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Section 12. Radiation effects. 1. Damage production and accumulation

Neutron energy spectrum and temperature effects on freely migrating defect concentrations and grain boundary segregation in α-Fe

R.G. Faulkner [a,*], D.J. Bacon [b], S. Song [a], P.E.J. Flewitt [c]

[a] *Institute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough, Leics LE11 3TU, UK*
[b] *Department of Materials Science and Engineering, Liverpool University, Liverpool L69 3BX, UK*
[c] *Magnox Electric, Berkeley Centre, Berkeley, Gloucestershire GL13 9PB, UK*

Abstract

Molecular dynamics (MD) calculations of cascades in α-Fe are used to predict the concentration of freely migrating defects. The single self-interstitial atoms (SIAs) are recognised to be important because they are more remote from the cascade and their migration energies are less than those of single vacancies. We are therefore able to estimate the enhanced concentration of freely migrating interstitial defects as a function of: (1) neutron energy spectrum, and (2) temperature. We compare our predictions with those obtained by diffusion experiments. The algorithms describing the temperature effect for a given neutron energy spectrum are incorporated in the models for radiation induced grain boundary segregation of P in α-Fe to produce an improved prediction of the temperature dependence of the segregation. Comments will be made on the implications of the new P segregation predictions for ferritic steels and on the importance of the low energy part of the neutron energy spectrum in determining freely migrating defect populations.

1. Introduction

Self-interstitial atoms (SIAs) and vacancies are formed in displacement cascades created by primary knock-on atoms (PKAs), which have a neutron energy distribution characteristic of a gas cooled reactor and position in the core.

At temperatures above that of stage I recovery (~50–100 K), SIAs are mobile (in the absence of strong traps at solutes) and it is assumed that a fraction escape their parent cascades as freely migrating defects (FMDs) and migrate to sinks or interact with defects from other cascades.

Those that do not escape from the parent cascades either recombine with vacancies (perhaps ~10–20% [1]) or form large, immobile, clusters. Some of these large clusters partially recombine with vacancies if they in turn are mobile and can migrate from their parent cascade region, i.e. at temperatures above stage III (~300–400 K).

Modelling the non-equilibrium processes such as neutron radiation-induced grain boundary segregation, which occur over long time periods can be done by Monte Carlo and other analytical methods. This paper indicates how the results of the molecular dynamics (MD) simulations, which only cover periods of picoseconds during the formation phase of the cascade, can help to predict effects such as segregation of solute or impurity atoms to grain boundaries, which occur over times of the order of years.

2. The model assumptions

Various *assumptions* are required to estimate the freely migrating defect fraction as follows.

(a) The interstitial freely migrating fraction is *independent* of the neutron irradiation temperature T for

* Corresponding author. Tel.: +44-1509 223 153; fax: +44-1509 223 949; e-mail: r.g.faulkner@lboro.ac.uk

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$T \geqslant 50$ K, i.e. the probability of a mobile interstitial defect escaping from the parent cascade is the same at all temperatures. This assumption is valid if the effect of a change in temperature is simply to increase or decrease the migration rate. It is supported by the recent Monte Carlo stochastic annealing simulation of high energy cascade damage in copper by Heinisch and Singh [1], which predicts that the fraction of interstitials that escape is ~0.4–0.5 for $T \geqslant 60$ K. However, similar simulations have not been performed for α-iron and it is possible that if the configuration of the mobile SIA changes with T, from the ⟨1 1 1⟩ crowdion at low T to the ⟨1 1 0⟩ dumbbell at high T, then the FMD fraction would be temperature dependent.

(b) For the transport of phosphorus solute atoms in α-iron to sinks such as grain boundaries via the interstitial migration process, we shall assume that only *single* SIAs couple with P atoms. Hence, we neglect the small cluster migration. If this assumption was not valid, a much more sophisticated model would be required.

On the basis of (a), we need to estimate only the number of single SIAs produced in cascades and the proportion that recombine. We assume that a fixed fraction of ≈80–90% give rise to the FMDs that couple with P solute atoms. Furthermore, since the FMD fraction is considered to be independent of temperature, *any temperature-dependence in the number of freely migrating single SIAs is due to the number created in the cascade at a given temperature*.

As a consequence, to estimate the number of single SIAs created in cascades as a function of neutron irradiation temperature, we can use the data from molecular dynamic computer simulations of cascade formation in α-iron reported in Refs. [2–5]. The simulations in Refs. [2,3] were based on the methodology and computer code used in Ref. [5], and cover a wide range of PKA energy, E_p, from 100 eV to 40 keV. Cascades for 20 and 40 keV have been studied only at a temperature of 100 K, but for cascades of up to 10 keV in energy, the temperature-dependence of defect production was investigated by choosing neutron irradiation temperatures of 100, 600 and 900 K. However, these simulations treated the MD cell as an adiabatic block, without heat extraction to balance the energy input due to E_p. Hence, the temperature of the MD cell at the end of a cascade simulation, i.e. after 5–10 ps, was typically 300–400 K higher than the specified temperature. The effect of this has been studied recently [4] using a new method to extract heat from the model cell during the lifetime of a cascade; the cell could then be imagined to be part of a much larger crystal. This has produced the most accurate data on the T-dependence of defect production to date, but was only carried out for E_p values of 2 and 5 keV. However, the new values enable us to test the reliability of the earlier data.

In using these data sets, we are mindful of the fact that no two cascades are the same in the number, size and distribution of defects produced, and that, as a consequence, many cascades should be simulated at each T and E_p condition to generate meaningful statistics. At least four cascades were created at each condition treated here, and in most cases many more were produced. This was sufficient to give reasonable predictions for the total number of Frenkel defect pairs, N_F, generated in a cascade, but still leaves considerable uncertainty in the number of defects of a given size, i.e. single and multiple SIA defects. This will be seen in the data presented below.

3. Results

The complete data set for the number, N_i^1, of *single* SIAs produced in displacement cascades in iron is plotted in Fig. 1. One observation inherent in these results is that there is no temperature dependence of N_i^1 in the energy range $E_p \leqslant 1.0$ keV. The large increase in N_i^1 as E_p increases from 20 to 40 keV is due to the onset of subcascade formation that Stoller [3] observes in his 40 keV simulations and there is a commensurate large increase in the total number, N_F, of Frenkel pairs.

The same data are plotted in terms of the variation of N_i^1 with E_p at each of the four temperatures 100, 400, 600 and 900 K in Fig. 2(a). Here, we label the energy axis as E_{dam}, the damage energy, rather than E_p, the PKA energy in the computer simulations. This is the energy used in the NRT estimate of defect production [6] and, since there are no inelastic energy losses in the MD simulations, we can take E_{dam} to be equal to E_p to a good approximation.

The energy spectrum for recoiling α-iron atoms in the fast neutron flux of a typical gas-cooled power reactor

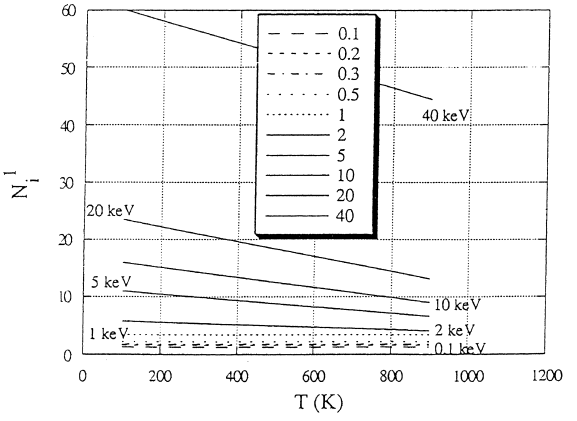

Fig. 1. Temperature dependence of single SIAs, N_i^1, formed as a function of $E_p = E_{dam}$ and absolute temperature.

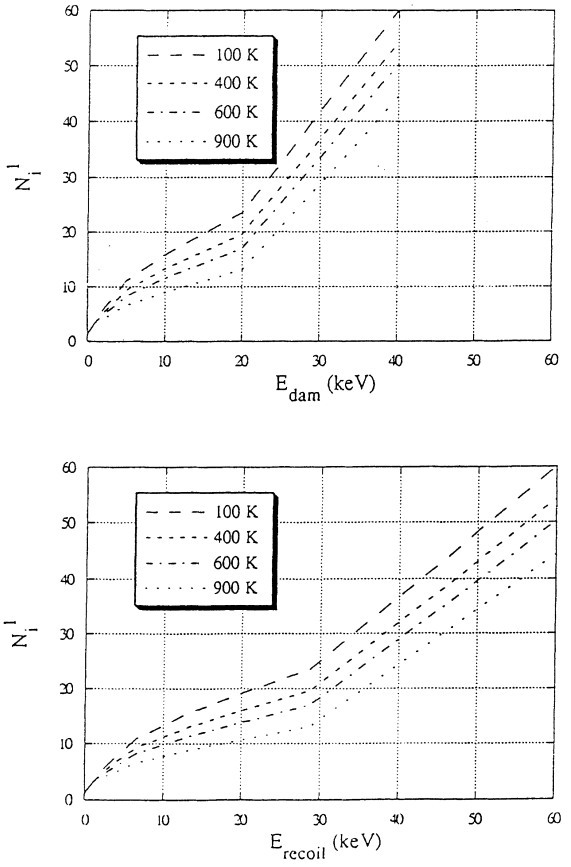

Fig. 2. (a) Number of freely migrating defects, single SIAs, N_i^1, formed as a function of $E_p = E_{dam}$ at different temperatures. (b) Number of freely migrating defects, single SIAs, N_i^1, formed as a function of recoil energy, E_{recoil}, as defined by the relation with E_{dam} in Fig. 4, at different temperatures.

reproduced in Fig. 3 is defined in terms of the recoil energy, E_{recoil}, which is larger than E_{dam} because of the inelastic losses suffered by a recoil in a metal. The empirical relationship between these two energies [6] for α-iron is plotted in Fig. 4. Using these data, the N_i^1 values in Fig. 2(a) can be re-expressed in terms of E_{recoil}, as shown in Fig. 2(b).

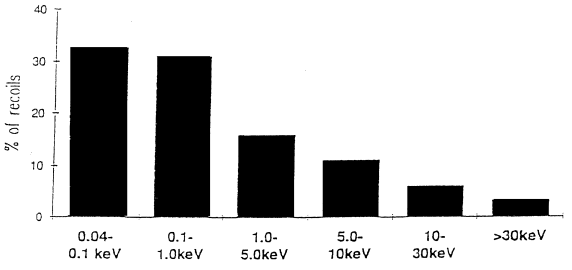

Fig. 3. Recoil energy spectrum for a typical gas cooled fission reactor system.

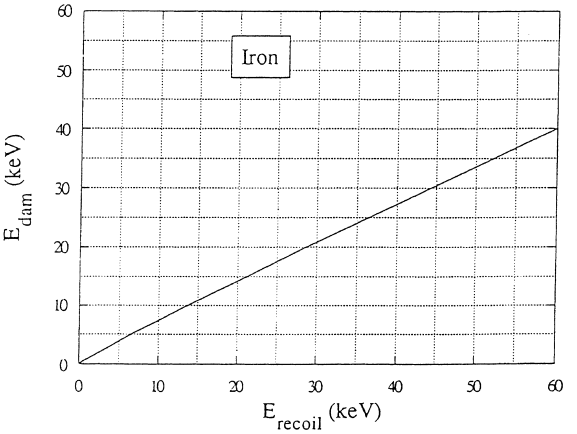

Fig. 4. Relationship between E_{dam} and E_{recoil}, which allows for inelastic losses in a real metal not considered in the MD simulation.

In order to estimate the total number of single interstitial atoms produced on the average by a recoil in the spectrum of Fig. 3, we note that the percentage population of recoils in the six bins of the histogram are 32.6%, 31.0%, 15.9%, 11.1%, 6.1% and 3.3%, respectively. This means that two thirds of the recoils fall in the energy range where the MD simulations suggest there is no temperature-dependence of N_i^1. This is demonstrated with greater clarity in Fig. 5, where the N_i^1 values from Fig. 2(b) are plotted as a function of the percentage of recoils occurring in each bin in Fig. 3. The bin boundaries are indicated by the E_{recoil} values at the top of the figure.

The average value, $\tilde{N}_i^1$, of the total number of single SIAs generated by a recoil with energy greater than 40 eV in the spectrum shown in Fig. 3 is simply the area

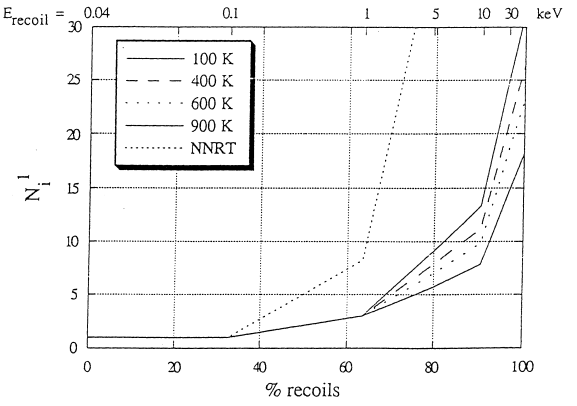

Fig. 5. Number of single SIAs, N_i^1, created at different temperatures as a percentage of the recoils in the various energy ranges defined by a typical gas cooled fission reactor neutron energy spectrum defined in Fig. 3.

under one of the plots in Fig. 5. It is given in the following:

T (K)	100	400	600	900
$\tilde{N}_i^1$	5.22	4.61	4.21	3.59
$\tilde{N}_i^1/\tilde{N}_{\mathrm{NRT}}$	0.183	0.161	0.147	0.126

Thus, our analysis predicts a reduction of about 30% in $\tilde{N}_i^1$ as the temperature increases from 100 to 900 K. The number given should be reduced by 10–20% based on the assumption about intracascade losses described in Section 2.

The area under the temperature-independent part of the N_i^1 plot in Fig. 5, i.e. that up to 63.6% of the recoils, is 0.95 and so the model used here predicts that 20–25% of the single interstitial atoms are produced by low-energy recoils for which temperature has no effect on the production efficiency.

The value, N_{NRT}, for the total number of SIAs, or vacancies, predicted by the binary collision model in Ref. [6] is also plotted in Fig. 5. It is simply $10E_{\mathrm{dam}}$ for α-iron when energy is in keV. The average, $\tilde{N}_{\mathrm{NRT}}$, for each recoil in the spectrum is 28.6, and so the ratio $\tilde{N}_i^1/\tilde{N}_{\mathrm{NRT}}$ for the spectrum considered decreases from about 18% to 12% over the temperature range, as indicated in the table above. Even if we assume that only 80–90% of the single SIAs escape from their initial parent cascades, this ratio is larger than the FMD fraction estimated from high voltage self-ion irradiation-enhanced diffusion measurements in copper and nickel by Naundorf et al. [7]. These workers estimate FMD concentrations of around 1.5% and the conclusions of the work suggest that vacancies and interstitials are produced in roughly equal quantities in these materials. Hence there can be no explanation for the difference between our work and that of Naundorf on the basis of vacancy domination in the experimental diffusion measurements and the reasons for the difference are therefore still not clear. Naundorf et al. [7] also determined the FMD fraction as a function of temperature and found no dependence. Since 300 kV self-ions were used in their work it is expected that the FMD fraction will be temperature-independent because presumably a sufficient number of recoil energies will be in the low energy range of the PKA spectrum, precisely where we have found temperature-independent FMD fraction behaviour.

Figs. 6–8 indicate the effect on the predicted segregation of P to grain boundaries in α-Fe as a result of neutron irradiation over a range of temperature, incorporating the above results concerning the freely migrating defect (FMD) fraction. Here the revised predictions are compared with those using the model described by Faulkner et al. [8]. The calculation of P

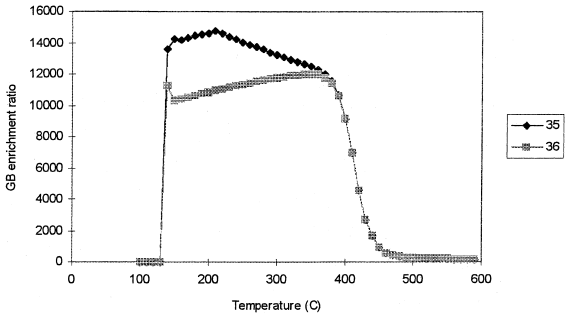

Fig. 6. Phosphorus grain boundary segregation, cb/cg, in α-Fe as a function of temperature showing the effect of including radiation enhanced diffusion and recombination into the non-equilibrium segregation model (curve 36) compared with the unmodified model (curve 35).

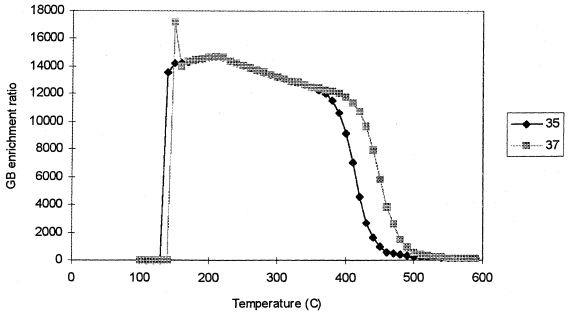

Fig. 7. Phosphorus grain boundary segregation, cb/cg, in α-Fe as a function of temperature showing the effect of including the temperature dependent FMD fraction for a typical gas cooled fission reactor neutron energy spectrum in the non-equilibrium segregation model (curve 37) compared with the unmodified model (curve 35).

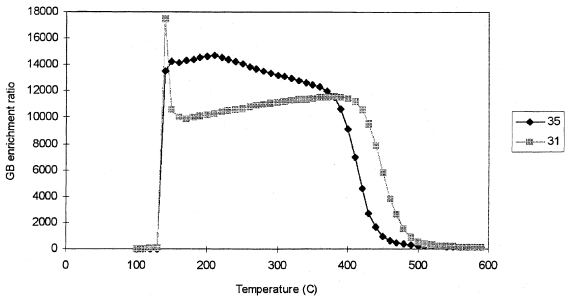

Fig. 8. Phosphorus grain boundary segregation, cb/cg, in α-Fe as a function of temperature showing the effect of including radiation enhanced diffusion, recombination and temperature dependent FMD fraction for a typical gas cooled fission reactor neutron energy spectrum into the non-equilibrium segregation model (curve 31) compared with the unmodified model (curve 35).

segregation to grain boundaries is calculated assuming the dose is 1 dpa; dose rate is 1×10^{-8} dpa s^{-1}; grain size is 10 μm; interstitial pre-exponential diffusion term is 5×10^{-6} m^2 s^{-1}; fixed FMD fraction is 1%; vacancy formation energy is 1.4 eV; and the pre-exponential vacancy concentration term is 1.0. It is assumed in this modification that there are no intra-cascade losses and so the data are taken directly from the table. Fig. 6 shows the effect of introducing recombination and neutron radiation enhanced diffusion (curve 36) to the latest published version of the model [8]. Fig. 7 shows the effect of simply incorporating the variable FMD fraction (curve 37), which follows an algorithm calculated using the data in the table, where the freely migrating defect fraction is given by

$$\text{FMD fraction} = -7 \times 10^{-5}\, T + 0.1898,$$

where T is the temperature in K. Fig. 8 shows the effect of introducing the recombination, neutron irradiation-enhanced diffusion and variable FMD fraction to the model (curve 31). This represents the best prediction of P segregation that we can currently make on the basis of recent model revisions and the above results concerning FMD fraction.

4. Discussion

This study has used simplifying assumptions and as a result has exposed several key issues in current understanding of defect production and damage evolution in metals exposed to a neutron flux.

Firstly, we have assumed that the number of self-interstitial atoms that can escape from their parent cascades is a fixed fraction of the total number created in the cascade process, independent of temperature. However in order to assess the validity of this it will be necessary to undertake computer simulations that model the long-term behaviour of defects produced in cascades over a wide range of energy and temperature values. A start in this direction has been established by the recent Monte Carlo calculations on copper of Heinisch and Singh [1], however there is a need to address the bcc structure specifically and α-iron would be an ideal material for investigating this.

Secondly, and as a corollary of the first assumption, we have considered that the temperature-dependence of the FMD fraction arises solely from the temperature-dependence of the number and configuration of the defects created during the lifetime of the displacement cascade process. Fortunately, the most extensive MD data on this for any metal are that generated at Liverpool (e.g., Calder and Bacon [5]) or by Stoller [3], using the Liverpool code for α-iron, and this has been used here. Nevertheless, it is clear that even with the large data set available, the trends in N_i^1 with T and E_p are not easy to discern with accuracy, and this must lead to corresponding uncertainty in the final values of $\tilde{N}_i^1$ calculated for the fission reactor spectrum employed. No attempt has been made to assess this at the present time, but it is clear that more extensive MD modelling over a wider range of energy is required using the new model reported in Ref. [4]. We have simply used what appears to be a reasonable fit to the MD data by assuming that N_i^1 is independent of T for $E_p \leqslant 1$ keV and has a linear dependence on T for $E_p \geqslant 2$ keV. Again, more MD modelling would be required to check the accuracy of this.

Thirdly, we have considered the number of single interstitial atoms, thereby assuming that these are the only defects that assist the transport of phosphorus solute atoms to grain boundaries. This gives rise, in part, to the uncertainties referred to in the preceding paragraph, because although the MD data are probably reasonable for the total number, N_F, of defects in a cascade, a larger set would be required to provide more confidence in the number of defects of a specified size. Furthermore, it may well be that small clusters of defects, which are also mobile in MD simulations, can couple with solutes. Assessment of this aspect requires atomic-scale computer simulation of the interaction of intrinsic point defects with solute atoms, which in turn requires the development of physically reasonable interatomic potentials and stochastic annealing (Monte Carlo) computer simulations of models containing both cascade damage and solute atoms.

Fourthly, it is clear from the grain boundary segregation models that recombination and neutron radiation-enhanced diffusion affect the P GB segregation results only slightly (Fig. 6), with a slight increase in segregation at lower temperatures between 423 and 623 K. The effects of the variable FMD fraction as predicted from the MD simulations for a typical gas cooled fission reactor neutron energy spectrum indicate a large extension of the neutron radiation induced segregation range by about 50° (Figs. 7 and 8) at temperatures above 400°C.

Finally, the results of the modelling show a considerable effect of FMD fraction on neutron radiation induced segregation and indicate that MD cascade simulation can be a valuable tool in helping to address the understanding of defect concentration for subsequent stochastic annealing modelling of solids at times beyond the few picoseconds that cascade simulations encompass.

5. Conclusions

We have shown that by modelling cascades in α-Fe, it is possible to make reasonable estimates of freely migrating SIA fraction of the NRT dpa dose value as a function of temperature and neutron energy spectrum. This has made possible a revised model for P segregation

to grain boundaries in ferritic alloys and steels. The report also highlights the importance of the temperature and energy dependence of the FMD fraction obtained from the MD simulation and also indicates that more modelling should be done to explore the influence of multiple defects on the segregation transport mechanism.

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References

[1] H.L. Heinisch, B.N. Singh, J. Nucl. Mater. 232 (1996) 206.
[2] W.J. Phythian, R.E. Stoller, A.J.E. Foreman, A.F. Calder, D.J. Bacon, J. Nucl. Mater. 223 (1995) 245.
[3] R.E. Stoller, Proc. MRS Fall Conference 1996, in press.
[4] F. Gao, D.J. Bacon, P.E.J. Flewitt, T.A. Lewis, J. Nucl. Mater. 249 (1997) 77.
[5] A.F. Calder, D.J. Bacon, J. Nucl. Mater. 207 (1993) 25.
[6] M.J. Norgett, M.T. Robinson, I.M. Torrens, Nucl. Eng. Des. 33 (1975) 50; Annual Book of ASTM Standards, vol. 12.02, Am. Soc. Test. Mater., Philadelphia, 1994.
[7] V. Naundorf, M.-P. Macht, H. Wollenberger, J. Nucl. Mater. 186 (1992) 227.
[8] R.G. Faulkner, S. Song, P.E.J. Flewitt, Mat. Trans. A 27A (1996) 3381.