EFFECT OF POST-IRRADIATION ANNEALING ON HARDENING, LOCALIZED DEFORMATION AND IASCC OF A PROTON-IRRADIATED 304 STAINLESS STEEL

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ABSTRACT

Post-irradiation annealing (PIA) is potentially an effective mitigation strategy for IASCC of stainless steels in light water reactor environments. Literature has shown that proper PIA conditions can fully recover some of the unirradiated properties including IGSCC resistance. However, the underlying process by which mitigation occurs is not well understood. In this study, a commercial purity 304 stainless steel was irradiated to 10 dpa using 2 MeV protons at 360°C. Irradiated samples were annealed at different conditions: 500°C to 1 and 15h, 550°C to 1h and 600°C for 10h. Constant extension rate tensile (CERT) tests were conducted in simulated BWR water at 288°C up to 10% plastic strain. Cracking susceptibility and dislocation channels were examined using SEM and LEXT interferometer, respectively. The results have shown that the decreasing trend in irradiation hardening with iron diffusion distance is consistent with the literature. IASCC susceptibility was significantly mitigated after PIA at 500°C for 1h and fully removed after PIA at 500°C for 15h or 550°C for 1h. The fraction of large dislocation channels dramatically dropped in the PIA samples that showed resistance to IASCC. The role of PIA in mitigation of IASCC is likely to be twofold. First, it decreases the overall yield stress of the material by removing part of irradiation hardening, thus decreasing the resolved normal stress at the grain boundaries. Second, it decreases the average dislocation channel height, which is probably linked to the decrease in the stress contribution from the channel-grain boundary intersection.

Keywords: IASCC, stainless steel, BWR, post-irradiation annealing

1. INTRODUCTION

Irradiation-assisted stress corrosion cracking (IASCC) of reactor core internals is a potential lifetime-limiting degradation mechanism for LWRs. It has taken on new urgency with the growing interest in extending operating licenses for the current generation of plants beyond 60 years. IASCC is largely controlled by the persistent damage induced by irradiation. That is, while radiation affects the environment through radiolysis, the onset of cracking in LWR environments is controlled by the radiation-induced persistent defects in the alloy [1.]. If some of the radiation-induced defects, including dislocation loops and radiation-induced precipitates, can be eliminated by methods such as post-irradiation annealing (PIA), IASCC susceptibility of the material is expected to be mitigated. Given that code qualification of new alloys could take one to two decades, and that an IASCC-resistant alloy has yet to be identified, PIA is one of the most promising near-term hopes for mitigating IASCC in today’s LWR fleet and to support life extension beyond 60 years.
The benefits of PIA have been shown in mitigating embrittlement of reactor pressure vessel (RPV) steels that mainly arises from radiation-induced copper precipitates or late blooming phases \[2,3\]. The effectiveness of PIA in mitigating IASCC in irradiated austenitic alloys has also been demonstrated in a number of studies \[4,7\]. For instance, Jacobs et al. \[4\] showed that the SCC behavior of 304SS irradiated to \(2.9 \times 10^{21}\) n/cm\(^2\) (E > 1 MeV) by fast neutrons was fully eliminated after PIA at 500°C for 1 hr. Two studies \[5,6\] have demonstrated that IASCC was significantly reduced in irradiated austenitic alloys after PIA for specific time-temperature combinations. These studies incorporate irradiation by both neutrons and protons, for which agreement is excellent.

Even though there are many instances that show the mitigation of IASCC by PIA, the mechanism how PIA leads to the mitigation of IASCC is not fully understood, mainly because the complexity of IASCC. The mechanism of IASCC is still being investigated actively. Without an understanding of the underlying mechanism of IASCC, it would be difficult to predict the effect of PIA. Yield strength correlates with IGSCC in austenitic stainless steels with high yield strength stainless steels show higher IASCC susceptibility \[5\]. Bruemmer et al. \[8\] found that there was a threshold of the increase in yield strength (600 MPa), above which IGSCC occurred. Localized deformation has recently emerged as a major contributor to IASCC \[9,12\], and recent data \[12\] has shown a strong correlation between IASCC and localized deformation. The objective of this paper is to examine the effect of PIA on these two aspects (irradiation hardening and localized deformation) with an ultimate goal of better understanding of the mechanism of IASCC and the role of PIA in mitigation of IASCC.

2. EXPERIMENTAL METHOD

2.1 Alloy and proton irradiation

A commercial grade 304SS (composition in wt%: Fe-18.3Cr 8.5Ni 1.4Mn 0.65Si 0.4Cu 0.03P 0.03S 0.04C) was used in this study because of its known susceptibility to cracking from previous studies \[10,12,13\]. Tensile samples (2×2mm\(^2\) cross-section and 21mm gage length) were made at Shular Tools (now Vacuum Technologies, Inc, TN) using electrical discharging machining. Prior to proton irradiation, the surface subject to irradiation was mechanically polished using up to #4000 grit SiC paper followed by electropolishing in a 10% perchloric acid in method solution at -40°C to obtain a mirror-like surface finish. Proton irradiation was conducted in the Tandem accelerator at Michigan Ion Beam Laboratory at the University of Michigan. Samples were irradiated to 10 dpa at 360 °C using 2 MeV protons. Sample temperature was monitored using a thermal imager during the irradiation and was kept within 10°C of the target temperature. The irradiation depth and dose rate was determined to be \(\sim 20 \, \mu m\) and \(1.2 \times 10^5\) dpa/s, respectively, using the SRIM code \[14\]. Raster beam was used during the irradiation and the full-cascade mode was used in SRIM for determining the damage rate. The detailed procedures for sample preparation of irradiations can be found in \[15\]. Only the center 10 mm of the gage length was irradiated.

2.2 Microhardness characterization

The microhardness in the following conditions: unirradiated, as-irradiated, and after PIA at 500-600°C up to 100 hours in the vacuum furnace following irradiation, was characterized using a Vickers hardness indenter (MICROMET II) with a load of 25g. At least 20 measurements with
spacing of at least 0.1 mm were performed to reduce statistical errors. The irradiation hardening is calculated by subtracting the unirradiated hardness from the irradiated hardness. The remaining irradiation hardening after PIA is calculated by subtracting the unirradiated hardness from the hardness of the irradiated sample after PIA.

2.3 CERT test in simulated BWR environment

Cracking susceptibility experiments were carried out in a high temperature, high pressure autoclave under simulated BWR normal water chemistry (NWC) conditions consisting of 288°C water containing dissolved oxygen (2 ppm) and a conductivity of 0.2 μS/cm at the outlet. The strain rate was $-3 \times 10^{-7}$ s$^{-1}$. Both the as-irradiated and after PIA samples were interruptedly strained to 2%, 4% and 10%. The irradiated and deformed surfaces were examined using SEM to check cracking susceptibility after each strain increment.

2.4 Characterization of localized deformation

The dislocation channel height measurements were taken utilizing the Olympus LEXT OLS4000 laser scanning confocal 3D measuring microscope at the Lurie Nanofabrication Facility at the University of Michigan. The channel height analysis was completed via the Gwyddion software. For each condition, at least 150 channels were characterized, with a maximum of four channels per grain to allow for statistics from a wide range of grains. Each channel was individually measured three times to provide a single average height. Channel height characterization was performed on samples after the final strain of 10% in BWR water. The sample surface was oxide-stripped before channel characterization.

3. RESULTS AND DISCUSSION

3.1 Irradiation hardening

The unirradiated hardness of the 304SS was 174±6 HV. Residual hardness values after irradiation and after PIA at 500°C:1h and 15h, 550°C:1h and 600°C:10h are given in Table 1. Irradiation hardening (the increase in hardness due to irradiation) was 211±20 HV in the as-irradiated condition and 120±13HV after PIA at 500°C:1h, and 20±12HV after PIA at 600°C:10h. The remaining irradiation hardening, which is shown as percentage of as-irradiated hardening, was 57% after PIA at 500°C:1h and only 9% after PIA at 600°C:10h. Irradiation hardening was fully removed (within statistical error) after PIA 600°C:30h.

Remaining irradiation hardening (expressed as % of the as-irradiated hardening) as a function of iron diffusion distance is shown in Figure 1, with available literature data. The iron diffusion distance, or $\sqrt{Dt}$ (where $D$ is the diffusivity of iron in stainless steels at the annealing temperatures and $t$ is the annealing time), contains information on both annealing temperature and time making it possible to compare different annealing conditions with various irradiation temperatures and durations. Data obtained in this study (black filled squares) from proton-irradiated 304SS to 10 dpa at 360°C followed by PIA at various conditions are shown in Figure 1 against the literature data from either proton-irradiated or neutron-irradiated stainless steels. The trend of decreasing hardness with the magnitude of $\sqrt{Dt}$ is consistent with the literature data.
Irradiation hardening originates from radiation-induced microstructures, including small defect clusters, dislocation loops and precipitates. Removal of irradiated microstructure by PIA leads to the decrease in irradiation hardening. As shown in Figure 1, the remaining hardening follows a much steeper slope with the diffusion distance starting at ~10^{-10} m (corresponding ~500°C:1h). This implies that the defect annihilation corresponding to hardening removal at the early stage may be different than that at a later stage. For instance, removal of small defect clusters and small loops may require short annealing time or lower annealing temperatures, while large loops or radiation-induced Ni/Si clusters/precipitates may require high annealing temperature and/or time. Microstructure analysis, which will be published elsewhere [16.], has shown the preferential annihilation of small dislocation loops after PIA and the relative insensitive of Ni/Si clusters to PIA. Therefore, radiation defects may have different annihilation rates, which leads to different hardening removal rates at the early and later stage of annealing.

3.2 Cracking susceptibility

Cracking susceptibility of the 304SS alloy in the as-irradiated and PIA conditions was examined in a simulated BWR-NWC environment. Samples were strained to 2%, 4% and 10% plastic strain and the crack number density and crack length per unit area for each strain level are given in Table 1. At 2% strain, only the as-irradiated sample showed susceptibility to IASCC. At 4% strain, cracks were also observed in the sample with PIA at 500°C:1h. However, the crack number density is only about half (30/cm^2 vs. 65/cm^2) and the crack length density is about 1/6th (42 μm/mm^2 vs. 240 μm/mm^2) that of the as-irradiated sample. Cracking susceptibility was significantly reduced after PIA at 500°C:1h. One crack was observed after PIA at 500°C:15h. However, careful examination of the crack reveals that it is a transgranular (TG) crack. Therefore, there is no IGSCC susceptibility after 500°C:15h. Crack susceptibility was completely removed after PIA at 550°C:1h. Figure 2 shows the sample surface after the final strain of 10%. The substantial difference in cracking susceptibility can be clearly seen. The as-irradiated sample shows many long cracks while the PIA at 500°C:1h shows a few short cracks. PIA appears to reduce not only the number density of cracks but also the ability of cracks to propagate.

3.3 Localized deformation

After the final strain of 10%, sample surface was oxide-stripped to remove the oxide film and oxide particles. The presence of oxides on the surface makes the characterization of channel difficult. Oxide stripping is not expected to affect channel height significantly and the ability to characterize samples after test in BWR-NWC water has the advantage over those tested in argon. Although the latter may preserve a much cleaner surface, the former is much closer to the real situation. The distribution of dislocation channels at the as-irradiated and PIA samples at 500°C:1h, 500°C:15h, and 550°C:1h are shown in Figure 3. The most distinct difference between the samples that are susceptible to IASCC (as-irradiated and PIA at 500°C:1h) and the samples that are not (PIA at 500°C:15h and 550°C:1h) is that the fraction of large channels (e.g. channels greater than 280 nm as indicated by the dash line in Figure 3) in the IASCC susceptible samples is much higher. The fractions of channels great than 280nm, 300nm and 320nm, respectively, for each condition are given in Table 1 and the comparison is shown in Figure 4. The as-irradiated condition shows the highest fraction of large channels among all the three channel categories. While PIA at 500°C:15h and 550°C:1h which exhibited no susceptibility to
IASCC both show substantially small fraction of large channels (less than half of the that at the as-irradiated condition).

Dislocation channeling is the dominant deformation mode at the testing temperature. Formation of dislocation channels is due to the interaction of dislocations with the irradiated microstructure under the applied stress. Dislocations annihilate some of the irradiation defects and form an easy path for subsequent dislocations. As dislocation slip is confined in the path, dislocation channels form with large deformation occurring in the channel. The degree of confinement of dislocations within channels depends on the nature of the irradiation defects. For instance, defect clusters and small dislocation loops are easier to annihilate by dislocations compared to voids. Therefore, defect clusters/dislocation loops are more important for channel formation compared to voids. In fact, the channel height has been shown to have a correlation with dislocation loop density [17.] but not void density. Ni/Si clusters can also be annihilated by dislocations, [13.] and therefore, they are expected to contribute to formation of dislocation channels.

PIA can partially or completely remove radiation-induced defects and therefore it would mitigate the degree of localized deformation in channels. PIA at 500°C:1h leaves ~23% of the as-irradiated dislocation loop density, which is further reduced to ~8% of the as-irradiated density after PIA at 500°C:15h, and to ~2% after PIA at 550°C:1h [16.]. Once the dislocation loops and Ni/Si clusters are completely removed (for instance, after PIA at 600 °C:10h), the deformed surface is indistinguishable from the unirradiated surface. Therefore, the decrease in dislocation channel height is primarily due to the removal of irradiation-induced defects by PIA.

3.4 IASCC mechanism and the role of PIA in IASCC

PIA removes both irradiation hardening and mitigates the degree of localized deformation in dislocation channels. But what is the ultimate role of PIA in mitigation of IASCC susceptibility? To answer this question, a better understanding of the IASCC mechanism is required. Yield strength of irradiated 304/316 stainless steels has been shown to correlate with IGSCC. Stainless steels with high yield strength are more susceptible to IASCC than those with low yield strength. A correlation between the irradiation hardening and the increase in yield strength has been established by Busby et al. [18.] in stainless steels and ferritic-martensitic steels. PIA reduces irradiation hardening/ yield strength therefore reduces the IASCC susceptibility of the material. However, although it correlates with IGSCC, yield strength is not directly connected to the IASCC mechanism, in which cracking of the passive oxide layer is a critical step in promoting IGSCC [19.],[20.],[22.].

A strong correlation was also established [12.] between the weighted average channel height and IASCC susceptibility. The argument was that a certain amount of localized deformation is essential in order to break the oxide film that covers the grain boundary so that the crack can initiate and advance. Therefore, there is a direct connection of localized deformation and the SCC process. The strong correlation between channel height and IASCC suggests that localized deformation is one of the major contributors to IASCC. However, the cause-and-effect relationship between channel height and IASCC has not been established. In other words, cracking of oxide film at the grain boundary by large dislocation channels, which results in crack initiation, needs to be demonstrated. Unfortunately, our work [21.] failed to establish the direct connection of large channels with crack initiation sites, however, IG cracks are preceded by
localized deformation as shown by Stephenson et al. [23.]. Dislocation channels associated with cracking initiation are not necessarily large channels. Note that, the correlation mentioned earlier was established based on the overall average channel height of the material, not on the observation of an individual channel and corresponding crack. The average dislocation channel height can serve as an indicator of the severity of degree of localized deformation in the material but is certainly not the only measure of localized deformation.

Besides dislocation channel height, which is an indicator of the localized plastic strain, there are a number of other factors that relate to localized deformation and may have a more direct connection with the IASCC mechanism. For instance, the localized stress at the grain boundary, which includes the resolved normal stress from the applied stress, and the dislocation-induced multiplication of stress at the interaction of channels and the grain boundary, can also play a critical role.

Normal stress was found to be closely related to the crack location as the cracked grain boundaries tend to be those aligned perpendicular to the tensile direction. The fraction of the cracked grain boundaries generally increases with grain boundary trace angle. The maximum cracking occurs when the grain boundary is about 90° to the tensile direction where the highest normal stress is expected. Normal stress, therefore, has a strong impact on crack initiation in the simulated BWR-NWC environment. West et al. [24.] used the Schmid factor of the neighboring grains to determine the normal stress acting on the grain boundary, resulting in the Schmid-Modified Grain Boundary Stress (SMGBS) model. This model showed that lower Schmid factors result in higher normal stress at the grain boundary.

The resolved normal stress is proportional to the applied stress for a given grain boundary with certain inclination. For the case of irradiated stainless steels, the yield strength increases significantly after irradiation and the normal stress on the grain boundary after yield is expected to be high. The positive correlation of cracking susceptibility with yield strength could be the result of the importance of normal stress. The stress at the grain boundary induced by the interaction of dislocation channels and the grain boundary can be significant. Evrard and Sauzay [25.], performed finite element modeling of the dislocation-grain boundary intersection and, found that the stress in the dislocation channels could be higher than the applied stress on the grain boundary by a factor of ~4. This could explain the observation of many instances of cracks initiated at the dislocation channel-grain boundary intersections.

The likely role of the stress at the grain boundary in the IASCC mechanism is to repeatedly rupture the oxide layer, exposing the underlying metal to the solution. Cracking could occur by high local stress that overcomes the cohesive strength of the oxide layer at the grain boundary, opening the crack and exposing the metal to the bulk solution [26.]. It is very likely that for a given grain boundary with certain cohesive strength of the oxide layer formed at or above the grain boundary, the overall stress state (resolved normal stress due to applied stress plus the contribution of dislocation channels) at the grain boundary will reach a critical value for cracking to occur. If stress is the determining factor for cracking, why is there a correlation of overall weighted average channel height with cracking susceptibility as shown in [13.]? It is believed that the average dislocation channel height indicates the overall level of localized deformation in
dislocation channels. Alloys with larger average channel height have higher probability of high stress level at the dislocation channel-grain boundary intersections. However, the situation for an individual grain boundary can be different. What is needed is a much more detailed analysis of the stress state including both the normal stress resulting from the applied stress and the contribution of the dislocation channel. Some grain boundaries may need a high fraction of contribution from dislocation channels while some other may need minimal. Characterization of the channel height alone is simply not enough for understanding the role of localized deformation in IASCC.

The role of PIA in mitigating IASCC is twofold. First, it decreases the overall yield stress of the materials by removing part of irradiation hardening, thus decreases the resolved normal stress at the grain boundaries. Second, it decreases the average dislocation channel height, which is believed to be linked to the decrease in the stress contribution at the channel-grain boundary interaction. Future work will be aimed at understanding the relative importance of the contribution of dislocation channels and the applied stress, which may be controlled by selecting proper PIA conditions. PIA can be a very useful tool to help understand the IASCC mechanism in this regard.

4.0 CONCLUSIONS

The effect of PIA on irradiation hardening, IASCC susceptibility and localized deformation was examined in 304 stainless steels following proton-irradiation to 10 dpa at 360°C. The trend of decreasing irradiation hardening following PIA is consistent with the literature, which includes data from both proton and neutron irradiations. Radiation-induced defects may have different annihilation rates leading to different hardening removal rates at the early and later stages of annealing. The decrease in average dislocation channel height following PIA is primarily due to the removal of irradiation-induced defect clusters, which contribute to the formation of dislocation channels. The as-irradiated condition shows the highest fraction of large channels. PIA at 500°C:15h and 550°C:1h exhibited no susceptibility to IASCC and both show a small fraction of large channels (less than half of that at the as-irradiated condition). IASCC susceptibility was significantly mitigated after PIA at 500°C for 1h and fully removed after PIA at 500°C for 15h and 550°C for 1h. The localized stress at the grain boundary, which includes the resolved normal stress from the applied stress and the addition of stress due to the interaction of channels and the grain boundary, can play a critical role in IASCC. The role of PIA in mitigating IASCC is twofold – decreasing the resolved normal stress at the grain boundaries and decreasing the stress contribution from the dislocation channel-grain boundary interaction.

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REFERENCES

Table 1: Irradiation hardening, cracking susceptibility and characterization of dislocation channels in 304SS following proton irradiation to 10 dpa at 360°C. Samples were strained in the simulated BWR water for cracking susceptibility. N.E.: not examined.

<table>
<thead>
<tr>
<th>PIA conditions</th>
<th>Remaining Irradiation hardness after PIA (ΔHV)</th>
<th>Number density (1/cm²) at 2%</th>
<th>Number density (1/cm²) at 4%</th>
<th>Number density (1/cm²) at 10%</th>
<th>Length per unit area (μm/mm²) 2%</th>
<th>Length per unit area (μm/mm²) 4%</th>
<th>Length per unit area (μm/mm²) 10%</th>
<th>&gt;280nm (%)</th>
<th>&gt;300nm (%)</th>
<th>&gt;320nm (%)</th>
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<tr>
<td>As-irradiated</td>
<td>211±20</td>
<td>100</td>
<td>10</td>
<td>65</td>
<td>100</td>
<td>23</td>
<td>240</td>
<td>48220</td>
<td>32.7</td>
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<tr>
<td>500°C:1h</td>
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<td>57</td>
<td>0</td>
<td>30</td>
<td>45</td>
<td>0</td>
<td>42</td>
<td>5388</td>
<td>24.8</td>
<td>21.6</td>
</tr>
<tr>
<td>500°C:15h</td>
<td>99±18</td>
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<td>N.E.</td>
<td>*</td>
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<td>N.E.</td>
<td>10.3</td>
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<tr>
<td>550°C:1h</td>
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<td>13.7</td>
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<tr>
<td>600°C:10h</td>
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*one transgranular crack was observed

Figure 1: Remaining irradiation hardening after PIA as a function of iron diffusion distance from multiple literature sources. The black filled squares are from this study of PIA of proton irradiated sample.
Figure 2: Cracking susceptibility of 304SS, as-irradiated (10 dpa at 360°C), and after PIA at 500°C:1h, 15h and 550°C:1h, following staining to 10% in simulated BWR water.

Figure 3: Distribution of dislocation channel heights in 304SS, as-irradiated (10 dpa at 360°C) and after PIA at 500°C:1h, 15h and 550°C:1h, following straining to 10% in simulated BWR water.
Figure 4: Comparison of the fraction of large channels, greater than 280, 300, and 320nm, respectively, in 304SS, as-irradiated (10 dpa at 360°C) and after PIA at 500°C:1h, 15h and 550°C:1h, following straining to 10% in simulated BWR water.