Positron confinement in ultrafine embedded particles: Quantum-dot-like state in an Fe-Cu alloy

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A quantum-dot-like positron state is demonstrated in the ''defect-free'' particles using coincidence Doppler broadening of positron annihilation radiation. The wave functions of all positrons are entirely confined spatially in all three directions within the embedded nanosize and subnanosize Cu particles in a dilute Fe-Cu alloy. With use of this probe, the ultrafine particles are revealed to have nearly the same electron momentum distribution as bulk Cu, to be free from Fe atoms and defects, three dimensional, and to have no open-volume defects at the interfaces which can trap the positron. These successes indicate that this positron state promises to be a powerful tool for the studies of mesoscopic systems in metals and semiconductors.

I. INTRODUCTION

Embedded nanoparticles in host materials, such as quantum dots in semiconductors[1] and ultrafine precipitates in metal alloys, have attracted extensive studies because of their application prospects as quantum devices and because of the fundamental interest in mesoscopic systems. Various experimental tools have been adopted to elucidate their atomic and electronic structures. However, the probes employed in the usual methods, such as photons (x ray), electrons, and neutrons, etc., have no ''site selectivity.'' The probes equally interact with both the embedded particles and the host materials. Thus it is difficult to extract unambiguously the useful (weak) interaction signals of the embedded particles from a much stronger background of the host. Therefore a method in which the probe is able to ''seek'' exclusively the embedded nanoparticles and to convey definite information on them will be extraordinarily useful.

In this paper, we report such a powerful method which uses the positron as a probe. The positron is well-known as a self-seeking probe for vacancy-type defects in solids.[2–5] For the defect concentration typically more than $10^{18}/cm^3$, all positrons are trapped by the defects and are exclusively annihilated there with the surrounding electrons, conveying significant information on the local electronic environment around the defect site with the emitted two γ photons. However, such a perfect trapping has not been evidenced so far for precipitates in materials in spite of extensive studies.[4–8] In this work, we employ an interesting technique: the coincidence Doppler broadening (CDB) of positron annihilation radiation,[9–14] which measures the momentum distributions of the core electrons specific to each element and is shown to be able to identify the elements definitely around the annihilation sites, to study the nano-scale particles embedded in the host materials. With the ultrafine Cu precipitates formed by the thermal aging in a very dilute Fe-Cu alloy as an example, we demonstrate that there is the other kind of positron trapping state in the solids, namely a quantum-dot-like state, at which the wave function of every positron is ''entirely'' confined spatially in all three directions (i.e., a complete positron trapping) within the nano and subnano embedded particle as electrons in their quantum dots. Its origin is found to be the difference of positron affinity between the particle and the host material.[4–6] With use of this probe, the rather small precipitates (~ 1 nm), which are expected to appear in the early aging stage but have never been observed even by high-resolution transmission electron microscope (HRTEM), are explored. The ultrafine precipitates are revealed to be free from Fe atoms and defects, three dimensional, and to have no open volume defects at the interfaces which can trap the positrons, thus being probably coherent with the Fe matrix. The present study demonstrates that the quantum-dot-like

positron state, combined with the well-established positron annihilation techniques, can be employed as a self-seeking probe for the studies of the atomic and electronic structures of the mesocopic systems in the materials.

II. EXPERIMENT

The Fe-1.0 wt % Cu samples were prepared from high-purity Fe ($4N$) and Cu ($5N$) by arc melting and cold rolled to 0.3 mm in thickness. They were heated to 825 °C and kept for 4 h, followed by quenching into iced water. Some of the samples were thermally aged at 550 °C for 0.1∼312 h. In the as-quenched state, Cu atoms are in a supersaturated solid solution, and precipitate by thermal aging.

Previous transmission electron microscopy (TEM) studies have revealed complex growing processes of the Cu precipitates in Fe-1.3 wt % Cu thermally aged at 550 °C:[15–17] (i) Cu particles of about 4 nm with coherent bcc structure after 2 h aging, (ii) the roughly spherical particles with twinned 9R structures of (5–20) nm, transformed from the bcc structure by (6∼100) h aging, (iii) ellipsoidal particles with untwinned $3R$ structure (larger than 18 nm) and eventual stable fcc structure for further aging. Peak hardening has been observed at about 2 h aging which is due to ultrafine Cu precipitates. However, it is difficult to observe the growth of the ultrafine precipitates of $\leqslant 2$ nm, which are expected to appear in the early aging stage, even by HRTEM. The present sample has peak hardening at about 10 h aging; the delay in the aging time for the peak hardening is mainly due to the lower Cu content compared with the previous works. This fact indicates that, in the present experiments, the Cu precipitates after 2 h aging is much less than 4 nm.

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 the 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 $E_T = E_1 + E_2$ equals 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.[13] Selection of coincidence events that fulfill the condition $2m_0c^2 - 2.4$ keV$< E_t < 2m_0c^2 + 2.4$ 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 ∼1.1 keV [full width at half maximum (FWHM)], which corresponds to the momentum resolution of $\sim 4.3 \times 10^{-3} mc$ (FWHM).

III. RESULTS AND DISCUSSION

Figure 1 shows the CDB spectra for the Fe-1.0 wt % Cu as quenched and after 2 h aging at 550 °C together with those for pure (bulk) Fe and Cu. For the as-quenched sample, the CDB spectrum is identical to that for the pure bulk Fe. This means that the positrons are not trapped by the isolated Cu

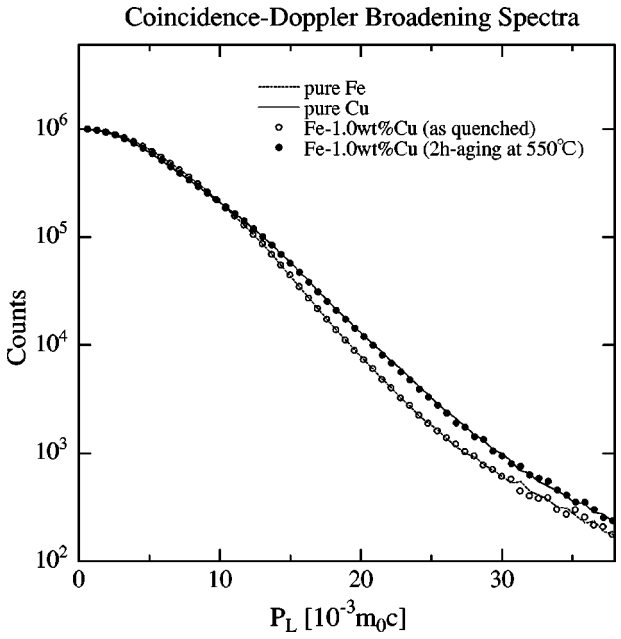

FIG. 1. CDB spectra for Fe-1.0 wt % Cu as quenched and after 2 h aging at 550°, compared with those for pure (bulk) Fe and Cu. Each spectrum is normalized to the same total count.

atoms in the supersaturated solid solution but annihilate only with the electrons of Fe atoms as expected for the low Cu content of 1.0 wt %. On the other hand, the spectrum for the 2 h aging is identical to that for the pure bulk Cu, and quite different from that for the pure Fe. This shows clearly that all the positrons annihilate with the electrons of Cu, but not with those of Fe. The concentration of the Cu precipitates is estimated to be the order of $10^{18}/\text{cm}^3$ by assuming that about 10% of Cu atoms have precipitated from the Fe matrix solid solution.

If positrons are trapped at possible open-volume defects such as vacancies or interfaces at the precipitates, they will have a longer positron lifetime than that for the pure bulk Cu and an enhanced momentum density at the low momentum region (for example, less than $4\times10^{-3}mc, 1\times10^{-3}mc = 0.137$ atomic unit) due to the annihilations with the electrons within these defects,[2–5] which would be detected by conventional positron annihilation techniques. However, we have neither such a longer positron lifetime [Fig. 2(a)] nor enhanced momentum density at low momentum region [Fig. 2(b)]. Furthermore, we have made first-principles two-component density-functional calculations for the momentum distributions and positron lifetimes[18–20] in the bulk fcc and bcc Cu. It is noteworthy that the calculated lattice parameter of bcc Cu (0.2961 nm) using a many-body interaction potential method[21] is very close to that of bcc Fe (0.2867 nm). Our calculation reveals that the momentum distribution for polycrystalline bcc Cu is very close to that for fcc Cu. The calculated lifetime of bcc Cu (109 ps) agrees very well with that for fcc Cu (107 ps) and the observed one (108 ps) for 2 h aging [Fig. 2(a)]. These results demonstrate that all the positrons in Fe-1.0 wt % Cu after 2 h aging are entirely confined into the Cu precipitates which are consisting of Cu only, free from vacancies, and no open volume defects which can trap the positrons at the interfaces between the matrix and precipitates, and thus suggesting coherent bcc Cu pre-

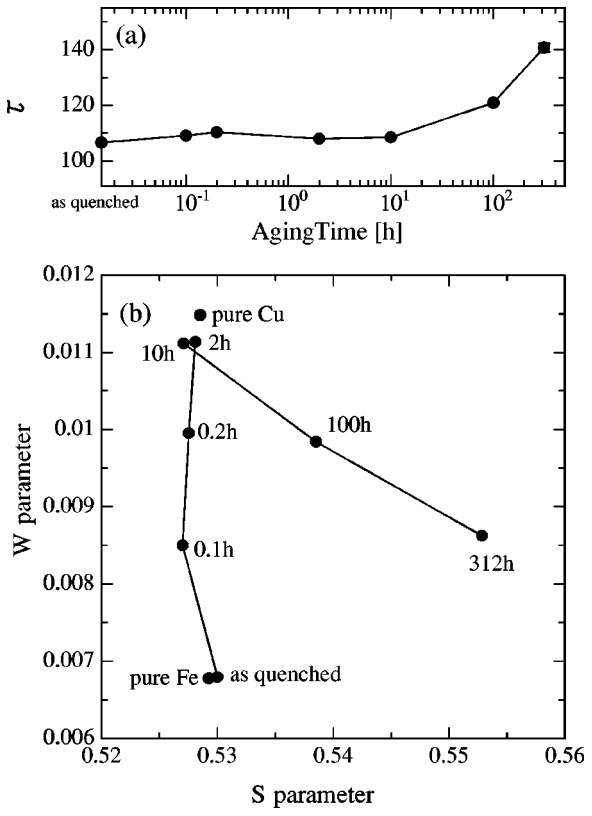

FIG. 2. Aging time dependence of (a) positron lifetime and (b) *S*- and *W*-parameter correlation (*S*-*W* plot). The *S* and the *W* parameters are defined as the ratio of low momentum ($|p_L|<4\times10^{-3}mc$) and high momentum ($18\times10^{-3}mc<|p_L|<30\times10^{-3}mc$) regions in the Doppler-broadening spectrum to the total region, respectively. The $S(W)$ parameter is a measure of the momentum density at low (high) momentum. The lifetime of bulk Fe is 107 ps (experimental), and that of bcc Cu is 109 ps (calculated).

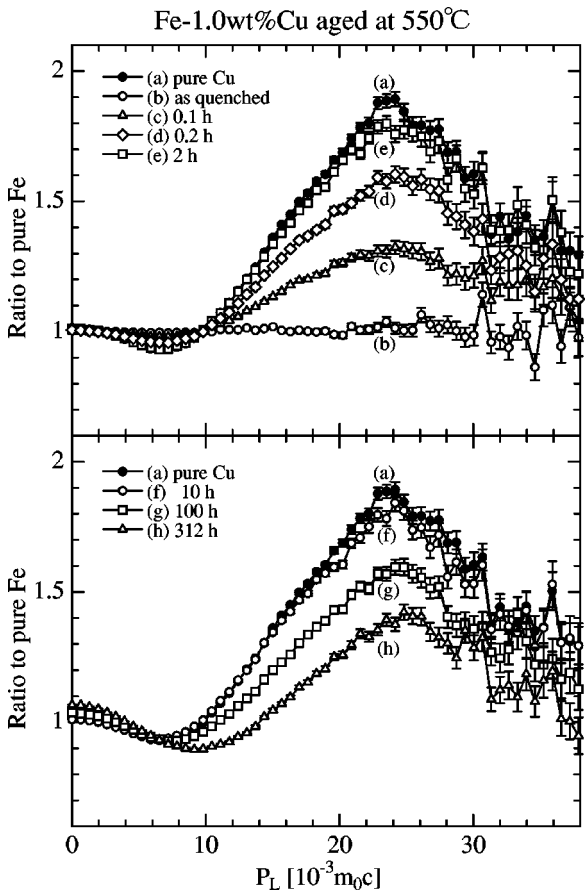

FIG. 3. Ratio curves of the CDB spectra of (a) pure Cu, the Fe-1.0 wt % Cu alloys (b) as quenched, after (c) 0.1 h, (d) 0.2 h, (e) 2 h, (f) 10 h, (g) 100 h, and (h) 312 h aging with respect to that of pure Fe. The shape of the ratio curve is characteristic of each chemical element.

cipitates. The coherent precipitates are consistent with previous studies by electron microscope.[15,16,22]

To see the aging evolution of the CDB spectra in Fe-1.0 wt % Cu, we have obtained ratio curves of the spectra which are given by the ratio of the spectra to that for a reference sample.[13] Figure 3 shows the ratios for pure Cu [curve (a)] and the samples with the different heat treatment [curves (b)–(h)] to that of the pure Fe. The ratio curve of pure Cu shows a broad peak around $24\times10^{-3}mc$ and a small valley at $6\times10^{-3}mc$, which are characteristic features of Cu in the ratio curve. For the as-quenched sample [curve (b) in Fig. 3], the ratio curve is constant at the value of 1. This means that the positrons annihilate only with the Fe electrons as shown in Fig. 1. For 0.1 h, 0.2 h, and 2 h aging (Fig. 3), every curve is similar to that for pure Cu [curve (a)] except for the amplitude, having the common characteristic peak and valley. As increasing the aging time, the amplitude also increases, and the curve for 2 h aging [Fig. 3(e)] is almost the same as curve (a) as expected from Fig. 1. Positron lifetime and *S* parameter of Doppler broadening spectrum show almost no change within 2 h aging time [Figs. 2(a) and 2(b)]. On the other hand, the *W* parameter, only obtainable from the CDB spectrum, changes sensitively in the initial stage of the thermal aging as is shown in Fig. 2(b).

This quantum-dot-like state of positron in the ultrafine particle can be explained in terms of the difference of positron affinity between the precipitates and the matrix.[4,23,24] The positron affinity of Cu (-4.81 eV) is ~1 eV lower than that of Fe (-3.84 eV),[4,23] thus the precipitated particle can be regarded as a potential well with a depth of 1 eV for the positron. If the spherical symmetry of the particle is assumed, there exists a bound positron state for particles larger than ~0.6 nm in diameter. For the particles smaller than 0.6 nm, the positron cannot be confined because the energy of the zero-point motion exceeds the depth of this affinity well. We can thus estimate that, the size of the Cu ultrafine particles after the first ~10 min aging, when the positron confinement rapidly increases [Figs. 3(c) and 3(d)], is about 0.6 nm. In addition, the Cu particles of less than 1 nm are three dimensional; if platelike (two dimensional), the positrons cannot be confined in a few atomic layers because of the large zero-point-motion energy in the perpendicular direction.

For longer aging time of 10, 100, and 312 h (Fig. 3), however, the broad peak around $24\times10^{-3}mc$ in the ratio curve, which originates from the annihilations with core electrons of Cu, decreases. A possible interpretation of this change would be that the density of the Cu precipitates decreases due to aggregation of the small precipitates and a part of positrons annihilates in the matrix. However, this picture is incorrect, and every positron is still confined in the Cu precipitates even after 312 h aging when the precipitate den-

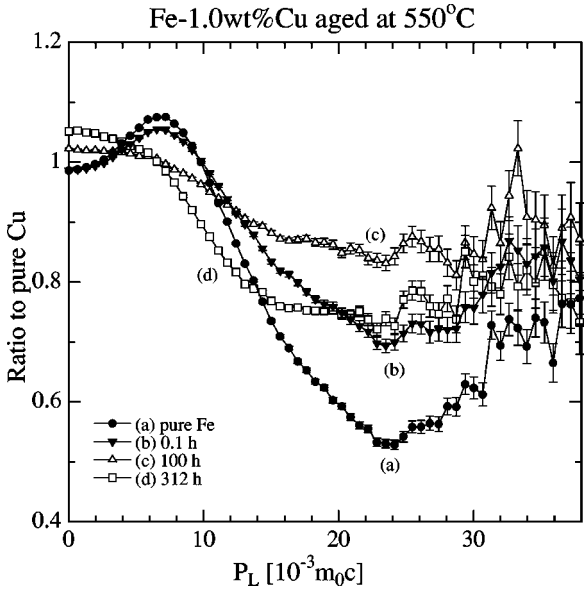

FIG. 4. Ratio curves of the CDB spectra of (a) pure Fe, the Fe-1.0 wt % Cu alloys after (b) 0.1 h, (c) 100 h, and (d) 312 h aging with respect to that of pure Cu.

sity decreases to $10^{16}\sim10^{17}/\mathrm{cm}^3$.

Figure 4 shows the ratio of the CDB spectra of (a) pure Fe, and the Fe-1.0 wt % Cu alloys after (b) 0.1 h, (c) 100 h, and (d) 312 h aging to that of pure Cu. While the ratio curve for 0.1 h aging is similar to that for pure Fe except for its small amplitude, the curves for 100 h and 312 h aging are quite different, namely, both the curves (a) and (b) have valleys at $24\times10^{-3}mc$, but (c) and (d) are almost flat in the high momentum ($>15\times10^{-3}mc$) region. This shows that the positrons do not yet annihilate with electrons in Fe after aging longer than 100 h. In addition, the enhancement in the low-momentum region in the curves (g) and (h) in Fig. 3 shows the positron trapping at some kind of vacancy-type defect. The existence of such defect is also supported by the changes in the positron lifetime [see Fig. 2(a)]. Thus the decrease of the broad peak around $24\times10^{-3}mc$ is due to the reduction of the annihilations with the core electrons by the trapping at the defect surrounded by Cu atoms, not due to the annihilations with Fe electrons. Therefore the defect is neither at the interface nor in the Fe matrix but in the Cu precipitates. The *S*-*W* plots for the longer aging time lie on a straight line as shown in Fig. 2(b), which suggests that the defects in them are the same kind. As the precipitates grow larger, they undergo transformations such as bcc to 9*R* structure to release the coherency strain energy, which will induce defects within the precipitates.

So far the structure of the subnanosize precipitates after ~10 min aging is still open. Curves (c) and (d) in Fig. 3 show that the positrons annihilate with both Cu and Fe electrons. This suggests that the Cu precipitates which are large enough to trap positrons are few. However, other interpretations, that the precipitates consist of both Fe and Cu atoms and that the positron wave functions spill out from the ultrafine precipitates, are also possible. Measurements of the temperature dependence of the positron annihilation may answer this question.

The Fe-Cu alloy presented in this work is a model alloy of nuclear reactor pressure vessel (RPV) steels. It is well known that the Cu precipitates play a significant role in the embrittlement by the neutron irradiation.[15–17] However, the detailed mechanism is poorly understood. The quantum-dot-like positron state is found to be able to reveal the structures of the ultrafine Cu precipitates in various Fe-Cu model alloys, especially their evolution under reactor neutron irradiation. The detailed results will be reported elsewhere.

The affinity-induced positron confinement occurs whenever the positron affinity for the particles is lower than that for the host material. The present success therefore suggests that the positron is a unique probe for nanoscale particles in materials, such as quantum dots in semiconductors[1] and precipitates in metallic alloys. The combination of positron confinement and well-established positron annihilation techniques together with first-principles calculations[18–20] promises to reveal the atomic and electronic structures of the ultrafine particles. For example, it is expected that by employing the angular correlation of positron annihilation radiation (ACAR) technique the Fermi surface of ''bcc'' Cu and the electronic structure of the ''electron'' quantum dots can be explored.

IV. CONCLUSION

The affinity-induced quantum-dot-like positron state is demonstrated by using the CDB technique. It is found that the wave function of all positrons can be entirely confined within the ultrafine particles embedded in a host material. Based on this positron state, many structural characteristics of the nanosize Cu particles in a dilute Fe-Cu are revealed successfully. Since the positron affinities for various elements or materials differ significantly from each other, this affinity-induced confinement state will appear widely in various ultrafine impurity particles in solids, such as quantum dots in semiconductors and precipitates in metallic alloys. The present study therefore suggests a ''high-sensitivity'' and ''self-seeking'' method to study the mesoscopic systems in solids.

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