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Irradiation-induced Cu aggregations in Fe: An origin of embrittlement of reactor pressure vessel steels

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Very dilute Fe-Cu systems, model alloys of nuclear reactor pressure vessel (RPV) steels, irradiated by fast neutrons, are studied by positron annihilation experiments and simple calculations. The ultrafine Cu precipitates, which are never formed by thermal aging in the dilute alloys, are observed clearly and are strongly suggested to be responsible for irradiation-induced embrittlement of RPV steels. The formation and recovery process of the precipitates are revealed: (i) irradiation-induced Cu-vacancy complexes aggregate into microvoids; (ii) around 400 °C the dissociation of vacancies from the microvoids leads to the formation of the Cu precipitates of about 1 nm in size; and (iii) the Cu precipitates anneal out at about 650 °C.

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Ensuring safe operation of nuclear power reactors is a recent urgent issue since the reactors of the first generation are going over their initially designed operating lifetimes. One of the menaces to the safety is the embrittlement of the reactor pressure vessel (RPV) steels, which is considered to be caused by the ultrafine precipitation of Cu impurities contained in the RPV steels ($\sim 0.3\%$) of the first generation induced by neutron irradiation.[1–5] In-service thermal annealing of the embrittled RPV steels is also planned in several countries.[6] However, little is known about the irradiation-induced Cu precipitates or aggregations because it is very difficult to observe them even by current high-resolution transmission electron microscopes (HRTEM).

Positron is well known as a sensitive probe for vacancy-type defects. Furthermore, we have found recently that the positron can be ''trapped'' by embedded ultrafine particles in materials, namely there is a quantum-dot-like positron state in a thermally aged Fe 1.0 wt % Cu alloy,[7] by using coincidence Doppler broadening (CDB) of positron annihilation radiation[8] and positron lifetime spectroscopy. The wave functions of positrons in this state are fully confined spatially in all three directions within the embedded (sub)nano-size Cu particles in Fe 1.0 wt % Cu even if they contain no vacancy-type defects. This state enables us to detect the defect free ultrafine Cu precipitates which cannot observed by HRTEM and to reveal their structure in atomic scale. For example, the Cu precipitates of ~ 1 nm, formed in Fe 1.0 wt % Cu by thermal aging at 550 °C for 2 h, are consisting of only Cu atoms, free from defects, three dimensional, and have no open-volume defects at the interfaces which can trap the positron.

In this paper, we show that the Cu aggregations are certainly produced by neutron irradiation even in very dilute Fe-Cu alloys, the model alloys of the RPV steels, using the positron annihilation method. The aggregations are observed in the alloys not only of higher Cu content (0.3%), but also of much lower content (0.05%), nearly the same level as that of recently manufactured RPV steels in which no degradation by Cu precipitation is anticipated. We also reveal the recovery process of the aggregations and the resulting precipitates by post-irradiation isochronal annealing (30 min) utilizing the quantum-dot-like positron state. The Cu precipitates survive up to about 600 °C. The results provide a clear guideline for the planned in-service annealing.

The RPV steels in the nuclear reactors of the first generation contain Cu impurities of more than 0.3% in weight. The steels of recently constructed power reactors contain about 0.05% Cu. Thus we prepared the following model alloys: Fe 0.3 wt % Cu, Fe 0.15 wt % Cu, Fe 0.05 wt % Cu, and pure Fe as a reference. These alloys are heated to 825 °C and kept for 4 h, followed by quenching into iced water. In the as-quenched state Cu atoms are in a supersaturated solid solution. It should be noted that in these alloys no Cu precipitate was observed even after thermal aging at 550 °C up to 312 h. The quenched samples were irradiated with fast neutrons for 144 h in the Irradiation Facility of Hydraulic Rabbit II of the Japan Material Testing Reactor (JMTR). The fast neutron fluence was 8.3×10^{18} n/cm^2, which corresponds to the irradiation dose, in general, of about 20 years for the RPV steels in the pressurized water reactors (PWR). The irradiation temperature was set at ~ 300 °C which is nearly the same as that of in-service RPV steels. Furthermore, in order to clarify the role of vacancies and microvoids (i.e., aggregations of vacancies) the samples for the post-irradiation annealing experiments are irradiated at ~ 100 °C, as a large part of the vacancies and microvoids disappear during the irradiation around 300 °C.

CDB spectra were measured using two Ge detectors. The details of the setup are described in Ref. 7. In the CDB method, momentum distribution of core electrons is measured,[8] based on which the chemical elements around the annihilation sites of positrons can be identified. The CDB ratio spectrum is the momentum distribution normalized to that of unirradiated (defect-free) pure Fe. The shape of the spectrum in high momentum region ($>10\times10^{-3}mc$, where c is the speed of light and m is the electron rest mass) exhibits characteristic signals from Cu or Fe through the positron annihilation with their core electrons specific to the elements. In the present experiments, the overall energy resolution was ~ 1.1 keV in full width at half maximum (FWHM), which corresponds to the momentum resolution of ~ 4.3

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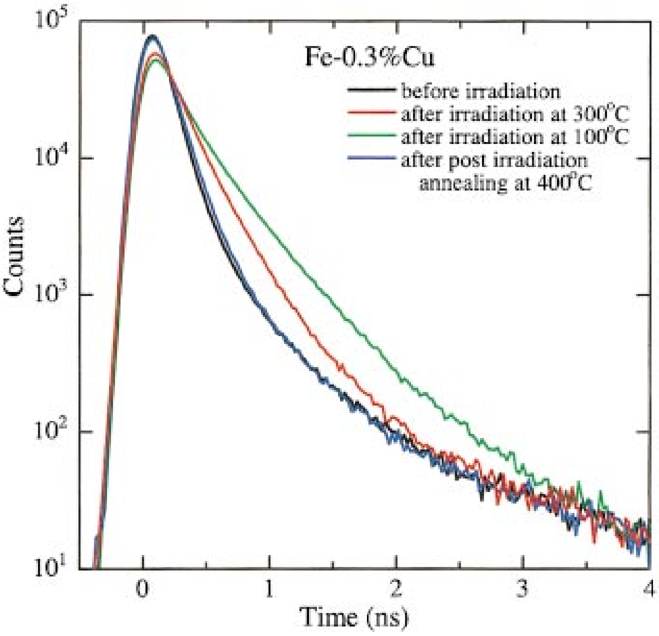

FIG. 1. (Color) Positron lifetime spectra for Fe 0.3% Cu. Black, red, green, and blue lines indicate before irradiation, after irradiation at about 300 °C, after irradiation at about 100 °C, and the post-irradiation annealing at 400°C, respectively.

$\times 10^{-3} mc$ (FWHM). Total counts more than 2×10^7 for each measurement were accumulated for 12 h. Positron lifetime measurements were carried out with a conventional fast-fast spectrometer with a time resolution of 190 ps (FWHM). Total counts of 4×10^6 were accumulated for 12 h.

Figure 1 shows positron lifetime spectra for Fe 0.3 wt % Cu. The spectrum after irradiation at ~300 °C (red curve) shows a long lifetime component of about 300 ps with the intensity of ~30% which evidences microvoids consisting of ~10 vacancies.[9,10] In addition, a relatively short lifetime component of about 160 ps which is arising from irradiation-induced dislocation loops and monovacancy-Cu complexes is observed. These two components appear in all the samples.

Figure 2 shows the CDB ratio spectra for the irradiated model alloys. The broad peak around $25\times 10^{-3} mc$ shows that positrons annihilate with core electrons of Cu atoms (see the ratio curve for unirradiated pure Cu). The enhancement in low-momentum region (less than $7\times 10^{-3} mc$) shows that positrons are trapped in the microvoids, vacancies, and dislocation loops induced by the irradiation. We can clearly see the broad peak for all the samples. The Cu CDB signal can be observed only when the positrons are localized around the Cu atoms in the dilute alloys: trapped at vacancy-type defects bound to Cu atoms or confined in Cu precipitates (i.e., the quantum-dot-like state).

Thus the long lifetime and the Cu CDB signal in the present case reveal that positrons are trapped at microvoids decorated with Cu aggregations, which are formed by the irradiation-induced vacancies bound to Cu solute atoms. The fractions of the covering with Cu on the inner surfaces of the microvoids and vacancies can be estimated from the amplitude of the broad peak in the CDB ratio spectra, taking account of correction of annihilation rate with core electrons:[11] about 94, 92, and 80% for Fe 0.3% Cu, Fe 0.15% Cu, and Fe 0.05% Cu, respectively. Thus we conclude that the inner surfaces of the resultant microvoids are mostly coated with Cu atoms. The other parts of surviving monovacancies would be surrounded by Cu atoms.

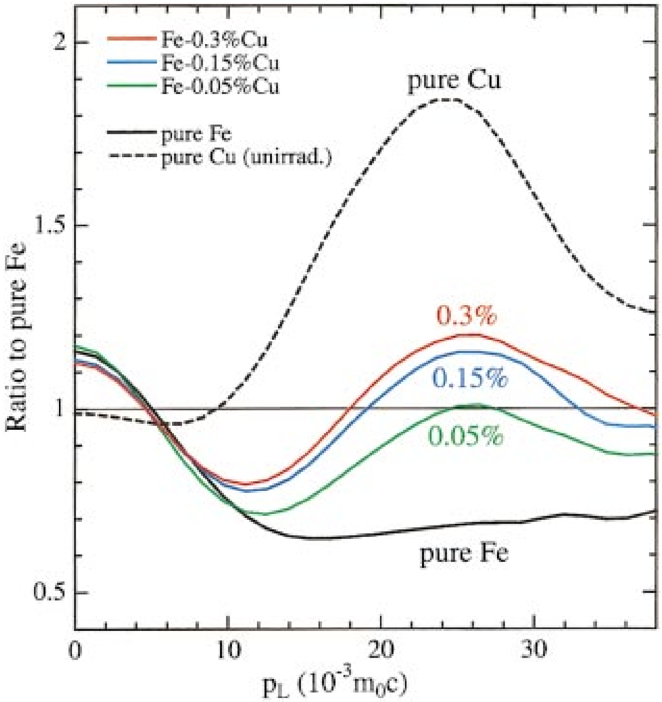

FIG. 2. (Color) CDB ratio spectra for Fe 0.3% Cu, Fe 0.15% Cu, Fe 0.05% Cu, and pure Fe irradiated with fast neutrons at about 300 °C, together with that for unirradiated pure Cu.

The Cu aggregation induced by electron and neutron irradiation have been studied by three-dimensional atom probe (3DAP); the results imply the Cu aggregation containing a high Fe content (~28%) after neutron irradiation but being nearly free from Fe after electron irradiation.[12] The difference between 3DAP and positron annihilation results for neutron irradiation might be due to the effect of microvoids involved in the Cu aggregations, which are not observed by 3DAP. Detailed measurements using both methods with the same samples are very necessary in order to explain this discrepancy.

Surprisingly, the Cu aggregations are detected clearly not only for the higher-Cu-content (0.3%) alloy in which the irradiation-induced precipitation is considered to be significant, but also for the lower-Cu-content (0.15 and 0.05%) alloys in which the Cu precipitation is hardly expected. The recent RPV steels with low Cu contents are believed to be free from the irradiation-induced Cu precipitates so that their embrittlement is caused mainly by matrix damage, such as dislocation loops, other than Cu(-rich) precipitates.[1,5] However, the present results show that the formation of the ultrafine Cu aggregations are strongly enhanced by the irradiation-induced vacancies with a high concentration and

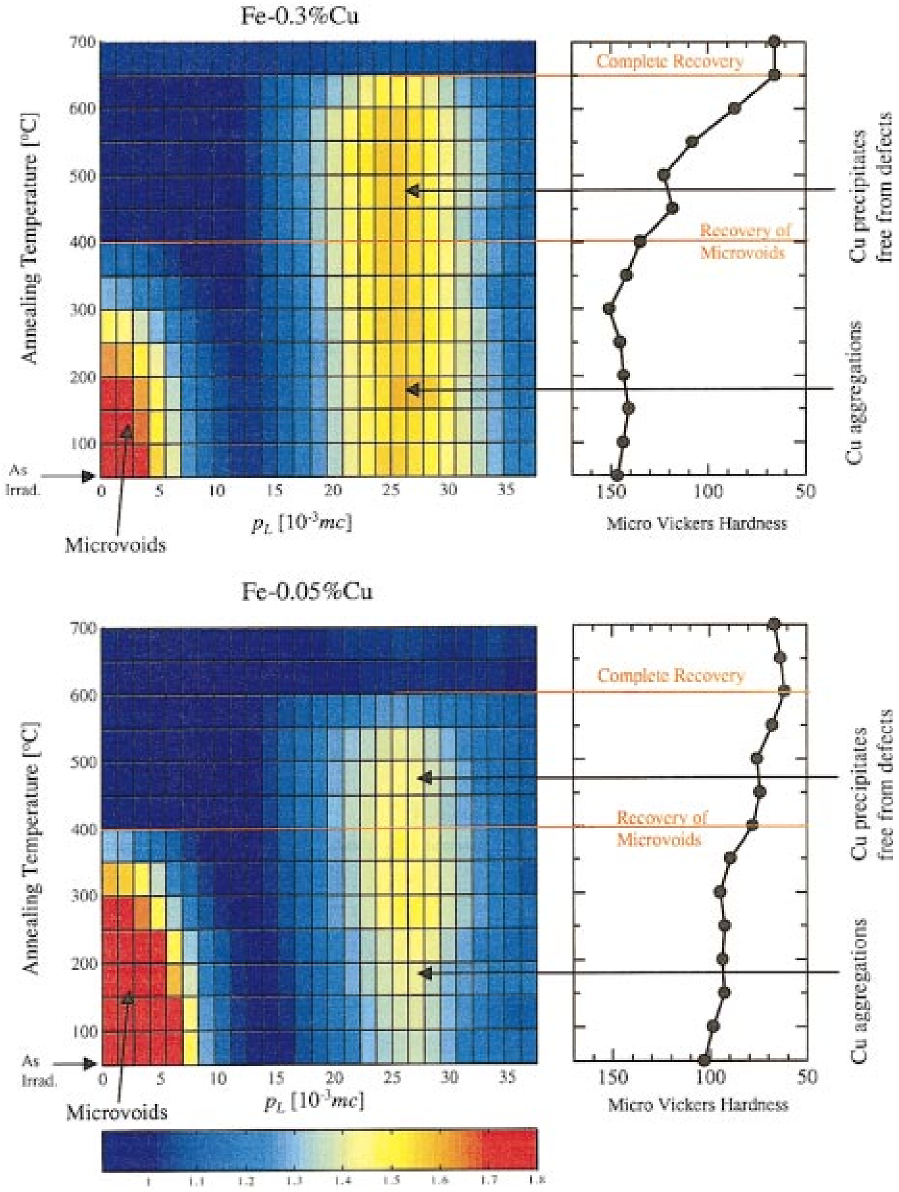

FIG. 3. (Color) Contour plots of isochronal (30 min) annealing behavior of the CDB ratio spectra for Fe 0.3% Cu and Fe 0.05% Cu after irradiation at about 100 °C. The ratio spectrum for each annealing temperature is normalized to have the same value of 1.0 at $13\times10^{-3}mc$.

hence suggest that the Cu precipitation may still be one of the reasons for the embrittlement even for the low Cu RPV steels.

These aggregations of vacancies and Cu atoms are originated from the following two facts: (i) that vacancies in Fe are mobile well below room temperature[13] and (ii) the high binding energy between a Cu and a vacancy in Fe, which could be due to a size effect[14,15] or to the high clustering tendency of the Fe-Cu system. The vacancies introduced by the irradiation around 300 °C can easily migrate during irradiation, and hence some of them encounter Cu impurity atoms and can diffuse as resulting vacancy-Cu impurity complexes. Eventually an agglomerate of about ten vacancy-Cu pairs is stabilized by aggregating with each other. Especially 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 strong Cu segregation on the microvoid surfaces could be due to the fact that Cu has a lower surface energy than Fe.[16] We should point out that such aggregation is never observed even in unirradiated high-Cu (0.3%) alloy by thermal aging at 550 °C for 312 h. Thus the aggregation is only possible by the irradiation.

In the next step, we studied how the Cu aggregations recover by thermal annealing. In several countries, in-service thermal annealing of the RPV steels is scheduled. The widely accepted condition, 454 °C heat treatment of 168 h, is believed to be enough for the annealing.[6] However, our work suggests that this is insufficient. Positron lifetime spectra for the samples irradiated at ~100 °C (green curve in Fig. 1) have a longer lifetime component of ~400 ps with the intensity (>50%) higher than that for the samples irradiated at ~300 °C, which indicates more and larger microvoids consisting of ~30 vacancies.[9,10] As shown in Fig. 1 (blue curve), the positron lifetime spectrum after post-irradiation annealing at 400 °C for 30 min recovers to the spectrum before irradiation. This means that the microvoids surrounded by the Cu atoms on their surfaces anneal out at

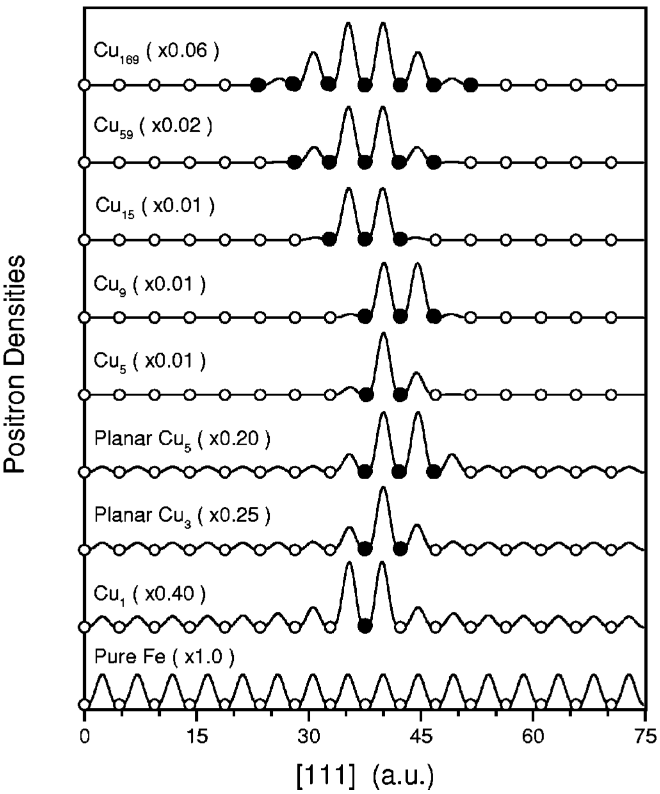

FIG. 4. Cross section of the calculated positron density distributions along the [111] direction for the bcc Cu precipitates coherent with bcc Fe matrix. Open circles and closed circles indicate Fe atoms and Cu atoms, respectively.

400 °C. However, this annealing does not lead to complete disappearance of the Cu aggregations. Figure 3 shows the contour plots of isochronal (30 min) annealing behavior in the CDB ratio spectra for Fe 0.3% Cu and Fe 0.05% Cu. The ratio spectrum for each annealing temperature is normalized to have the same value of 1 at $13\times 10^{-3}mc$. The peak in the low-momentum region (less than $7\times 10^{-3}mc$) due to the microvoids disappears around 400 °C, while the broad peak around $25\times 10^{-3}mc$, the signals of the Cu atoms, is clearly observed even after the higher temperature annealing, which indicates the positron confinement in defect-free Cu precipitates. As shown in Fig. 3, the precipitates recover at much higher temperatures: 650 °C for Fe 0.3% Cu and 600 °C for Fe 0.05% Cu. These recovery temperatures of the precipitates are consistent with the solubility limits of Cu in Fe.[17]

The issue of the positrons annihilating with the electrons of the Cu precipitates is further investigated by theoretical calculations. For this purpose, the superimposed-atom method developed by Puska *et al.*[9] is adopted. In this scheme, the electron density distribution in the crystal and the Coulomb potential for the positron are constructed by superimposing the free atomic charges and Coulomb potentials, respectively. The positron-electron correlation potential is calculated based on the two-component density-functional theory.[18] The positron wave function is then obtained by the numerical relaxation technique.[9] To simulate the Cu precipitates in iron, an 1024-site bcc iron supercell is employed in the present calculations, and various coherent bcc Cu precipitates (as large as containing 169 Cu atoms) are generated in the supercell by replacing corresponding Fe atoms by Cu atoms. Figure 4 shows the cross section of the calculated positron density distributions along the [111] direction for these Cu precipitates. It is found that the positron can be trapped even by a coherent precipitate containing only five Cu atoms. In particular, the complete confinement, namely the quantum-dot-like positron state, are realized when the precipitate is grown to 0.5 nm (which contains 59 Cu atoms) in its radius. On the other hand, it is found that the lifetime of the positron trapped at the defect-free precipitate is nearly the same as that of the positron annihilating at the Fe matrix (104 ps for bcc Fe matrix and 110 ps for Cu_{59} precipitates). The size of the Cu precipitates in Fe which can confine positrons completely has been already estimated in our previous work[7] from the viewpoint of positron affinity.[19] The estimated minimum size of ~0.6 nm in diameter is consistent with the present calculations. These calculations indicate that the experimental CDB and lifetime results after post-irradiation annealing at 400 °C are originated from the positron annihilation at the defect-free Cu precipitates. That is to say, the recovery of the microvoids by dissociating their vacancies around 400 °C leads to formation of the ultrafine Cu precipitates free from vacancies.

We also measured Vickers microhardness which is closely related to the embrittlement (Fig. 3). The recovery temperature of the microhardness exactly agrees with that of the Cu precipitates. Therefore the ultrafine Cu precipitates are, at least, one of the origins of the embrittlement by neutron irradiation.

In summary, we revealed the following two points in the present work. (i) Ultrafine Cu aggregations involving microvoids, which are the origin of the embrittlement of neutron irradiated RPV steels, are observed. The irradiation induced Cu aggregations form even in a very dilute alloy (Fe 0.05% Cu), which strongly suggests that the recently constructed power reactors still suffer from the Cu aggregation and precipitation. (ii) Upon the recovery of the microvoids by dissociating their vacancies around 400°C, the Cu atoms on the microvoid surfaces form the resulting ultrafine Cu precipitates free from vacancies. In addition, it is found that the recovery temperature of the Cu precipitates depends on the Cu content in the alloys. Thus the positron annihilation technique is a promising tool to optimize the in-service annealing condition of the RPV steels from the microscopic mechanism.

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