collected from a long-cracked GB region in the sample A98-1-2-C. The crack is more than 10  $\mu$ m long along the GB. The data show the flanks of the cracked surfaces consist of a three-layers structure, an Fe-rich spinel oxide layer, a Cr-rich layer and a Ni-rich layer underneath.



Figure 49. (a) and (b) are BF and STEM-HAADF images of a long-cracked GB in the A98-1-2-C sample, (c)-(f) are corresponding Fe, Cr, O and Ni maps, respectively, (g) and (h) are mixed elemental maps with two line profiles displayed as insets.

Figure 50 displays STEM-SI EDS data showing the distributions of Cr, Fe, Ni, and O, maps of another region centering to a long-cracked GB in the A98-1-2-D sample. The data indicate that the surface was oxidized forming large, isolated Fe(Ni)-rich oxide particles which might be the spinel phase and a continuous Cr-rich oxide layer with a Ni-rich layer underneath. The data also show that the crack stopped at a Ni-rich region.



Figure 50. (a) is a STEM-HAADF images taken from a region with a long-cracked GB in the A98-1-2-D sample and (b) is its corresponding O-map; (c)-(f) and (g)-(j) are Fe-, Cr-, Ni- and O-maps from the outlined region 1 and 2 in (a), respectively.

| Table 10. The Summary of the depth of attacked/cracked GBs in the selected neutron irradi | ated and |
|---|----------|
| strained 304 samples.   |          |

| Samples | <b>GB</b> Labels | GB degradation mode | Cracked/Attack depth (nm) |
|---------|------------------|---------------------|---------------------------|
|         | А                | Attacked            | 100 nm                    |
|         | В                | Attacked            | 250 nm                    |
| A98-1-1 | С                | Attacked            | 250 nm                    |
|         | D                | Short-cracked       | 400 nm                    |
|         | E                | Short-cracked       | 460 nm                    |
| A       |                  | Attacked            | 600 nm                    |
|         | В                | Short cracked       | 350 nm                    |
| A98-1-2 | С                | Long cracked        | >10,000 nm                |
|         | D                | Cracked             | 6,600 nm                  |
|         | Е                | Cracked             | >10,000 nm                |
|         | F                | Attacked            | 100 nm                    |

Table 11. The Summary of the surface oxide film of the selected samples and conditions.

|   | A98-1-1  | A98-1-2  |
|---|--|--|
| Averaged inner oxide<br>film thickness (nm) | 35   | 30   |
| Compactness                                 | Isolated Fe-rich spinel<br>(Fe, Cr, Ni) <sub>3</sub> O <sub>4</sub> / continuous Cr <sub>2</sub> O <sub>3</sub> /<br>continuous Ni | Isolated Fe-rich spinel (Fe, Cr, Ni) <sub>3</sub> O <sub>4</sub> /<br>continuous Cr <sub>2</sub> O <sub>3</sub> /continuous Ni |
| Oxide Structure                             | Fe-rich spinel (Fe, Cr, Ni) <sub>3</sub> O <sub>4</sub> /<br>Cr <sub>2</sub> O <sub>3</sub> / Ni                                   | Fe-rich spinel (Fe, Cr, Ni) <sub>3</sub> O <sub>4</sub> / Cr <sub>2</sub> O <sub>3</sub> /Ni                                   |

# 4. **DISCUSSION**

# 4.1 Effect of Grain Boundary Oxidation on IG Cracking

Straining of pristine samples of irradiated 304 SS (69 dpa) showed no evidence of cracking after being strained to 0.8YS. In fact, continued straining into the plastic zone by several percent failed to produce any IG cracks. However, the sample A98-1-2 (69 dpa; SA304 SS) that was strained dynamically to 0.8YS in simulated PWR primary water at 320°C initiated 7 cracks (see Table 9). Dynamic straining in high temperature water leads to severe oxidation and subsequent cracking when the generated DCs intersect an oxidized GB, as shown in Figure 51. The BSE and SE micrographs given in Figures 51c and 51d, clearly show that no cracking occurred in an unoxidized sample A98-3 (69 dpa) even after straining to 0.8YS in Ar at 320°C despite the generated DCs intersecting GBs. These results establish the high temperature water environment as being a key factor in the intergranular cracking of irradiated 304 SS. Further, observations have indicated that cracked GBs are often oxidized prior to cracking. However, due to the coincident application of stress and an oxidizing environment in these experiments, the role of the environment is not clearly established. As such, the separation of the oxidation and straining processes was designed to provide insight into the role of grain boundary oxidation on IG cracking.



(a) BSE - 0.8YS-PW - A98-1-2 (69 dpa)



(c) BSE - 0.8YS-Ar - A98-3 (69 dpa)



(b) SE - 0.8YS-PW - A98-1-2 (69 dpa)



(d) SE - 0.8YS-Ar - A98-3 (69 dpa)

Figure 51. (a, and b) The BSE and the corresponding SE micrographs showing the cracked GBs in A98-1-2 (69 dpa; SA304 SS) sample upon straining to 0.8YS in primary water at 320°C, and (c, and d) the BSE and the corresponding SE micrographs showing the uncracked GBs in A98-3 (69 dpa; SA304 SS) sample upon straining to 0.8YS in Ar at the same temperature. Sample A98-3 is oxide free, thus, no IG cracking occurred.

By separating the oxidation and straining steps, the influence of stress on oxidation was removed. While grain boundary oxidation has been suspected as one of the major factors in IASCC, the IG fracture of grain boundaries of samples exposed to PW and strained in high purity Ar clearly establishes grain boundary oxidation as a necessary and sufficient process for IASCC. The oxidation of the GB weakens it, increasing the susceptibility to cracking. Where dislocation channels terminate at the grain boundary, the local stress can exceed 1 GPa [14], providing a large amplification to the applied stress. The observation of cracks initiating at dislocation channel-grain boundary. This result also agrees well with the degradation of GB strength in Alloys 600 and 690, due to oxidation along the GBs [15-17], meaning that the (Cr-rich) oxidized GB is brittle and can easily be fractured. It should be noted that while discontinuous DC-GB intersections necessarily experience the same local stress for a given applied load. Factors such as variation in local chemistry of the oxidized GB and/or the structure plays a role on crack nucleation. This, along with other factors such as the orientation of the GB to the applied stress and to the slip plane, helps to explain the low fractions of boundaries that actually crack.

## 4.2 Role of Exposure Time on IG cracking

In the current work, the bend sample A84-3 (5.4 dpa) was exposed to primary water at 320°C for 210 h without application of load, whereas the companion sample A84-4 (5.4 dpa) was exposed for 1010 h. Based on the SEM micrographs presented in Figures 11 (A84-3) and 15 (A84-4), long-term exposure (1010 h) leads to severe grain boundary oxidation as well as relatively compact coverage of outer Fe-rich oxide micro-crystallites, ultimately impacting the cracking characteristics. Both the pre-oxidized samples (A84-3 and A84-4) were strained in Ar individually, in an interrupted manner until crack initiation. As shown in the results section, sample A84-3 cracked at 0.6YS whereas the long-term exposed sample A84-4 cracked at 0.5YS. Thus, the first obvious effect of exposure time from the current work on 5.4 dpa sample is that an increase of exposure time leads to lowering of the crack initiation stress due to the more severe grain boundary oxidation during long-term exposure in PW.

Based on the crack quantification data summarized in Table 9, the following points can be considered as an effect of exposure time on cracking. Comparing the cracks in these two experiments, the cracks found in 1010 h – oxidized sample were of greater length and at a higher density than those in the sample oxidized for 210 h – oxidized sample. At every stress level, the 1010 h – oxidized sample had a significantly higher average crack length, number density and crack length per unit area than the samples oxidized for 210 h. It should be noted that only the 5.4 dpa samples were taken to different exposure times in the separation of oxidation and straining approach. However, sample A98-1-1 (69 dpa) was also subjected to a 210 h preoxidation without applying load, followed by straining in Ar. The 210 h - pre-oxidized 69 dpa sample initiated cracks at a stress of 0.5YS itself, similar to that of the 1010 h 5.4 dpa sample A84-3. While 11 cracks were formed at that stress, they were very short and quite similar in average length to that for the 210 h 5.4 dpa sample A84-3. Thus, the sample response of the 69 dpa sample to pre-exposure and straining in Ar fell somewhere between the two cases for the 5.4 dpa samples, perhaps indicating a small effect of irradiation damage level on cracking propensity.

## 4.3 Effect of Stress during Oxidation on IG Cracking

The role of stress can be determined via comparison of the pre-exposure-Ar straining experiments with those strained dynamically in water. For the 5.4 dpa samples, A84-1-1 and A84-3, cracking initiated at the same stress, 0.6YS, but the crack lengths were substantially different. Average crack length of the sample strained dynamically was 58  $\mu$ m compared to 4  $\mu$ m for the pre-exposed and Ar-strained sample. The difference was maintained at the higher stress increment of 0.7YS (see Table 9). The sample pre-exposed for 1010 h prior to Ar straining had greater crack lengths, but still less than half that of the dynamically strained sample. Thus, more time at temperature in PW results in longer cracks, but loading while in the environment produces the longest cracks. The effect of time under load in 320°C PW is shown in Figure 52 that plots the average crack length on the surface as a function of time. The data in blue refer to time under load and the data in red is for exposure time without load, followed by straining in Ar. Note that despite samples with different dpa, the effect of stress during oxidation is dramatic. A plot of crack length per unit area shows exactly the same behaviors.



Figure 52. Effect of the time over which the sample was under stress during oxidation on average IASCC crack length compared that for samples exposed without load and subsequently strained in purified UHP Ar gas.

Stress accelerated oxidation and subsequent cracking is probably the main reason for larger average crack length (58.1 µm at 0.6YS and 62.8 µm at 0.7YS) in sample A84-1-1 (5.4 dpa) that underwent an interrupted straining in PW. Overall exposure time upon three steps of straining in PW for A84-1-1 (5.4 dpa) sample is around 146 h, even then the average crack length and length density is much higher than the companion samples (A84-3; A84-4) that were pre-exposed in PW for 210 h and 1010 h followed by straining in Ar. A wide crack observed in A84-1-1 (5.4 dpa) sample that was dynamically strained to 0.7YS in water whereas a very narrow crack occurred in A84-4 (5.4 dpa) sample exposed to PW for 1010 h without application of stress followed by straining to 0.6YS in Ar, as shown in Figure 53. Despite the lower exposure time (146 h) for a sample A84-1-1 that was dynamically strained in water, an observation of wide

and long cracks supports an interaction between stress and corrosion on IG cracking. While measurements of crack depth are fewer in number, it can be seen from Table 10 that while the greatest depth of attack or cracking of a GB in the case of pre-exposure followed by straining in Ar is 460 nm, three of the 6 cracked/attacked GBs in the group that was stressed during oxidation had depths over 6,600 nm and two were over 10,000 nm. Thus, the crack length on the surface is likely a good indicator of the crack depth.



(a) SE - 0.7YS-PW - A84-1-1 (5.4 dpa)

(b) SE - 0.6YS-Ar-(1010 h pre-oxidized A84-4 (69 dpa))

Figure 53. The high magnification SE images showing a crack occurred in SA304 SS (5.4 dpa) samples, (a) Sample A84-1-1 dynamically strained in primary water (PW), and (b) A84-4, pre-oxidized for 1010 h in PW without applying load followed by straining in high temperature Ar. The sample A84-1-1 strained in PW showing a wide crack due to stress accelerated GB oxidation, and the synergistic effect of stress and corrosive environment.

The importance of combined stress and PW exposure is substantiated by the constant load test for 200 h in PW (A84-1-2) in which the crack length was double that of the dynamically strained sample (A84-1-1). In 200 h of constant load exposure at 0.5 YS in PW, the bend sample A84-1-2 (5.4 dpa) showed very lengthy cracks as a consequence of stress accelerated GB oxidation. The time in PW under load for the constant load test was considerably longer than that for the dynamically strained sample and the BSE and SE images in Figure 54 show an example of enhanced oxidation at the DC-GB triple junction intersection. This suggests a synergistic effect of applied stress and corrosive environment on GB oxidation. As a consequence, crack openings are very wide even at a low stress level of 0.5YS, as can be seen in Figure 55, which is a good example of stress accelerated GB oxidation that leads to IG cracking at low stress level. As can be noted from the crack summary Table 9, this sample had an average crack length of 136.9  $\mu$ m which is by far the largest among all test conditions. So, in addition to the exposure time in PW, stress plays a major role in accelerating GB oxidation and, as a result, IG cracking occurs at low stress level with lengthy cracks.



Figure 54. The BSE and SE images obtained from the surface of A84-1-2 (5.4 dpa) sample upon constant load bend test at 0.5YS for 200 h in PW at 320 °C, showing accelerated oxidation at GB triple junction.



(a) BSE – 0.5YS-PW – 200 h – Constant load A84-1-2 (5.4 dpa)



(b) SE – 0.5YS-PW – 200 h – Constant load A84-1-2 (5.4 dpa)



(c) SE – 0.5YS-PW – 200 h – Constant load A84-1-2 (5.4 dpa)

Figure 55. The BSE and SE images obtained from the surface of A84-1-2 (5.4 dpa) sample upon constant load bend test at 0.5YS for 200 h in PW at 320°C, showing a wide crack due to stress accelerated GB oxidation, and synergistic effect of stress and corrosive environment.

Another important observation is that accelerated oxidation at GBs and IG cracking occurs mainly for the GBs that were perpendicular to the straining direction. This agrees well with the several earlier studies [12-14] that have shown that normal stress plays a major role in IG cracking.

# 4.4 Effect of Ferrite

Observation of crack at the retained ferrite-austenite boundary (see Fig. 21), and at the boundary that bridges the retained ferrite phases in austenite matrix (see Fig. 36), as well as the crack formation at inclusion site GB clearly signaling the role of local chemistry on IASCC susceptibility. To the extent to known, there were no reports available concerning the influence of retained ferrite phase on IASCC, and no GB cracks were observed in these samples at a ferrite boundary. Though retained ferrite phase does not induce IASCC, oxidation of the ferrite-austenite boundary was observed. It is well known [18], that ferrite facilitates the Cr-rich oxide formation at the ferrite-austenite interface (as can be seen in Fig. 22). The direction of the ferrite with respect to the loading and the strain incompatibility at the interface of ferrite-austenite raises the local stress, as reported for fatigue cracks [19] and may lead to cracking at these interphase boundaries.

## 5. CONCLUSIONS

To understand the role of GB oxidation on IG cracking, the neutron-irradiated SA304 SS (5.4 dpa and 69 dpa) four-point bend samples were tested in various methods such as separation of oxidation and straining, constant load and an interrupted straining mode. Particularly, in this work, the separation of oxidation in simulated PWR primary water at 320 °C followed by straining in Ar at the same temperature was exclusively implemented on 5.4 dpa samples. The following conclusions can be made out of this work:

- Separation of oxidation and straining approach confirms that GB oxidation is both a necessary and sufficient condition to initiate IASCC. Pre-oxidation without application of load in simulated PWR primary water followed by straining in high temperature Ar clearly showed the effect of exposure time on GB oxidation and the impact on lowering the stress to initiate crack. Exposure of SA304 SS (5.4 dpa) for 210 h in high temperature water initiated the cracks at 0.6YS in Ar whereas the companion sample of same dose level exposed to 1010 h in primary water cracked at low stress level 0.5YS in Ar. The long-term exposure in water leads to oxidation of the grain boundary that ultimately lowering the crack initiation stress. The decrease in stress to initiate crack with long-term exposure substantiates the role of GB oxidation on IASCC.
- Increased exposure time in water results in more severe GB oxidation and a lowering of the stress to crack the grain boundary. A factor of 5 increase in exposure time from 200 to 1000 h produced a lower failure stress, and for the same stress level, a greater number of cracks, greater crack length and higher crack length per unit area.

- While pre-exposure experiments followed by straining in high purity Ar has shown that grain boundary oxidation is a necessary and sufficient condition to initiate IASCC, the application of stress during exposure results in more and longer cracks. As shown, both the surface crack length and the crack length per unit area are much greater than that in the pre-exposed and subsequently tested samples in Ar. Stress accelerated oxidation and subsequent cracking is probably the main reason for larger average crack length, which also likely results in greater crack depths. The depth of cracks in the samples stressed during oxidation can exceed 10,000 nm while of those tested in the pre-exposed + straining in Ar had a maximum depth of 460 nm.
- There was no evidence of cracking upon straining of an unoxidized SA304 SS (69 dpa) sample to 0.8YS in high temperature Ar whereas the same dose level sample pre-oxidized in water for 210 h followed by straining in Ar cracked at much lower stress level of 0.6YS. These findings confirm that the samples are not inherently susceptible to IG cracking and that oxidized GBs serve as initiation sites for IG cracking. The DC-GB intersections and/or triple junction sites can promote cracking only when the GB is oxidized.

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