JOURNAL OF MATERIALS SCIENCE 25 (1990) 649-653

A new computer model of grain boundary segregation

N. C. WAITE, R. G. FAULKNER
Institute of Polymer Technology and Materials Engineering, University of Technology, Loughborough, Leicestershire LE11 3TU, UK

Improvements have been made to an earlier model of grain boundary segregation. The new model includes an influx of vacancies into the region of the material considered by the model, and accounts for the effect of a grain boundary on defect-binding energies. The model predictions for boron segregation in steel are compared with the original model.

1. Introduction

The grain boundary segregation of impurity atoms in an alloy is thought to occur by two main mechanisms, equilibrium [1] and non-equilibrium segregation [2, 3]. The driving force of equilibrium segregation is the reduction in free energy which occurs when an impurity atom moves into the disordered regions which surround grain boundaries, free surfaces, dislocations and stacking faults. In non-equilibrium segregation the rate of movement of impurity atoms towards a sink is enchanced by a flux of vacancies towards that sink. This will lead to a higher than equilibrium value of the impurity concentration at the sink, which will continue until either the vacancy flux or the impurity flux becomes depleted. At this stage the concentration gradient of impurity atoms will cause the impurities to diffuse away from the grain boundary.

The combined effects of equilibrium and non-equilibrium segregation mean that the amount of segregation taking place during a quenching operation depends not only on the temperature range of the quench, but also on the cooling rate applied. For any starting temperature there exists a critical cooling rate at which maximum segregation can take place, but desegregation is halted by the reduction in diffusion rates during cooling. This critical rate of cooling has been modelled [4, 5] using diffusion-rate equations. This model gives an equivalent isothermal heat-treatment time for the critical cooling rate from any temperature: this time is known as the critical time t_c. For the segregation of boron in steel, the critical time for the quench start temperature 1320 K is 3.6 msec [4].

One of the main difficulties in predicting the amount of segregation which occurs under a given heat treatment is the need to estimate the relative contributions of equilbrium and non-equilbrium segregation. Attempts have been made [5] to combine the two mechanisms into one theory, but this work is still in its early stages.

Another approach to the prediction of the amount of segregation is the computer model proposed by Chapman and Faulkner [6]. This model attempts to simulate impurity atom segregation by considering the interactions that take place between impurity atoms, lattice vacancies and the grain boundary. These interaction energies are calculated from the binding energies of the various defects. The computer model assumes that the interaction energy between two defects is equal to the binding energy of those defects divided by the square of their separation.

Each defect is given a mean kinetic energy, due to vibration, of 3 kT. The direction of this vibration is chosen at random. The factors affecting whether or not the defect can diffuse in the chosen direction are: (i) the kinetic energy of the defect; (ii) the migration energy required for diffusion; and (iii) the change in the total interaction energy of the defect during the diffusion jump. Assuming a Boltzmann distribution of kinetic energies, the probability of a defect making a particular jump can be calculated. This probability is multiplied by an acceleration factor, F, to reduce the computation time. During each cycle of the model each defect is considered in turn. A probability is calculated, as described above, and is compared to a random number. If the random number is less than the probability values then the defect is moved to its new position. If a vacancy reaches the grain boundary in the model then it is annihilated. Each cycle of the program models $F \times 10^{-13}$ seconds of real time.

2. Modelling

The computer model discussed above had several faults, amongst which were:

(i) After about 5000 cycles, most of the vacancies had migrated to the grain boundary and been annihilated there. This meant that there was no vacancy flux to encourage impurity atom segregation. Tank [7] attempted to overcome this by introducing vacancies into the matrix after every 1000 cycles as to restore the total number of vacancies in the grid to its original starting value.

(ii) It was found that after about 20 000 cycles, maximum segregation was achieved but no subsequent desegregation was observed. Tank [7] showed that desegregation could be introduced by setting the binding energies of the vacancies and impurities to

0022-2461/90 $03.00 + .12

the grain boundary equal to zero after maximum segregation was achieved.

Both of these alterations are physically unrealistic. The introduction of vacancies into the matrix is better modelled using a diffusion-theory-based equation as described below. A consideration of defect-to-defect binding energies at the grain boundary leads to the proposal of a variation of such binding energies with the position of the defects in the matrix. This also is detailed below.

2.1. Diffusion of vacancies into the matrix

Drawing an analogy between the diffusion of vacancies to the grain boundary and the diffusion of carbon atoms in the carburization of a semi-infinite block of steel, the vacancy concentration profile at time t is given by [8]

$$C_b - C = (C_b - C_0)\left[1 - \text{erf}\left(\frac{x}{(Dt)^{1/2}}\right)\right] \quad (1)$$

where x is the distance from the grain boundary, C_b is the bulk vacancy concentration in the grain boundary region and D is the vacancy diffusion coefficient. From Fick's first law this produces a flux of vacancies towards the grain boundary (J) of

$$J = \frac{D(C_b - C_0)}{(\pi Dt)^{1/2}} \exp(-x^2/4Dt) \quad (2)$$

If the lattice parameter of the matrix is a, then the number of vacancies diffusing into a lattice site during an interval dt will be $Ja^2\,dt$, that is, the number of vancancies diffusing through an area a^2. If this number is less than one, then it can be taken as the probability of a vacancy entering the lattice site during the interval dt. If the matrix is an $m \times m$ grid of lattice sites then there are $2m$ possible sites for a vacancy to enter the grid. These are along the two edges of the grid parallel to the grain boundary. These edges are at a distance $x = ma/2$ from the grain boundary. Hence the probability of a vacancy entering the grid during the interval dt is:

$$P = 2ma^2\,dt\,\frac{D(C_b - C_0)}{(\pi Dt)^{1/2}} \exp\left(\frac{-m^2a^2}{16Dt}\right) \quad (3)$$

If n_0 is the number of vacancies originally in the grid, and n the number present at time t, then $C_b = n_0/m^2a^3$ and $C_0 = n/m^2a^3$. dt is the time modelled by one cycle of the model, and so [6] $dt = F \times 10^{-13}$ sec where F is the acceleration factor applied to the model.

At the end of the sth cycle, $t = s\,dt$ and so

$$P = \frac{2}{ma}\left(\frac{D\,dt}{\pi}\right)^{1/2} s^{-1/2} \exp\left(-\frac{m^2a^2}{16D\,dt}\,1/s\right)(n_0 - n) \quad (4)$$

$(n_0 - n)$ is the number of vacancies that the computer model lists as having been annihilated. The probability of a vacancy entering the grid is therefore

$$P' = \frac{2}{ma}\left(\frac{D\,dt}{\pi}\right)^{1/2} s^{-1/2} \exp\left(-\frac{m^2a^2}{16D\,dt}\,1/s\right) \quad (5)$$

per annihilated vacancy.

This equation is used in the section of the computer program which checks for vacancies that have reached the grain boundary. For every vacancy that is listed as having been annihilated a random number is generated and compared with the value of P' given by Equation 5. If the random number is less than this value then a vacancy is introduced at one of the available lattice sites, that is, an empty site along either the front or back edges of the grid.

2.2. Variation of defect to defect binding energies

In the original computer model, it was assumed that defect binding energies remain the same irrespective of the positions of the defects within the matrix. Such an assumption conflicts with other assumptions made about the grain boundary. At the grain boundary it is assumed that there is no lattice distortion and that vacancies are annihilated at the boundary. From this it can be shown that all the defect-to-defect binding energies fall to zero at the grain boundary.

This implies that the defect–defect binding energies should vary with the distance of the defects from the grain boundary. This can also be seen from the fact that the formation energies calculated in [6] assume that the surrounding medium is homogeneous. This is obviously not true near a grain boundary.

The modified version of the computer model assumed that the binding energy between two defects is given by

$$E = E_0\left(1 - \frac{0.25}{s_a s_b}\right) \quad (6)$$

where E_0 is the binding energy between the defects at a large distance from the grain boundary, as calculated in [6], and s_a, s_b are the distances of the defects from the grain boundary. The factor 0.25 appears in the equation because, in the model, a defect at the grain boundary is defined to be at a distance of 0.5 units.

It should also be noted that Equation 6 is basically an inverse square law. This is consistent with the defect interaction energy dependence on distance used in [6].

3. Results

The computer model was run to simulate the segregation of boron in an austenitic stainless steel. The following conditions were used:

Impurity atom concentration	0.75 at %
Vacancy concentration	0.75 at %
Temperature	1300 K
Acceleration factor	10^6

The impurity atom concentrations are artificially high in order to promote segregation. Concentrations of under 0.001 at % are more typical. The temperature of 1300 K is also kept high so that high diffusion rates occur. The value of the lattice parameter used is $a = 3.56 \times 10^{-10}$ m. The value of the vacancy diffusion coefficient is given by

$$D = 1.5 \times 10^{-7} \exp\left(\frac{E_m}{kT}\right) \text{m}^2\,\text{sec}^{-1} \quad (9)$$

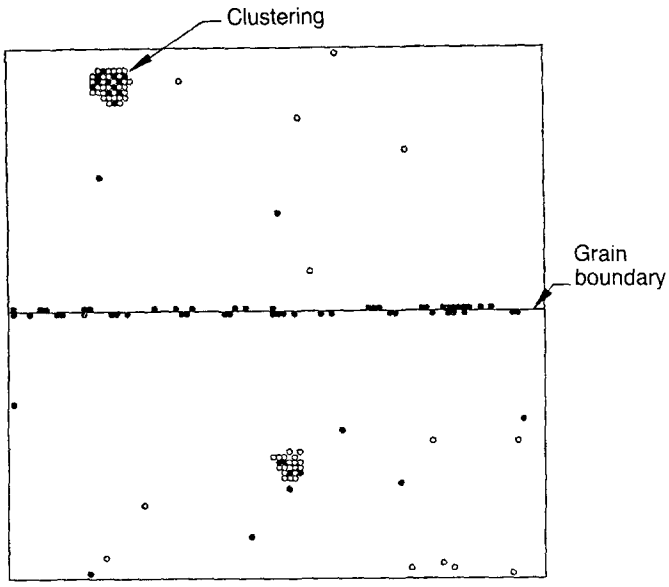

Figure 1 A typical matrix grid output by the computer model. ○, Vacancies; ●, impurity atoms.

where $E_m = 1.6\,eV$ [6]. The computer model starts off with the vacancies and impurities distributed at random throughout the matrix. The segregation process is then modelled using the method described in [6]. Every 3000 cycles the program outputs the positions of the vacancies and impurity atoms in the grid. A typical plot of these positions is shown in Fig. 1. This figure shows the impurity atoms which have segregated to the grain boundary and also the formation of large vacancy-impurity clusters. These clusters are practically immobile and act as secondary sinks for the vacancies and impurities. The distribution of the clusters affects the segregation of the impurities to the grain boundary.

Figure 2 shows the variation of grain-boundary segregation with time for three runs of the computer model. The flux of vacancies towards the grain boundary is assessed by counting the number of vacancies present in the matrix which are not bound to the large clusters. This is indicated in Fig. 2 as the "free vacancies" curve.

As can be seen in Fig. 2 the computer model shows equilibrium desegregation of the impurity atoms after maximum segregation has occurred. The peak value of the segregation curve seems to depend on the magnitude of the vacancy flux. Fig. 2b shows a peak value of 43 impurities at the grain boundary (equivalent to 21.5 at % boron) whereas Fig. 2c, which has a much higher vacancy flux, shows a peak segregation of 58 impurities or 29 at % boron. The results shown in Fig. 2a lie in between these two, both in terms of the magnitude of the vacancy flux and in the peak boron segregation of 50 atoms or 25 at %. However, for all three figures, the peak in the segregation curve lies at

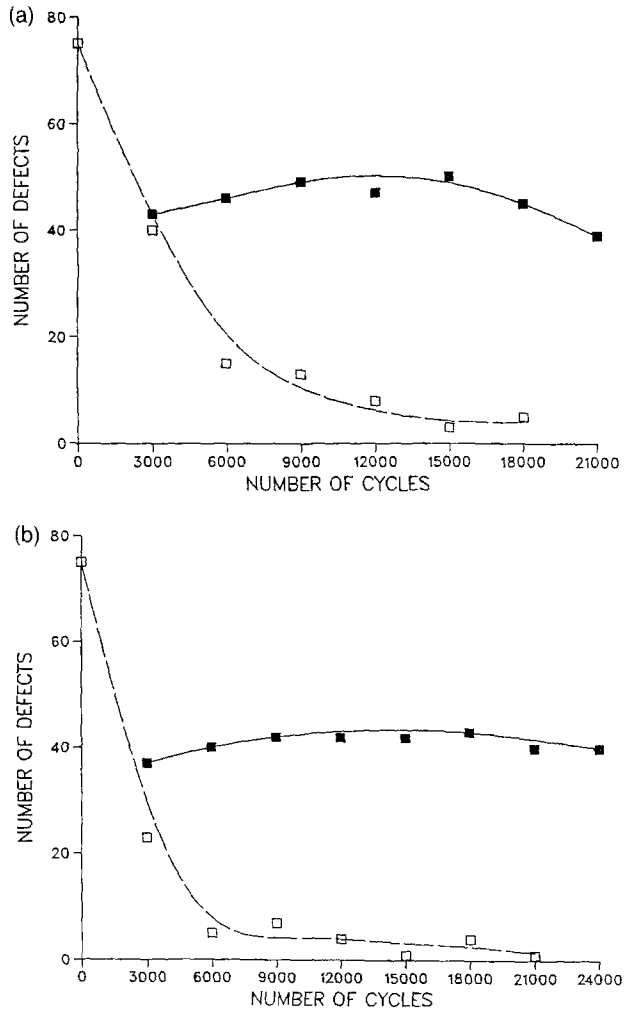

Figure 2 (a) to (c) Variation of impurity atom segregation and the number of free vacancies with number of cycles for three runs of the computer model. ■, Impurities at grain boundary; □, free vacancies.

between 12 000 and 15 000 cycles, or between 1.2 and 1.5 msec, since each cycle models 10^{-7} seconds of real time. This segregation time seems to be independent of the vacancy flux.

The program was run on the Honeywell Multics at Loughborough University. The maximum CPU time that could be used at any one time was 3 h. It was found that 3000 cycles took 2.5 h to evaluate. It was required to calculate at least 20 000 jump probabilities. This limitation was overcome by storing the coordinates of the vacancies and impurities in a file after a run of 3000 cycles and then resubmitting the program. However this meant that a simulation took up to a week to complete.

4. Discussion

Figure 2 clearly shows that this computer model provides a qualitative simulation of grain boundary segregation of boron atoms in an austenitic steel. The model predicts that maximum segregation occurs at between 1.2 and 1.5 msec at a heat treatment temperature of 1300 K. Faulkner [4] has predicted that for a temperature of 1320 K, maximum segregation should occur after 3.6 msec. This is in fairly close agreement given the approximations used in the model.

The computer model predicts that the maximum segregation occurring in the matrix is between 21.5 and 29 at % boron. After a similar amount of time, the Chapman–Faulkner model predicted a segregation of 13.2 at % [6] while that of Tank predicted a segregation of 34.5 at % [7]. These differences can be explained in terms of the different vacancy fluxes implemented in the three models. In the Chapman–Faulkner model, no new vacancies were introduced into the matrix after the modelling was started, which resulted in a very low vacancy flux. In the Tank model, vacancies were introduced into the matrix every 1000 cycles in order to return the vacancy concentration back to its original level. This resulted in a very high vacancy flux. The results of the present model show that the amount of segregation is strongly dependent upon the vacancy flux.

Neither the Chapman–Faulkner model nor the Tank model predicted desegregation of the impurity atoms. However the inclusion of binding energy variation in the computer model, as described above, has produced desegregation. This is due to the fact that in the earlier models, once impurities reached the grain boundary, they formed clusters which were practically immobile. The variation in binding energy assumed in Equation 6 means that there is no binding energy between impurities at the grain boundary. At very high impurity concentrations it may even be energetically favourable for an impurity to move away from the grain boundary.

As can be seen from Fig. 1, the model also predicts the formation of large, immobile clusters of vacancies and impurities in the matrix. The size and distribution of these clusters has a great influence on the segregation that occurs. However the formation of the clusters is controlled by the defect–defect binding energies. These energies are calculated from the formation energies of defect pairs and so are probably not valid for large clusters. Hence the present model exaggerates the effect of clustering upon segregation.

The present model can be extended to include the effects on interstitials upon segregation and to model radiation-induced segregation. However, as mentioned above, the model requires considerable computing time in order to produce any results. Increasing the complexity of the model would increase the amount of computing time needed.

This model also has other faults. The variation of binding energy assumed in Equation 6, while giving better results than the assumption of constant binding energy used previously, still has no theoretical or experimental justification. Another problem is that impurities will inevitably enter the reference lattice in a similar manner to that in which the vacancy injection has been assumed. This has currently not been allowed for in the model and must represent a serious inadequacy. It should also be noted that Equation 1 includes the idea that vacancy creation does not occur at the grain boundary. If this were not the case in practice, the vacancy flux to the boundary would never approach zero, as it should do when equilibrium conditions are approached after very long times. That is $C_b - C_0$ is always greater than 1.

Overall, although approximations still exist the model represents a considerable step forward from the earlier approach [6] and does qualitatively predict the trends of non-equilibrium segregation. It is based on a small, two-dimensional simple cubic lattice and better results would be obtained by using larger, three-dimensional lattices. The acceleration factor used to reduce the amount of computation needed to run the model also results in some of the probabilities calculated being greater than unity, thus introducing errors into the model. These errors would be reduced by using a smaller acceleration factor but this would increase the amount of computation time required.

5. Conclusions

Grain boundary segregation can be modelled by considering interaction energies between impurity atoms, vacancies and grain boundaries. The model shows that at a temperature of 1300 K maximum segregation of boron in stainless steel occurs after about 1.2 to 1.5 msec. The magnitude of the peak segregation depends upon the vacancy flux present. A large flux produces a large segregation peak. This method of modelling segregation may be extended to incorporate interstitials and the effects of irradiation. However, the method does not allow for interstitial injection into the lattice, or vacancy generation at the boundary, and it requires large amounts of computing time to produce meaningful results.

Acknowledgements

The authors appreciate the assistance of Mr G. P. Gerrard of the Loughborough University of Technology Computer Centre.

References

1. E. D. HONDROS and M. P. SEAH, *Int. Met. Rev.* **222** (1977) 262.

2. K. T. AUST, J. S. ARMIJO, E. F. KOCH and J. H. WESTBROOK, *Trans. Amer. Soc. Met.* **60** (1967) 360.
3. T. R. ANTHONY, *Acta. Met.* **17** (1969) 603.
4. R. G. FAULKNER, *J. Mater. Sci.* **16** (1981) 373.
5. *Idem, Acta. Metall.* **35** (1987) 2905.
6. M. A. V. CHAPMAN, and R. G. FAULKNER, *ibid.* **31** (1983) 677.
7. J. TANK, Final Year Project Report, Dept. of Materials Engineering, Loughborough University (1986).
8. R. G. FAULKNER, D. J. FRAY and R. D. JONES, "Worked Examples in Mass and Heat Transfer in Materials Engineering" (Institute of Metallurgists, London, 1983) p. 26.
9. R. G. FAULKNER, *Mater. Sci. Tech.* **1** (1985) 442.

Received 23 May 1988
and accepted 14 April 1989