Comparison of hardness and XPS measurement on austenitic stainless steel irradiated by He^+ or Fe^+ high energy ions

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Type 304 stainless steel (304SS) used in a nuclear power plant could suffer a disastrous damage called irradiation assisted stress corrosion crack (IASCC). It has been recognized that the radiation induced segregation (RIS) exerts an important effect on IASCC [1]. Wu *et al.* also did some work on SCC resistance of sensitized 304SS in high-temperature water [2, 3]. Both U-bend and slow strain rate stress corrosion tests were performed, complemented by the electrochemical polarization curve measurement and extensive oxide film analysis by Auger electron spectroscopy (AES). Besides, a considerable effort has already been made to study the relation of electrochemical corrosion potential (ECP) to IASCC under various conditions [4–6]. Lately, some modified measurements have been tried to study the IASCC phenomenon. These methods included electrochemical noise measurement [7], *in-situ* electrochemical impedance measurement [8], and acoustic emission response measurement [9]. On the other hand, some studies were conducted with ion irradiation. Microstructure and micro-chemical changes of type 304 stainless steel irradiated by protons were quantified and compared with literature results for irradiated specimens [10]. Lee *et al.* observed effects of helium on radiation-induced defect microstructure in austenitic stainless steel with 360 keV He^+ and 3500 keV Fe^+ ions beams at 200 °C [11]. Distinct swelling was noted by atomic force microscopy observation in austenitic stainless steel SUS316 specimens irradiated by He^+ ions [12]. In this work 304SS was irradiated by 460 keV Fe^+ ion beam with dose up to 1×10^{21} ions/m^2 or by 500 keV He^+ ion beam with dose up to 1×10^{21} ions/m^2. The micro-hardness and XPS measurement were taken on for the irradiated specimens and the annealed specimen.

The material used in the work was commercial 304SS plate with a thickness of 2 mm. The chemical compositions (mass%) of the material was 18.33% Cr, 8.49% Ni, 1.08% Mn, 0.54% Si, 0.066% C, 0.009% S, 0.024% P, and Fe balanced. Specimens of 10×10 mm^2 square were cut by electrodischarge machine, and were mechanically polished with 1500 grit SiC paper. All specimens were enveloped in a quartz tube (1.33 Pa vacuum degree), annealed at 1050 °C for 30 min, and quenched by water. All treated specimens were electrochemically polished for further irradiation or for other measurement.

One group of specimens was irradiated using 460 keV Fe^+ ions at a rate of $1.5–2.5 \times 10^{16}$ ions/m^2/s (1×10^{-3} dpa/s) and the irradiation dose was up to 1×10^{21} ions/m^2. Another group of specimens was irradiated using 500 keV He^+ ions at a rate of 1×10^{18} ions/m^2/s (5×10^{-3} dpa/s) and the irradiation dose was also up to 1×10^{21} ions/m^2. Three groups of specimens such as annealed or irradiated by Fe^+ or He^+ ions respectively were included in following measurement.

The hardness measurement was taken on by the Fischerscope H100VP mechanical probe. The beginning load value was 0.4 mN and max load value was 20 mN. When the load was up to 20 mN, it was removed after remaining 5 s. 10 curves were obtained at different micro-area of the same surface for every specimen. These curves were averaged to become an effective curve.

The XPS measurement instrument was MICROLAB MK II using Mg-K_α as light source with the power of 300 W. All specimens were cleaned twice in acetone liquid with supersonic vibration. Then dried specimen was clipped in a support tray with the irradiated surface against the light source. Measurement started by scanning from 0 to 1000 eV with 1 eV step span. Further narrower range scanning was taken on with 0.5 eV step span.

The press depth of annealed specimen was the deepest among the three specimens under the same loading and unloading condition in Fig. 1a. While the load started from the beginning value to 7.5 mN the press depth of No.3 specimen was deeper than that of No. 2 specimen. The depth was almost the same for both irradiated specimens during the load between 7.5 and 12.5 mN. The depth of No. 2 specimen was deeper than that of No. 3 specimen while the load increased continuously from 12.5 to 20 mN, remained 5 s at 20 mN, and then unloaded. The same tendency appeared in Fig. 1b. The hardness value of No. 1 specimen was always the lowest whereas the hardness value of No. 2 specimen was the highest between the beginning load value and 7.5 mN and the hardness value of No. 3 specimen was the highest with loading from 7.5 to 20 mN and thereafter. The max hardness value was 18 000 and 14 000 for No. 2 and No. 3 specimen respectively.

The micro-hardness measurement result showed that the effect of hardness improvement was larger and

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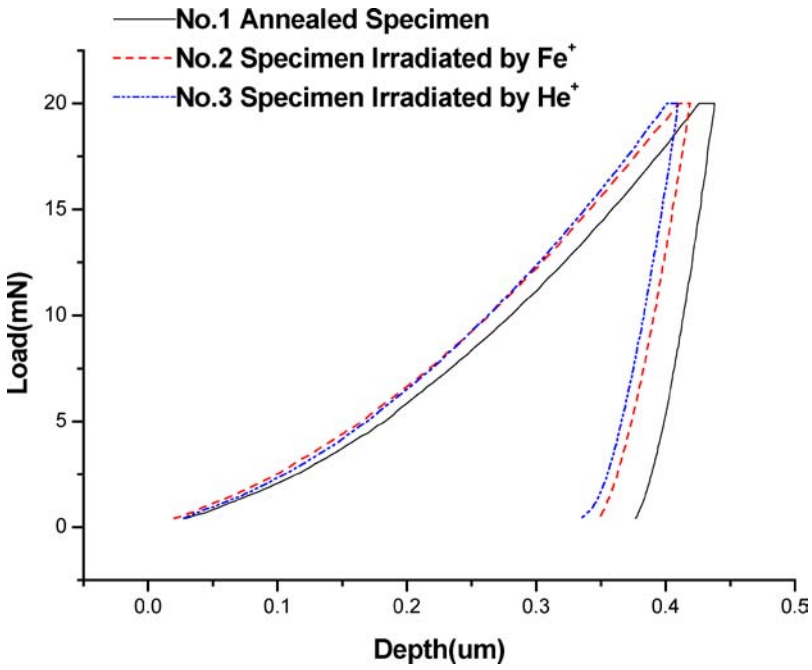
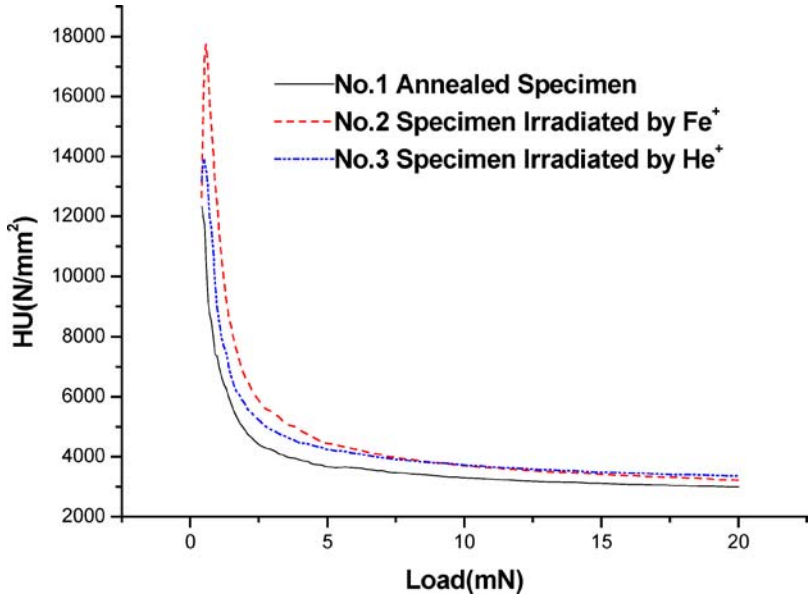


(a)



(b)

Figure 1 Micro-hardness measurement curves: (a) Relation curve between load and depth and (b) Relation curve between HU and load.

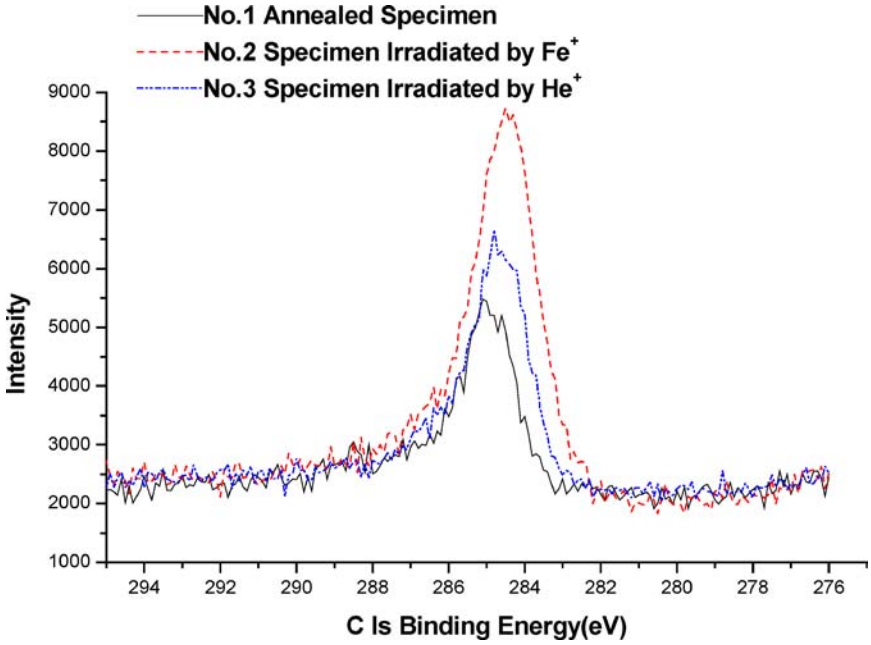
nearer to the surface for the specimen irradiated by Fe^+ than that for the specimen irradiated by He^+ although the dose and energy of Fe^+ and He^+ ions were selected almost the same. The discrepancy between these two kinds of ions was due to the fact that Fe^+ ion was heavier than He^+ ion so that Fe^+ entered specimen with more difficulty. The shot distance of Fe^+ was shorter and a larger amount of it stopped in a shallower surface layer. This meant that micro-defects were more severe for No. 2 specimen than for No. 3 specimen. The hardening effect of No. 3 specimen irradiated by He^+ was weaker but its hardening depth was deeper than that of No. 2 specimen.

Fig. 2 is the results of XPS spectra obtained from the surface of specimens, showing the elements of C, O, Fe, Cr and Ni. The binding energy of C and O was of 1s line. The binding energy of Fe, Cr and Ni was of 2p line. The peak of C 1s binding energy for No. 2 specimen was the highest and the peak of C 1 s binding energy of No. 1 specimen was the lowest (Fig. 2a) while the peak of O 1s binding energy of No. 2 specimen was the lowest and the peak of O 1s binding energy of No. 1 specimen was the highest (Fig. 2b). This phenomenon might suggest that the absorbability of carbon and oxygen for specimens irradiated by ions changed. The surface of specimen irradiated by Fe^+ absorbed the largest amount of carbon and the least amount of oxygen whereas the surface of annealed specimen absorbed the largest amount of oxygen and the least amount of carbon. The absorption amount of C or O on the surface of the specimen irradiated by He^+ was in the middle. Besides O 1s binding energy of the specimen irradiated by He^+ reduced 1.5 eV about and C 1s binding energy of the specimen irradiated by Fe^+ reduced 1 eV about

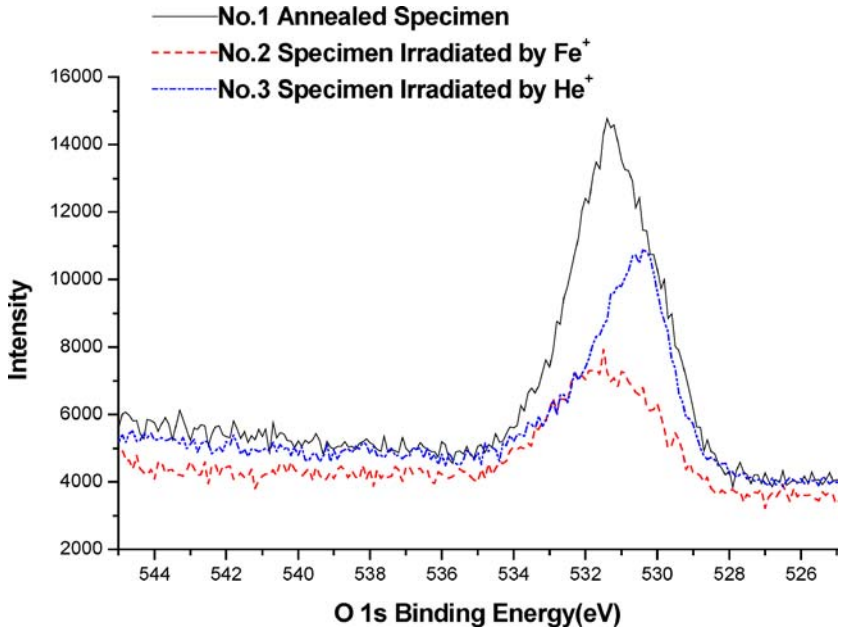
comparing to that of annealed specimen. This result suggested that the chemical environment changed for carbon or oxygen atoms absorbed on the surface of the irradiated specimen.

Fig. 2c to e shows the binding energy of three main elements in type 304 austenitic stainless steel. Fe 2p binding energy of both irradiated specimens was evidently smaller than that of the annealed specimen (Fig. 2c). ΔE_{Fe2p} was 5 eV. Cr 2p binding energy of both the annealed specimen and the specimen irradiated by He^+ was the same. The Cr 2p binding energy of the specimen irradiated by Fe^+ was slightly reduced and the peak height was much lower than that of Nos. 1 and 3 specimens (Fig. 2d). There was no difference among the three specimens considering Ni 2p binding energy (Fig. 2e). The above measurement suggested that Fe^+ or He^+ irradiation greatly increased the density of the valence electrons of Fe atoms. However the irradiation did not evidently change the chemical environment of Cr or Ni atoms. There was no evident difference in XPS results between Fe^+ and He^+ ions.

In summary, Fe^+ or He^+ irradiation increased microhardness of the surface layer. The hardening effect of He^+ ions was weaker than that of Fe^+ ions but the hardening depth was deeper than that of Fe^+ ions. Fe^+ or He^+ irradiation changed Fe 2p binding energy greatly; however, the binding energy of Cr or Ni did not exhibit any difference between the annealed specimen and the irradiated specimens. There was no obvious diversity between Fe^+ and He^+ irradiations considering the

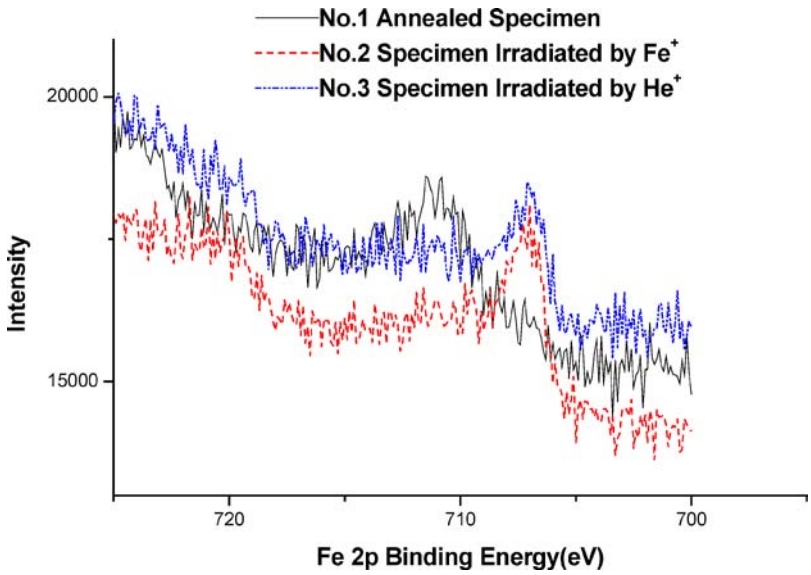


(a)

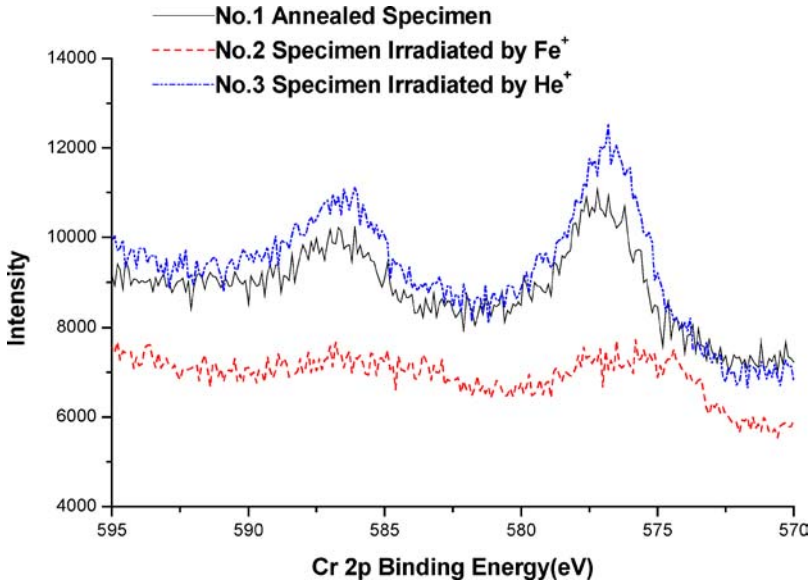


(b)

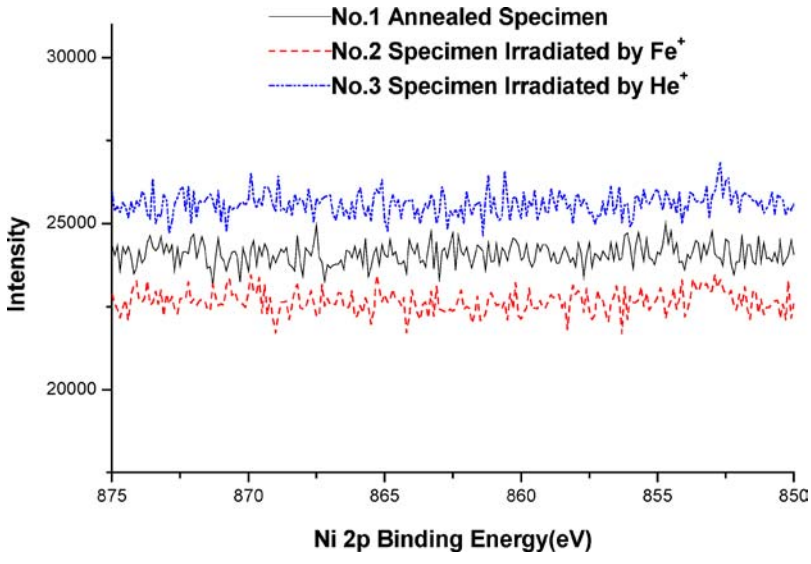
Figure 2 XPS measurement curves: (a) C 1s binding energy, (b) O 1s binding energy, (c) Fe 2p binding energy, (d) Cr 2p binding energy, and (e) Ni 2p binding energy. *Continued*



(c)



(d)



(e)

Figure 2 (Continued)

irradiation effect on electron binding energy of the 304SS. He^+ ions may be more suitable in simulating neutron irradiation.

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