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Positron annihilation spectroscopy of proton irradiated single crystal BCC iron

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Abstract

Positron annihilation spectroscopy was used to analyze the open-volume defects created in single crystal, body-centered cubic iron irradiated with 1.0 MeV protons. The effects of irradiation dose and temperature were investigated. A novel technique utilizing a Bremsstrahlung beam to activate and induce positron decay in the bulk specimens, followed by Doppler broadening spectroscopy, was employed. No open-volume defects were detected in the 0.03 dpa irradiated specimens. However, the 0.3 dpa specimens exhibited an increase in the *S* parameter when compared to the 0.03 dpa specimens at 723 K. The 0.3 dpa specimen at 723 K indicated an increase in open-volume defects, as the radiation temperature increased compared to the 573 K, 0.3 dpa specimen. This was thought to be a consequence of the void and dislocation loop density decreasing while the void and dislocation loop diameter was increasing.

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1. Introduction

Ferritic–martensitic steels are candidate structural materials for Generation IV reactors, fusion systems, and accelerator driven systems (ADS). These steels have been selected because of their resistance to void swelling [1], irradiation creep [2], and helium (He) and hydrogen (H) embrittlement [3,4] at higher temperatures ($T/T_m > 0.4$). During fusion or ADS reactor operations the structural materials will be subjected to displacement damage, as well as the generation of He and H via (n, α) and (n, p) transmutation reactions, respectively. Also, protons can be directly implanted from the beam in an ADS. In fusion and ADS environments the He generation is approximately 10 appm/dpa [5]

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and 150 appm/dpa [6], respectively. The H generation is approximately three to ten times higher than He production in ADS environments [7,8]. Although it is known that the introduction of He and H in pure iron (Fe) and iron alloys leads to cavity growth [9–12] and dislocation loop production [11,13,14], the impact of these generation rates of He and H impurities on microstructural evolution during irradiation is still not well understood. However, it is known that the presence of both He and H within Fe materials have a synergistic effect with respect to hardening [15]. Also, this further leads to additional hydrogen retention [15]. If the effects of the ions are considered individually, He atoms are more effective than H atoms in microvoid formation in Fe between 423 and 573 K [16]. Also the temperature dependence of microvoid formation in Fe is more evident following H irradiation versus He irradiation between 423 and 573 K [16]. In this study BCC Fe was investigated since it is the crystallographic form of iron found in ferritic–martensitic steels. However, the ultimate goal of this research is to study damage processes and microstructural evolution resulting from irradiation effects in ferritic–martensitic steels used in nuclear reactors.

Positron annihilation spectroscopy (PAS) is a non-destructive, analytical technique that can be utilized to characterize defects in solids, such as vacancies, voids, bubbles, and dislocation loops at low concentrations. Bubbles and voids can be detected in the sub-nanometer range, which is below the resolution of transmission electron microscopy. These characteristics make PAS an ideal technique for studying irradiation damaged material.

The PAS Doppler broadening technique analyzes the profile of the momentum distribution of the electrons that have annihilated with positrons. Doppler broadening gives information about the electronic characteristics where the annihilation occurred [17] and is given by [18]

$$\Delta E = 1/2 p_x c, \tag{1}$$

where p_x is the longitudinal component of the momentum in the direction of the emitted γ-ray and c is the speed of light. The Doppler broadening energy spectrum consists of two main parts: (1) the narrow, central region (S parameter) of the Gaussian that accounts for positron annihilation with the valence electrons and unbound electrons and (2) the wing region (W parameter) of the Gaussian that is a result of positron annihilation with the core electrons. In irradiated materials that contain vacancies or open-volume defects, positron annihilation will occur at these open sites. This results in a greater contribution to the central region and a decreased contribution of the wing region.

In this study Doppler broadening spectroscopy was utilized to investigate the defects formed in single crystal, body-centered cubic (BCC) Fe irradiated with 1.0 MeV protons at varying doses and temperatures. A novel technique using a Bremsstrahlung beam to activate and induce positron decay in the specimens was employed.

2. Experimental procedures

A single crystal BCC Fe (99.99%) ingot was grown by MaTecK with an orientation of a few degrees off of (1 1 1). The specimen dimensions were 9.6 mm × 6.0 mm × 1.3 mm. The specimens were mechanically polished prior to irradiation with a series of SiC papers, followed by polishing with polycrystalline diamond suspensions. The final polishing step utilized a colloidal silica suspension. All of the specimens were carefully polished utilizing the same process to minimize variations created during polishing that would affect the PAS results.

Proton irradiations were carried out using the Tandetron accelerator at the Michigan Ion Beam Laboratory at the University of Michigan. The 1.0 MeV H^+ irradiations were conducted at a dose rate of 1×10^{-5} dpa/s. Specimens were irradiated at 573 or 723 K to a dose of 0.03 or 0.3 dpa. The experimental dose and dose rates were calculated with SRIM-2003 [19] with a displacement energy of 40 eV. The dose rate versus depth for a representative irradiation is shown in Fig. 1. The dose and dose rates described above were calculated for the approximately uniform proton damage region,

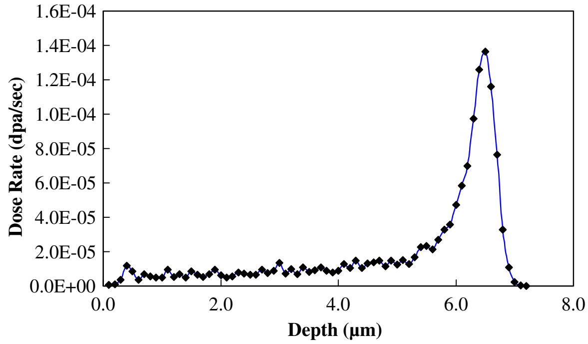

Fig. 1. 1.0 MeV H^+ irradiation to a dose of 0.03 dpa at the 1–4 μm region.

located at a depth range of ~1–4 μm. Two control (un-irradiated) specimens were prepared by annealing at 573 or 723 K for 2 h in vacuum.

The specimen irradiation temperatures were controlled by a temperature regulated irradiation stage. The copper irradiation stage was heated from the back with a cartridge heater. Also an air cooling loop passed through the copper block to assist in temperature control. The stage temperature was monitored with a thermocouple inserted in the back of the stage. Thermocouples were also mounted on template samples or directly on the specimens to calibrate and monitor the temperatures. The specimen temperatures were calibrated to a pyrometer once the desired irradiation temperature was achieved with the cartridge heater (no beam was present). Throughout the irradiation, the pyrometer was used to monitor the specimen temperatures. A set of tantalum apertures allowed for control of the beam to ensure that the beam was uniformly irradiating the specimens as it was raster-scanned across the stage. The electrically isolated apertures measured the beam current on all four sides throughout the irradiation. The opening on the apertures measured 18 mm × 10 mm. Additional details of the irradiation setup are described by Was et al. [20].

Doppler broadening spectroscopy was carried out at the Idaho Accelerator Center at Idaho State University. Six single crystal BCC Fe specimens were analyzed: 0.03 dpa irradiated with 1.0 MeV H^+ at 573 or 723 K, 0.3 dpa irradiated with 1 MeV H^+ at 573 or 723 K, and un-irradiated samples annealed at 573 or 723 K. Prior to the Doppler broadening measurements, the specimens were activated to induce positron decay within the Fe. This novel Doppler broadening technique via Bremsstrahlung activation was developed by Selim et al. [21,22]. Typically, Doppler broadening measurements are carried out using a radioactive source (i.e. ^{22}Na) or a positron beam. The advantage of this technique is that it is non-destructive and the highly penetrating γ-rays activate the entire sample, hence allowing a bulk measurement. The samples were activated with a 20 MeV pulsed electron Linac (pulse width of 2.0 μs and repetition rate of 60 Hz) that impinged on a tungsten converter, as illustrated in Fig. 2. This converter then produced Bremsstrahlung radiation (γ-rays), which was then further filtered. Finally, the γ-rays impinged on the specimen. The γ-rays induced photonuclear reactions (γ, n) in the Fe, specifically ^{54}Fe(γ, n)^{53}Fe. A characteristic γ-ray of 378 keV is emitted upon the decay of ^{53}Fe, which has a half-life of 8.5 min. Positron decay also occurred within the specimens from the decay of ^{53}Fe, allowing for the detection of the annihilation radiation (two 511 keV photons). The specimens were activated for 20 min.

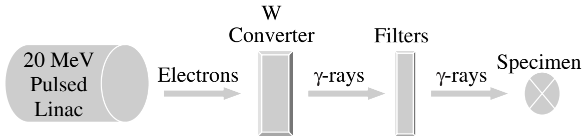

Fig. 2. Schematic of the specimen activation method for generation of positrons.

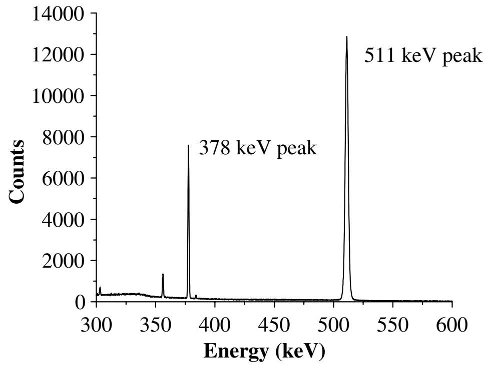

Fig. 3. Spectrum with the 511 keV annihilation peak and 378 keV characteristic γ-rays from Fe-53 for a dose of 0.3 dpa.

Immediately following activation, the specimens were counted for 1000 s with a high resolution HPGe detector. The energy resolution of the detector at the 662 keV γ-ray from ^{137}Cs was 1.4 keV (FWHM). The energy resolution was 1.1 keV (FWHM) at the 356 keV γ-ray from ^{133}Ba. The specimens were counted at a rate of 3.2 kHz. The annihilation radiation, as well as the characteristic γ-rays were detected and recorded. A representative spectrum obtained from the HPGe is illustrated in Fig. 3. Note the 378 keV characteristic γ-rays from the ^{53}Fe decay and the 511 keV annihilation peak.

3. Results and discussion

The 511 keV peaks from the Doppler broadened spectra were analyzed for the *S* and *W* parameters. The *S* and *W* parameters were calculated from the program STW_PPandACT_2005 [23]. The *S* parameter encompassed ±1σ (±1.3 keV) from the 511 keV peak and the *W* parameter encompassed the 3–5σ regions. The *S* parameter results for the

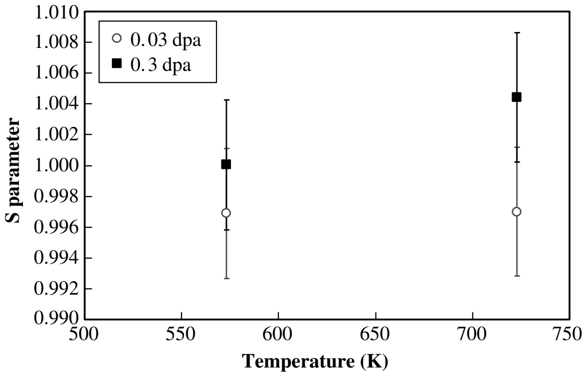

Fig. 4. S parameter ratio of irradiated specimen to the control versus irradiation temperature for single crystal BCC Fe irradiated with protons.

proton irradiations (0.03 and 0.3 dpa) at 573 and 723 K are shown in Fig. 4. The S parameter is shown as a ratio of the irradiated to the un-irradiated specimens. Hence a ratio of 1 indicates that there was no damage observed via Doppler broadening. The control specimens possess the same S parameter. Fig. 4 indicates that there was no damage (open-volume defects) observed by Doppler broadening for the 0.03 dpa samples at both irradiation temperatures. However, the 0.3 dpa specimens exhibited an increase of open-volume defects as the irradiation temperature increased, shown by a 0.4% increase in the S parameter. The S parameter also increased by 0.3% for the 573 K specimens and by 0.7% for the 723 K specimens as the dose increased from 0.03 to 0.3 dpa.

As expected, the 0.3 dpa samples demonstrated a greater S parameter ratio than the 0.03 dpa since the defect number density increases with increasing proton dose [13,24,25], until it saturates at ~1 dpa. However, due to the nature of the bulk irradiation of the specimen, the entire specimen was activated. This resulted in positrons generated throughout both the irradiated (0–7 μm) and un-irradiated regions (7 μm to 1.3 mm). Therefore only ~0.5% of the spectrum was generated from the damaged region, assuming an equal distribution of positrons. This bulk technique demonstrated that the open-volume defects generated in the 0.03 dpa specimens were below the threshold of detection when examining the S parameter.

The S parameter is determined by contributions from annihilation in the bulk and at defects. When the bulk annihilation rate is much less than the defect specific trapping rate multiplied by the defect concentration, the S parameter observed is primarily determined by the defect contribution to the S parameter and not the bulk contribution [26]. However, if this assumption is not valid, then the measured S parameter is determined by both the bulk and defects. The inability to observe a response from the S parameter at the lowest dose indicates that the bulk contributions may be too large to observe the defect contribution. Note that in the study conducted by Iwai et al. [26], which utilized a 15 keV positron beam to investigate the dose dependence of the S parameter for various ion irradiations in polycrystalline Fe, an increase in the S parameter was detected at $\sim 10^{-4}$ dpa. This positron energy coincided with the damage regions analyzed, allowing the positrons to thermalize and annihilate in the damaged region.

The T parameter is defined as a ratio of the wing parameter to the shape parameter ($T = W/S$). As previously described, the S parameter accounts for annihilation with low momentum electrons (valence and unbound), which indicates the presence of open-volume defects. The W parameter results in contributions from the annihilation with high momentum core electrons. Therefore a high concentration of open defects or an increase in defect size results in a greater contribution of annihilation photons from low momentum electrons due to the positron trapping at defects. This results in an increase in the S parameter and a decrease in the W parameter. Hence, as the open-volume defects increase in size or number, the T parameter will decrease. The results for the T parameter are shown in Fig. 5. No change in the T parameter was observed for the 0.03 dose samples when compared to the un-irradiated specimens. Again, this demonstrated the

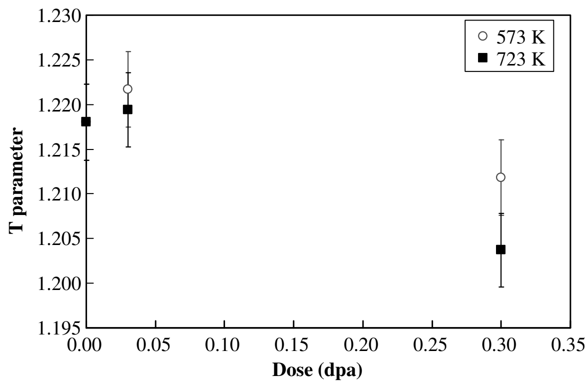

Fig. 5. T parameter versus irradiation dose for single crystal BCC Fe irradiated with protons.

insensitivity of this technique to Fe irradiated at low dose levels due to the annihilation in both the bulk and at defects. However, an expected decrease was observed in the *T* parameter for the highest dose of 0.3 dpa. Also at this damage level, the 723 K specimen exhibited more damage than the 573 K sample.

Results from Figs. 4 and 5 indicated that at a dose of 0.3 dpa at 723 K, more open-volume defects were detected than at 573 K. Recall that the *S* parameter is sensitive to both the size and concentration of defects. It has been shown that as the proton irradiation (3.2 MeV, 0.5 dpa) temperature increases, the void and dislocation loop density decreases while the void and dislocation loop diameter increases in austenitic steel [27]. At temperatures greater than ~673 K the void and dislocation loop density begins to dramatically decrease, while the void and dislocation loop diameter dramatically increase. For example, the dislocation loop density decreased from 10^{15} to 10^{14} cm^{-3} as the temperature increased from 673 to 773 K [27]. The dislocation loop diameter increased from 16 to 49 nm over the same temperature region [27]. Therefore, this large decrease in void and dislocation loop density, as well as the corresponding increase in void and dislocation loop diameter at higher temperatures may explain the increase in the *S* parameter and decrease in the *T* parameter at the higher temperature of 723 K at a dose of 0.3 dpa.

4. Conclusions

A novel technique utilizing a Bremsstrahlung beam to induce bulk positron decay in single crystal BCC Fe specimens was utilized. These specimens were then analyzed via Doppler broadening spectroscopy. It was found that the lowest proton dose specimens (0.03 dpa) irradiated at 573 and 723 K did not exhibit any open-volume defects measurable with the bulk Bremsstrahlung activation technique. This was attributed to the bulk annihilation contributions to the *S* parameter. As expected, the 0.3 dpa samples exhibited an increase in the *S* parameter and a decrease in the *T* parameter, when compared to the 0.03 dpa specimens. The 0.3 dpa specimens also demonstrated an increase in the *S* parameter and a decrease in the *T* parameter, hence an increase in open-volume defects, as the radiation temperature increased. This was thought to be a consequence of the void and dislocation loop density decreasing while the void and dislocation loop diameter was increasing.

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