Positron annihilation study of vacancy-solute complex evolution in Fe-based alloys

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Irradiation-induced vacancy-type defects in Fe-based dilute binary alloys (Fe-C, Fe-Si, Fe-P, Fe-Mn, Fe-Ni, and Fe-Cu), model alloys of nuclear reactor pressure vessel steels, are studied by positron annihilation methods, positron lifetime, and coincidence Doppler broadening (CDB) of positron annihilation radiation. The vacancy-type defects were induced by 3 MeV electron irradiation at room temperature. The defect concentrations are much higher than that in pure Fe irradiated in the same condition, indicating strong interactions between the vacancies and the solute atoms and the formation of vacancy-solute complexes. The vacancy-solute complexes in the Fe-Cu, Fe-Ni, and Fe-C alloys are definitely identified by the CDB technique. In particular, the single vacancies in Fe-Cu are surrounded by Cu atoms, resulting in vacancy–multi-Cu-atom complexes of V-Cu$_n$ ($n \geqslant 6$). The vacancy clusters are formed in Fe-Ni and Fe-P, while they are not observed in the other alloys. The isochronal annealing behavior is also studied. The ultrafine Cu precipitates coherent with the Fe matrix are formed in Fe-Cu after annealing at 350 °C, while the other alloys show complete recovery without forming any precipitate that traps the positrons.

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I. INTRODUCTION

Our previous work, using the defect-sensitive positron annihilation technique, has revealed aggregations of Cu atoms and vacancies in dilute Fe-Cu alloys induced by neutron irradiation.[1] The vacancy-Cu complexes formed by irradiation aggregate into nanovoids. The inner surface of the nanovoids is covered by Cu atoms. We have found that the positron is also sensitive to ultrafine particles embedded in materials, even if they have no defect, due to affinity-induced positron confinement [positron *quantum-dot-like* state (see Ref. 2)]. By utilizing such positron confinement, it has been revealed that the ultrafine Cu precipitates of ~1 nm in size, too small to observe even by current high-resolution transmission electron microscopes, are formed after the dissociation of the vacancies from the nanovoids by the postirradiation annealing around 400 °C. The Cu precipitates are coherent with the Fe matrix, i.e., bcc structure, consist of only Cu atoms, and anneal out around 650 °C. In addition, the electronic structure of the metastable bcc Cu embedded in Fe has been also revealed by two-dimensional angular correlation of positron annihilation radiation (2D-ACAR) measurements;[3] the topology of the Fermi surface of the bcc Cu has been directly observed, which is an experimental demonstration of the Fermi surface observation of the embedded nanoparticles.

These results have significant impact not only on the fundamental understanding of the solute clustering mechanism and electronic structure of embedded nanoparticles but also on the nuclear industry. The main origin of the embrittlement of the nuclear reactor pressure vessel (RPV) steels due to long-term in-service exposure to neutron irradiation is considered to be the ultrafine precipitation of Cu impurities contained in the old RPV (~ 0.3%) enhanced by the neutron irradiation.[4–9]

In the practical RPV steels, it is considered that other impurities and alloying elements, for example, Ni, P, Mn, affect the Cu precipitation process. In order to reveal this effect, the vacancy-solute complex evolution for these elements should be well understood. For this purpose, we have irradiated model alloys (Fe-C, Fe-Si, Fe-P, Fe-Mn, Fe-Ni, and Fe-Cu) by 3 MeV electrons to introduce simple monovacancies and have studied the defect-solute interaction by using positron annihilation methods: positron lifetime and coincidence Doppler broadening (CDB) of positron annihilation radiation. The formations of vacancies, vacancy clusters, and vacancy-solute complexes induced by the irradiation are clarified. Their recovery process by postirradiation isochronal annealing is also revealed.

The positron is the only probe that is able to detect sensitively vacancy-type defects in metals.[10–13] Since positively charged nuclei are absent at vacancy-type defects, positrons are trapped and annihilate there with the surrounding electrons, conveying the information on the local electronic environment around the vacancy-type defects. The positron lifetime spectroscopy provides information on the size of the vacancy clusters and their number density. The CDB enables us to identify the chemical element whose electron annihilates with the positron,[14–16] by measuring the electron momentum distribution in the high-momentum region, given by the positron annihilation with the inner orbital electrons. We can identify the chemical environment where the positron is trapped, because the inner orbital electrons are tightly bound to the nuclei and are almost unaffected by the chemical bonding and crystal structure. Thus, the CDB method is expected to prove the formation of vacancy-solute complexes. The positrons are also sensitively trapped at the positron affinitive ultrafine precipitates.[2,17] In the present systems, the nanosize Cu and Ni precipitates in Fe are the positron trapping sites.[12,18] Thus, the CDB can also detect such ultrafine precipitates.

In the present paper, the CDB and lifetime methods will

be used as tools to study the interaction of vacancies with solute atoms in the Fe-based alloys. The information obtained gives direct confirmation of the identification of the vacancy-solute complexes and Cu precipitates.

II. EXPERIMENT

The model alloy samples under study were Fe–0.2 wt % C, Fe–0.5 wt % Si, Fe–0.04 wt % P, Fe–1.5 wt % Mn, Fe–0.7 wt % Ni, and Fe–0.3 wt % Cu. They were made from high-purity Fe (99.99%) and Ni (99.99%), Si (99.999%), Cu (99.999%) and ferroalloys (Fe-C, Fe-P, and Fe-Mn) by arc melting and cold rolled to a thickness of 0.3 mm. The solute content of each model alloy was set to be similar to that of the practical RPV steels. Pure Fe samples were also prepared as a reference. The samples were heated to 825 °C and kept for 4 h, followed by quenching into iced water. They were bombarded with 3 MeV electrons below 50 °C to a fluence of 2.0×10^{18} e/cm^2 using a Dynamitron accelerator of the JAERI-Takasaki Institute. In this condition, only Frenkel pairs are introduced, which is desirable for the study of the basic interaction between vacancies and solute atoms. The as-irradiated samples were employed to perform the positron annihilation measurements at first, and then were isochronally annealed for 30 min from 100 °C to the temperature of complete recovery of the defects.

Positron lifetime measurements were carried out using a conventional fast-fast spectrometer with a time resolution of 190 ps in full width at half maximum (FWHM). About 4×10^6 coincidence events were accumulated for each measurement for 12 h. After subtracting the source component and background, the spectra after irradiation were decomposed into two components (τ_1 and τ_2). In order to identify the size of the vacancy clusters (V_n, where n is the number of vacancies), the experimental results were compared with the calculated positron lifetimes in the vacancy clusters by using a simple superimposed atom method.[19] The details of the method are described in Ref. 20.

The CDB spectra were measured with two Ge detectors in coincidence. The energies of the annihilating γ-ray pairs were simultaneously recorded with these detectors located at an angle of 180 ° relative to each other. The details of this method are described by Asoka-Kumar *et al.*[15] The overall energy resolution is $\sim$ 1.1 keV (FWHM), which corresponds to a momentum resolution of $\sim4.3\times10^{-3}m_0c$ (FWHM), where c is the speed of light and m is the electron rest mass. The sample-detector distance is 20 cm, and the strength of the ^{22}Na positron source is $\sim$ 1 MBq. Total counts of more than 2×10^7 for each measurement were accumulated for 12 h. The CDB ratio spectrum was obtained by normalizing the momentum distribution of each spectrum to that of the unirradiated (defect-free) pure Fe. The shape of the spectrum in the high-momentum region (typically $>10\times10^{-3}m_0c$) exhibits characteristic signals of the elements through the positron annihilation with their inner orbital electrons. The S and the W parameters are defined as the ratios of low momentum ($|p_L|<4\times10^{-3}mc$) and high momentum ($18\times10^{-3}mc<|p_L|<30\times10^{-3}mc$) regions in the CDB spectrum to the total region, respectively. When the positron is trapped at a vacancy-type defect, the S parameter increases, while the W parameter decreases. In addition, the W parameter strongly depends on the chemical environment of the positron trapping site. We also measured the Vickers microhardness with a conventional apparatus with a load of 200 g for 15 s in each step of the isochronal experiments.

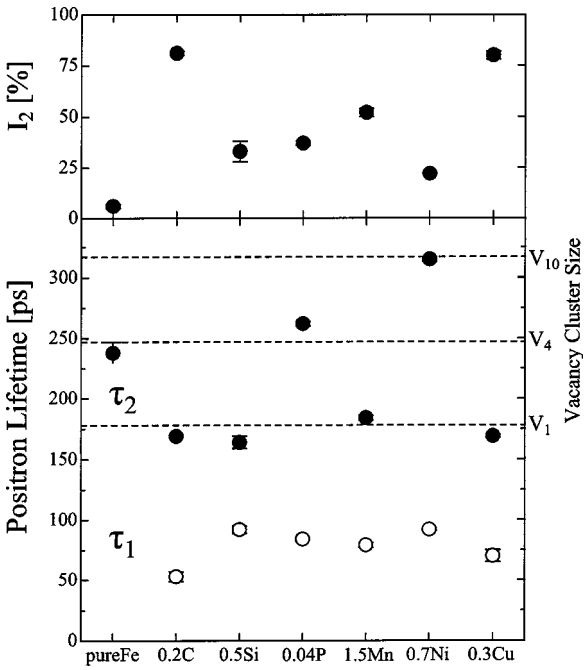

FIG. 1. Positron lifetimes in pure Fe and model alloys: Fe–0.2 wt % C, Fe–0.5 wt % Si, Fe–1.5 wt % Mn, Fe–0.04 wt % P, Fe–0.7 wt % Ni, and Fe–0.3 wt % Cu as irradiated by 3 MeV electrons. Calculated positron lifetimes for V_1, V_4, and V_{10} in Fe are also shown by horizontal dashed lines.

III. RESULTS AND DISCUSSION

A. As irradiated

Figure 1 shows the results of the positron lifetime measurements in the model alloys and pure Fe as irradiated by 3 MeV electrons. The calculated positron lifetimes for some vacancy clusters (V_1, V_4, and V_{10}) in Fe are also shown by horizontal dashed lines. [The lifetimes of the alloy samples before irradiation have been measured although the results are not shown in Fig. 1. All the lifetime spectra consist of one component about 107 ps similar to that of well-annealed pure Fe, indicating that the defect concentrations in the samples before irradiation are less than the lower limit ($\sim10^{-6}$) of the detection by positron annihilation.]

In the case of pure Fe after irradiation, the longer lifetime component (τ_2) of 240 ps, which corresponds to V_4, is observed. However, its relative intensity (I_2) is only few percent. This means that most of the vacancies induced by the electron irradiation recover during the irradiation, which is consistent with the fact that vacancies in Fe are mobile well below room temperature,[21] but some of the vacancies survive as their clusters.

For the Fe-P and Fe-Ni alloys, τ_2 corresponding to V_4 and V_{10} are obtained, respectively, with much higher I_2 than that

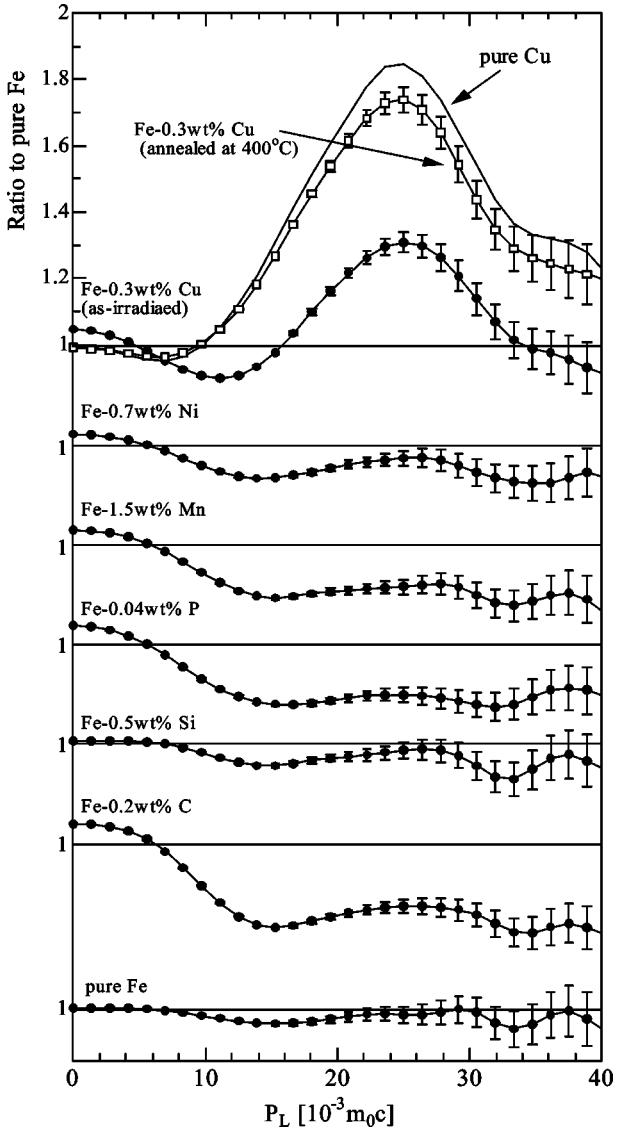

FIG. 2. Ratio curves of CDB spectra in as-irradiated pure Fe and model alloys: Fe–0.2 wt % C, Fe–0.5 wt % Si, Fe–1.5 wt % Mn, Fe–0.04 wt % P, Fe–0.7 wt % Ni, and Fe–0.3 wt % Cu, normalized to the momentum distribution of well-annealed (defect free) pure Fe.

for pure Fe, indicating that the addition of P and Ni promotes the formation of vacancy clusters. It should be noteworthy that P atoms of only 0.04 wt % affect the vacancy cluster formation.

The τ_2 for Fe-C, Fe-Si, Fe-Mn, and Fe-Cu are about 175 ps, close to the calculated positron lifetime in V_1 (178 ps). This suggests that the irradiation induced vacancies are stabilized by forming vacancy-solute complexes. In particular, the high I_2 values ($\sim$80%) for Fe-C and Fe-Cu indicate the strong interaction between the vacancies and the solute (C and Cu) atoms.

Figure 2 shows the CDB ratio spectra for the as-irradiated samples (pure Fe and the model alloys) normalized to the momentum distribution of the well-annealed (defect-free) pure Fe. The ratio spectrum for well-annealed pure Cu is also shown as a reference. For the Fe-Cu sample, the broad peak

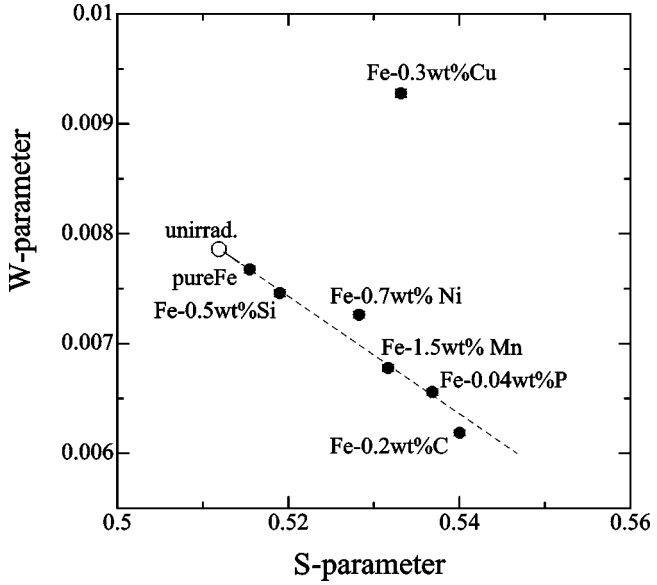

FIG. 3. *S*-*W* plots of as-irradiated pure Fe and model alloys: Fe–0.2 wt % C, Fe–0.5 wt % Si, Fe–1.5 wt % Mn, Fe–0.04 wt % P, Fe–0.7 wt % Ni, and Fe–0.3 wt % Cu.

around $25\times10^{-3}m_0c$ in the spectrum shows that the positrons annihilate with the inner $3d$ orbital electrons of Cu atoms (see the ratio spectrum for pure Cu).[22] The enhancement in the low-momentum region (less than $7\times10^{-3}m_0c$) shows that the positrons are trapped in the vacancies, consistent with the result of the positron lifetime stated above. Thus, we conclude that the positrons are trapped at the vacancies decorated with Cu atoms. The fraction of the positron annihilation with Cu electron is estimated to be $\sim$80% from the amplitude of the broad peak in the CDB ratio spectra, taking account of the correction of the annihilation rate with the inner orbital electrons.[23] This suggests that more than $\sim$80% of eight nearest-neighbor atoms of the vacancy site are Cu atoms, indicating that the vacancy–multi-Cu-atom complexes of V-Cu$_n$ ($n\geqslant6$) are introduced by the electron irradiation. We have already reported the formation of vacancy clusters covered by Cu atoms in the same Fe-Cu alloy by neutron irradiation.[1] In the case of neutron irradiation, vacancy-rich regions are created in the small area of the collisional cascade of the primary knock-on atom, which facilitates the aggregation. The present study, however, shows that the Cu atoms aggregate at room temperature accompanying monovacancies without the collisional cascade.

For the other alloys (Fe-C, Fe-Si, Fe-Mn, Fe-P, and Fe-Ni), no remarkable structure in the CDB ratio spectra is observed in the high-momentum region while the enhancement in the low-momentum region due to the positron trapping at vacancies or vacancy clusters is observed. This indicates that the solute aggregation as in the case of Fe-Cu does not take place, although the formation of the vacancy-solute complexes are suggested from the results of the positron lifetime of $\tau_2\simeq175$ ps. To see the shape of the CDB ratio spectra more quantitatively, the *S*- and *W*-parameter correlation (*S*-*W* plot) is shown in Fig. 3. Reflecting the positron anni-

hilations with the $3d$ electrons of Cu, the W parameter for Fe-Cu is high.

For the other samples, the (S,W) points are distributed along a straight line (dashed line in Fig. 3). However, the point for Fe-Ni is slightly above the line and the point for Fe-C is slightly below the line. These deviations from the linear correlation of the S and W parameters are due to the positron annihilation with the electron of Ni and C; $3d$ electrons of Ni contribute to a higher W parameter and no $3d$ electron in C results in a lower W parameter.[24] Thus, the vacancy clusters ($\sim V_{10}$) in the Fe-Ni and the vacancies in the Fe-C are associated with Ni and C atoms, respectively.

The (S,W) points for Fe-Mn, Fe-Si, and Fe-P lie just on the straight line, i.e., no indication of association of vacancies with these solute element atoms. For Fe-Mn, this is because the electron momentum distribution of Mn in the high-momentum region is similar to that of Fe.[24] For Fe-Si and Fe-P, the electron momentum distributions of Si and P in the high momentum region are different from that of Fe due to the lack of 3d electrons. However, the defect-trapping component in the positron lifetime spectra is much lower than that for Fe-C (see I_2 in Fig. 1). Thus, the dehancement of the W parameter due to the positron annihilations with Si or P electrons should be too small to be observed.

B. Annealing behavior

Figure 4 shows the isochronal annealing behavior of the positron lifetime in pure Fe and the model alloys: (a) pure Fe, Fe-C, and Fe-Si, and (b) Fe-P, Fe-Mn, Fe-Ni, and Fe-Cu. While the vacancy clusters ($\sim V_4$) in pure Fe recover at 250 °C, the vacancy clusters with a similar average size formed in Fe-P survive up to 300 °C and recover at 350 °C, which suggests that P atoms stabilize the vacancy clusters. The vacancy clusters ($\sim V_{10}$) formed in Fe-Ni become larger ($\sim V_{15}$) by annealing at 200 °C–300 °C and then recover at 350 °C. The recovery temperature of the vacancies formed in Fe-Si, Fe-Mn, and Fe-Cu is similar to that of the vacancy clusters in Fe-P and Fe-Ni (350 °C). On the other hand, the vacancies formed in Fe-C recover by annealing at 200 °C, which corresponds to the recovery temperature of the vacancy-C complexes reported previously.[25]

The annealing behavior of the CDB spectra is shown in Fig. 5 by the S-W plot. The change of the (S,W) point of Fe-Cu is markedly different from the other alloys. After small increases both in the S parameter and the W parameter by annealing at 150 °C, the (S,W) point moves to the point close to that of the well annealed pure Cu along a straight line by annealing up to 350 °C, and then moves to the point of the unirradiated state by annealing at 550 °C–650 °C. The CDB ratio spectrum for Fe-Cu annealed at 400 °C is shown in Fig. 2. The curve is very close to that for the pure Cu, which indicates that most of the positrons (about 85%) are annihilated with the Cu electrons.[23] We should notice that the irradiation-induced vacancies already recover at 400 °C, as shown in Fig. 4(b). Thus, it is concluded that the positrons are trapped at the ultrafine Cu precipitates consisting of Cu atoms (at least 85%) without defects, i.e., bcc structure coherent with the Fe matrix.[2] We have confirmed that the ultrafine Cu precipitates form in the Fe–0.3 wt % Cu irradiated by fast neutrons after the similar annealing as stated above.[1] It should be noted that the irradiation dose in the present study [9.9×10^{-5} dpa (displacement per atom)] is much lower (about two order of magnitude) than that in the previous study of the neutron irradiation (1.2×10^{-2} dpa). It should be also noted that no precipitation is observed by

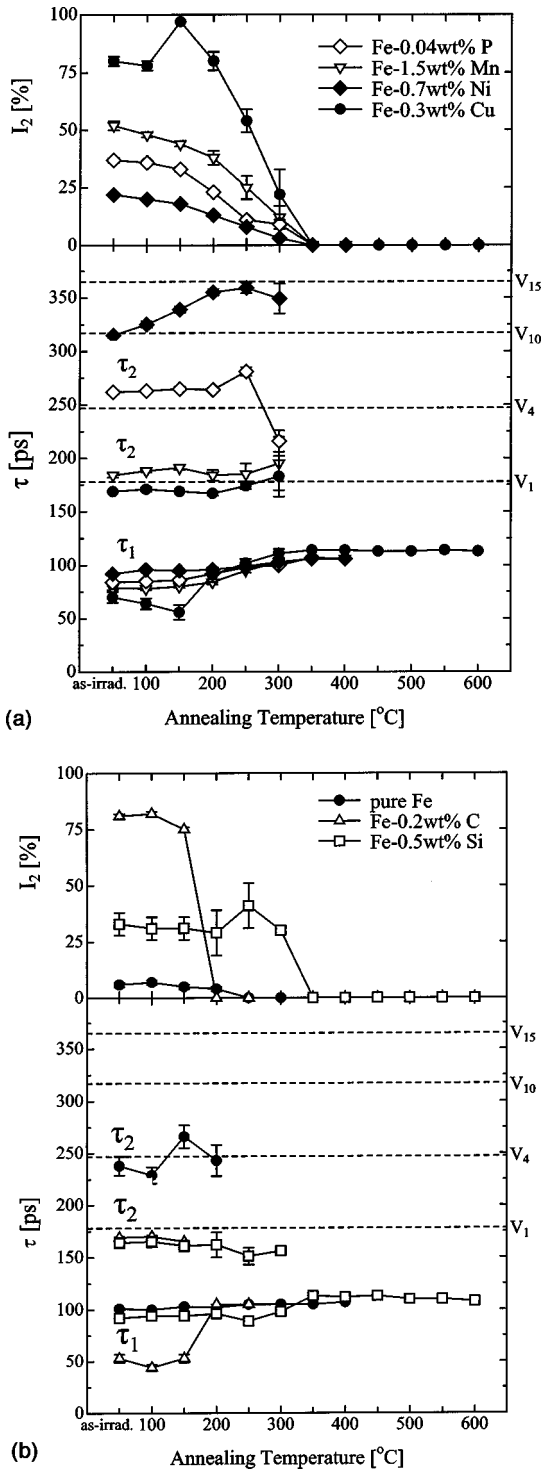

FIG. 4. Isochronal annealing behavior of positron lifetime in pure Fe and model alloys: (a) pure Fe, Fe-C, and Fe-Si, and (b) Fe-Mn, Fe-P, Fe-Ni, and Fe-Cu.

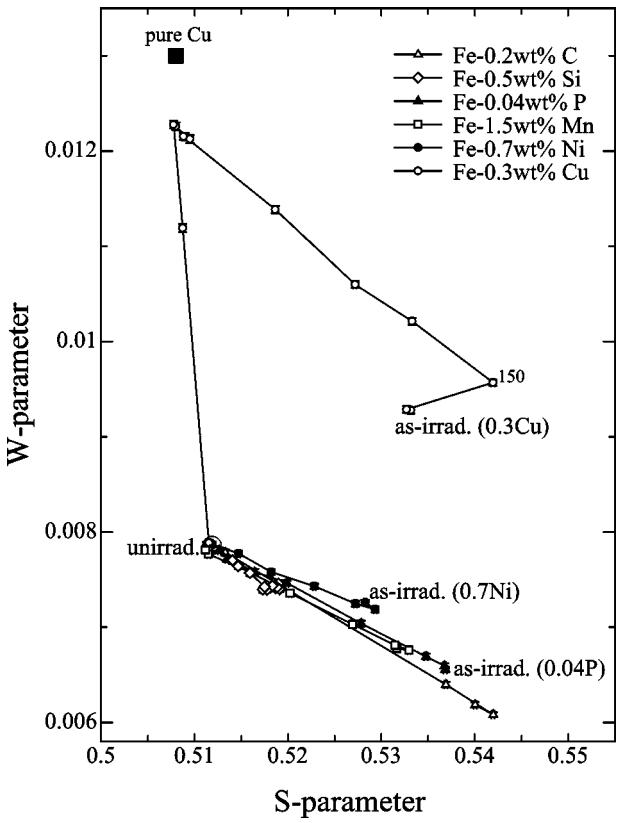

FIG. 5. Isochronal annealing behavior of the S-W plot.

thermal aging without irradiation even for two weeks at 550 °C.[1] These indicate that the introduction of small amount of vacancies highly enhances the aggregation of the Cu atoms in Fe.

In the case of the other alloys, the (S,W) points move to the point before irradiation along straight lines directly. This suggests that the irradiation effects completely recover by annihilation of the vacancies and the vacancy clusters without forming any precipitate which traps positrons. Figure 6 shows the annealing behavior of the Vickers microhardness (H_V). For the Fe-Cu sample, H_V increases with the formation of the Cu precipitates and decreases upon their dissociation. However, the H_V for the other alloys show almost no change. This also supports no precipitation of the solutes (Si, P, Mn, Ni). For Fe-C, carbide is formed before the irradiation. However, the positrons are not sensitive to the carbide because its positron affinity is lower than that of the Fe matrix.[18] The present results imply that the electron irradiation and the postirradiation annealing do not affect the carbide seriously.

IV. CONCLUSION

The binary model alloys (Fe-C, Fe-Si, Fe-P, Fe-Mn, Fe-Ni, and Fe-Cu) of the nuclear RPV steels irradiated by 3

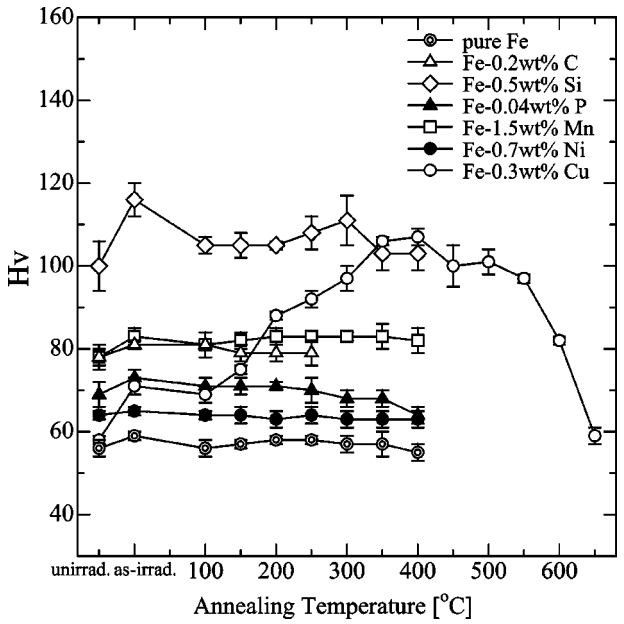

FIG. 6. Isochronal annealing behavior of Vickers microhardness (H_V).

MeV electrons at room temperature are studied by the positron lifetime and the CDB methods. Vacancies are formed in Fe-C, Fe-Si, Fe-Mn, and Fe-Cu, indicating formation and evolution of vacancy-solute complexes. In particular, the single vacancies in Fe-Cu are associated with Cu atoms to form vacancy-multi-Cu-atom complexes of V-Cu_n $(n \geqslant 6)$. Ultrafine Cu precipitates coherent with the Fe matrix are formed in Fe-Cu after the postirradiation annealing around 350 °C, while the other alloys show complete recovery without forming any precipitate which traps positrons. Vacancy clusters are formed in Fe-P $(\sim V_4)$ and Fe-Ni $(\sim V_{10})$; doping with P and Ni markedly enhances the vacancy aggregation. The vacancy-solute complexes and the vacancy clusters in Fe-Si, Fe-P, Fe-Mn, Fe-Ni, and Fe-Cu recover around 350 °C, while the complexes in Fe-C recover around 200 °C. These results are important for understanding the fundamental vacancy-solute interaction and the mechanism of the embrittlement of the RPV steels.

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