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Radiation-induced grain boundary segregation in nuclear reactor steels

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Abstract

The paper will review the various mechanisms of grain boundary segregation. These are: thermal equilibrium segregation (TES); neutron irradiation enhanced equilibrium segregation; thermal non-equilibrium segregation; and radiation-induced segregation (RIS). The neutron irradiation-induced mechanisms will be discussed in detail. Modelling of the neutron irradiation segregation effects will be outlined with reference to two approaches: non-equilibrium theory based models and rate theory models. Both models have been successful in predicting phosphorus grain boundary segregation in pressure vessel steels as a function of irradiation conditions and examples of this success will be given in the paper. In addition the models have recently been adapted to account for the behaviour of Cr in austenitic steels with a view to understanding irradiation-assisted intergranular stress corrosion (IASCC). The use of predictive modelling of this kind in forecasting the embrittled state of grain boundaries as a function of reactor operating conditions will be emphasised. The influences of neutron dose, dose rate, temperature and microstructure will be mentioned. © 1997 Elsevier Science B.V.

1. Introduction

Radiation-induced segregation (RIS) to grain boundaries in steels is receiving increasing attention because of low dose rate reactor pressure vessel embrittlement and IASCC in austenitic steel reactor core components. Both of these phenomena are explained on the basis of grain boundary segregation: P in the pressure vessel situation; and Cr in the IASCC problem. This paper outlines various attempts to model the segregation process and highlights selected experimental observations of RIS. The paper concludes with some examples of modelling/experimental approaches to the specific cases of P in ferritic steels and Cr in austenitic steels.

2. Modelling of radiation-induced grain boundary segregation

2.1. Non-equilibrium segregation (NES)-based models

Radiation-induced segregation (RIS) arises because of point defect excesses being created around sinks like grain boundaries by the neutron damage process. The grain boundary acts as a perfect sink and so the thermal equilibrium concentration is maintained in these regions of the microstructure. The point defect excesses are entirely analogous to those produced during quenching, except that vacancies are the major point defect contributing to the quenching situation. The subsequent diffusion of point defects and associated complexed impurities down the concentration gradients created by the neutron irradiation can be quantified by similar methods to those for thermally induced non-equilibrium segregation (NES) [1,2]. The major difference with RIS is the involvement of interstitials

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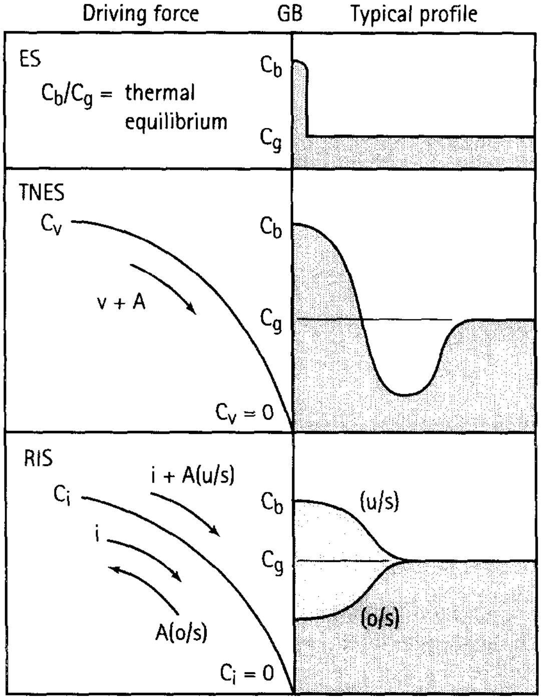

Fig. 1. Summary of equilibrium segregation (ES), thermal non-equilibrium segregation (TNES) and radiation-induced segregation (RIS).

as well as vacancies. There appears to be stronger binding of impurities with interstitials than with vacancies and so interstitial–impurity complexes feature more strongly in RIS theory. Fig. 1 shows the concentration distributions of vacancies (v), interstitials (i) and impurity atoms (A) expected for equilibrium Gibbsean segregation (ES), NES and RIS.

A key feature of the RIS theory is the requirement of a knowledge of the point defect–impurity atom binding energy. The reasons for this are twofold. In the first place this quantity determines the proportion of complexed to freely migrating impurities, and thus the absolute magnitude of the impurity segregation on the boundary plane. This is because it is the complexed impurities that are accumulated on the boundary plane during the segregation process. In the second place the binding energy is very important in determining the diffusion coefficient of the complexes as they move from the supersaturated regions to the grain boundary plane. Fig. 2 shows some recent results of Faulkner [3] for binding energies calculated for steel matrices. As can be seen from Fig. 2, the binding energy is somewhat different for interstitials compared to vacancies. As a rule, vacancy–impurity complexes form when there is any misfit, whether it be positive (o/s) or negative (u/s). This is not so for interstitial–impurity complexes: strong binding only occurs with negative misfits, i.e., when the impurity atom is smaller than the matrix atom (undersize – u/s). Negative NES can occur for cases of positive misfit and when this happens the process is called radiation-induced depletion (RID). There are some exceptions to this rule, e.g., Ni–Ge, but this objection seems to be overcome by redefining the misfit term in this case [4]. This subject has received detailed attention for interstitial complexes from Dederichs et al. [5] and Robrock [6], Ehrhart et al. [7] and Faulkner et al. [8].

The Faulkner calculations are based purely on strain energy arguments: no electronic contribution is included.

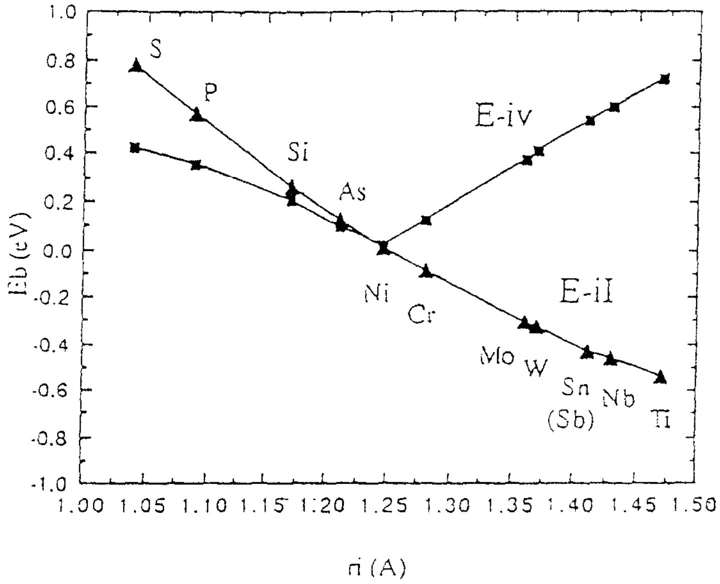

Fig. 2. Impurity-point defect binding energies as a function of impurity atom radius in a ferritic steel matrix.

Table 1
Vacancy–solute complex binding energies (in eV): comparison of data

Element	In Ni				In Cu		
	Ref. [3]	Ref. [9]	Ref. [10]	exp. [11,12]	Ref. [3]	Ref. [9]	exp. [9,13–16]
Si	0.19		0.73	0.18 (11)	0.26		
Ge	0.073	0.35	0.55	0.2(11), 0.2 (12)	0.15	0.28	0.23, 0.27, 0.18
Zn	0.25	0.14			0.14	0.10	0.07, 0.05

There are similar calculations made based on interatomic potential models but these do not seem to produce any more accurate values than the strain energy calculation, at least for the case of transition metals. Experimental, interatomic potential and strain based calculated values for various impurities in nickel and copper matrices are given in Table 1 [3]. Another factor which controls the magnitude of RIS is the relative diffusion rate of the complexed and free impurities in the matrix, with additional factors built in for radiation enhanced diffusion.

The NES modelling approach is easily extended to point defect–impurity complex driven non-equilibrium segregation caused during irradiation of dilute alloys and a series of equations has been developed by Faulkner [17,18] to quantify the process. Modelling is performed by solely monitoring the diffusion of point defect–solute complexes near to grain boundaries during neutron irradiation. Major variables in the model are the diffusion coefficients for impurities and interstitial–impurity complexes, microstructural parameters, neutron dose, dose rate, interstitial formation and binding energy with the impurity, and temperature.

2.2. Rate theory-based models

Rate theory approaches have been applied to the problem of modelling RIS in both dilute and concentrated alloys with some success (Johnson and Lam [19], Simonen et al. [20] and Druce et al. [21]). The fluxes of all atomic species are defined by a series of partial differential diffusion equations which are solved simultaneously to yield the elemental distribution. The modelling approach has commonly assumed the title of inverse Kirkendall effect modelling, because of the similarities of the process with that of the Kirkendall effect. In this case point defect concentration gradients create unequal fluxes of solute atoms: in the Kirkendall effect case, unequal flows of solute atoms create point defect concentration gradients. Normally Kirkendall effect models assume the point defects to be vacancies. It should be stressed that in the irradiation case the point defects of interest are interstitials and so strictly the term inverse Kirkendall effect cannot be applied to the irradiation case. The diffusion coefficients used in the solutions are dependent upon the interaction with other elements present in the system, so-called site

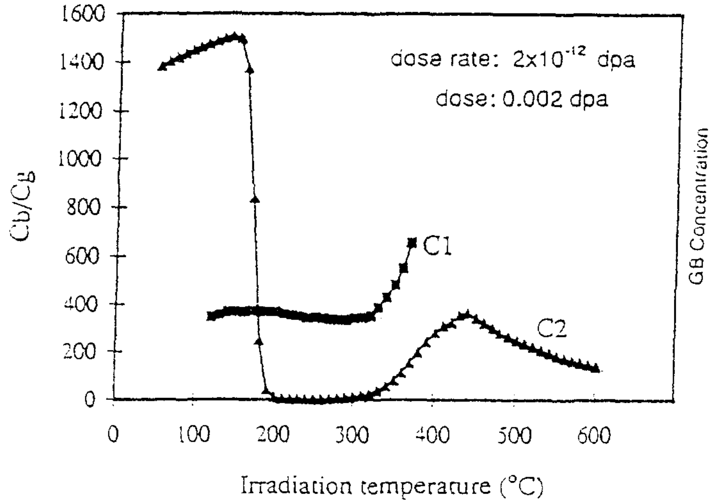

Fig. 3. Temperature dependences of phosphorus grain boundary segregation in neutron irradiated ferritic steels: curve C1 after rate theory (Druce et al. [21]); curve C2 from NES theory (Faulkner et al. [18]). Dislocation density 10^{18} m^{-2}; grain size = 1 μm.

competition effects. A revised approach to the problem, specifically allowing for concentrated alloy matrix effects has been proposed by Grandjean et al. [22].

2.3. *Comparison of NES and rate theory models*

An example of the rate theory as opposed to the NES theory predictions is given in Fig. 3 for P grain boundary segregation in a ferritic steel matrix. These results are taken from the work of Faulkner et al. [18] and Druce et al. [21], and are for very high dislocation densities. In all of these cases the NES model seems to give more 'peaky' predictions of segregation as a function of temperature than the rate theory or, as will be shown in a later section, from experimental results. This may be due to experimental measurements not having sufficient resolution to detect the true composition on the grain boundary. Alternatively the rate theory approach may be more general but it should be stressed that currently it does not fully account for microstructural effects such as grain size, or dislocation density in the same way as does NES modelling. However it should be noted that NES theory is a form of rate theory where we are considering the point defects' motion in relation to one atomic species at a time, without regard to the interdiffusion effects with other species present. We maintain that for dilute alloys this approach is reasonably valid. Clearly rate theory is rigourously more correct but there are so many interaction coefficients involved, which are difficult to find in the literature, that practically the NES method leads to equally accurate predictions. It also has the advantage that it uses simple analytical equations which can indicate directly how various reactor operating conditions will alter segregation of elements of interest to the reactor materials engineer.

3. Experimental studies of radiation-induced grain boundary segregation

The original ideas of RIS were developed by Johnson and Lam [19] and by Okamoto and Wiedersich [23]. These workers supported their theoretical models with observations of RIS to free surfaces in Zn–Ag and stainless steels respectively. Other evidence for surface segregation is available from the work of Harries and Marwick [24], Rehn and Okamoto [25], and Druce et al. [21]. RIS to internal interfaces such as grain boundaries is more difficult to monitor but progress has been made using Auger electron spectroscopy (AES) and field emission gun scanning transmission electron microscopy (FEGSTEM) methods by Nandenkar and Kesternich [26], Mahon et al. [27], Norris et al. [28], Clausing et al. [29], and Kenik [30]. Kenik's work and independent studies by Shepherd [31] are some of the most spectacular in that they have detected segregation to line defects occurring by the NES mechanism. Atom probe field ion microscopy methods have also studied the effect with some success [32].

4. Applications of NES modelling

4.1. *Phosphorus grain boundary segregation in pressure vessel steels*

Fig. 4 shows the predicted dose and temperature dependence of P GB segregation in a ferritic pressure vessel steel. The data used and analytical approach can be found in Ref. [18]. There are two peaks in the temperature profile at any given dose rate. The higher temperature peak is due to equilibrium segregation. This dies away at high temper-

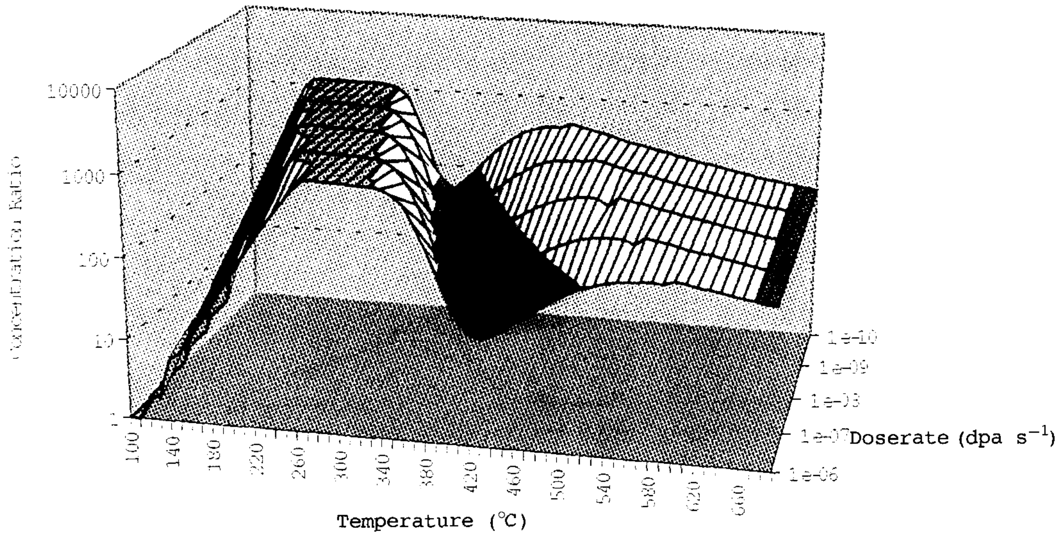

Fig. 4. Predictions of NES RIS for P in ferritic steel as a function of irradiation temperature and dose rate (dose = 0.25 dpa).

Table 2
Comparison of theoretical and experimental predictions of GB phosphorus radiation-induced segregation

Material	Irradiation temp. (°C)	Bulk P content (wt%)	Irradiation condition	Observed value (at.%)	Predicted value (at.%)
1	198	0.039	$\sim 2 \times 10^{-12}$ dpa/s, 9.4×10^{-4} dpa	20	22
1	260	0.039	$\sim 2 \times 10^{-9}$ dpa/s, 9.2×10^{-3} dpa	37	35
2[a]	292	0.040	$\sim 2 \times 10^{-9}$ dpa/s, 9.5×10^{-3} dpa	42	38

Dislocation density constant; $\rho_0 = 5.5 \times 10^{12}$ m^{-2} for material 1 and 3.0×10^{15} m^{-2} for material 2; grain size: $R = 20$ μm.
[a] AES results; all the others obtained by FEGSTEM.

atures because the thermal motion in the lattice makes it less energetically favourable for misfitting impurity atoms to sit on the disordered grain boundary. In other words there is increasing solubility in the lattice due to increasing entropy at higher temperatures. At low temperatures the diffusion kinetics limit the amount of segregation possible. The lower temperature peak is due to a mixture of NES and radiation enhanced diffusion-based ES. The NES low temperature cut-off is due to restricted diffusion at these temperatures. The high temperature cut-off is caused by the thermal equilibrium concentrations of point defects present on the grain boundaries becoming equal to the concentrations being produced by the neutron irradiation, thus removing the driving force for the process. Fig. 4 expresses the situation for a dose of 0.25 dpa. The limited experimental data available confirm the validity of the NES-based model. Table 2 shows the comparison between predictions and AES and FEGSTEM observations of P segregation in C–Mn pressure vessel steels. Fig. 5 shows the predicted temperature dependence for P in a 2.25Cr1Mo steel. At present we have one data point at 280°C which indicates very little segregation. This is at the bottom of the trough between the NES and ES peaks for this steel. Other data from FBR irradiations at much higher temperatures (465°C) and higher doses (46 dpa) indicate P enrichments of about 50 [33].

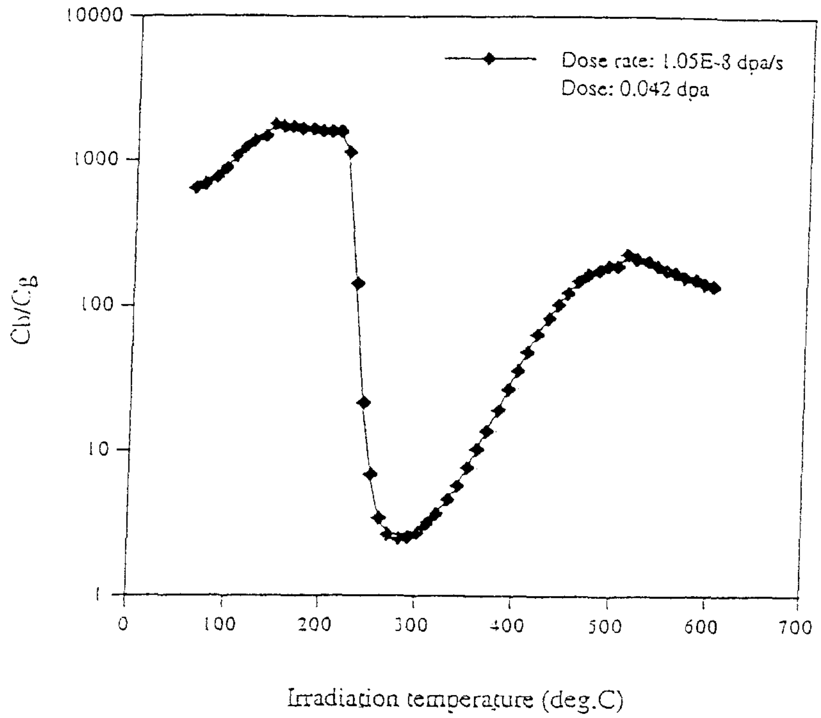

Fig. 5. Predicted temperature dependence of phosphorus segregation in the irradiated α-Fe for neutron dose rate = 1.05×10^{-8} dpa/s and neutron dose = 0.042 dpa ($B = 0.01$, $\varepsilon = 0.1$, $R = 1$ μm, $\rho_0 = 5 \times 10^{18}$ m^{-2}).

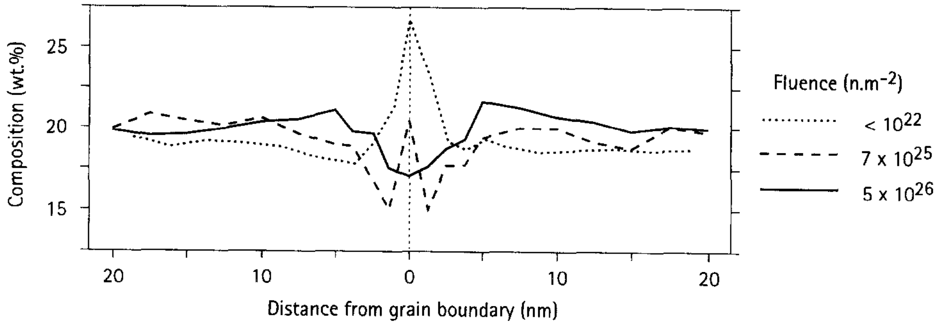

Fig. 6. FESTEM-EDS Cr GB concentration profiles in 304 austenitic steel, indicating the transition between TNES and RIS.

4.2. Chromium radiation-induced depletion in austenitic steels

Most of the experimental data on Cr behaviour near to grain boundaries in austenitic alloys is confused by the situation which very often exists as a result of prior processing. Thermal annealing, solution heat treatments and post weld heat treatment can leave the grain boundary enriched in Cr. The mechanism responsible for this is thermal non-equilibrium segregation (TNES). This process has been well-documented [1,2] and is caused by non-equilibrium supersaturations of vacancies created during cooling from high temperatures. Vacancy–impurity complexes are formed and they diffuse towards the boundary down the vacancy concentration gradient created by the non-equilibrium cooling process. Since there is always a positive binding between vacancies and impurities, irrespective of misfit (Fig. 2), the impurity is always attracted towards the boundary by this mechanism. Thus segregation of impurities always occurs. An example of this can be seen in Fig. 6 [34]. If a steel in this state is subsequently neutron irradiated, then the Cr will be driven away from the boundary. This is because RIS is an interstitial driven mechanism and a figure similar to Fig. 2 shows that Cr in austenitic steel has a positive misfit and that there is therefore a negative binding between the interstitials and the Cr atoms. Thus Cr depletion or RID occurs. Fig. 6 confirms this by showing that a W shaped profile develops during irradiation as the RID mechanism removes the enriched layer of Cr created by the prior heat treatment.

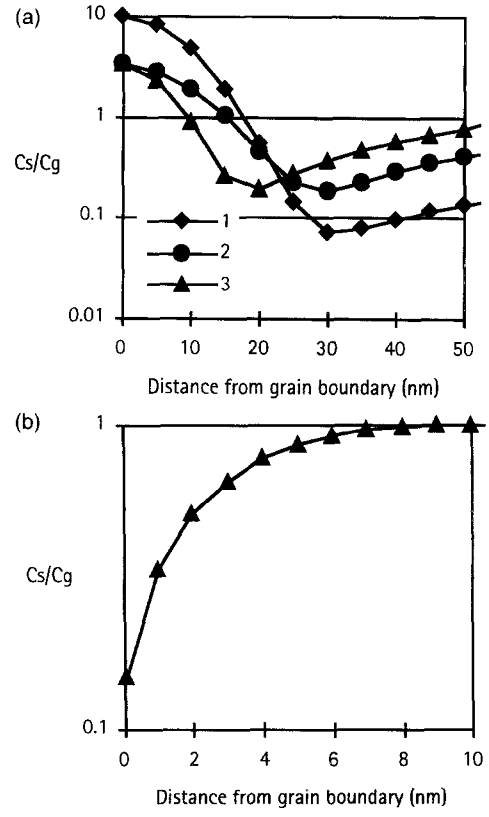

Fig. 7. Predicted GB Cr concentration profiles in austenitic steel resulting from RIS (a) and TNES (b).

Modelling of this has been completed by Goodwin et al. [35] and the results are presented separately for TNES and RID in Fig. 7. The curve on the right indicates the TNES profiles predicted for a variety of starting temperatures and cooling rates. The left-hand picture indicates the RID effect.

Rate theory has also been applied successfully to model the effect in austenitic steels by Simonen et al. [36]. They conclude that modelling of the effect can be successfully accomplished by altering the Ni to Cr diffusion coefficient ratios. This work was substantiated by experimental FEG-STEM studies [36,37] with similar results to those shown in Fig. 6.

5. Conclusions

Neutron irradiation induced grain boundary segregation mechanisms have been discussed. It is shown that the phenomenon can be modelled by non-equilibrium-based theories using the idea of complexed impurity atom-point defect entities being dragged to the boundaries by the non-equilibrium conditions prevailing during irradiation (NES model), or by the rate theory model. Both models are shown to make similar predictions, although the rate theory does not take microstructual variations so fully into account.

The NES complex models are applied to the neutron irradiation-induced problems of P grain boundary segregation in pressure vessel steels and chromium depletion in austenitic steels. Reasonable fits between modelling predictions and experimental results are found.

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