Effect of electron- and neutron-irradiation on Fe-Cu model alloys studied by positron annihilation spectroscopy

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Abstract. Electron- and neutron-irradiation effects on dilute Fe-Cu model alloys of nuclear reactor pressure vessel steels are studied by positron annihilation spectroscopy. We have found that, not only by high-dose neutron-irradiation but also by low-dose electron-irradiation, the aggregation of Cu atoms and vacancies takes place and the ultrafine Cu precipitates are formed after post-irradiation annealing at 400°C. In spite of large difference in the irradiation doses between the electron- and the neutron-irradiated samples, no significant difference is observed in the isochronal annealing behaviour above 400°C of positron annihilation and micro-hardness, indicating that small amount of extra vacancies enhance the aggregation of Cu atoms in Fe during the annealing-out process of the vacancies.

1. Introduction
Since light water reactors supply a large part of the electric power, their prolonged and safe operation is indispensable. In particular, the embrittlement of the reactor pressure vessel (RPV) steels due to long-term in-service exposure to neutron irradiation is one of the topical issues in the field of nuclear power energy. Therefore, the understanding of the detailed mechanism of the embrittlement is very important. The ultrafine precipitation of Cu impurities contained (~0.3%) in old RPV enhanced by the neutron irradiation is considered to be one of the main origin of the embrittlement of RPV steels (low alloy steels: mainly A533B) [1-6]. In spite of extensive studies, however, little is known about the irradiation enhanced Cu precipitation because it is very difficult to observe the ultrafine Cu precipitates even by current high-resolution transmission electron microscopes.

Recently, we have revealed the formation and recovery process of the ultrafine Cu precipitates in Fe-Cu model alloys formed by neutron irradiation using positron annihilation technique [7]. Vacancy-Cu complexes are formed by neutron irradiation and aggregate into nanovoids. The inner surface of the nanovoids is covered with Cu atoms. The dissociation of vacancies from the nanovoids by annealing at ~400°C leads to the formation of the ultrafine Cu precipitates. The Cu precipitates are
coherent with Fe matrix and they are annealed out at ~650°C. In this paper, we study electron irradiated Fe-Cu alloys as well as neutron irradiated ones using positron annihilation spectroscopy (coincidence Doppler broadening (CDB) and positron lifetime) and Vickers micro-hardness, and compare the results for both irradiations.

Positron is the only probe that is able to detect vacancy-type defects in metals sensitively [8-11]. In addition, it is found that positron is also a sensitive tool to defect-free ultrafine Cu precipitates in Fe due to their positron affinity trapping [12]. Positron lifetime spectroscopy provides information on the size of the vacancy clusters and their number density. The CDB enables us to identify the chemical environment surrounding the site where the positron is trapped by measuring the electron momentum distribution. The high momentum region is namely the result of the positron annihilation with the inner shell electrons [13, 14]. Thus, the CDB method can reveal the formation of vacancy-Cu complexes, their aggregations and (defect free) ultrafine Cu precipitates.

In this paper, we report that, in spite of the much lower electron dose (10^{-4} dpa: displacement probability per atom) than the neutron dose (10^{-2} dpa), Cu atoms aggregate around vacancies and the ultrafine Cu precipitates are formed after post-irradiation annealing at 400°C even in the electron-irradiated dilute Fe-Cu alloys. This indicates that small amount of extra vacancies enhances much the aggregation of Cu atoms in Fe during the annealing-out process of the vacancies.

2. Experimental procedure

The prepared samples were Fe-0.3wt%Cu and -0.05wt%Cu. They were made from high purity Fe (4N) and Cu (5N) by arc melting and cold rolled to 0.3 mm in thickness. The high and low Cu samples are the model alloys of the practical old RPV steels (~0.3wt%) and recent RPV steels (~0.05wt%), respectively. The samples were heated to 825°C and kept for 4h, followed by quenching into iced water. Some of the samples were bombarded with 3 MeV electrons below 50°C using a dynamiton accelerator of the JAEA-Takasaki Institute. In this condition, only Frenkel pairs are introduced and no collisional cascade is formed. The electron fluence was 2.0×10^{18} e/cm^{2}, which corresponds to the irradiation dose of 9.9×10^{-5} dpa (displacement probability per atom). Other samples were irradiated with fast neutrons in the Irradiation Facility of Hydraulic Rabbit II of the Japan Material Testing Reactor (JMTR) at ~100°C. The neutron fluence was 8.3×10^{18} n/cm^{2}, which corresponds to the irradiation dose of 1.2×10^{-2} dpa. In this condition, vacancy-rich regions are created in the small area of the collisional cascade of the primary knock-on atom [15].

Isochronal annealing experiment from 100°C to 750°C with 50°C step (30 min) of positron annihilation and Vickers micro-hardness were performed. Positron lifetime measurements were carried out using a conventional fast-fast spectrometer with a time resolution of 190 ps (FWHM). About 4×10^{6} coincidence events were accumulated for each measurement for 12h. After subtracting the source component and background, the spectra were decomposed into two components (τ_1 and τ_2). In order to identify the size of the vacancy clusters (V_n, n: 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 [16]. The detail of the method is described in ref. [17].

The CDB spectra were measured using two Ge detectors. The details of this method are described by Asoka-Kumar et al. [14]. The overall energy resolution is ~1.1 keV in full width at half maximum (FWHM), which corresponds to the momentum resolution of ~4.3×10^{-3} m_0 c (FWHM), where c is the speed of light and m_0 is the electron rest mass. Total counts of more than 2×10^{5} 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 unirradiated (defect free) pure Fe. The shape of the spectrum in high momentum region (typically >10×10^{-3} m_0 c) exhibits characteristic signals of the elements through the positron annihilation with their inner shell electrons. In the case that positron annihilates with Cu 3d electrons, a broad peak around 25×10^{-3} m_0 c appears [12]. The S- and the W-parameters are defined as the ratios of the counts in low momentum (|p_L| < 4×10^{-3} m_0 c) and high momentum (18×10^{-3} m_0 c < |p_L| < 30×10^{-3} m_0 c) regions in the Doppler-broadening spectrum to the total counts, respectively. When the positron is trapped at vacancy-type defect, the S-parameter increases and the W-parameter...
decreases. In addition, the $W$-parameter increases when positron annihilates with Cu electrons corresponding to the broad peak around $25 \times 10^{-3} m_0 c$ in the CDB ratio spectrum.

We also measured Vickers micro-hardness with conventional apparatus with a load of 200 g for 15 sec in each step of the isochronal experiments.

3. Results and discussion

Figure 1 shows the CDB ratio spectra of as-irradiated (a) Fe-0.3wt%Cu and (b) Fe-0.05wt%Cu, together with well annealed pure Cu as a reference. Broad peak around $25 \times 10^{-3} m_0 c$ characteristic of Cu 3$d$ electrons is clearly observed for both the electron- and neutron-irradiated Fe-0.3wt%Cu and Fe-0.05wt%Cu. Enhancement in the low momentum region and dehancement (except the broad peak around $25 \times 10^{-3} m_0 c$) in the high momentum region due to positron trapping at vacancy-type defects are also observed. These results indicate that vacancy-type defects associated with Cu atoms are formed.

![Figure 1](image-url)

**Figure 1.** CDB ratio spectra of electron- and neutron-irradiated Fe-Cu alloys: (a) Fe-0.3wt%Cu, (b) Fe-0.05wt%Cu.

The results of positron lifetime measurements in the irradiated samples are shown in figure 2 ((a) electron- and (b) neutron-irradiation). The calculated positron lifetimes for some vacancy clusters in Fe are also shown by horizontal dashed lines. For the neutron-irradiated samples, the longer lifetime $\tau_2$ of 400ps arising from three dimensional vacancy clusters (nanovoids) consisting of ~30 vacancies and the shorter lifetime $\tau_1$ of ~170ps arising mainly from monovacancies ($V_1$) are consistent with our previous report [7], indicating that the irradiation-induced vacancies, binding with Cu solute atoms, aggregate into the nanovoids. The surfaces of the nanovoids are mostly covered with Cu atoms. The other parts of vacancies, as $V_1$, are surrounded by Cu atoms. On the other hand, for the electron-irradiated samples, the longer lifetime $\tau_2$ are ~170ps for Fe-0.3wt%Cu with the intensity $I_2$ of 80% and ~220ps for Fe-0.05wt%Cu with $I_2$ of 60%. These values are close to the calculated positron lifetime in $V_1$ and $V_3$, respectively. Although large vacancy-clusters are not observed because of low energy (3MeV) electron irradiation, the irradiation induced vacancies certainly survive at room temperature as $V_1$ and $V_3$ surrounded by Cu atoms. It should be noted that the vacancy-Cu aggregation takes place by
low dose (~$10^{-4}$ dpa) electron irradiation even in the very dilute Fe-0.05wt%Cu where the Cu precipitation is hardly expected so far.

We have also performed three-dimensional atom probe (3D-AP) observations for the electron irradiated samples. 3D-AP is a unique method to map out the alloying elements in three dimensional space with nearly atomic scale. However, no Cu precipitate is observed. The vacancy-Cu aggregation should be too small to be detected even by 3D-AP.

The isochronal annealing behaviour of positron lifetime is shown in figure 2: (a) electron- and (b) neutron-irradiated Fe-Cu alloys. The longer lifetime components disappear by the annealing above 350°C for the electron irradiation and 400°C for the neutron irradiation, and positron average lifetime decreases to the value (~110ps) for bulk pure Fe or Cu, indicating that the vacancy-type defects are annealed out. However, the recovery is not complete recovery. The CDB ratio spectra of the irradiated Fe-Cu alloys annealed at 450°C are shown in figure 1. The shape of the spectra having a broad peak around $25 \times 10^{-3} \text{m}_0\text{c}$ is very similar to the ratio spectrum of pure Cu. This means that defect-free ultrafine Cu precipitates are formed.

![Figure 2](image_url). Isochronal annealing behaviour of positron lifetime of the irradiated Fe-Cu alloys: (a) electron-irradiation, (b) neutron-irradiation.

The isochronal annealing behaviour of $S$- and $W$-parameters, and Vickers micro-hardness are shown in figure 3. The $S$-parameters, sensitive to vacancy-type defects, decrease to the value for well annealed pure Fe or pure Cu up to 400°C annealing, consistent with the results of positron lifetime. Correspondingly, the $W$-parameters increase by the annealing up to the temperature where the vacancy-type defects are annealed out. They hold high values until high temperature values, up to 500°C for Fe-0.05wt%Cu and 550°C for Fe-0.3wt%Cu. They completely recover to the values of well annealed pure Fe at 600°C and 650°C for Fe-0.05wt%Cu and Fe-0.3wt%Cu, respectively. These results indicate the dissolution of the defect-free ultrafine Cu precipitates. The dissolution temperatures are consistent with the solubility limit of Cu in Fe [19].
The micro-hardness in the neutron-irradiated samples shows two-step recovery; the first is due to the annealing out of the vacancy-type defects and the second due to the dissociation of the Cu precipitates. On the other hand, the micro-hardness in the electron-irradiated samples increases with the recovery of the defects and spontaneous Cu precipitate formation, and then recovers with the dissociation of the Cu precipitates.

![Diagram of isochronal annealing behavior of S- and W-parameter and Vickers micro-hardness of the irradiated Fe-Cu alloys: (a) Fe-0.3wt%Cu, (b) Fe-0.05wt%Cu.](image)

It should be noted that the values of $W$-parameter and the micro-hardness for the electron irradiated and neutron irradiated samples are very similar to each other above the annealing temperature (400–450°C) where the vacancy-type defects are annealed out, in spite of the large difference in the irradiation dose. This indicates that small amount of extra vacancies enhance the aggregation of Cu impurity in Fe during the migration process of the vacancies. The difference in the $W$-parameter and micro-hardness between the electron- and neutron-irradiated samples below the annealing temperature dominantly comes from the Cu precipitates including nanovoids in addition to so-called matrix defects, considered to be dislocation loops formed by high dose neutron irradiation.

4. Conclusions
Electron- and neutron-irradiated Fe-Cu model alloys of nuclear reactor pressure vessel steels are studied by using positron annihilation spectroscopy. Not only by high dose neutron-irradiation but also by low dose electron-irradiation, vacancy-Cu aggregations are formed in dilute Fe-(0.05, 0.3wt.%)Cu model alloys and ultrafine Cu precipitates are formed after post-irradiation annealing at 400°C. In spite of large difference in the irradiation doses between the electron- and the neutron-irradiated samples, no significant difference is observed in the isochronal annealing behaviour above 400°C of both
positron annihilation and micro-hardness results. These indicate that small amount of extra vacancies enhance the aggregation of Cu impurity in Fe during the annealing-out process of the vacancies.

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References
[1] Phythian W J and English C A 1993 J. Nucl. Mater. 205 162
[2] Othen P J, Jenkins M L and Smith G D W 1994 Phil. Mag. A 70 1
[3] Buswell J T, Phythian W J, McElory R J, Dumbill S, Ray P H N, Mace J and Sinclair R N 1995 J. Nucl. Mater. 225 196
[4] Stoller R E 1996 Effects of Radiation on Materials: 17th International Symposium, ASTM STP 1270, ed D S Gelles, R K Nanstad, A S Kumar and E A Little, American Society for Testing and Materials 25
[5] Odette G R and Lucas G E 1998 Rad. Eff. Def. Sol. 144 189
[6] Carter R G, Soneda N, Dohi K, Hyde J M, English C A and Server W L 2001 J. Nucl. Mater. 298 211
[7] Nagai Y, Tang Z, Hasegawa M, Kanai T and Saneyasu M 2001 Phys. Rev. B 63 134110
[8] 1979 Positron in Solids ed P Hautojärvi (Berlin: Springer-Verlag)
[9] 1983 Positron Solid-State Physics ed W Brandt and A Dupasquier (Amsterdam: North-Holland)
[10] Puska M J and Nieminen R M 1994 Rev. Mod. Phys. 66 841
[11] 1995 Positron Spectroscopy of Solids ed A Dupasquier and A P Mills Jr (Amsterdam: IOS Press)
[12] Nagai Y, Hasegawa M, Tang Z, Hempel A, Yubuta K, Shimamura T, Kawazoe Y, Kawai A, Kano F 2000 Phys. Rev. B 61 6574
[13] Lynn K G, MacDonald J R, Boie R A, Feldman L C, Gabbe J D, Robbins M F, Bonderup E and Golovchenko J 1977 Phys. Rev. Lett. 38 241
[14] Asoka-Kumar P, Alatalo M, Ghosh V J, Kruseman A C, Nielsen B and Lynn K G 1996 Phys. Rev. Lett. 77 2097
[15] for example, 1976 Radiation Damage in Metals ed N L Peterson and S D Harkness (American Society for Metals)
[16] Puska M J and Nieminen R M 1983 J. Phys. F.: Met. Phys. 13 333
[17] Ohkubo H, Tang Z, Nagai Y, Hasegawa M, Tawara T and Kiritani M 2003 Met. Sci. Eng A 350 95
[18] Salje G and Feller-Kniepmeier 1977 J. Appl. Phys. 48 1833
[19] Toyama T, Nagai Y, Tang Z, Hasegawa M,almazouzi A, van Walle E and Gerard R 2007 Acta Materialia 55 6852