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Positron-lifetime study of electrically hydrogen charged Ni, austenitic stainless steel and Fe

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Abstract

Positron-lifetime study has been made for the electrically hydrogen charged Ni, austenitic stainless steel (316 stainless steel), and Fe in order to investigate the structural changes due to the presence of high concentration of hydrogen atoms in the bulk, such as hydrogen-induced defects, hydrogen-induced phase transformation and so on. Increase of mean lifetime was observed for Ni and 316 stainless steel, but almost no change was observed for Fe. The introduction of a long lifetime of about 150 ps to the Ni specimen was interpreted as the generation of vacancies by the hydrogen charging. But in the case of Fe, no vacancy generation was observed probably due to the low concentration of hydrogen atoms, even by the electrical hydrogen charging. In 316 stainless steel, both the phase transformation and the generation of vacancies were observed by the presence of high concentration of hydrogen atoms in the bulk. Elastic recoil detection (ERD) method showed that the hydrogen concentration reaches about 40% (H/atom = 0.4) near the surface region of 316 stainless steel, electrically hydrogen charged.

1. Introduction

It has recently been recognized that the presence of hydrogen atoms of high concentration in metals might introduce crystal defects like vacancies, due to the lowering of the formation energy of vacancies by trapping hydrogen atoms [1,2]. This is a very important phenomenon both in the fundamental field of lattice defects, and in the practical field like plasma-facing materials, which are subject to hydrogen-recycling phenomenon. In order to investigate the possibility of the vacancy formation due to the presence of hydrogen atoms of high concentration, positron annihilation technique will be very useful because this method is very sensitive to vacancy-type defects in the crystals confirmed by a large number of studies performed in last two decades. Furthermore, the calculation of positron lifetime in various defect sites has recently become possible and then the comparison between the experimental result and the lifetime calculation will be made to clarify the hydrogen-induced defects. In the case of austenitic stainless steel like 316 stainless steel, it is well known that hydrogen-induced phase transformation also occurs and the situation will be more complex [3–6].

2. Experimental

High-purity Ni and Fe specimens were prepared by zone-melting refining process in high-purity hydrogen gas in a high-frequency induction heating apparatus. As starting materials, Johnson & Matthey high-purity Ni, and Showa Denko high-purity Fe were used. The obtained rods were rolled into plates and cut into square specimens of a size 8 mm × 8 mm × 0.2 mm. After that, they were annealed in high-purity hydrogen gas at 800°C following the lower temperature (about 300°C) annealing for degassing of hydrogen. As austenitic stainless steel, 316 stainless steel with the chemical composition

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Table 1
Chemical analysis of alloying elements in 316 stainless steel (wt%)

	C	Cr	Ni	Mo	Mn	S	P
SUS316	0.07	17.25	12.07	2.09	1.23	0.008	0.028

shown in Table 1 was used after solution annealing for 1 h at 1050°C.

The electrical hydrogen charging was made in the bath of 1 N H_2SO_4 under the conditions of various current densities and charging times.

Positron annihilation lifetime measurement was performed by using the conventional fast–slow coincidence circuit with BaF_2 scintillators and H3378 Hamamatsu phototubes, the time resolution of which is about 210 ps. The lifetime spectra obtained were analyzed by the Resolution program and the Positronfit program. Elastic recoil detection (ERD) measurement to obtain the depth distribution of hydrogen atoms in the surface region of a specimen was also made by using a 3-MeV He ion beam generated by the tandem accelerator [7].

3. Results and discussion

3.1. Ni

In Fig. 1, the result of positron-lifetime measurement for a Ni specimen electrically hydrogen charged under the current density 10 mA/cm^2 for 24 h is shown as a function of aging time at room temperature. It is seen that, by hydrogen charging, the second lifetime component (long lifetime component) was introduced and with increasing aging time, this lifetime increased. After 150 days at room temperature, this second lifetime reached about 350 ps, which corresponds to microvoids consisting of about 15 vacancies [11]. Then, lifetime 150 ps observed just after hydrogen charging is considered to be a positron lifetime trapped in a vacancy. But this value is shorter than that obtained in Ni irradiated with electrons at low temperature, which is about 175 ps [8,9]. Then, the lifetime obtained in the present study is considered to correspond to a vacancy with hydrogen atoms inside, which might give a shorter positron lifetime than that of an empty vacancy. The increase of the second lifetime during aging can be considered to be due to two processes, i.e. (i) thermal release of hydrogen atoms from vacancies, and (ii) migration of vacancies and formation of vacancy clusters. In high-purity Ni, vacancies become mobile around room temperature and then during long-term aging at room temperature, it is possible for vacancy clusters to be formed. Just after finishing long-term aging, the isochronal annealing above room temperature was made in order to investigate the thermal stability of microvoids in Ni and the result is shown in Fig. 2. It is seen that the lifetime gradually decreases with increasing annealing temperature, which can be considered to be due to the collapse of microvoids to stacking fault tetrahedra (SFTs). Corresponding to this decrease, the second intensity increases because SFTs have higher trapping cross-section for a positron than microvoids consisting of vacancies of the same number. SFTs become unstable and almost disappear until 400°C as seen in the figure.

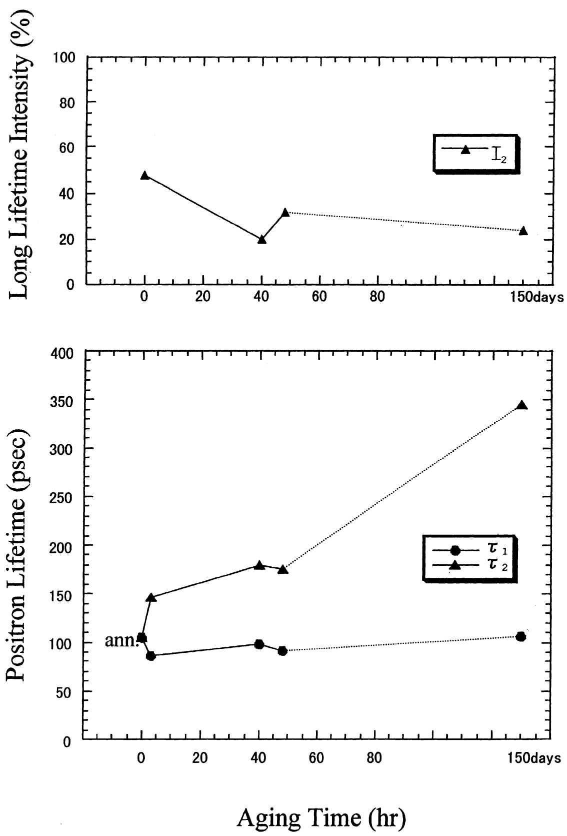

Fig. 1. Result of positron-lifetime measurement for Ni specimen electrically hydrogen charged under the current density 10 mA/cm^2 for 24 h as a function of aging time at room temperature.

To confirm the decrease of positron lifetime for a vacancy with hydrogen atoms inside, positron-lifetime calculation was made for a vacancy with hydrogen atoms inside. Hydrogen atoms were placed at the octahedral site (O-site), but at a site shifted inward by a

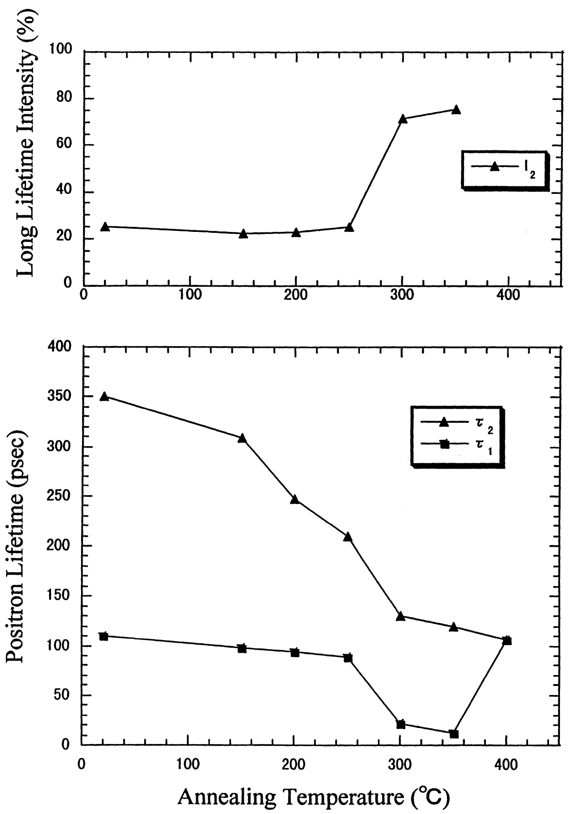

Fig. 2. Result of the isochronal annealing above room temperature for Ni specimen electrically hydrogen charged under the current density 10 mA/cm^2 for 24 h just after finishing long-term aging at room temperature.

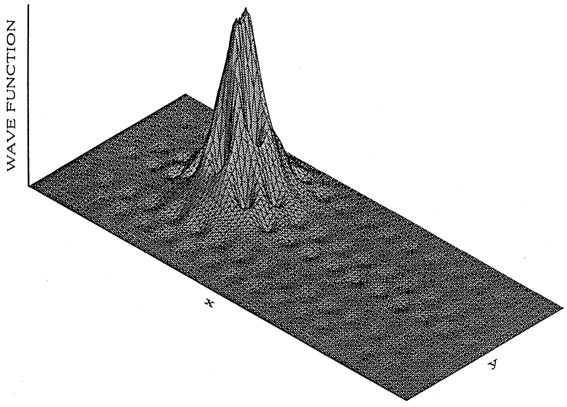

Fig. 3. Wavefunction of a positron trapped in a vacancy with one hydrogen atom inside in Ni (view on {1 1 2} plane in which a vacancy is located).

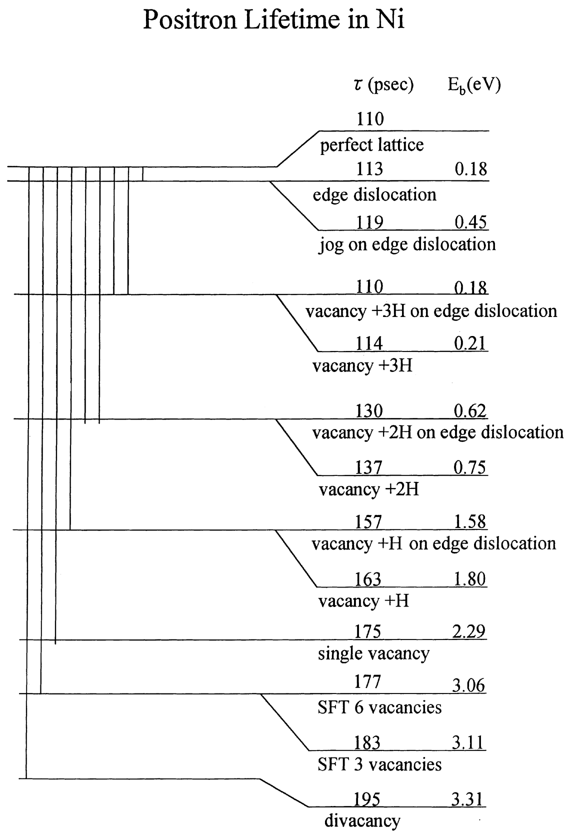

Fig. 4. Calculated values of positron lifetime and binding energy for various defects in Ni, edge dislocation, vacancy, vacancy with hydrogen atoms, vacancy with hydrogen atoms on an edge dislocation, and SFT.

certain distance depending on the number of hydrogen atoms in a vacancy. Assumption was made as follows, taking into account the research on deuterium atoms in a vacancy in Ni given by Myers et al. [10]. When one or two hydrogen atoms were placed in a vacancy, the amount of distance shifted was selected 20% of the distance between the O-site and the center of a vacancy. Three or four hydrogen atoms were placed at sites 10% shifted inward and five or six hydrogen atoms were placed exactly at the O-sites. Positron lifetime was calculated on the basis of the atomic superposition method with the local density approximation (LDA) for the correlation potential [11–14]. One example of a wavefunction of a positron trapped in a vacancy with one hydrogen atom inside is shown in Fig. 3. Introduction of hydrogen atoms into a vacancy in Ni decreases positron lifetime as shown in Fig. 4, where values of positron lifetime at various defect sites in Ni and values of binding energies are shown. With increase in the number of hydrogen atoms in a vacancy, positron lifetime decreases as 175, 163, 137 and 114 ps, for a vacancy with no hydrogen, one hydrogen atom, two hydrogen atoms, and three hydrogen atoms, respectively. Positron lifetimes in a vacancy with hydrogen atoms on an edge dislocation are also shown. The positron lifetime 150 ps obtained just after hydrogen charging is then considered to be corresponding to a vacancy with one or two hydrogen atoms inside.

3.2. Fe

The same experiment was performed for high-purity Fe, but almost no change in positron lifetime was observed before and after hydrogen charging (10 mA/cm^2, 24 h) namely, 106 ps before charging and 107 ps after charging. The reason for this is considered to be due to higher heat of solution for Fe, 0.25 eV, than that for Ni, 0.17 eV, resulting in the low hydrogen concentration in the Fe matrix during hydrogen charging and then almost no formation of vacancies.

3.3. 316 Stainless steel

It is well known that the electrical hydrogen charging causes phase transformation in austenitic stainless steel, e.g. from γ-phase to ε-phase or α-phase, especially by X-ray diffraction method. But hydrogen-induced vacancy formation has not been investigated yet. The positron-lifetime measurement was made before and after the electrical hydrogen charging for 316 stainless steel. In Fig. 5, the mean positron lifetime obtained for 316 stainless steel specimens electrically hydrogen charged under 100 mA/cm^2 for 24 h is plotted as a function of aging time at room temperature. The increase of the mean lifetime is seen from 106 ps to 118 ps.

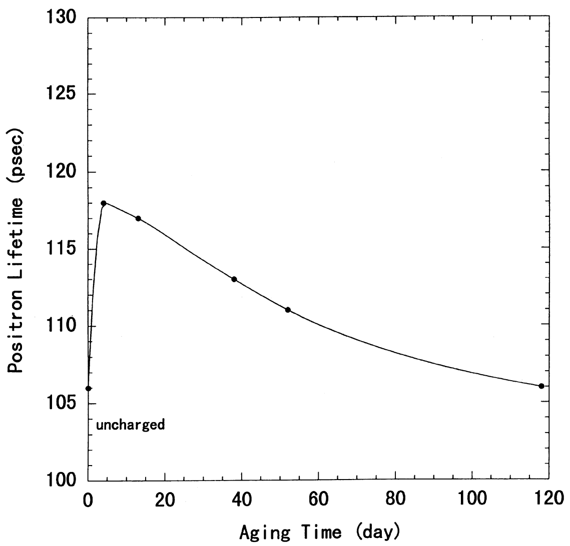

Fig. 5. Mean positron lifetime obtained for 316 stainless steel specimens electrically hydrogen charged under 100 mA/cm^2 for 24 h.

Two-component analysis of the positron annihilation spectrum was made and the second (long) lifetime component of about 300 ps was obtained as shown in Fig. 6. This long lifetime component is considered to be corresponding to microvoids of about 15 vacancies [11]. This result suggests that during hydrogen charging, single vacancies are produced and form clusters like microvoids. This is not so easy to be understood because vacancies in 316 stainless steel are much less mobile than those in pure Ni at room temperature. Hence vacancies in 316 stainless steel must be considered to be formed locally with high density, e.g. in the vicinity of the phase-transformed region. Then in this case, two processes are going in parallel, that is, hydrogen-induced phase transformation and hydrogen-induced vacancy formation are taking place together. ERD method was used to detect the depth distribution of hydrogen atoms in the surface region of 316 stainless steel specimens electrically hydrogen charged. A 3-MeV He ion beam was produced by the tandem accelerator and by this beam, hydrogen atoms in the surface region (until 350 nm) were forward scattered and detected by the silicon surface barrier detector (SSBD). The result showed that the hydrogen concentration reaches about 40% (H/atom = 0.4) near the surface region. It is then recognized that this high value of hydrogen density enables the phase transformation and generation of vacancies in the bulk.

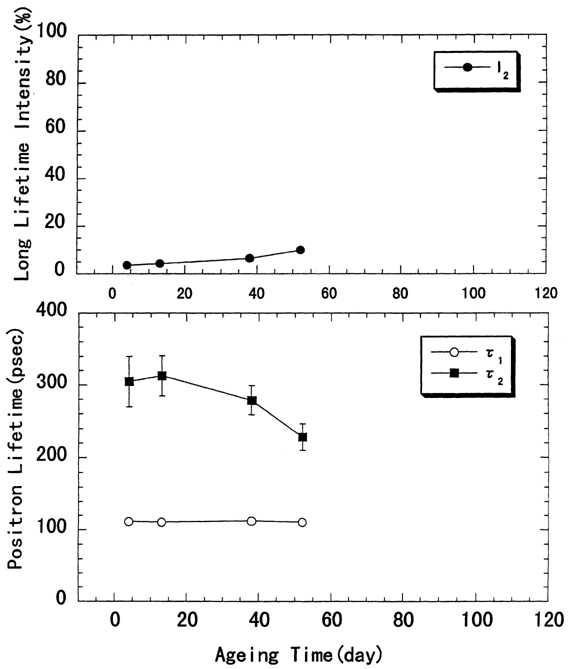

Fig. 6. Two-component analysis of the positron annihilation spectrum for 316 stainless steel specimens electrically hydrogen charged under 100 mA/cm^2 for 24 h.

4. Conclusion

By the electrical hydrogen charging, the increase of mean lifetime was observed for Ni and 316 stainless steel, but almost no change was observed for Fe. The appearance of a long lifetime of about 150 ps in Ni specimen was interpreted as the generation of vacancies by the hydrogen charging. But in the case of Fe, no vacancy generation was observed, probably due to low concentration of hydrogen atoms even by the electrical hydrogen charging. In 316 stainless steel, both the phase transformation and the generation of vacancies were observed by the presence of high concentration of hydrogen atoms in the bulk. ERD method showed that the hydrogen concentration reaches about 40% (H/atom = 0.4) near the surface region of 316 stainless steel electrically hydrogen charged.

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