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Radiation-induced segregation in desensitized type 304 austenitic stainless steel

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ABSTRACT

Radiation-induced segregation (RIS) in desensitized type 304 stainless steel (SS) was investigated using a combination of electrochemical potentiokinetic reactivation (EPR) test and atomic force microscopy (AFM). Desensitized type 304 SS was irradiated to 0.43 dpa (displacement per atom) using 4.8 MeV protons at 300 °C. The maximum attack in the EPR test for the irradiated desensitized SS was measured at a depth of 70 μm from the surface. Grain boundaries and twin boundaries got attacked and pit-like features within the grains were observed after the EPR test at the depth of 70 μm. The depth of attack, as measured by AFM, was higher at grain boundaries and pit-like features as compared to twin boundaries. It has been shown that the chromium depletion due to RIS takes place at the carbide–matrix as well as at the carbide–carbide interfaces at grain boundaries. The width of attack at grain boundaries after the EPR test of the irradiated desensitized specimen appeared larger due to the dislodgement of carbides at grain boundaries.

1. Introduction

Radiation-induced segregation (RIS) is non-equilibrium segregation of alloying elements caused by generation and diffusion of point defects [1–4]. The RIS is typically observed for in-core components in light water reactors (LWR). The RIS is considered to be part of a complex process that increases the susceptibility to irradiation assisted stress corrosion cracking (IASCC) of austenitic stainless steel (SS) in LWR [1–5]. RIS leads to depletion of chromium at grain boundaries, without formation of chromium rich carbides in contrast to chromium rich carbide formation leading to chromium depletion in the case of thermally sensitized material [6].

The studies to relate the effects of neutron irradiation on intergranular stress corrosion cracking (IGSCC) of thermally sensitized SS have shown [7–9] an increase in susceptibility to IGSCC with neutron fluences up to 1.1×10^{24} n/m^2 ($E \geqslant 1$ MeV). Studies [10–12] have also indicated that prior thermal sensitization increased the susceptibility to IGSCC in irradiated austenitic stainless steel. For example, in sensitized type 304 SS, equivalent amount of chromium depletion was attained for a neutron fluence of 1.0×10^{24} n/m^2 as compared to 1×10^{26} n/m^2 for the non-sensitized material [10]. The effect of sensitization on RIS has been studied extensively [11–13] and is shown to result in narrower chromium depletion zones [11] and nickel enrichment under Helium-ion damage [12]. It has been shown [13] that the chromium-concentration profile gets narrower and deeper upon proton-irradiation. It was argued that [13] during irradiation, concentration flux and the inverse Kirkendall flux compete with each other and Cr will be further depleted at grain boundaries if the inverse Kirkendall flux is greater than the concentration flux. The Cr profile would be narrower if the concentration flux is greater than the inverse Kirkendall flux.

Though there are many studies [7–13] showing enhanced RIS in sensitized austenitic stainless steels, the effects of desensitization on the RIS behavior have not been investigated. It may be noted that desensitization in austenitic stainless steels leads to formation of $M_{23}C_6$ (M = Cr, Fe) hence to an indirect enrichment of Cr at grain boundaries without any chromium depletion zones adjacent to grain boundaries. Such an indirect enrichment of Cr at grain boundaries may help in reducing the extent of RIS (particularly Cr depletion) at grain boundaries. As RIS is a part of the complex process that leads to irradiation assisted stress corrosion cracking (IASCC), improvement in resistance to RIS may also improve the resistance to IASCC. In this study, effect of desensitization on the nature and extent of RIS in type 304 SS was investigated using 4.8 MeV proton-irradiation at 300 °C. A combination of double loop electrochemical potentiokinetic reactivation (DL-EPR) test and atomic force microscopy (AFM) was used to characterize the extent of RIS and to link the RIS behavior with different microstructural features. The EPR method was used in the past to characterize RIS in austenitic SS [14–19]. AFM examination was done to evaluate the depth of attack on various microstructural features after the

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DL-EPR test for the irradiated specimen. It may be noted that characterization of RIS by analytical techniques (such as scanning transmission electron microscopy–energy dispersive spectroscopy: STEM–EDS and Auger electron spectroscopy: AES) reveal information about irradiation induced microstructural and microchemical changes and electrochemical techniques yield information about the influence of irradiation induced microstructural and microchemical changes on the corrosion characteristics of the material [16].

2. Material and experimental

2.1. Materials and heat-treatment

The material chosen for the present investigation was obtained in the form of a 3 mm thick plate. The chemical composition (in wt.%) of this alloy is C: 0.054, Cr: 19.97, Ni: 7.97, Si: 0.59, Mn: 1.85, P: 0.035 and S: 0.006. The desensitization was carried out on the as-received material at 750 °C for 360 h [20]. The desensitization heat treatment results in grain boundaries saturated with chromium-rich $M_{23}C_6$ carbides and no chromium depleted regions adjacent to grain boundaries. To check the sensitization behavior of the as-received material, a specimen was subjected to a sensitization heat-treatment at 675 °C for 1 h. A smaller sample was cut from the plate and was polished metallographically followed by electro-polishing before proton irradiation. An electrolyte of 90% methanol and 10% perchloric acid solution was used at a temperature of −30 °C and at 20 V dc for electro-polishing.

2.2. Proton-irradiation

Proton irradiation was performed using a specifically designed assembly at PELLETRON accelerator, a joint Bhabha Atomic Research Centre–Tata Institute of Fundamental Research (BARC–TIFR) facility. Proton-irradiation was carried out using a 4.8 MeV proton beam at a dose rate of 1.4×10^{-6} dpa/s (displacement per atom/s). The irradiated surface area was approximately 7 mm^2. The specimen temperature was maintained during irradiation at 300 ± 5 °C and the level of vacuum was at 1.3×10^{-5} N/m^2. The proton-irradiated specimen was allowed to cool down for a period of a month before doing further analysis to remove any residual radioactivity. The average current during proton-irradiation was approximately 500 nA and the specimen was irradiated to 0.43 dpa. The experimental doses and dose rates were calculated using SRIM2003 software [21], while accumulated irradiation damage due to proton-irradiation, in terms of dpa, was estimated using NRT equation [22],

$$\mathrm{dpa} = \frac{0.8}{2E_d}\left(\frac{dE}{dx}\right)_n \frac{\phi_t}{\rho} \quad (1)$$

where E_d is the displacement energy, $(dE/dx)_n$ is the linear energy transfer (LET) per ion to target by nuclear processes, Φ_t is the fluence per unit area and ρ is the atomic density. $(dE/dx)_n$ and was obtained from SRIM by summing up phonon and binding energy profiles. The binding energy profile was obtained by vacancy profile multiplied by binding energy (3 eV). The damage profile obtained using SRIM for proton-irradiation was given a curve-fitting using the following equation (4-parameter Pseudo-Voigt equation):

$$y = a\left[c\left(\frac{1}{1+\alpha^2}\right) + (1-c)\exp(-0.5\alpha^2)\right], \quad (2)$$

where $\alpha = (x - x_o)/b$ and a, b, c, x_o are constants, x is depth (in micron) and y is the damage corresponding to given x.

2.3. Electrochemical potentiokinetic reactivation (EPR) test

The extent of chromium depletion in un-irradiated as received, sensitized, and desensitized as well as the irradiated desensitized SS specimens was evaluated using the DL-EPR test. The DL-EPR test was carried out [23] in a solution of 0.5 mol/l H_2SO_4 and 0.01 mol/l KSCN (de-aerated) at room temperature. The potential was scanned from −30 mV vs. open circuit potential (OCP) to +300 mV_{SCE} (mV vs. saturated calomel electrode) and then back to OCP at a scan rate of 6 V/h. The non-irradiated area on each specimen was masked with a lacquer and only the irradiated area was exposed to the solution. The result of the DL-EPR test is reported as DL-EPR value which is the ratio of the maximum current in the backward loop to that in the forward loop, multiplied by 100. The maximum damage due to proton irradiation to occur at 70 μm [21] below the surface for 4.8 MeV protons. Therefore, starting from the as-irradiated surface, the DL-EPR test was repeated after removing the affected-layer after each test, until the un-irradiated/un-affected material was reached. The thickness of the specimen after each DL-EPR test was measured using a micrometer screw with a least count of 1 μm. After each DL-EPR test, the affected layer was removed by grinding using fine emery-papers followed by polishing using 0.5 μm diamond paste.

2.4. AFM examination

After each DL-EPR test, the specimen was examined using NT-MDT Solver Pro scanning probe microscope in semi-contact mode. The extent of attack caused by the DL-EPR test was measured as depth of attack on various microstructural features like grain boundaries, twin boundaries, and any other feature within the grains.

3. Results

3.1. Characterization of the un-irradiated material

The hardness of the as-received material was 205 HV (Vickers hardness), higher than that of a typical solution-annealed type 304 SS (i.e. 170 HV). The grain size of the as-received material was 18 μm, corresponding to an ASTM grain size number 9. After the desensitization heat treatment, the hardness reduced to 180 HV with no change in grain size. The respective DL-EPR values for the as-received, sensitized and desensitized samples were 0.07, 3.89 and 0.06. Optical micrographs after DL-EPR test and the DL-EPR curves for the as-received, sensitized and desensitized samples are shown in Fig. 1. Optical micrographs (Fig. 1a and c) for the as-received and the desensitized specimen did not show significant attack on the grain boundaries, while the same for the sensitized sample demonstrated severe attack on almost all the grain boundaries, as depicted in Fig. 1b. The DL-EPR curves for the as-received sensitized and desensitized specimens are shown in Fig. 1d, indicating a higher current during the reactivation loop for the sensitized specimen. On the other hand, a very low current during the reactivation loop for the desensitized sample indicated the effectiveness of the desensitization heat-treatment in removing chromium depletion (with chromium below 12 wt.% [20]) regions adjacent to grain boundaries.

3.2. Electrochemical characterization of the irradiated specimen

Fig. 2 shows the damage profiles calculated using Eq. (1) and the variation of DL-EPR values with depth. The typical profile consisted of a uniform damage region for the first 70 μm of depth, followed by the peak damage region between 70 and 80 μm. The variation of