Coincidence Doppler Broadening of Positron Annihilation Radiation for Detection of Helium in Irradiated Ni and Cu

Q. Xu¹, T. Ishizaki², K. Sato¹, T. Yoshiie¹ and S. Nagata³

¹Research Reactor Institute, Kyoto University, Sennan-gun, Osaka 590-0494, Japan

²Toyota Central R&D Labs., Aichi-gun, Aichi 480-1192, Japan

³Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

A new composition analysis method, namely, coincidence Doppler broadening (CDB) of positron annihilation radiation, was employed to detect He atoms in ion irradiated Ni and neutron irradiated Cu. The results of positron lifetime and transmission electron microscopy (TEM) show that microvoids and voids were formed in ion-irradiated Ni and neutron-irradiated Cu, respectively. The results of CDB measurements indicate that He atoms were present in the microvoids and voids, even in microvoids annealed at 1273 K in ion-irradiated Ni. Coincidence Doppler broadening measurement, which is a nondestructive technique for testing materials, is effective for detecting He atoms.
[doi:10.2320/matertrans.47.2885]

(Received July 18, 2006; Accepted September 15, 2006; Published November 15, 2006)

Keywords: helium, microvoids, voids, positron annihilation

1. Introduction

Interest in the behavior of He in solids has increased with advances in nuclear power technology, in particular, fusion reactor technology. He atoms can be generated in materials by the nuclear reaction of (n, α) . The production of He atoms induced by nuclear reactions increases with increasing neutron energy since the cross section of the (n, α) reaction generally increases with neutron energy. In addition, He atoms are introduced directly in plasma-facing materials by the He plasma in fusion reactors. These He atoms produce damage not only on the surface of materials, such as erosion, sputtering and blistering, but also in the bulk because He easily diffuses deep into the specimens.^{1,2)} He atoms are insoluble in most metals and alloys,³⁾ and the presence of He atoms in metals may have a great impact on the microstructure. He atoms promote the growth of cavities,^{4,5)} dislocation loops^{6,7)} and induce void swelling. These microstructural changes lead to the degradation of mechanical properties.

Thermal desorption spectrometry (TDS) is commonly used to detect He in materials. TDS detects He atoms exiting the sample. However, the TDS method has two disadvantages: i) the sample must be heated during the measurement, and ii) TDS is unable to provide information on sites trapping He.

Positron annihilation spectroscopy is a powerful tool for detecting vacancy-type defects in condensed matter.⁸⁾ Doppler broadening of positron annihilation radiation is a nondestructive technique for testing defect clusters. In the dominant decay mode of a thermal positron and electron, two gamma rays are emitted. In the laboratory frame, the energy of two photons emitted by the annihilation of a positron and an electron is different. The difference in photon energy is proportional to the longitudinal component of the electron-positron momentum in the direction of gamma emission. Measurement of photon energies yields information about the momentum distribution of core electrons. Thus, Doppler broadening measurements can provide useful information about the distribution of elements around annihilation sites.

Recently, Doppler broadening measurements have been improved by a two-Ge-detector coincidence system, which decreased the background of high momentum contributions by about two or three orders of magnitude compared with traditional measurements using a single Ge-detector.⁹⁾ Coincidence Doppler broadening (CDB) has been used widely to detect precipitates in alloys,^{10,11)} however, it has not yet been used to detect gaseous atoms. The main objective of the present work was to develop a new nondestructive technique for detecting He atoms in metals and alloys using CDB.

2. Experimental Procedure

In the case of ion irradiation, well annealed high-purity (99.99%) Ni supplied by Johnson & Matthey Chemicals Ltd. was irradiated with 3.3-MeV He ions at 423 K using an accelerator in the Institute for Materials Research, Tohoku University, at an irradiation dose of 9.6×10^{15} He ions/cm². The damage and the concentration of He at the peak region (about 6 μ m from the specimen surface) were 0.3 dpa (displacements per atom) and 300 appm based on calculations using TRIM code,¹²⁾ where the threshold displacement energy of Ni was assumed to be 24 eV. The peak width was 1 μ m. The isochronal annealing experiments for irradiated Ni were carried out for 1 h at increments of 50 K from the irradiation temperature. To compare the formation of microvoids produced by He ion irradiation and neutron irradiation, where He production can be neglected, well annealed Ni was irradiated at the Kyoto University Reactor (KUR)¹³⁾ at 573 K to 4.4×10^{-3} dpa.

Natural Cu is composed of 69.1 at% ⁶³Cu and 30.9 at% ⁶⁵Cu. The (n, α) and (n, p) reaction typically produces He and H in Cu during neutron irradiation. In order to avoid the effects of H, the Cu isotope ⁶³Cu, which was prepared by reductive reaction of ⁶³CuO, was used in the neutron irradiation since He is produced only from ⁶³Cu by a (n, α) reaction. The irradiation was conducted in a Fast Flux Test Facility (FFTF) reactor using the Materials Open Test

Assembly (MOTA) below a core canister during its cycle 12 operation. The irradiation temperature and doses were 646 K and 7.3 dpa. The amount of He produced in ^{63}Cu was estimated to be 0.214 appm based on dosimetry measurements and calculations.¹⁴⁾ As in the case of Ni, to compare the formation of microvoids produced by He ion irradiation and neutron irradiation, where He production can be neglected, well annealed Cu was irradiated at the KUR at 573 K to 2.8×10^{-3} dpa.

Positron lifetime and coincidence Doppler broadening (CDB) 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 1.0×10^6 counts. To discriminate between bulk and defect components, after subtracting the source and background components, the lifetime spectrum $L(t)$ was decomposed into two components using the programs Resolution and Positronfit:¹⁵⁾

$$L(t) = (I_1/\tau_1)\exp(-t/\tau_1) + (I_2/\tau_2)\exp(-t/\tau_2) \quad (1)$$

where, τ_i are the lifetimes and I_i are the intensities. The long lifetime τ_2 comes from vacancies and vacancy clusters, if any, and the short lifetime τ_1 results from the positron lifetime of free electrons and other defects, such as dislocations.

The average positron lifetime τ_m is defined as:

$$\tau_m = I_1\tau_1 + I_2\tau_2. \quad (2)$$

Doppler-broadening spectra were accumulated to a total of 2.0×10^7 counts. The energy resolution was 1.4 keV at 511 keV.

3. Results and Discussion

After irradiation to 9.6×10^{15} He ions/cm² in Ni, the long lifetime τ_2 was 278.8 ps with an intensity of 13.6%, which corresponded to a cluster of four vacancies V_4 .¹⁶⁾ Figure 1 shows the lifetimes and intensities of long lifetime τ_2 during annealing irradiated Ni to 1273 K. The intensity of long lifetime almost did not change up to 723 K, and then decreased with increasing annealing temperature. Meanwhile, the long lifetime decreased slightly during annealing from 623 to 823 K, and then increased at 873 K. The long lifetime increased to about 350 ps at 1123 K, which corresponded to a V_{10} . These results indicate that the microvoids are stable at temperatures below 623 K. It is believed that the decrease and increase in long lifetime were caused by microvoids absorbing the interstitials produced by dissociation or movement of tiny interstitial clusters and the migration of tiny microvoids such as V_2 and V_3 , respectively. In addition, the lifetime spectra could not be decomposed into three components. In other words, positronium formation was not observed in lifetime measurements.

Figure 2 shows typical ratio curves of He-ion-irradiated Ni and after annealing at 1273 K to unirradiated Ni. In order to identify He, the figure also shows the ratio curve of neutron-irradiated Ni, where there was no He production, relative to Ni. After irradiation, the ratio curves were higher than 1 in the low momentum region because more positrons were annihilated by valence electrons at vacancies in the irradiated

Fig. 1 Positron lifetimes and intensities of long lifetime in He-ion-irradiated Ni during isochronal annealing experiments.

Fig. 2 Typical CDB ratio curves for He-ion-irradiated Ni after annealing at 1273 K and neutron-irradiated Ni relative to unirradiated Ni.

samples. In addition, the ratio curve of He-ion-irradiated Ni, especially after annealing at 1273 K, shows a peak at about $13.5 \times 10^{-3} m_0c$, where m_0 is the electron rest mass, and c is the velocity of light. However, there was no such peak in neutron-irradiated Ni at $13.5 \times 10^{-3} m_0c$. In the present study, we introduced two parameters, namely S and W , defined as the ratio of the low-momentum ($|P_L| < 4 \times 10^{-3} m_0c$) and high-momentum ($11.5 \times 10^{-3} m_0c < |P_L| < 15.5 \times 10^{-3} m_0c$) regions in the Doppler broadening spectrum to the total region, respectively. S represents the smaller Doppler shift resulting from the annihilation at the valence electrons of Ni. In the same materials, the increase in S relative to a well-annealed sample comes from the annihilation at vacancy-type defects. W comes from the annihilation at electrons of He, which is used to estimate the number of He atoms around positrons when they are annihilated. Figure 3 shows the results of S and W parameter correlations for He-ion-irradiated Ni during the annealing

Fig. 3 Annealing temperature dependence of the S-W plot.

experiment. S increased and W decreased from 423 to 523 K. The irradiation-induced vacancies became mobile at temperatures above 423 K, and microvoids nucleated and grew though they could not be observed in the lifetime measurement. Then, S decreased and W increased with increasing annealing temperature. On the basis of the lifetime results described above, the decrease in S corresponded to annihilation with interstitials at relatively low temperatures (< 873 K) and to a decrease in the microvoid concentration during growth of microvoids at temperatures above 873 K. The (S , W) points of annealed Ni were almost aligned on the same line segment, which indicated that the variation in S and W was only caused by the changes in microvoid size. In addition, with increasing annealing temperature, S closed to the value of unirradiated Ni, but W remained higher than that of unirradiated Ni. This means that He atoms were present even in microvoids annealed at high temperatures (1273 K). As the affinity of positrons is higher for microvoids than for He atoms, the positrons trapped at microvoids were annihilated with the electrons in He, *i.e.*, He was present in the microvoids.

In order to identify the He peak shown in Fig. 2, CDB measurements were carried out in neutron-irradiated isotope ^{63}Cu , where He was produced homogeneously in the matrix by the nuclear reaction of (n, α) . Figure 4 shows ratio curves of neutron-irradiated ^{63}Cu relative to unirradiated Cu. The figure also shows the ratio curve of low dose neutron-irradiated natural Cu, where the neutron dose was 0.0028 dpa and He production could be neglected, relative to Cu. Low dose neutron-irradiated Cu was selected because S is almost the same as that in neutron-irradiated ^{63}Cu , which allows easy comparison. Though not prominent, there was a peak at about $13.5 \times 10^{-3} m_0c$ in neutron-irradiated ^{63}Cu . However, there was no peak in low dose irradiated Cu. The low peak was due to the low concentration of He produced by the nuclear reaction, which was estimated to be 0.214 appm as described above. There were peaks at the same positions in He-ion-irradiated Ni and neutron-irradiated ^{63}Cu . This indicates that the momentum distribution of He in metals is not influenced by the metallic element. The TEM observation shows that large voids with an average diameter of 100 nm were formed in neutron-irradiated ^{63}Cu . The long lifetime τ_2

Fig. 4 Typical CDB ratio curves for neutron-irradiated ^{63}Cu and natural Cu relative to unirradiated Cu.

was 439.2 ps with an intensity of 11.3%. The long lifetime corresponded to the lifetime of the void surface since the voids were large. However, no formation of positronium was observed.

4. Conclusion

The present study employed a new detection method involving CDB to detect He in metals. He could be detected by CDB measurements even at low concentrations. The microvoids containing He were stable at the high temperature of 1273 K. No positronium formation was detected in microvoids containing He.

REFERENCES

- 1) Q. Xu, N. Yoshida and T. Yoshiie: *Mater. Trans.* **46** (2005) 1255.
- 2) Q. Xu, N. Yoshida and T. Yoshiie: *J. Nucl. Mater.* (2006) in press.
- 3) M. D'Oleslaeger, G. Knuyt, L. De Schepper and L. M. Stals: *Fundamental Aspects in Inert Gas in Solids* Ed. by S. E. Donnelly and J. H. Evans, (Plenum, 27, 1991).
- 4) J. B. Condon and T. Shober: *J. Nucl. Mater.* **207** (1993) 1.
- 5) K. Farrell: *Rad. Eff.* **53** (1980) 175.
- 6) K. Ono, T. Kino, S. Furuno, K. Hojou, K. Izui, K. Mizuno and K. Ito: *J. Nucl. Mater.* **179-181** (1991) 978.
- 7) K. Niwase, T. Ezawa, T. Tanabe, M. Kiritani and F. E. Fujita: *J. Nucl. Mater.* **203** (1993) 56.
- 8) A. Dupasquier and A. P. Mills, Jr.: *Positron Spectroscopy of Solids* (IOS Press, Amsterdam, 1995).
- 9) P. Asoka-Kumar, M. Alatalo, V. J. Ghosh, A. C. Kruseman, B. Nielsen and K. G. Lynn: *Phys. Rev. Lett.* **77** (1996) 2097.
- 10) Q. Xu, T. Yoshiie and K. Sato: *Phys. Rev. B* **73** (2006) 134115.
- 11) Q. Xu and T. Yoshiie: *Mater. Sci. Forum* **445-446** (2004) 216.
- 12) J. P. Biersack and L. G. Hagmark: *Nucl. Instrum. Meth.* **174** (1980) 257.
- 13) T. Yoshiie, Y. Hayashi, S. Yanagita, Q. Xu, Y. Satoh, H. Tsujimoto, T. Kozuka, K. Kamae, K. Mishima, S. Shiroya, K. Kobayashi, M. Utsuro and Y. Fujita: *Nucl. Instrum. Methods, Phys. Res. A* **498** (2003) 522.
- 14) L. R. Greenwood: *Fusion Reactor Mater. Semiann. Prog. Rep. DOE/ER-0313/18*, 27 (1995).
- 15) P. Kirkegaard, M. Eldrup, O. E. Morgensen and N. J. Pedersen: *Comput. Phys. Commun.* **23** (1981) 307.
- 16) M. J. Puska and R. M. Nieminen: *J. Phys. F: Met. Phys.* **13** (1983) 333.