Deformation-enhanced Cu precipitation in Fe-Cu alloy studied by positron annihilation spectroscopy

T. Onitsuka,[1] M. Takenaka,[2] E. Kuramoto,[2] Y. Nagai,[3] and M. Hasegawa[3]
[1]*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580, Japan*
[2]*Research Institute for Applied Mechanics, Kyushu University, Kasuga, Fukuoka 816-8580, Japan*
[3]*The Oarai Branch, Institute for Materials Research, Tohoku University, Oarai, Ibaraki 311-1313, Japan*
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The formation of Cu precipitates in Fe-1.0 wt % Cu alloy specimens enhanced by deformation has been studied by positron annihilation technique, coincidence Doppler broadening, and the positron lifetime method. In the alloy specimens quenched and 20% rolled at room temperature, the formation of Cu-vacancy clusters was observed, which evidenced the enhanced diffusion of Cu atoms by deformation-induced excess vacancies mobile at room temperature. By annealing up to 400 °C following the deformation, vacancies and vacancy clusters were dissociated from these Cu-vacancy clusters, and ultrafine Cu precipitates coherent with the Fe matrix were formed. The increase of the hardness was also observed and was attributed to the precipitation.

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I. INTRODUCTION

In order to study the fundamental features of very localized sites in host materials, (that is, embedded nanoparticles), such as quantum dots in semiconductors and ultrafine precipitates in metal alloys, it is essential to adopt a measuring technique which has the ability of so-called "site selectivity." One such powerful methods, the positron annihilation technique,[1–4] has become very popular. In particular the coincidence Doppler broadening (CDB)[6–11] of positron annihilation radiation is very powerful; it measures the momentum distribution of the core electrons specific to each element, and is able to identify the elements definitely around the annihilation sites.

It was recently recognized that the fundamental behavior of the irradiation embrittlement of pressure vessel steels in a light water reactor is an irradiation-enhanced formation of fine Cu precipitates in the matrix. It is, however, very difficult to observe this precipitation process, especially the initial stage of the precipitation.

It has so far been clarified that Cu precipitates are formed during thermal aging,[12–14] and furthermore during or after irradiation this precipitation process is enhanced by the presence of radiation-induced vacancies.[13,15] On the other hand, it is well known that deformation also induces a significant amount of vacancies into a specimen.[18] In the present paper, the possibility of deformation-enhanced Cu precipitation in an Fe-Cu alloy will be studied by using the CDB method. It is known that in an Fe-Cu alloy system Cu precipitates are perfect trapping sites for a positron, and that the wave function of every positron is "entirely" confined spatially within fine precipitates, which can be recognized as a "quantum-dot-like positron state."[12] The reason for this positron trapping is considered to be due to the positron affinity of Cu being larger than that of Fe.[3–5]

II. EXPERIMENT

Fe-1.0 wt % Cu samples were prepared from high-purity Fe ($4N$) and Cu ($5N$) by the zone-leveling method in high-purity hydrogen gas, and cold rolled into a sheet of 0.4-mm thickness. The size of the specimen is $8\times8\times0.4$ mm.[3] Specimens were heated to 825 °C in high-purity hydrogen gas and kept for 4 h, followed by quenching into iced water. In the as-quenched state, Cu atoms are in a supersaturated solid solution. Deformation of samples were made by a 20% reduction of the thickness by rolling at room temperature. CDB measurement was made by using a sandwich of two samples and a positron source (^{22}NaCl). Samples were repeatedly used for the isochronal annealing experiment in a vacuum of 10^{-4} Pa, and also for measurement of the micro-Vickers hardness made at the peripheral region of the square-shaped samples.

CDB spectra were measured using two Ge detectors. The energies of annihilating γ-ray pairs (denoted by E_1 and E_2) in coincidence were simultaneously recorded by two detectors located at an angle of 180° relative to each other. The difference in energies of the two γ rays, $\Delta E=E_1-E_2$, is cp_L, and the sum energy $E_T=E_1+E_2$ is equal to the total energy of the electron-positron pair prior to annihilation, i.e., $2m_0c^2-E_B$ (neglecting the thermal energies and chemical potentials), where p_L is the longitudinal component of the positron-electron momentum along the direction of the γ-ray emission, c is the speed of light, m_0 is the electron rest mass, and E_B is the electron binding energy.[10] The selection of coincidence events that fulfill the condition $2m_0c^2-2.4\,\mathrm{keV}<E_T<2m_0c^2+2.4\,\mathrm{keV}$, results in a significant improvement in the peak to background ratio (by three orders of magnitude) over conventional one-detector measurements. This enables us to observe positron annihilation with element-specific high-momentum core electrons. The overall energy resolution was $\sim$ 1.1 keV [full width at half maximum (FWHM)], which corresponds to the momentum resolution of $\sim4.3\times10^{-3}$ mc (FWHM).

Positron lifetime measurements were carried out with a conventional fast-fast spectrometer with a time resolution of 190 psec (FWHM). The total counts of 4×10^6 were accumulated for 12 h. Lifetime spectra were decomposed into two components by using the Resolution and Positronfit programs.[16]

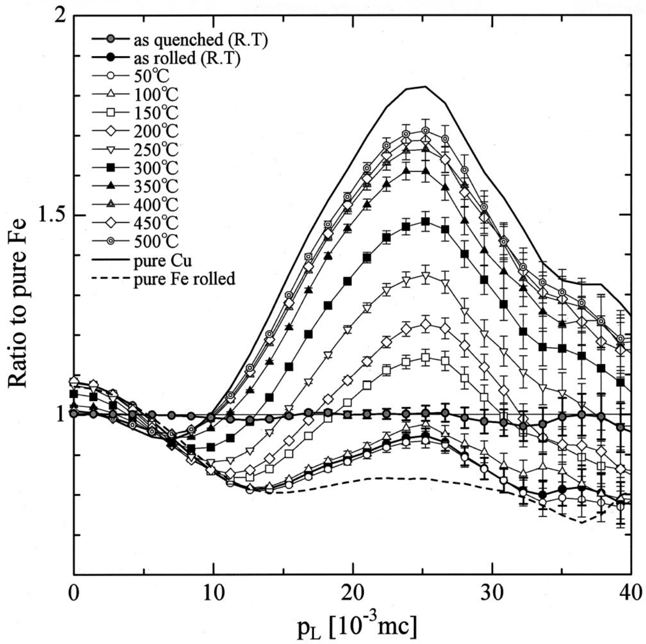

FIG. 1. CDB ratio curves [momentum distribution normalized to that of annealed (defect-free) pure Fe] of an Fe-1.0 wt % Cu alloy, quenched and then 20% rolled, followed by a subsequent isochronal annealing up to 500 °C, together with the curves for pure bulk Cu, a pure Fe 20% rolled alloy, and an Fe-1.0 wt % Cu as-quenched alloy.

III. RESULTS AND DISCUSSION

In order to investigate the deformation enhanced Cu precipitation in an Fe-Cu alloy system-the CDB and the positron lifetime measurements were made for Fe- 1.0 wt % Cu alloy specimens quenched and 20% rolled. Figure 1 shows the CDB ratio curves [momentum distribution normalized to that of annealed (defect-free) pure Fe] of these specimens followed by a subsequent isochronal annealing up to 500 °C, together with those for pure bulk Cu, pure a Fe 20% rolled alloy, and an Fe-1.0 wt % as-quenched Cu alloy.

The CDB ratio curve for the pure bulk Cu shows a broad peak around 25×10^{-3} mc and a small valley at 7×10^{-3} mc, which is the characteristic feature of Cu in the ratio curve. The CDB ratio curve for an as-quenched is Fe-1.0 wt % Cu alloy almost constant at about 1.0, namely, almost identical to that for the pure Fe. This means that the positrons are not trapped by the isolated Cu atoms in the supersaturated solid solution but annihilate only with the electrons of Fe atoms, as expected from the low Cu content of 1.0 wt %.

On the other hand, the CDB ratio curve for the pure Fe 20% rolled allay is quite different from the value of 1.0, that is, the increase in the low p_L region and the decrease in the high p_L region, which is considered to be due to the positron trapping at open-volume defects such as deformation-induced vacancies where positron annihilation with core electrons is significantly reduced.

The CDB ratio curve for an Fe-1.0 wt % Cu quenched alloy and a 20% rolled alloy is already different from that for the pure Fe 20% rolled alloy showing a small broad peak around 25×10^{-3} mc. This means that a small number of Cu-vacancy clusters are already formed through the migration of Cu atoms caused by deformation-induced excess vacancies in the as-rolled state. This is very clear evidence of the fact that vacancies in an Fe matrix are already mobile even at room temperature, which is consistent with the previous result obtained by the positron annihilation lifetime measurement for Fe irradiated with electrons at low temperature.[17,18]

To study the aging evolution of the CDB spectra for an Fe-1.0 wt % Cu quenched alloy and a 20% rolled alloy, CDB ratio curves obtained after each heat treatment between 50 and 500 °C, in steps of 50 °C, are also shown in Fig. 1. As seen from this figure, the peak which originates from Cu-vacancy clusters continuously grows with an increase of the annealing temperature up to 500 °C and almost reaches the CDB ratio curve for pure Cu. This result clearly shows that most of the positrons annihilate with electrons of Cu, but only a few positrons do so with elements of Fe, which suggests that Cu-vacancy clusters change to Cu precipitates with large enough sizes for positrons to annihilate in them at 500 °C, not at the boundaries and not at open-volume defects such as vacancies.

It is considered that a positron has a quantum-dot-like state in Cu precipitates, as discussed in a previous paper.[12] This state can be explained in terms of the difference in positron affinity between the precipitates and the matrix.[3,19,20] The positron affinity of Cu (-4.81 eV) is ~1 eV lower than that of Fe (-3.84 eV).[3,19] Thus the precipitated particle can be regarded as a potential well with a depth of 1 eV for a positron. If the spherical symmetry of the particle is assumed, there exists a bound positron state for particles larger than $\sim$ 0.6 nm in diameter. The concentration of the Cu precipitates is estimated to be the order of $10^{18}/\mathrm{cm}^3$ by assuming that about 10% of Cu atoms precipitated from the Fe matrix solid solution.

In order to clarify the transition process from Cu-vacancy clusters to Cu precipitates, information about vacancies is definitely needed. For this purpose, a *S*-parameter and positron lifetime measurements are very useful. In the following results of these measurements are shown.

Figure 2 shows the result of *S*-and *W*-parameter correlations (*S*-*W* plot) for an Fe-1.0 wt % Cu quenched alloy and a 20% rolled alloy, followed by subsequent isochronal annealing up to 500 °C together with those for pure bulk Cu and Fe,[5] pure Fe 20% rolled alloy and an Fe- 1.0 wt % Cu as-quenched Cu alloy. The *S* and *W*-parameters are defined as the ratio of low-momentum ($|p_L|<4\times10^{-3}$ mc) and high-momentum ($18\times10^{-3}\,\mathrm{mc}<|p_L|<30\times10^{-3}$ mc) regions in the Doppler-broadening spectrum to the total region, respectively. The $S(W)$ parameter is a measure of the momentum density at low (high) momentum.

The pure Cu is located at a low *S* site and a high *W* site, but the pure Fe is located at a low *S* site and a low *W*. On the other hand, the pure Fe 20% alloy rolled is located at a high *S* site and a low *W* site, corresponding to the fact that the CDB ratio curve for the pure Fe 20% alloy rolled is quite different from the value of 1.0 (pure Fe) due to deformation induced defects such as vacancies as shown in Fig. 1.

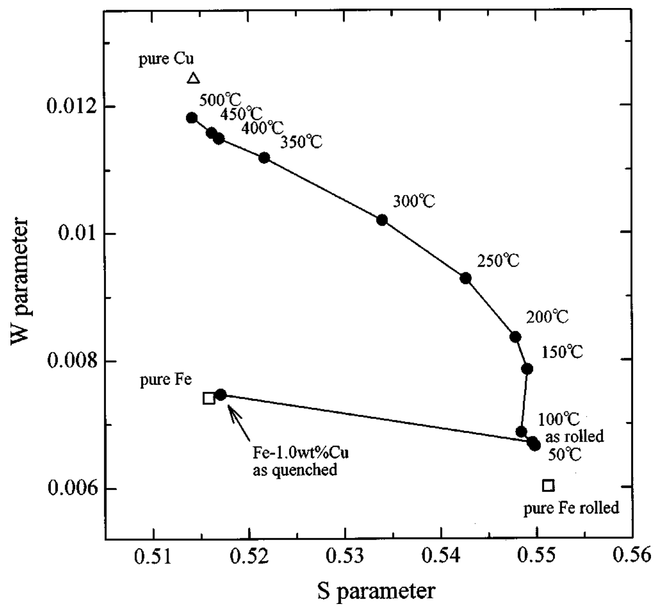

FIG. 2. Result of *S*-and *W*-parameter correlations ($S-W$ plot) for an Fe-1.0 wt % Cu alloy quenched and 20% rolled, followed by a subsequent isochronal annealing up to 500 °C together with those for pure bulk Cu and Fe, a pure 20% rolled Fe alloy, and a Fe-1.0 wt % as-quenched Cu alloy.

It is seen that Fe-1.0 wt % Cu as-quenched alloy is located at a site almost identical to that for pure Fe. This is consistent to the fact that the CDB ratio curve for Fe-1.0 wt % Cu as-quenched alloy is almost constant at the value of 1.0 (pure Fe). Furthermore, an Fe-1.0 wt % Cu quenched alloy and a 20% rolled alloy is located near the Fe 20% rolled, alloy but has a slightly larger *W* parameter, which is consistent with the result of the CDB ratio curves for both specimens; that is, the former already has a small amount of Cu-vacancy clusters.

During isochronal annealing up to 500 °C for an Fe-1.0 wt % Cu quenched alloy and a 20% rolled alloy, data points are shifted from a region of high *S* and low *W* to that of low *S* and high *W*, that is, near the pure Cu site. The increase of the *W* parameter corresponds to the growth of the peak which originates from Cu-vacancy clusters on the CDB ratio curves in Fig. 1, showing that most of the positrons annihilate in Cu-vacancy clusters formed by the aid of deformation-induced excess vacancies. The decrease of the *S* parameter means that vacancies and vacancy clusters are annealedout with an increase of the annealing temperature. During an isochronal annealing below 200 °C the *W* parameter increases without an decrease of the *S* parameters, suggesting that Cu-vacancy clusters are rapidly growing with the aid of deformation-induced excess vacancies. To obtain more detailed information about vacancies in Cu-vacancy clusters, the result of positron lifetime measurement is definitely important, which is shown in the following.

Figure 3 shows the result of the positron annihilation lifetime measurement for an Fe-1.0 wt % Cu quenched alloy and a 20% rolled alloy followed by an isochronal annealing up to 500 °C together with the result of the hardness measurement. In this figure τ_{av} is the average positron lifetime, τ_1 the first component of the positron lifetime, τ_2 the second component of the positron lifetime, I_2 the intensity of the second component, I_{Cu} the intensity for positrons trapped at Cu-vacancy clusters or Cu precipitates, and H_V the Vickers hardness. I_{Cu} is obtained from the result of the CDB ratio measurement in Fig. 1, taking into account the position of the data point in the range spanning from 1.0 (pure Fe) ($I_{Cu}=0\%$) and pure Cu ($I_{Cu}=100\%$) values together with the effect of deformation induced vacancies which reduces the data values.[22]

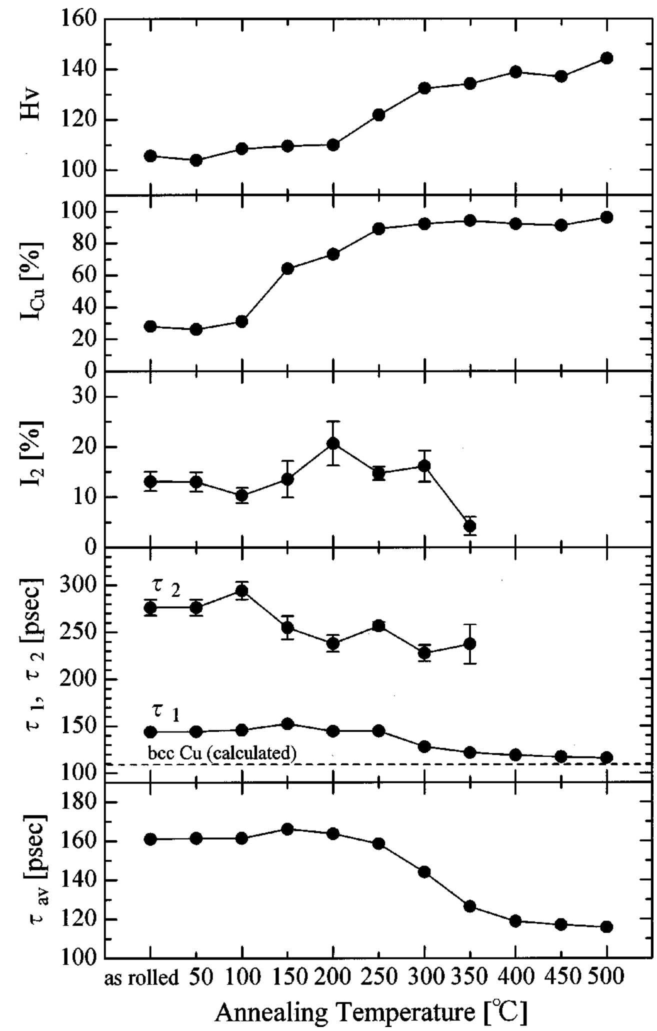

FIG. 3. Result of the positron annihilation lifetime measurement for an Fe-1.0 wt % Cu alloy quenched and 20% rolled followed by the isochronal annealing up to 500 °C together with the result of the hardness measurement, where τ_{av} is the average positron lifetime, τ_1 the first component of the positron lifetime, τ_2 the second component of the positron lifetime, I_2 the intensity of the second component, I_{Cu} the intensity for trapped positrons at Cu-vacancy clusters or Cu precipitates, and H_V the Vickers hardness.

In the as-rolled state, information about vacancy clusters is obtained in τ_2, which is about 280 psec, corresponding to three dimensional vacancy clusters of about five vacancies.[21,23] On the other hand, τ_1 is about 150 psec, which is shorter than a positron lifetime at a single vacancy in Fe [~175 psec (experimental[17,18])], and is considered to be including a matrix component [the positron lifetime of bulk Fe is 107 psec (experimental), and that of bcc Cu is 109 psec (calculated)]. A single vacancy in Fe is already mobile at room temperature, and this must correspond to single vacancies trapped at Cu atoms. I_2 is only around 12%, suggesting that fraction of vacancy clusters is not so high compared with other vacancy component, probably single vacancies trapped at Cu atom sites. I_{Cu} is about 30%, suggesting that positrons annihilate at vacancy and vacancy cluster sites 30% of the neighboring atoms of which is Cu atoms in average.

In the process of increasing the annealing temperature a prominent change occurs at about 150 °C where I_{Cu} rapidly increases, suggesting that the number of Cu atoms in positron annihilation sites increases. I_{Cu} increases toward a value close to 100% above 250 °C annealing. On the other hand, the long lifetime component I_2 is almost annealed out after 400 °C annealing, suggesting that vacancy clusters became unstable at high temperature and are dissociated from Cu-vacancy clusters, and thus ultrafine Cu precipitates coherent with Fe matrix are formed. At the same time, the first lifetime τ_1 decreases with an increase of the annealing temperature, and comes very close to the lifetime at matrix. This must be caused by the fact that positrons are trapped and annihilate at small Cu precipitates with a quantum-dot-like state at the end of the isochronal annealing, i.e., at 500 °C as known from the CDB measurement mentioned above. This result is corresponding to the change observed in S-W plot. H_V increases at high temperature region, which means that Cu precipitates contribute to the hardness in the Fe-1.0 wt % Cu alloy.

IV. CONCLUSION

In a Fe-1.0 wt % Cu quenched alloy and a 20% rolled alloy, it was observed by the CDB method that, during the isochronal annealing process up to 500 °C Cu-vacancy clusters were formed by the aid of deformation-induced excess vacancies, and changed into fine Cu precipitates above 400 °C. The positron lifetime measurement was also made parallel to the CDB measurement, and it revealed that vacancies and vacancy clusters contribute to the nucleation and growth process of small Cu-vacancy clusters at a relatively low-temperature region, but are annealed out after 400 °C annealing, where Cu precipitates free from vacancies and Fe atoms are formed. In small Cu precipitates in a high-temperature region, trapped positrons are considered to have a quantum-dot-like state, that is, a bound state in a potential well, which is induced by the difference of positron affinity between the precipitates and matrix.

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