Detection of Hydrogen in Vacancies and Voids in Nickel by Positron Annihilation Lifetime Measurement

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A positron lifetime study was performed on nickel to investigate the detection of hydrogen in nanovoids. The introduction of hydrogen into well-annealed nickel by electrochemical hydrogen charging increased the positron lifetime by inducing the formation of vacancy-type defects. Hydrogen was released from 323 K to 423 K and the defects introduced disappeared at 573 K. The Vickers hardness recovered at 323 K with the escape of interstitial hydrogen atoms. The size and number of hydrogen atoms in voids were estimated through calculations. The positron lifetimes in quenched and neutron-irradiated Ni were shortened after electrochemical hydrogen charging due to the trapping of hydrogen in vacancy clusters. The hydrogen in nanovoids escaped during annealing at 373 K.
Keywords: positron annihilation spectroscopy, hydrogen, vacancies, voids, nickel

1. INTRODUCTION

Energy generation is key for the accomplishment of a sustainable society. Nuclear energy is an important energy system now and is expected to remain so in the future. Development of nuclear materials is important for a safe, economical and effective nuclear energy system. Nuclear materials are used under radiation. Voids are major defects formed in nuclear materials by neutron irradiation and induce embrittlement in materials. Gas atoms produced by nuclear reaction promote the nucleation and growth of voids. Helium and hydrogen are formed in nuclear materials by (n,α) and (n,p) reactions, respectively.

A nondestructive method for detecting the size of nanovoids and the number of gas atoms in voids is required for the prediction of materials degradation in nuclear power plants. As positron annihilation spectroscopy is greatly affected by gas atoms [1], it can be used for the detection of gas atoms. In this paper, in order to establish a new method to detect the size of nanovoids and the number of gas atoms in nanovoids, positron annihilation spectroscopy was used.

Hydrogen was introduced into nickel by electrochemical charging. It is well known that the presence of a high concentration of hydrogen atoms in metals induces the formation of vacancies and clusters thereof [2-5]. Thus, hydrogen charging induces vacancy clusters as well as hydrogen atoms. The effect of hydrogen atoms in vacancy clusters was also studied.

2. EXPERIMENTAL

The purity and size of the nickel plate used were 99.99% and 10×10×0.2 mm, respectively. The plates were annealed at 1173 K for 1 h. Vacancies were introduced into nickel by quenching in ice water from 1523 K. The plates were annealed at 573 K for 0.5 h to form stable vacancy clusters. Neutron-irradiated nickel was formed by the SSS facility [6] at the Kyoto University Reactor at 573 K to a dose of 1.3×10^{-3} dpa. Electrochemical hydrogen charging was performed in a 4-N H_2SO_4 solution using a current density of about 20 mA/cm^2 over a period of 10 h. To examine the retention behavior of hydrogen, the hydrogen-charged specimens were isochronally annealed for 1 h in the temperature range from 323 K to 573 K using a mass spectrometer (ANELVA AQA-100R).

Positron lifetimes were measured at room temperature. The positron lifetime spectrometer had a time resolution of 190 ps (full width at half maximum), and each spectrum was accumulated to a total of over 1.0×10^6 counts. To discriminate between bulk and defect components, after subtracting the source and background components, the lifetime spectrum was broken down into two components.

3. RESULTS

Fig. 1 shows the lifetime and intensity of the long lifetime in nickel after hydrogen charging and following annealing for 1 h from 323 K to 573 K. The mean lifetime of annealed nickel (106 ps) increased to 118 ps and was divided into two components. The long lifetime and its intensity increased during the annealing at 323 K. The intensity started to decrease from 373 K, while the long lifetime increased up to 423 K and then decreased. By annealing at 573 K, almost
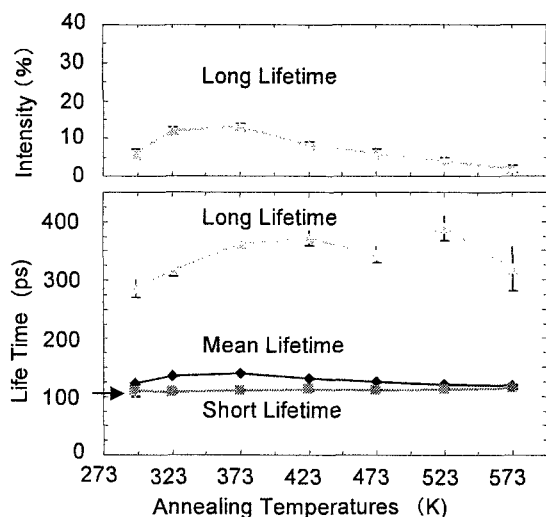
Fig. 1   Positron annihilation lifetimes and the long lifetime intensity of hydrogen-charged annealed nickel after isochronal annealing for 1 h. The arrow indicates the mean lifetime before hydrogen charging.

all the defects introduced were recovered. The thermal desorption spectrum of hydrogen was obtained between 323 K and 573 K, as shown in Fig. 2.   Fig. 3 (a) indicates that the maximum desorption occurred at 373 K.   The change in the Vickers hardness of the specimen as a result of hydrogen charging and subsequent annealing are shown in Fig. 3 (b).   After annealing at 323 K, although the amount of hydrogen release was small, the hardness recovered remarkably.
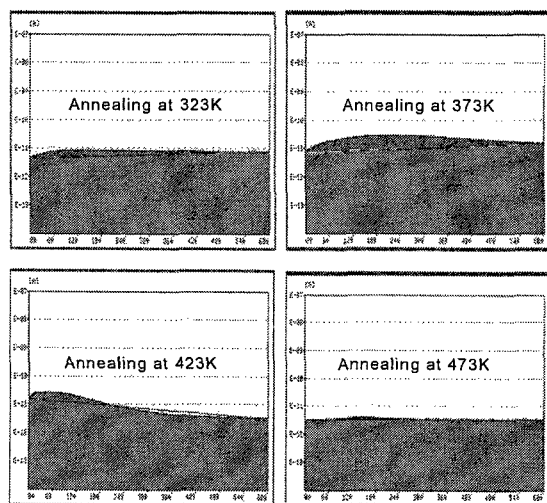

Fig. 2   Thermal desorption spectrum (TDS) from 323 K to 473 K of hydrogen-charged annealed nickel after isochronal annealing for 1 h.

After quenching and annealing at 573 K for 30 min, a long lifetime of 351 ps, which indicates nanovoids of 12 vacancies, was detected. The
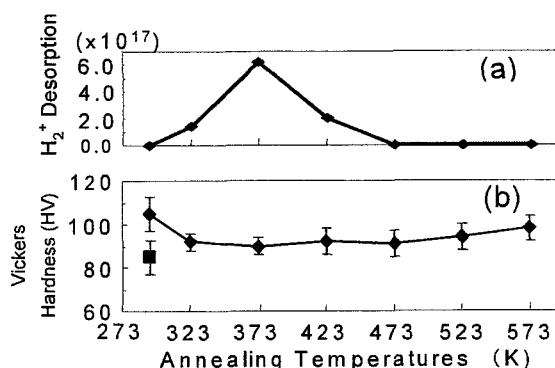

Fig. 3   (a) thermal desorption spectrum (TDS) and (b) Vickers hardness changes of hydrogen-charged annealed nickel after isochronal annealing for 1 h.   The solid square represents the Vickers hardness before hydrogen charging.
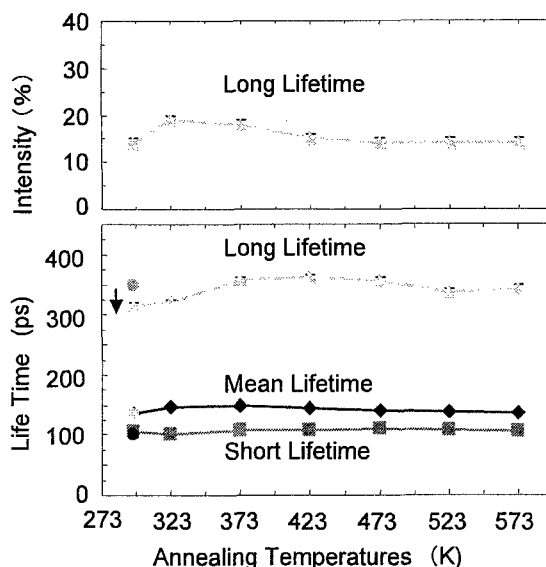

Fig. 4   Positron annihilation lifetimes and long lifetime intensity of hydrogen-charged quenched nickel after isochronal annealing for 1 h. The solid circles represent the lifetimes and the intensity before hydrogen charging. The arrow indicates the decrease in long lifetime.

number of vacancies in nanovoids was estimated using the calculation by Shivachev *et al.* [1]. As shown in Fig. 4, after hydrogen charging, the lifetime decreased to 313 ps as a result of hydrogen absorption.   Although the lifetime was constant, the intensity of long lifetime increased during the annealing at 323 K.   After subsequent annealing, the lifetime increased and then decreased to the value before hydrogen charging. The hydrogen desorption spectrum and Vickers hardness variation are shown in Fig. 5.   As in the case   of hydrogen-charged nickel, the hardness recovered at 323 K.   The positron lifetimes and the intensity of long lifetime of neutron-irradiated nickel are shown in Fig. 6.   The

long lifetime of 394 ps indicates the presence of nanovoids with 18 vacancies [1]. The annealing behavior of lifetimes and the intensity were almost the same as those in quenched nickel. After annealing at 573 K, the long lifetime and the intensity recovered to the values before hydrogen charging.
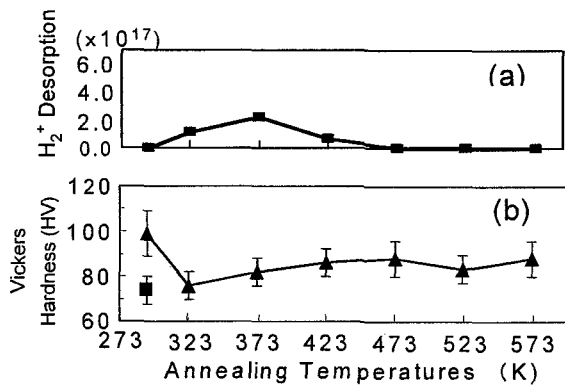

Fig. 5   (a) thermal desorption spectrum (TDS) and (b) Vickers hardness changes of hydrogen-charged quenched nickel after isochronal annealing for 1 h.   The solid square represents the Vickers hardness before hydrogen charging.
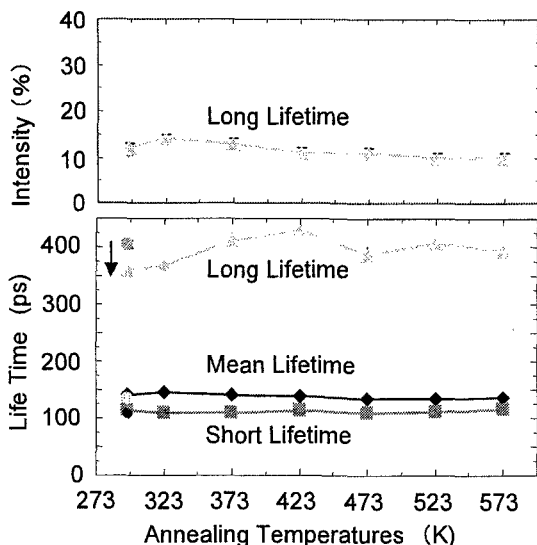

Fig. 6   Positron annihilation lifetimes and long lifetime intensity of hydrogen-charged neutron-irradiated nickel after isochronal annealing for 1 h.   Solid circles represent the lifetimes and the intensity before hydrogen charging.   The arrow indicates the decrease in long lifetime.

4. DISCUSSION

According to Fukai et al. [7], vacancies are formed when hydrogen atoms accumulate in the interstitial sites of a nickel atom.   The formation energy of vacancies drops from 1.8 eV for the non-hydrogen case to 0.3 eV with the accumulation of six hydrogen atoms.   The increase in mean lifetime and the long lifetime observed after

hydrogen charging were due to the vacancies induced by hydrogen.   The Vickers hardness recovered as a result of the escape of hydrogen at 323 K.   As the most unstable hydrogen sites are found in interstitial sites, the hydrogen atoms that escaped at 323 K must be from interstitial sites.

The long lifetime and its intensity increased simultaneously at 323 K, as shown in Fig. 1. The increase was caused by the agglomeration of vacancies into nanovoids.   An intensity increase usually indicates an increase in defect concentration or positron trapping rate.   In this case, however, the increase in nanovoids due to clustering of vacancies does not contribute to the intensity increase because of the decrease in vacancy concentration.   The same intensity increase was observed in quenched nickel and neutron-irradiated nickel at the same temperature. In both cases, the lifetime did not change and only the intensity increased.   These results lead us to conclude that the positron trapping rate in the matrix changed during annealing at 323 K. Electrons near interstitial hydrogen may increase the trapping rate of positrons in the matrix. Upon the escape of interstitial hydrogen, the trapping rate in the matrix decreased and the trapping rate at nanovoids increased.

The long lifetime increased during the annealing at 373 K with a small change in intensity, as shown in Fig. 1.   This was caused by the escape of hydrogen from nanovoids.   In hydrogen-charged annealed nickel, the change in long lifetime from 306 ps (nanovoids + hydrogen) to 356 ps (nanovoids of 12 vacancies) was caused by the desorption of hydrogen from nanovoids. The calculation results [1] indicate that the number of hydrogen atoms was 5 in each nanovoid. The trapping rate is the product of the defect concentration and the capture probability.   The capture probability, μ, was calculated using the diffusion model, via $\mu = 4\pi RD / \Omega$ [8].   For the diffusion coefficient of positrons, D, 2×10^{-5} m^2/s was used, which was derived by fitting the observed number density and size of voids formed by neutron irradiation in nickel at 563 K [9].   R and Ω are the radius and atomic volume of nanovoids, respectively.   The concentration of nanovoids at 373 K was found to be 1.1×10^{-7}, and the number of hydrogen atoms at 323 K was 5.   The total concentration of hydrogen molecules released at 373 K was 3.4×10^{-4} according to TDS measurement.   The hydrogen trapped in nanovoids was only 0.07 % of the total release.   Thus, it is concluded that there are three main trapping sites for hydrogen in charged nickel.   First, there are the interstitial sites in the matrix (hydrogen escapes to surfaces or grain boundaries at 323 K).   Second, there are the highly concentrated areas near grain boundaries (hydrogen escapes at 373 K).   After hydrogen charging, vacancies and clusters thereof are formed in these areas and are annihilated below 573 K because of the easy escape to grain boundaries and surfaces.   Third, there is the

hydride at grain boundaries.   Rommal *et al.* reported the presence of hydride along grain boundaries.   Presumably, the hydride is stable and decomposes during annealing at 423 K [10].

5. CONCLUSION

In this paper it was demonstrated that positron annihilation lifetime measurements are sensitive to the presence of hydrogen and are capable of detecting it.   However, the lifetime depends on the nanovoid size and the number of hydrogen atoms in them.   It takes another set of experiments to find out the size and number of hydrogen atoms separately.   Xu *et al.* reported the results of coincidence Doppler broadening measurements for detecting gas atoms [11].   In a helium-irradiated nickel, they detected a peak that indicated the annihilation of positrons with electrons localized near helium in coincidence Doppler broadening measurements.   Although they have not succeeded in obtaining the number of helium atoms in nanovoids, their method is highly promising.   Further studies are required.

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