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DEFECT RECOVERY IN α-Fe e^--IRRADIATED AT 300 K

G.H. DAI

Department of Chemistry, College of Arts and Science
University of Missouri-Kansas City, Kansas City, MO 64110, USA

X.H. LI*, P. MOSER

Centre d'Etudes Nucléaires de Grenoble, DRFMC/SP2M/MP, 85X
38041 Grenoble Cedex, France

G. MOYA

Faculté des Sciences et Techniques de Saint Jérome
Département de Science des Matriaux, 13397 Marseille Cedex 13, France

AND J.C. VAN DUYSEN

Electricité de France, Direction des Etudes et Recherches
Département Etudes des Matériaux, les Renardières, 77250 Ecuelles, France

Defect annealing recovery has been studied, by measuring positron lifetime spectra, in high-purity α-iron irradiated at 300 K with 3 MeV electrons to a fluency of 7×10^{19} cm^{-2}. Vacancy clusters containing 6–10 single vacancies were observed immediately after irradiation during which they were possibly forming (the so-called "irradiation annealing"). With increasing temperature, the agglomerates continually grow in size at the expense of their concentration, giving rise to the formation of microvoids ($>$ 15 vacancies). Also present were other types of defects, probably immobile vacancies trapped by impurity (e.g. carbon) atoms and dislocation/loops generated presumably from collapse of voids during the relatively high dose irradiation and/or the annealing. The immobile vacancies eventually became movable at around 350 K, supplying the growing clusters and thus leading to a stabilization in their concentration till around 500 K. Between 500 and 700 K, microvoids gradually evaporated, but the dislocation-associated defects were able to survive annealing at temperatures as high as 700 K. The void size and concentration and their evolution have been evaluated on the basis of both the to date theoretical and experimental studies. The temperature dependence was also observed of positron trapping into vacancy agglomerates of various sizes.

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*Permanent address: Department of Physics, Wuhan University, Wuhan 430072, China.

1. Introduction

In recent years, more and more research work by various experimental techniques, such as the small angle neutron scattering (SANS), field ion microscopy (FIM), transmission electron microscopy (TEM), positron annihilation (PA), and extended X-ray absorption fine structure (EXAFS), etc., has been carried out on stainless steels (or model alloys) used as shielding or vessel materials in nuclear reactors. Under the practical operational conditions of power reactors, the steel materials usually suffer neutron irradiation at rather high temperatures ($\approx 300°C$). However, most of the published results up till now concerning irradiation damages in iron and alloys as well as some steels have been obtained by irradiation at low temperatures. To simulate the real irradiation conditions, it is thus important to investigate metals/alloys irradiated at ambient temperatures or temperatures similar to those in power reactors. We have started to perform a series of investigation using PA methods on pure iron and various model Fe alloys containing different alloyed metal elements, such as Cu, Mn, and Cr, etc., or different amounts of various alloyed metals, electron irradiated at such high temperatures.

The e^+ lifetime technique has proved to be a powerful tool to observe vacancy-type defects and particularly agglomeration of vacancies (in the case of Fe and alloys, see Refs. [1–6]). All the previous irradiations have been carried out at low temperatures (e.g. 20 K) and the major purpose of them has been to detect and understand vacancy formation, migration and clustering processes undergoing at relatively low temperatures (e.g. below room temperature). It is well known that in hyper pure α-iron, vacancy migration begins at around 200 K [1, 4–6] while agglomeration occurs simultaneously, and the vacancy clusters or microvoids anneal out above 500 K. It is therefore interesting to see the defect structure in α-iron just after electron irradiation at 300 K (27°C) and its evolution during subsequent isochronal annealing treatments.

High-purity α-Fe e^--irradiated at 20 K was carefully studied about ten years ago [1, 4]. During the 80's, the attention has been shifted onto the effects of various metal elements on the annealing behaviors of dilute iron alloys [5, 6]. In this paper, we not only report the first experiment on the defect recovery of ultra pure α-Fe e^--irradiated at 300 K followed by positron lifetime measurements, but also manage to furnish as much as possible quantitative information from the experimental point of view on the basis of the up to date theoretical studies released in the past few years, in the hope of trying to combine relevant results of the experimental and theoretical efforts in the positron annihilation studies on vacancy-type defects in metals and thereby to go deeper into the understanding of the behavior and process of defect formation, migration and clustering, etc.

2. Experimental

The α-Fe used in the present study is the ultra pure iron produced by Centre d'Etudes Nucleaires de Grenoble (CENG) [7, 8]. The samples with dimensions of $5 \times 7 \times 1$ mm^3 were annealed for 12 h at 1100 K under hydrogen atmosphere, slowly cooled to room temperature, thinned by electrolytic polishing and then irradiated at 300 K (27°C) by 3 MeV electrons to a fluency of 7×10^{19} cm^{-2} using a Van de Graaff accelerator.

The isochronal annealing was carried out *in situ* in the e^+ lifetime setup over the temperature range 300–500 K, whereas above 500 K it was done in a separate stove. The positron lifetime spectra were recorded using a conventional fast-slow coincidence system with γ detectors consisting of plastic scintilators and with a time resolution (FWHM) of about 235 ps. The positron source was about 20 μCi ^{22}NaCl sandwiched by two identical cold-rolled 1μm thick Ni foils. Measurements were made at both 77 K and T_{ann}, at each step ($\Delta T = 25$ K, $t = 5$ h and 30 min for $T_{ann} \leq 500$ and > 500 K, respectively) of the annealing treatment.

After source and background corrections, all the spectra were resolved into two lifetime components. Two major source components were subtracted, arising from annihilation of positrons: (1) in source-supporting foils (e.g. Ni, Al, kapton, and mylar, etc.) and (2) at surfaces plus in the ^{22}NaCl source material. The fraction of the former can be evaluated using the following formula [9]:

$$I_{foil}(\%) = 0.324 Z_{sample}^{0.93} \sigma_{foil}^{(3.45/Z_{sample}^{0.41})}, \qquad Z_{sample} \leq 30$$

$$I_{foil}(\%) = 0.905 Z_{sample}^{0.619} \sigma_{foil}^{(1.49/Z_{sample}^{0.235})}, \qquad Z_{sample} \geq 30$$

where σ_{foil} is the thickness of the foil in the units of mg/cm^{-2} and Z_{sample} is the average atomic number of the sample material given by [10]

$$Z_{sample} = \frac{\sum p_i Z_i^2 / A_i}{\sum p_i Z_i / A_i},$$

in which p_i is the percentage content, and Z_i and A_i are the atomic number and weight of the i-th component. The lifetime of this source component is characteristic of the foil material. In the present case, τ_{foil} was taken to be 155 ps, corresponding to cold-worked Ni, while for the sample Fe, 1μm Ni foil gives $I_{foil} = 6\%$. The surface/salt component is usually obtained from the spectra of well-annealed samples, with an intensity $\approx 5\%$ and a lifetime $\approx$ 400–500 ps (depending on the sample).

3. Results and discussion

Figure 1 shows the lifetime spectra taken at several critical annealing temperatures; the selected adjacent spectra can be easily distinguished from one another. The evolution of the positron lifetime parameters during the isochronal annealing is shown in Fig. 2. To check the internal consistency in a one-trap analysis, we calculated τ_1's, assuming the well-known τ_b(Fe) = 110 ps; the results are also shown in Fig. 2 (the lines in the block of τ_1). The deviation of the experimental τ_1's from their calculated counterparts indicates the two-state trapping model inappropriate to the current problem and more than one sort of defects co-present in the specimen during the annealing processes. Therefore, following Vehanen et al. [4], we have also analyzed the data in terms of the two-trap model.

It is noticed that just after irradiation at 300 K (T_{irr}) the measured lifetime spectrum is already separable to two exponentials, different from those after low-temperature (20 K) electron irradiations [1, 4–6] where the positron lifetime spectra are one-exponential at 77 K (the usual first measurement after irradiation at 20 K), with a mean lifetime about 175 ps characteristic of single vacancies in α-iron, i.e. τ_v(Fe), since all positrons are trapped by monovacancies produced in

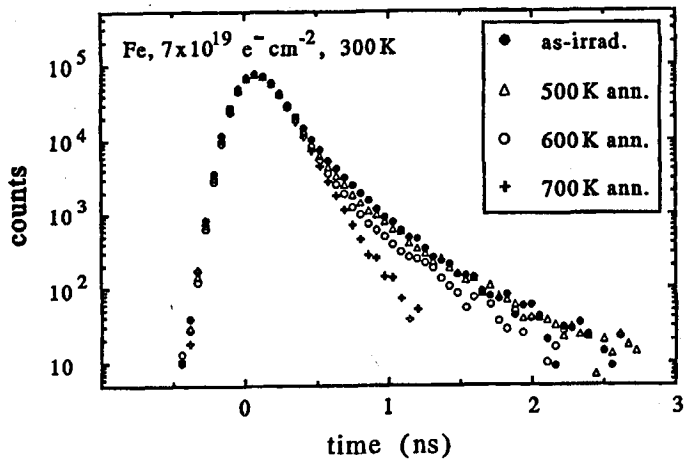

Fig. 1. Positron lifetime spectra, measured at 77 K, of high-purity α-iron e^--irradiated at 300 K to 7×10^{19} cm^{-2} after the source and background correction (described in the text).

electron irradiation. But here at 300 K, a distinct long-lifetime component having the intensity $I_2 \approx 20\%$ is readily observable; its lifetime τ_2 is already 320 ps, clearly indicating the presence of small vacancy clusters, since the lifetime value is much higher than τ_v(Fe). The three-dimensional vacancy clusters have formed during the irradiation (the so-called "irradiation annealing") because the monovacancies can migrate freely at T_{irr} that is far beyond around 200 K, the temperature where monovacancy migration and clustering in high-purity α-Fe begin to occur [1, 4–6, 11]. The value of τ_2 at 300 K corresponds very well to the previous results obtained at $T_{ann} = 300$ K during the annealing of α-iron specimens (of the same quality as used here) e^--irradiated at 20 K [5, 6]. According to Puska and Nieminen [12], the vacancy cluster sizes are about 6–10 single vacancies at 300 K, and the evolution of the average number of vacancies in the voids during the whole annealing process has been estimated, as given in Fig. 3.

Two recovery stages can be easily seen from Fig. 2, divided by $T_{ann} = 500$ K, if we first consider the 77 K measurements. Comparing the spectra of the as-irradiated and annealed at 500 K shown in Fig. 1, one could note that the slope of the long tail of the spectra decreases and the spectra has been a little shifted to the left after annealing at 500 K, indicating the increase of τ_2 and decrease of I_2. The interpretation comes naturally in the light of a number of previous investigations [1, 4–6]. During the first stage, with the increase of T_{ann}, positrons see that the vacancy agglomerates continuously grow in size (Fig. 3), accompanied by a gradual decrease in their concentration as indicated by the decrease of I_2. Above 500 K, microvoids containing > 15 single vacancies form and then evaporate rapidly with increasing temperature, evidenced from the sharper drop in I_2 and τ_m shown in Fig. 2, and interestingly as could be noted from Fig. 1 that the major legible changes in the spectrum shape occur over the temperature range of

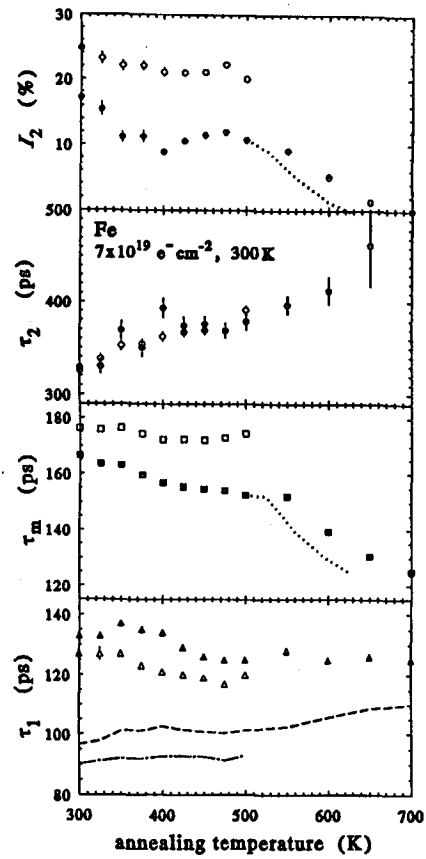

Fig. 2. Variation in positron lifetime parameters I_2, τ_2, τ_m and τ_1 as a function of the isochronal annealing temperature in ultra pure α-Fe electron irradiated at 300 K to 7×10^{19} cm^{-2}. The spectra were measured at both 77 K (full markers) and T_{ann} (open markers) over the temperature range of 77–500 K. The variation in τ_1 expected on the basis of the two-state trapping model is also indicated for measurements at 77 K (dashed line) and T_{ann} (dash-dotted line). The dotted lines in the blocks of I_2 and τ_m indicate the expected curves from an isochronal annealing of 5 h, the same as that used in the temperature range of 77–500 K, rather than the actual 30 min. The error bars are statistical resulting from standard deviations in the positron parameters.

500–700 K. These vacancy agglomerates anneal out finally around 700 K.

Here, it should be mentioned that during the second recovery stage, the annealing time was only 30 min, compared to 5 h for T_{ann} in the range of 300–500 K where it was prolonged due to measurements at both 77 K and T_{ann}. So the drop in τ_m and I_2 should have been sharper over 500–700 K if the annealing time had been longer; a simple estimation yields a 50 K shift to low temperatures of this recovery stage if the annealing time becomes 5 h (shown as the dotted line in Fig. 2).

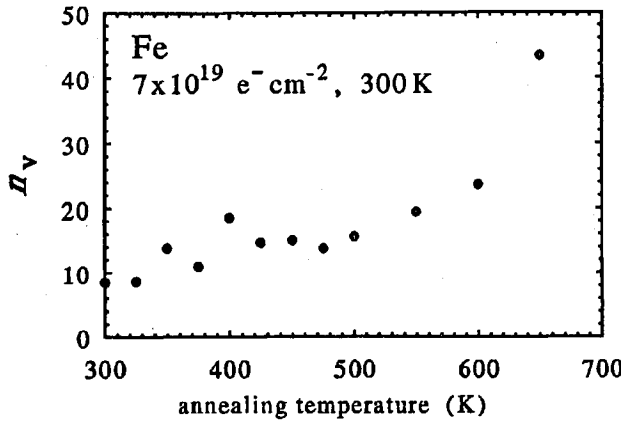

Fig. 3. The average number of single vacancies, n_v, in the vacancy clusters as a function of annealing temperature in e^--irradiated α-Fe, estimated from the experimental τ_2 values according to Puska and Nieminen [12].

When we consider the behavior of τ_1, we notice that the measured values of τ_1 are clearly above the dashed line that, as mentioned above, shows the value of τ_1 when vacancy clusters are assumed to be the only positron trap present in the lattice. Thus the vacancy clusters alone cannot explain the results, a fraction of other vacancy-like defects survive in the lattice (see below the calculated cluster and vacancy concentrations). This might be assigned to vacancy capture by immobile impurities resulting in a complex still capable of trapping positrons. Another possibility might be formation of dislocation loops, whose effect is relatively stronger in the present specimen, compared to previous studies [1, 4–6], as τ_m or τ_1 never reaches $\tau_b(\mathrm{Fe}) = 110$ ps even after the final annealing at 700 K, that is to say, the sample is not fully recovered. This is probably due to the much higher irradiation dose and temperature. Since annealing was already going on during the irradiation, giving rise to formation of vacancy agglomerates, the local vacancy concentration, as irradiation continues, became so high that the clusters collapsed either to voids or dislocation loops. Dislocations, as shown by Vehanen et al. [4], may stand annealing temperature as high as 800 K in plastically deformed high-purity iron. Hence, this gives a reasonable explanation to the non-complete recovery of our specimen up to the 700 K annealing.

It is interesting to note that the positron lifetime parameters (in particular, I_2) measured at the annealing temperatures (open symbols in Fig. 2) are markedly different from those taken at 77 K (full symbols). This has been well accounted for as the positron trapping dependence into vacancy agglomerates on the temperature by Nieminen et al. [13]. That is to say, the specific trapping rate ν_{cl} increases with the temperature linearly and the trapping is transition-limited at low temperatures, whereas at temperatures higher than about 200 K, the trapping tends to be diffusion-limited and the increase in ν_{cl} is slowed down, showing

a saturation-like behavior. This temperature dependence of ν_{cl} manifests itself via a remarkable variation in I_2 but with τ_2 unaffected [13], in agreement with our experiments.

From the experimental data given in Fig. 2, we have evaluated the positron trapping rates κ_v and κ_{cl} into vacancy-type defects and vacancy agglomerates, respectively, at both 77 K (full symbols) and T_{ann} (open symbols), as shown in Fig. 4. The evolution of κ_{cl} is similar to that of I_2. With increasing annealing

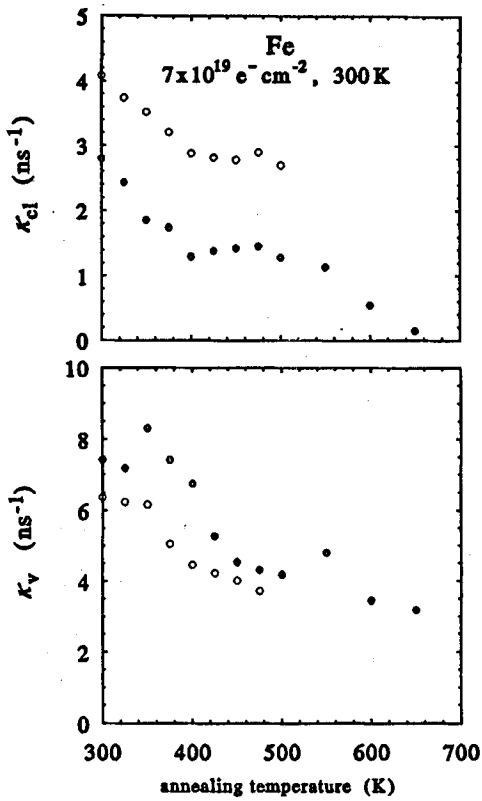

Fig. 4. Positron trapping rates into monovacancies κ_v, and vacancy agglomerates κ_{cl} as a function of annealing temperature in e^--irradiated pure α-Fe, calculated from the results in Fig. 2 via the three-state trapping model. The solid and open circles correspond to the measurements at 77 K and T_{ann}, respectively.

temperature, even if the size of the voids gradually grows, giving rise to higher and higher specific trapping rate ν_{cl}, the concentration of them, c_{cl}, decreases more rapidly, thereby leading to an overall decrease of κ_{cl}, according to $\kappa_{cl} = \nu_{cl} c_{cl}$. On the other hand, the trapping rate of vacancy-type defects κ_v gradually decreases, but does not approach 0 up to the highest annealing temperature, reflecting that the positron lifetime has not yet reached τ_b(Fe) at 700 K.

The temperature dependence of positron trapping into vacancy clusters is clearly seen here, since $\kappa_{cl} = \nu_{cl} c_{cl}$ with c_{cl} the same at 77 K as at T_{ann}. As is well known, there is essentially no temperature dependence of positron trapping into monovacancies in metals (see, e.g. Ref. [14]). However, κ_v's obtained at T_{ann} (open circles in Fig. 4) deviates slightly from their 77 K values (full circles). This indicates that, as speculated above, there are dislocation-type defects present in the specimen because κ_v is lower at higher temperatures than at 77 K (see, e.g. Ref. [15]). It is these dislocation-type defects that have not yet been completely removed by the annealing till 700 K. We have also estimated the defect concen-

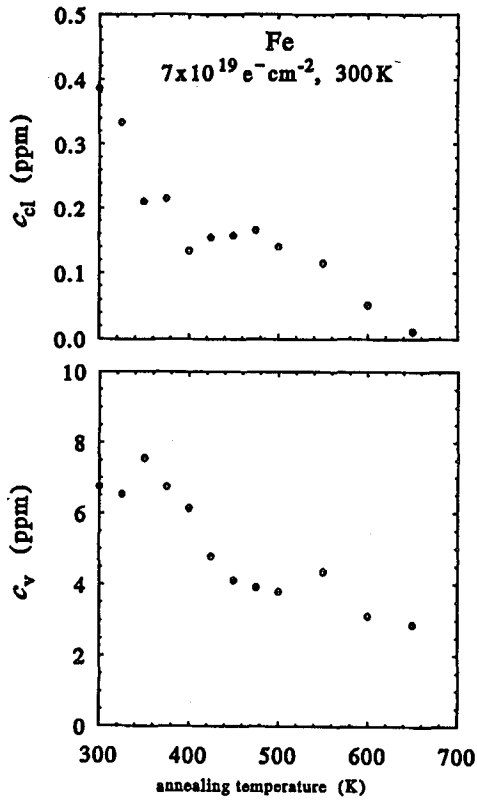

Fig. 5. Concentrations of monovacancies c_v, as well as the vacancy clusters c_{cl} as a function of annealing temperature in e^--irradiated high-purity iron, constructed from the data in Fig. 4 and the specific trapping rates given in the literature [4, 12, 16].

tration c_v and c_{cl} via the relations $\kappa_v = \nu_v c_v$ and $\kappa_{cl} = \nu_{cl} c_{cl}$ using the 77 K data. For the vacancy-type defects, we have used $\nu_v = 1.1 \times 10^{15}$ sec^{-1} for iron [4], so the variation of c_v follows exactly that of κ_v. For the vacancy agglomerates, the specific trapping rate ν_{cl} is dependent on both the void size and sample temperature. Nieminen and Laakkonen [16] have calculated theoretically ν_{cl} in aluminum as a function of the number of single vacancies n_v in the void. As an approximation,

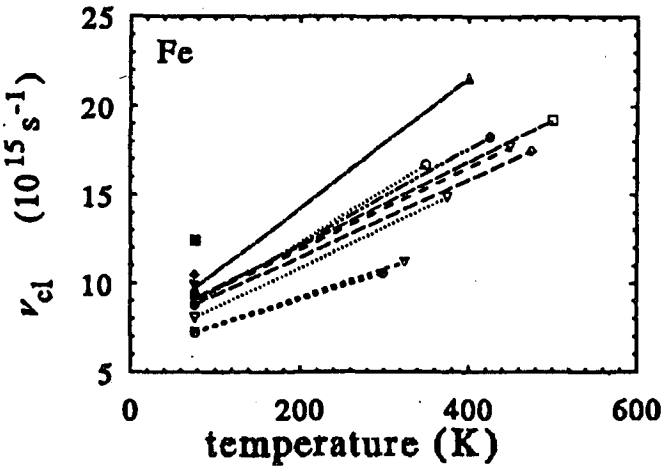

Fig. 6. Specific positron trapping rates (ν_{cl}) into vacancy clusters of different sizes in Fe at 77 K and T_{ann}. Each pairs of specific symbols connected with a specific line corresponds to the two measurements or sample temperatures at 77 K and T_{ann}, respectively. They are all in all showing the general temperature dependence of ν_{cl}, in spite of the scatter in its quantity.

it is reasonable to assume the same n_v dependence of ν_{cl} in Fe and, by simply re-scaling the curve for Al using the multiplying factor $\nu_v(\text{Fe})/\nu_v(\text{Al})$, we could obtain $\nu_{cl}(n_v)$ for iron. On the other hand, the positron lifetimes in the vacancy clusters containing n_v monovacancies have been theoretically calculated by Puska and Nieminen [12]. Hence, on the basis of the results of the two theoretical investigations, we estimated ν_{cl}'s at 77 K for each T_{ann} from the measured τ_2 values, and successively reckoned c_{cl} shown in Fig. 5. From this figure, we note that more than half of the vacancy agglomerates disappear in the T_{ann} range of 300–400 K, while c_v stays at around 7 ppm. Above around 350 K, some immobile vacancies perhaps bound to impurity atoms start to move and strongly annihilate into the vacancy clusters, leading to a rapid drop in c_v and a stabilization in c_{cl} in the T_{ann} range 400–500 K. Above 500 K, microvoids collapse into dislocation loops, giving rise to the drop in c_{cl} but non-vanishing c_v.

From κ_{cl} at T_{ann} (open circles in Fig. 4) and c_{cl} (Fig. 5), we have evaluated ν_{cl} at each T_{ann}, shown in Fig. 6 together with ν_{cl}(77 K) mentioned above. In spite of the only two respective data points, these temperature dependencies of ν_{cl} of the vacancy clusters with the various average sizes are in general agreement with expectation and previous investigations (see, e.g. Refs. [13] and [15]).

4. Conclusions

We have studied the defect annealing recovery in high-purity α-iron irradiated at 300 K with 3 MeV electrons to a fluency of 7×10^{19} cm^{-2}, using positron lifetime spectroscopy. Vacancy clusters containing 6–10 single vacancies were observed immediately after irradiation. With increasing annealing temperature, the

agglomerates continually grow in size at the expense of their concentration, leading to the formation of microvoids (> 15 vacancies). Other types of defects were also present, probably immobile vacancies trapped by impurity atoms and dislocation/loops generated presumably from the collapse of voids during the relatively high dose irradiation and/or the annealing. The immobile vacancies eventually became movable at around 350 K, supplying the growing clusters and thus leading to a stabilization in their concentration till around 500 K. With T_{ann} going up from 500 to 700 K, microvoids gradually evaporated, but the dislocation-associated defects were able to survive annealing temperatures as high as 700 K. The void size and concentration and their evolution have been evaluated and presented based on both the to date theoretical and experimental studies. The temperature dependence was also observed of positron trapping into vacancy agglomerates of various sizes. Largely differing from the phenomenon observed on the samples irradiated at low temperatures, the results on the pure α-iron irradiated at 300 K are helpful in clarifying what happened in stainless steels used as shielding or vessel materials usually undergoing irradiation at ambient or high temperatures in nuclear reactors.

References

[1] P. Hautojärvi, T. Judin, A. Vehanen, J. Yli-Kauppila, J. Johansson, J. Verdone, P. Moser, *Solid State Commun.* **29**, 855 (1979).

[2] P. Hautojärvi, J. Johansson, A. Vehanen, J. Yli-Kauppila, P. Moser, *Phys. Rev. Lett.* **44**, 1326 (1980).

[3] P. Hautojärvi, L. Pöllänen, A. Vehanen, J. Yli-Kauppila, *J. Nucl. Mater.* **114**, 250 (1983).

[4] A. Vehanen, P. Hautojärvi, J. Johansson, J. Yli-Kauppila, P. Moser, *Phys. Rev. B* **25**, 762 (1982).

[5] C. Corbel, P. Moser, P. Hautojärvi, in: *Positron Annihilation*, Eds. P.C. Jain, R.M. Singru, K.P. Gopinathan, World Scientific, Singapore 1985, p. 524.

[6] P. Moser, C. Corbel, P. Lucasson, P. Hautojärvi, *Mater. Sci. Forum* **15-18**, 925 (1987).

[7] F. Vanoni, Ph.D. Thesis, Université de Grenoble, Grenoble 1973.

[8] J. Dufresne, A. Seeger, P. Groh, P. Moser, *Phys. Status Solidi A* **36**, 579 (1976).

[9] D. Huguenin, Ph.D. Thesis, Université Joseph Fourier–Grenoble 1, Grenoble 1989.

[10] H.-W. Thümmel, *Isotopenpraxis* **6**, 214; 254 (1970).

[11] L. De Schepper, G. Knutt, L.M. Stals, D. Segers, L. Dorikens-Vanpraet, M. Dorikens, P. Moser, *Mater. Sci. Forum* **15-18**, 131 (1987).

[12] M.J. Puska, R.M. Nieminen, *J. Phys. F* **13**, 333 (1983).

[13] R.M. Nieminen, J. Laakkonen, P. Hautojärvi, A. Vehanen, *Phys. Rev. B* **19**, 1397 (1979).

[14] M.J. Puska, R.M. Nieminen, *J. Phys. F* **17**, 2235 (1987).

[15] M.D. Bentzon, J.H. Evans, *J. Phys., Condens. Matter* **2**, 10165 (1990).

[16] R.M. Nieminen, J. Laakkonen, *Appl. Phys.* **20**, 181 (1979).