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Vacancy defects in Fe: Comparison between simulation and experiment

M.R. Gilbert [a,b,*], Z. Yao [b], M.A. Kirk [c], M.L. Jenkins [b], S.L. Dudarev [a,d]

[a] EURATOM/UKAEA Fusion Association, Culham Science Centre, Oxfordshire, OX14 3DB, UK
[b] Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH, UK
[c] Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA
[d] Department of Physics, Imperial College, Exhibition Road, London, SW7 2AZ, UK

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ABSTRACT

The evolution of radiation damage under heavy-ion irradiation in thin foils of pure bcc Fe has been investigated by simulation and experiment. Simulations showed that vacancy loops are about as mobile as interstitial loops, and can be lost to the surface of a foil. Consistent with this, *in situ* real-time dynamic observations of the damage evolution showed that loops, many of which are believed to be of vacancy nature, were mobile and were often lost during irradiation. Atomistic simulations of vacancy defects in Fe showed that spherical voids, rather than vacancy loops, represent the lowest energy configurations for clusters of vacancies of any size. The simulations also indicated that the stability of loops strongly varies depending on their size. Closed loops above a critical diameter (~2 nm) are highly metastable due to the difficulty of their transformation into voids. The greater stability of voids explains why the loop yield in Fe and other ferritic materials is very low.

1. Introduction

Ferritic–martensitic steels are candidate materials for structural applications in fusion power plants and for other advanced nuclear applications, where they will suffer from radiation damage caused by fast neutrons. The accumulation of this radiation damage may adversely affect the structural integrity of the materials, leading to a range of deleterious effects, including, for example, low-temperature hardening [1]. There is therefore an urgent need to understand the formation and behaviour in ferritic materials of vacancy and interstitial clusters, which constitute the accumulated damage produced by irradiation-induced displacement cascades.

In order to address this need, we have carried out studies of the relative stability and mobility of vacancy and interstitial clusters in Fe, which was chosen as the simplest model ferritic material. Simulations were performed using Molecular Dynamics (MD) and Molecular Statics on lattices of pure Fe with periodic boundary conditions. The interactions between atoms in the simulations were described by the recently developed 'magnetic' many-body magnetic interatomic potential [2]. In parallel we have performed *in situ* transmission electron microscope (TEM) experiments to study the evolution of radiation damage under heavy-ion irradiation in thin foils of pure Fe, where the incident ions mimic the primary knock-on atoms produced in neutron irradiation. These experiments were carried out using the Argonne IVEM-Tandem Facility which consists of a Hitachi H-9000NAR transmission electron microscope interfaced to a 2 MV tandem ion accelerator and a 0.65 MV ion implanter, only the latter of which was used in the present experiments [3]. Specimens of Fe of different purities, as well as various FeCr alloys, were irradiated with 100 or 150 keV Fe^+ and Xe^+ heavy ions at room temperature (RT) and 300 °C (573 K) to doses up to 2×10^{18} ions m^{-2}.

This paper reports on results from these two parallel investigations, focusing on those elements which allow for a direct link to be drawn between the two. In particular, we consider the vacancy clusters which are present in thin-foil irradiations. At the low doses of the present experiments many if not all of the clustered defects are likely to be vacancy in nature. Interstitial damage is less commonly seen in thin foils at low doses because the expected high mobility of single interstitials and small clusters causes most of them to be lost from the foil, although interstitial clusters are present at higher doses [1]. A more detailed description of the present results can be found in [4] for the atomistic simulations, which also consider tungsten, and in [1] for the experiments, where full results from irradiations of FeCr alloys are also presented.

2. Mobility of vacancy dislocation loops

In thin-foil experiments the vacancy or interstitial nature of very small clusters is difficult to determine. However, the so-called black–white (B–W) contrast technique does allow for the nature of some loops lying close to the foil surface to be determined. When

* Corresponding author. Address: EURATOM/UKAEA Fusion Association, Culham Science Centre, Oxfordshire, OX14 3DB, UK.
E-mail address: mark.gilbert@ukaea.org.uk (M.R. Gilbert).

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imaged under two-beam dynamical imaging conditions loops lying within layers close to the surface may exhibit B–W contrast, characterised by a B–W contrast vector **l**. The technique relies on the direction of **l** relative to the diffraction vector **g** and a determination of the depth of the loop in the foil (see [5] for full details of the technique). An experiment was performed in Fe-11%Cr irradiated with 30 keV Ga^+ ions. Because of the low energy of the ions, it was expected that most loops would be produced close to the surface, within the so-called first depth layer. It was found that all loops which exhibited strong B–W contrast had the same direction of **l** and were of vacancy nature, if they lay in the first depth layer. Whilst we have not yet analysed loops in pure Fe irradiated with Fe^+ or Xe^+ ions, it seems likely that a proportion of the loops observed in thin foils are also vacancy in nature in these cases.

MD simulations such as those by Calder and Bacon [6] have demonstrated that interstitial clusters can form directly in cascades, and so it is widely held that the reason for the absence or scarcity of interstitial loops in experiments such as ours is that such clusters are highly mobile, and so most are lost from the foil, either via migration to surfaces or by recombination. However, this prompts the question as to how mobile are vacancy clusters relative to interstitial clusters.

In the present work cluster mobility was investigated using long-timescale (in MD terms) simulations of equivalently-sized interstitial and vacancy loops in pure bcc Fe. For each loop, 2 ns simulations were performed at temperatures ranging from 100 to 800 K. The position of the loop was measured at 0.1 ps intervals throughout each simulation and then the diffusion coefficient D was evaluated by taking the statistical average over many subsets of the full set of positions. A typical trajectory is shown in Fig. 1 for a vacancy loop with Burgers vector $1/2\langle 1\,1\,1\rangle$ at 700 K. Here the position of the vacancy loop was determined by averaging the positions of the atoms that bounded the loop and therefore had energies significantly divergent from that of bulk atoms. In the case of interstitial loops, the loop position was the average of the atoms making up the loop. Fig. 2 shows the variation of diffusion coefficient D with temperature for $1/2\langle 1\,1\,1\rangle$ loops of diameter 1.9 nm (comprising 61 vacancies or interstitials). Note that the trend lines drawn in the graph here, and elsewhere in the paper, are continuous interpolations of the discrete data.

Fig. 2 shows that interstitial loops are systematically more mobile than vacancy loops at the same temperature. However, the results also indicate that vacancy loops do diffuse at rates of the same order of magnitude as interstitial loops. A similar pattern was observed in simulations of 3.1 nm diameter $\langle 0\,0\,1\rangle$ loops (185 vacancies/interstitials), although in this case the difference between the two loops types was less pronounced. The simulations also indicated that a $1/2\langle 1\,1\,1\rangle$ vacancy loop could be lost to a surface on a timescale of 100 ps once it approached the surface closer than 5 nm. Therefore, in experiments, it is probable that both interstitial and vacancy dislocation loops are lost to surfaces. This will be more significant for interstitial loops due to their higher mobility and hence higher escape probability.

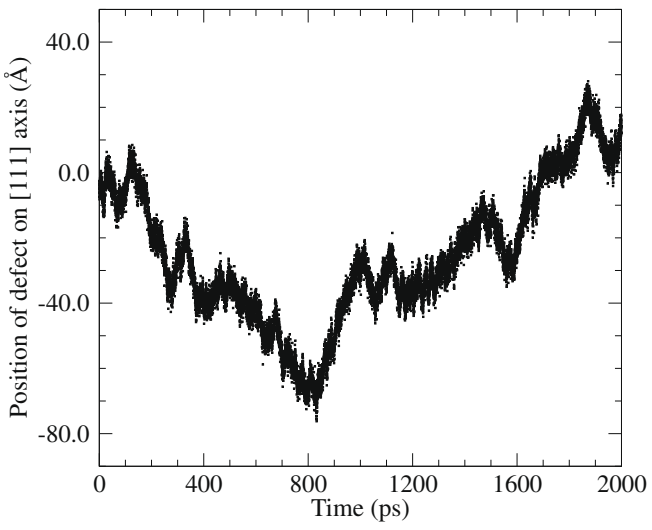

Fig. 1. Defect trajectory of a 1.9 nm diameter $1/2\langle 1\,1\,1\rangle$ vacancy loop (61 vacancies) during 1 D vertical motion in the [1 1 1] direction in a MD simulation at 700 K. Loop position marked every 0.1 ps.

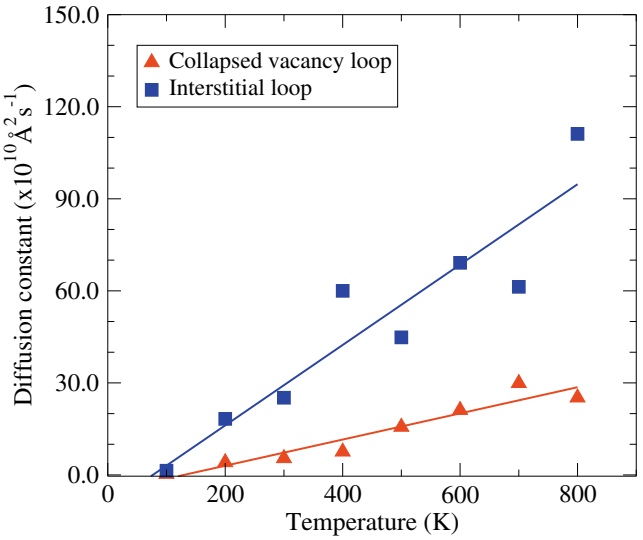

Fig. 2. Plot of calculated diffusion coefficients as a function of temperature in Fe for 1.9 nm $1/2\langle 1\,1\,1\rangle$ (61 vacancies/interstitials) interstitial and vacancy dislocation loops. Here 'collapsed vacancy loop' is an alternative description of a vacancy dislocation loops.

In some of the *in situ* experiments is was possible to perform dynamic observations using a CCD camera connected to a video (DVD) recorder, which allowed recording of images during and immediately after irradiation. The motion of individual loops was observed in all materials, including FeCr alloys, although it was most pronounced in Ultra-High Purity (UHP) Fe. The motion consisted of sudden, discrete hops over distances of several nanometres or more, and occurred both during irradiation and afterwards under observation in the electron microscope and at both RT and 300 °C.

Fig. 3(a) shows an example of a loop in UHP Fe which moved one-dimensionally over the course of three image frames. This motion occurred under electron illumination alone with the specimen at 300 °C. The direction of hopping is parallel to the projection of the $1/2\langle 1\,1\,1\rangle$ Burgers vector. The time spacing between frames is approximately 34 ms and a clearly visible hop occurs between the first and second frames. From this observation, and many others like it, it is clear that many of the loops formed under irradiation are mobile. Whilst this does not confirm directly the MD results discussed above, because the nature of the hopping loops is uncertain, there is a significant probability that some of the mobile loops were vacancy in nature. In addition, we have also observed that in some cases the loops formed during ion irradiation were lost from the foil, as demonstrated by the sequence of images shown in Fig. 3(b), in which a loop disappeared over the course of three frames in UHP Fe in the same specimen as Fig. 3(a). These losses occurred both during and after irradiation, and may (but not necessarily) be caused by glide of the loop to the surface [1]. The timescale of loss was longer than in the atomistic simulations of migration to surfaces, but if escape to surfaces is the preferred

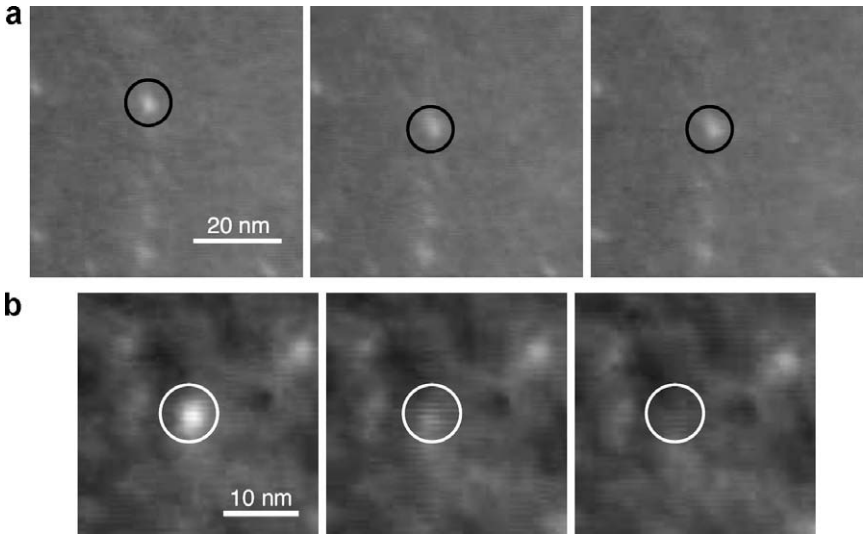

Fig. 3. Frames of video recording during dynamic observations of UHP Fe irradiated with 150 keV Fe^+ ions at 300 °C, showing (a) the 'hopping' of a loop under electron irradiation alone, and (b) the loss of a loop during ion irradiation. In each sequence the images are approximately 34 ms apart.

mechanism then it still appears to be a rapid process occurring in fractions of a second or less.

By analysing successive video frames of UHP Fe observations it was possible to measure the frequency and amplitude (to the nearest nanometre) of jumps for individual loops. The results from one such analysis are shown in Fig. 4. In this case the motion represents a $1/2\langle 1\,1\,1\rangle$ loop hopping backwards and forwards under electron illumination at 300 °C. In the figure the loop seems to occupy several discrete positions and performs jumps of several nanometres between them from one frame to the next, although it spends a large proportion of its time in the 'zero' position, possibly due to a particularly deep energy minimum at this position arising from local defects or impurities. Results shown in Fig. 4 are in good qualitative agreement with observations performed by Arakawa et al. [7].

We note that the motion of loops observed in experiments is much more discrete than the motion seen in the atomistic simulations (Fig. 1). Also, the experimental observations extend over much longer timescales. It is likely that the behaviour observed experimentally is related to the loop moving between pinning sites in the lattice, perhaps caused by impurities and solute atoms, with the motion in-between being so rapid that it does not register on the 34 ms frame-interval timescale of the video recording. Indeed, estimates from the atomistic simulations suggest that the loop velocity is of the order of 100 ms^{-1} or greater, indicating that a hop of around 4 nm would occur in 4×10^{-11} s (40 ps), and so it is reasonable to expect the hops to appear as instantaneous events in experiments.

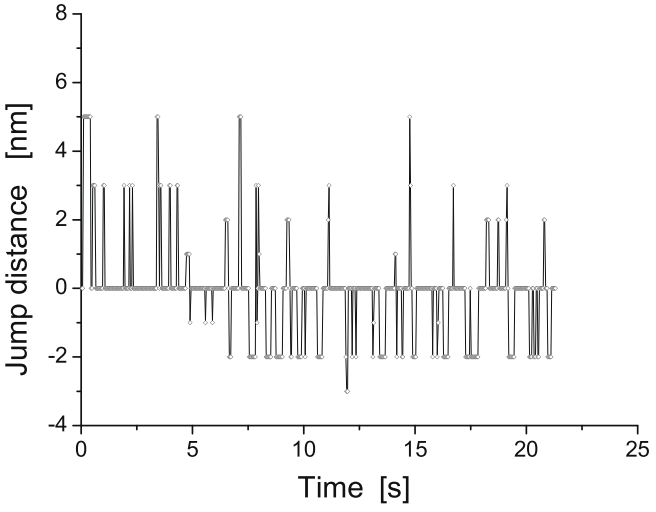

Fig. 4. One-dimensional hopping of $1/2\langle 1\,1\,1\rangle$ loops in UHP Fe under the electron microscope beam after ion irradiation.

3. Defect yield and size constraints

In self-ion irradiations of UHP Fe, the formation of dislocation loops was not observed until the dose was sufficiently high to produce significant cascade overlap in the foil. At this point, loops may be produced in regions containing sub-microscopic vacancy clusters from previous cascades [1]. These findings agree with previous studies, such as those of Robertson et al. [8], who also proposed that spatial overlap of the diffuse cascades induced by Fe^+ ions was required to produce loops. Meanwhile, in the Xe^+ irradiation experiments, the formation of loops was seen at lower doses, possibly because the heavier Xe^+ ions produce compact cascades, without break-up into sub-cascades. This may give rise to a sufficiently high local vacancy density to produce loops directly from the collapse of single cascades in some cases.

However, under irradiation with either ion, the loop yield was very low when compared to many other metals. In Cu, for example, the yield is close to unity, which implies that each incoming ion produces a visible loop – the process known as cascade collapse. To understand why it is so difficult to produce vacancy loops in Fe, we have performed extensive molecular statics simulations (the energy minimisation form of MD), to determine how the relaxed formation energies of different kinds of vacancy cluster vary with cluster size. Specifically, we have investigated collapsed vacancy dislocation loops and planar disc-voids (open loops or vacancy platelets) with both $1/2\langle 1\,1\,1\rangle$ and $\langle 0\,0\,1\rangle$ Burgers vectors, as well as spherical clusters of vacancies (spherical voids).

Fig. 5 shows how the energies of the five different types of cluster vary with size. The planar voids were created by removing a disc of atoms of a given diameter, whilst equivalent collapsed loops were created with the opposing faces of these same discs 'pushed' together. It can be seen from the plot that spherical voids are the most favourable configurations for vacancy clusters of any size, and that their stability relative to the other cluster types increases

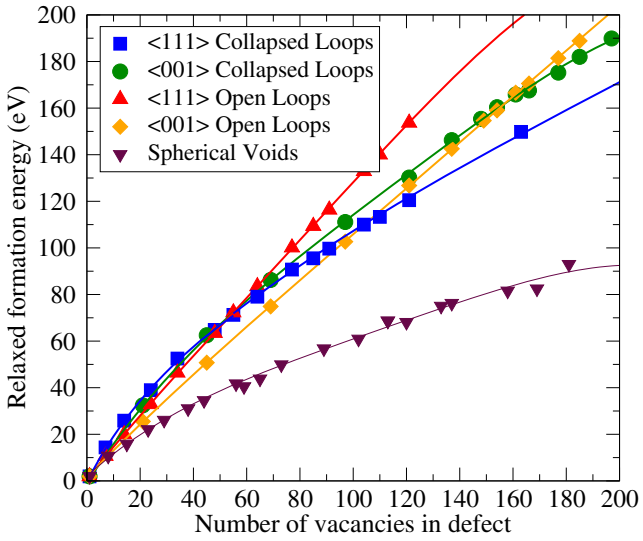

Fig. 5. Plot showing the variation in formation energy of vacancy defects of different type and orientation as a function of their size.

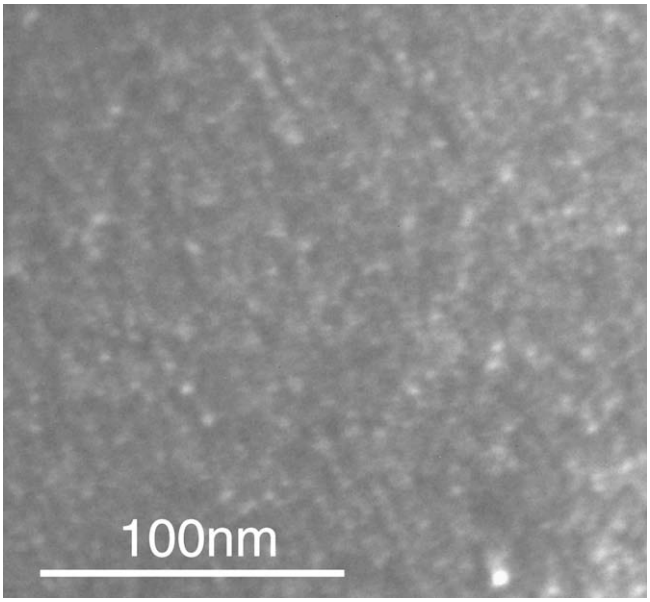

Fig. 6. Weak-beam dark field contrast image of Fe8%Cr irradiated with 150 keV Fe^+ ions at 300 °C to a dose of 10^{18} ions m^{-2}. The image is taken under somewhat unusual (2 g, 4 g) conditions with $\mathbf{g} = 1\bar{1}0$. Possible alignment of small voids is seen. The scale in the corner demonstrates that the defects shown are very small.

with size. It is therefore likely that stable voids rather than loops are formed in most cascades, which would explain why the visible loop yields are low in our experiments. Even if a loop does form, there is a good chance that it will transform into the more favourable spherical structure. This is particularly true for very small loops because, as Fig. 5 indicates, planar void configurations are then also more favourable than equivalent collapsed vacancy loops. Finite temperature MD simulations showed that very small collapsed loops have an easy transformation route to the ideal spherical structure via the planar void configuration (see [4]).

Only when clusters reach a critical size, which is roughly 2 nm in diameter for $1/2\langle 1\,1\,1\rangle$ loops (~52 vacancies) and 3 nm for $\langle 0\,0\,1\rangle$ loops (~150 vacancies), do planar voids become less favourable than collapsed loops. At this point, the straightforward collapsed loop → planar void → spherical void transformation pathway is removed. Collapsed vacancy loops then become metastable, and so may remain in the material for sufficiently long to be observed in experiments. Note here that large planar voids (vacancy platelets) remain stable during the energy minimisation because the separation of the opposing faces of the defect is larger than the range of the interatomic potential. In a more realistic simulation, it would be expected that planar voids above the critical size would collapse readily. However, this does not affect the conclusion that at small sizes collapsed loops are highly unstable because of the high elastic energies associated with their perimeters.

Very small spherical voids (<2 nm) are generally difficult to observe experimentally [5], and so it is difficult to find *direct* evidence to support the above conclusions derived from simulations. It is not clear if there is an abrupt size constraint on the dislocation loops produced in cascades since the 2–3 nm critical size regions are on the limit of experimental resolution. At the same time, it is difficult to determine the nature of such small loops, leading to the possibility of mistaking interstitial loops, which have no size constraint, for vacancy ones. However, we have been able to observe in experiments, where the resolution was particularly good, a 'sea' of tiny unidentified defects present at a much higher density than larger (>2 nm) loops. An example of one such experiment is shown in Fig. 6, which is a weak-beam image (taken under somewhat unusual diffraction conditions) of a small region of Fe8%Cr foil irradiated with 150 keV Fe^+ ions at 300 °C to a dose of 10^{18} ions m^{-2}. Defects appear as white dots, some of which may be interstitial loops, but some of which may be small voids. This is tentative evidence to support the view that small voids are the predominant defect produced in cascades, whereas under the right circumstances long-lived metastable vacancy dislocation loops can be formed. Further evidence for this view has been seen in the neutron irradiation experiments of Horiki et al. [9,10], where an observed reduction in interstitial clusters, under certain experimental conditions, was thought to be due to the production of a large number of small, and in their case invisible, vacancy clusters or voids.

More recently, Eldrup et al. [11,12] have been able to detect small (typically less than 1 nm in diameter) void defects produced in Fe (and Cu) using Positron Annihilation Spectroscopy (PAS). This technique is based on the concept of positrons, which can be injected into a material, becoming trapped in vacancy defects due to their reduced atomic, and hence electron density, compared to the bulk. When the positron finally annihilates with an electron the spectrum of the emitted gamma ray gives information about the defect that trapped the positron. Alternatively, the lifetime of the trapped positron (i.e., the time between trapping and annihilation), which varies according to the trapping defect, can also be measured. This is the method employed by Eldrup et al. In Fe, the small voids they detect are produced in large numbers (~10^{24} m^{-1} [12]) at relatively low doses, which is further evidence for the preferential formation of small voids over vacancy dislocation loops of the same size.

4. Summary

In thin-foil experiments in Fe dislocation loops formed under heavy-ion irradiation, of which a proportion are probably of vacancy type, were seen to be highly mobile and were often lost from the foil, probably by glide to the surface. MD simulations showed that vacancy loops diffuse through pure Fe at comparable rates to interstitial loops, which have traditionally been considered as significantly more mobile.

Atomistic simulations have indicated that a spherical cluster of vacancies is systematically more stable than a vacancy loop of equivalent size. This offers a possible explanation for the low loop

yields seen in the experiments: namely, that most vacancies form voids and that the right conditions for loop formation occur very infrequently. There is some evidence from experiment that small spherical clusters of vacancies are indeed formed in large numbers under irradiation in Fe.

Acknowledgements

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References

[1] Z. Yao, M. Hernández-Mayoral, M.L. Jenkins, M.A. Kirk, Philos. Mag. 88 (2008) 2851;
M. Hernández-Mayoral, Z. Yao, M.L. Jenkins, M.A. Kirk, Philos. Mag. 88 (2008) 2881.
[2] S.L. Dudarev, P.M. Derlet, J. Phys.: Condens. Matter 17 (2005) 7097.
[3] C.W. Allen, L.L. Funk, E.A. Ryan, Mater. Res. Soc. Symp. Proc. 396 (641) (1996).
[4] M.R. Gilbert, S.L. Dudarev, P.M. Derlet, D.G. Pettifor, J. Phys.: Condens. Matter 20 (2008) 345214.
[5] M.L. Jenkins, M.A. Kirk, Characterisation of Radiation Damage by Transmission Electron Microscopy (Series in Microscopy & Materials Science), Institute of Physics, 2001.
[6] A.F. Calder, D.J. Bacon, J. Nucl. Mater. 207 (1993) 25.
[7] K. Arakawa (2007), private communication, see also: K. Arakawa, M. Hatanaka, E. Kuramoto, K. Ono, H. Mori, Phys. Rev. Lett. 96 (2006) 125506;
K. Arakawa, K. Ono, M. Isshiki, K. Mimura, M. Uchikoshi, H. Mori, Science 318 (2007) 956.
[8] I.M. Robertson, M.A. Kirk, W.E. King, Scr. Metall. 18 (1984) 317.
[9] M. Horiki, T. Yoshiie, M. Iseki, M. Kiritani, J. Nucl. Mater. 271&272 (1999) 256.
[10] M. Horiki, T. Yoshiie, Q. Xu, M. Iseki, M. Kiritani, J. Nucl. Mater. 283–287 (2000) 282.
[11] M. Eldrup, B.N. Singh, S.J. Zinkle, T.S. Byun, K. Farrell, J. Nucl. Mater. 307–311 (2002) 912.
[12] M. Eldrup, B.N. Singh, J. Nucl. Mater. 323 (2003) 346.