Vacancy evolution in Ni during irradiation at high temperatures studied by in situ positron annihilation spectroscopy

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Abstract. We present experimental results for in situ study of atomic-vacancy production and its evolution occurring during irradiation by using a slow-positron beam. Thermal stability of the vacancy produced during irradiation is investigated under elevated temperature conditions. An annealed Ni specimen was irradiated with 400 keV He ions at three different temperatures of 296 (RT), 368 and 713 K. Doppler broadenings of positron-annihilation γ-rays were measured and variation of the line-shape parameter S was observed under beam-on (during irradiation) and beam-off (non-irradiation) conditions. Results indicate that variation of the S depends on the specimen temperature, showing that vacancy cluster consisting of about 15 vacancies is formed predominantly via thermal evolution of atomic-sized vacancies under irradiation at high temperatures. We found that formation of the activated vacancies occurs during irradiation, which leads to vacancy clustering.

1. Introduction
Studies of radiation defects in materials have been carried out for many years. Considerable interest has been devoted to study radiation damage (degradation of materials) in radiation environments. Recent investigations focus on an understanding of a characteristic of defects under irradiation to reveal the dynamics underlying defect production, accumulation and evolution. To this end, various apparatus or techniques have been developed for performing in situ observation of irradiation behaviour in materials [1].

Irradiation of energetic ions is known to produce a large number of point defects in a nanometer-sized region near an ion trajectory (collision cascade region). In the cascade region, activated defects are formed, and then they annihilate via interaction with one another, or with various sinks such as

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dislocations and a surface. On the other hand, defect clustering occurs via thermal diffusion or migration of the activated defects. In the initial stage of defect clustering, a small-sized vacancy cluster or a latent vacancy cluster, which is invisible in observation of electron microscope, is formed [2]. The formation of latent vacancy cluster plays an important role in processes of void nucleation resulting in void swelling in materials [3].

At present little is known experimentally about the void nucleation because of the experimental difficulty in observation of a small-sized vacancy cluster at nucleation stage during irradiation. Positron annihilation spectroscopy is a powerful technique with a high sensitivity to such atomic-scale open-volume defects or nanovoid. We have recently investigated transient vacancies produced during ion irradiation of non-annealed Ni with positrons [4]. In situ positron annihilation Doppler broadening measurement was performed during ion irradiation at room temperature by using a specially developed experimental system combined with a slow-positron-beam apparatus and a high-energy ion accelerator. The results showed that an increase in the Doppler broadening line-shape parameter $S$ occurs during irradiation, implying that vacancy concentration is higher and larger-sized vacancy clusters are formed during irradiation, compared with those of vacancies that have survived after irradiation.

In the present work, we report on thermal stability of vacancies produced during irradiation. A well-annealed Ni was used as a target specimen. The specimen was irradiated with 400 keV He ions at three different temperatures of 296 (RT), 368 and 713 K, and in situ positron annihilation Doppler broadening measurement was performed simultaneously. Temperature dependence of evolution of atomic-scale vacancy defects produced by irradiation is investigated.

![Figure 1. Positron implantation profile for 20 keV positrons in Ni and the number of vacancies produced by one incident ion (400 keV He ion) calculated from TRIM, as a function of the specimen depth.](image)

2. Experimental techniques
The experiments were carried out at High Fluence Irradiation Facility of the University of Tokyo (HIT). The apparatus and experimental procedure were essentially the same as those described in Ref. 5, and only a brief outline is given. A specimen was Ni of 10 µm in thickness that was annealed at 1173 K for an hour in vacuum. The specimen was mounted on a target holder equipped for heating the specimen up to 773 K. Three different specimen-temperature of RT, 368 and 713 K were chosen because mobility of vacancy in Ni differs at each temperature. Temperature of the specimen was
measured with a thermocouple, and was monitored continuously during irradiation experiments. Fluctuation of the temperature during the experiments was ±4 K.

Mobility of vacancies in a thermally activated process can be estimated by $v = v_0 \exp(-E_a/kT)$, where $v$ the number of atomic jumps per second, $v_0$ the lattice vibration frequency ($10^{13}$ s$^{-1}$), $k$ the Boltzmann constant, $T$ the temperature. The migration energy of single vacancies and divacancies in Ni are $E_a = 1.25$ eV and $E_a = 0.75$ eV, respectively [8]. At the low temperature of 368 K, the value of $v$ is $7.9 \times 10^5$ jumps/s for single vacancies and $5.5 \times 10^2$ jumps/s for divacancies. This indicates that single vacancy is immobile below 368 K. On the other hand, at the high temperature of 713 K, the value of $v$ is $1.5 \times 10^4$ jumps/s for single vacancies and $5.1 \times 10^7$ jumps/s for divacancies, indicating that both single vacancies and divacancies are mobile.

An irradiation chamber was connected with both slow positron apparatus and high-energy ion accelerator. This experimental system enables to observe in situ vacancy-type defects in materials produced under an ion irradiation environment. Beams of 400 keV He ions were incident on a specimen at 30° to the surface normal, and monoenergetic positron beams were directed parallel to the surface normal. A positron with the incident energy of 20 keV was used so that depth profile of positron implantation overlaps with that of defects produced by the ions. Figure 1 shows depth profile for 20 keV positrons and vacancy defect distribution by 400 keV He ions in Ni, where the defect depth profile by ions was calculated from the TRIM code [6] and the positron implantation profile was calculated using the formula described in Ref. 7.

For the specimen during irradiation and non-irradiation, we performed measurements of the positron annihilation Doppler-broadening spectroscopy. Positron-annihilation $\gamma$-rays emitted from the specimen were detected with a high-purity Ge detector (ORTEC GEM-20180-P). A Doppler broadening spectrum of the annihilation $\gamma$-rays was characterized by the line-shape parameter $S$ defined as the ratio of counts in the central portion of the annihilation photopeak (ranging from 510.2 keV to 511.8 keV) to the total counts in the peak (from 507.0 keV to 515.0 keV). Overall experimental errors for the $S$ parameter due to a statistical error were ±0.0015. In each run of annihilation spectrum measurements, data-acquisition time was 20 min, and the average fluence of ion beams was $\sim 2.3 \times 10^{14}$ ions/cm$^2$ (where the average flux was $\sim 1.9 \times 10^{11}$ ions/(cm$^2$ s$^{-1}$)).

3. Results and discussion

Figure 2 shows a typical result for $S$-parameter variation measured sequentially during non-irradiation (open symbols or odd-numbered runs) and irradiation (closed symbols or even-numbered runs) at temperatures of RT, 368 and 713 K. One can see zigzag variation of $S$-parameter: values of $S$ observed during irradiation are larger than those measured under non-irradiation condition. This zigzag variation has been also observed in our previous study for non-annealed Ni irradiated with 2.5 MeV C ions at RT [4]. For observations at the low temperature of RT and 368 K, comparing between the value of $S$ for run 1 and that for run 3, the $S$-parameter changes significantly, indicating that accumulation of surviving or immobile vacancies. On the other hand, such significant change in the $S$-parameter was not observed at the high temperature of 713 K, suggesting inhibition of defect accumulation.

In order to obtain information on temperature dependence of the variation of $S$-parameter in more details, the type of defects was studied for the specimens (run 13 shown in Fig. 2) irradiated at a fluence of about $1.0 \times 10^{15}$ ions/cm$^2$ by positron lifetime measurements. The measurements were carried out using the high-intensity slow-positron microprobe apparatus at National Institute of Advanced Industrial Science and Technology (AIST) [9]. Time resolution of the spectrometer was typically $\sim 280$ ps. Beam spot size of the positron was 200-300 µm in diameter. Although an incident positron energy of 20 keV was used in the measurements, the component of kinetic energy of the positron in parallel direction with the surface normal was about 14 keV. This results from a focusing
Figure 2. Temperature dependence of $S$-parameter variation measured sequentially during ion irradiation (closed symbols) and non-irradiation (open symbols) for an annealed Ni foil of 10 µm in thickness irradiated by 400 keV He ions.

condition of positron beams. In this case, a mean implantation depth of the positron is about 300 nm. Total counts of more than $1\times10^6$ were corrected in each lifetime spectrum.

Figure 3 shows experimental results of positron lifetime measurements. Two-component analysis of the lifetime spectra was done. We used the calculated value of positron lifetime taken from Ref. 10 in order to determine the type of vacancies. For the specimen without irradiation, the value of $\tau_1$ corresponds to the bulk lifetime in Ni. The $\tau_2$ component with intensity $I_2$ of about 18% is attributed to the surface annihilation occurring as a result of back-diffusion of positrons. This is due to that an implantation depth of the positron is short: about 300 nm, as described above. The fraction of positrons diffusing back to the surface, corresponding to the intensity $I_2$, can be estimated by analysing experimental data of the $S$-$E$ curve (the $S$-parameter as a function of an incident positron energy) with the model developed by Britton et al. [11]. The intensity $I_2$ was estimated as about 15 %, indicating that the calculation is in good agreement with the experiment. It should be noted that the back-diffusing fraction is significantly affected by the defect concentration, because positrons was trapped at defects before reaching the surface; hence, the back-diffusing fraction reduces significantly for specimen containing defects.

For the specimen irradiated at RT, the value of $\tau_1$ was found to be 207 ps, corresponding to vacancy cluster consisting of about 3 vacancies. The same result was observed for the specimen at 368 K, except for the intensity of the $\tau_1$ component. Result of the $\tau_2$ component (about 300 ps) shows the formation of larger-sized vacancy clusters. The vacancy clusters may be latent vacancy clusters directly formed from collision-cascade damage. The occurrence of the latent vacancy clusters has been observed in the experiment for Ni irradiated with MeV neutrons [2]. On the other hand, the size of vacancies corresponding to the $\tau_2$ component observed at 368 K is larger than that observed at RT. This suggests that vacancy evolution occurs via thermal migration process of vacancy clusters such as divacancies at 368 K.

Remarkably, it is found that for the specimen at the high temperature of 713 K the $\tau_1$ component (115 ps) with intensity of about 60 % corresponds to the bulk lifetime in Ni, and result of the $\tau_2$ component
(360 ps) shows formation of a large-sized vacancy cluster consisting of about 15 vacancies. This evidently indicates that atomic vacancies produced during irradiation agglomerate and they develop into a large-sized vacancy cluster.

We consider the increase of S-parameter observed during irradiation. The factor may be due to the following process occurring after irradiation. Radiation-induced defects are produced continuously during irradiation (beam-on), and also their evolution (vacancy clustering) takes place simultaneously. After irradiation (beam-off) production of defects completely stops, and then the defect recombination resulting from migration of interstitials occurs mainly because a high-mobility of interstitials. Consequently, a part of the vacancy formed during irradiation is deflated via absorption of a freely migrating interstitial into the vacancy. Therefore, it is likely that the variation of S-parameter observed is attributed to a relaxation process occurring between the vacancies produced during irradiation and a freely migration interstitials. This implies that the size of vacancy cluster formed during irradiation is large compared to that survived after irradiation.

4. Conclusions

Using the in situ positron-annihilation Doppler broadening technique, we investigated the vacancy production during irradiation and its thermal evolution for annealed Ni irradiated with 400 keV He ions. We demonstrated that the present in situ observation technique is applicable for the study, in particular of latent vacancy cluster produced in materials under irradiation environments. It was found that (1) vacancy concentration during irradiation is high at each of the temperatures studied compared to that survived after irradiation, (2) stable atomic-scale defects consisting of about 3 vacancies are formed predominantly below the temperatures of 368 K, and (3) agglomeration of the activated vacancies occurs significantly at the high temperature of 713 K, where defect cluster consisting of about 15 vacancies was formed and atomic-sized vacancies annihilate via recombination with a freely migrating interstitial.
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