Influence of cluster mobility on Cu precipitation in χ-Fe: A cluster dynamics modeling

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Received 23 November 2009; received in revised form 4 February 2010; accepted 8 February 2010
Available online 5 March 2010

Abstract

A cluster dynamics model has been parametrized to quantitatively reproduce results obtained by atomistic kinetic Monte Carlo (AKMC) modeling on the precipitation of Cu in χ-Fe under thermal aging. The cluster mobility, highlighted by AKMC, is shown to have a significant effect on the precipitation kinetics and can reconcile the experimentally observed fast kinetics with the relatively low diffusivity of Cu monomers.

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Keywords: Precipitation; Kinetics; Modeling; Monte Carlo techniques

1. Introduction

The precipitation of copper in iron during thermal aging or under irradiation in reactor pressure vessel steels is known to lead to the hardening and embrittlement of these materials. Given that the solubility limit in χ-Fe is lower than 2% even at high temperatures (850 °C) [1], such effects can be expected at low Cu concentrations. For supersaturations as low as 1.2%, the precipitation has been shown to be homogeneous until approximately 600 °C [2]. Under irradiation, this conclusion still holds and no significant induced segregation is observed [3,4]: the kinetics is accelerated because of the supersaturation in vacancies. Due to the small lattice mismatch, the precipitates are spherical and are coherent with the matrix for a radius lower than 2 nm [5,6].

This coherency at small sizes has turned Fe–Cu alloy into a model system to validate numerical methods such as the rigid lattice atomistic kinetic Monte Carlo [7–9] (AKMC) model. In addition, the spherical shape of the precipitates, the low concentration of Cu necessary for the precipitation and the almost pure Cu content of the precipitates [10,11] greatly simplify the use of mesoscopic simulation approaches such as cluster dynamics (CD) [12,3].

Using this latest method, Christien and Barbu obtained a good agreement with the experimental mean radius of clusters after around 1 h under thermal aging [13], using a capillary approximation for the binding energies and a Cu diffusivity of $7 \times 10^{-15}$ cm$^2$ s$^{-1}$ at 500 °C. Possible reasons for the discrepancy at short times were a finite reaction kinetics at the interface or heterogeneous nucleation on impurities [3]. Golubov et al. used a lower value for the diffusivity $2.26 \times 10^{-16}$ cm$^2$ s$^{-1}$ at 500 °C with different binding energies accounting for the structural transformation body-centred cubic (bcc) $\rightarrow$ 9R that the Cu clusters undergo at a radius of around 2 nm [14]. However, using these values the coarsening rate was lower than the experimental one. Similar results were obtained by Wagner and Kampmann [15], even by taking into account the increase of the coarsening rate through the overlapping of the diffusion fields.

Recently, AKMC simulations [16], parametrized by ab initio calculations, have shown that due to the trapping of vacancies inside Cu clusters, these clusters can be considered as mobile for sizes up to several hundreds of atoms for...
all the temperatures considered (from 127 to 327 °C). The mobility of small clusters is a few orders of magnitude higher than the mobility of monomers. At 500 °C, the AKMC simulations are in very good agreement with the experimental measurements. The monomer diffusivity is 3.8 × 10^{-18} \text{ cm}^2 \text{ s}^{-1}, so around 2–3 orders of magnitude lower than the values used in CD, assuming only mobility of monomers. As pointed out by the authors, the value of the monomer diffusivity is closer to the self-diffusivity of Fe and is more probable. An interesting point is that the marked growth and coarsening stages present in CD simulations cannot be clearly distinguished in the AKMC simulations and in the experiments.

As the AKMC simulation is limited to the onset of precipitation for computation time reasons, it is interesting to investigate the effect of cluster mobility in CD. This is the main objective of this work. Given the structural transformation bcc → 9R that appears at a radius of around 2 nm, we will focus only on the precipitation kinetics before this mean radius is reached. The first part of this article is devoted to the parametrization of the CD model, in order to reproduce the AKMC results when the mobility of clusters is artificially suppressed. In the second part we investigate the role of the cluster mobility and compare results with AKMC results and experimental measurements.

2. Cluster dynamics model

Modeling precipitation by CD only requires a few parameters, as it is based on a number of key assumptions that appear to be satisfactory in most cases. A review of CD is available in Ref. [17]. The model is based on the cluster gas model: clusters can capture and emit monomers that diffuse in the pure solvent.

The spatial correlations are not considered in CD, which turns the problem into solving a set of ordinary differential equations involving the number of clusters per lattice site containing \(n\) solute atoms \(C_n\):

\[
\frac{dC_n}{dr} = J_{n-1 \to n} - J_{n \to n+1}, \quad n \geq 2, \tag{1}
\]

\[
\frac{dC_1}{dr} = -2J_{1 \to 2} - \sum_{n \geq 2} J_{n \to n+1}. \tag{2}
\]

The flux between two classes reads:

\[
J_{n \to n+1} = \beta_n C_n C_{n+1} - x_{n+1} C_{n+1}, \tag{3}
\]

where \(\beta_n\) is the capture coefficient of a monomer by a cluster containing \(n\) solute atoms, and \(x_{n+1}\) is the emission rate by a cluster of size \(n + 1\).

The following assumptions are commonly made for the capture and emission coefficients:

- The capture coefficient \(\beta_n\) can be obtained by the solution of the stationary diffusion equation, considering that the cluster is spherical and isolated. We will neglect the possible finite reaction kinetics at the interface, in agreement with AKMC. In this case we obtain

\[
\beta_n = 4\pi (r_n + r_i) D_1 / \Omega,
\]

where \(r_n\) is the reaction radius of a cluster of size \(n\), \(D_1\) is the monomer diffusivity and \(\Omega\) is the atomic volume.

- The emission rate \(x_n\) by a cluster of size \(n\) is taken as an intrinsic property of this cluster and can be determined at equilibrium. Assuming that the alloy is very dilute, the equilibrium concentration \(\overline{C}_n\) of a cluster of size \(n\) is obtained by minimizing the free energy of the cluster gas, for an undersaturated solution [18]:

\[
\overline{C}_n = \exp \left( - \frac{G_n - n \mu}{kT} \right),
\]

where \(\mu\) is the difference between the chemical potentials of the solute and the solvent, and \(G_n\) is the free energy of a cluster of size \(n\). To define the emission rate, the equilibrium concentrations must ensure a stationary state, i.e., the flux (3) between two classes must be zero. This leads to:

\[
x_{n+1} = \beta_n \exp \left( - \frac{G_1 + G_n - G_{n+1}}{kT} \right).\]

The parameters needed are the reaction radius \(r_n\), the cluster free energy \(G_n\) and the monomer diffusivity \(D_1\). For the reaction radius, we have adopted the value deduced from the atomic volume, \(r_n = (3n/8\pi)^{1/3}a\), where \(a\) is the lattice parameter. Previous attempts to model precipitation by CD have highlighted the need for a precise evaluation of the free energies, at least for small cluster sizes [19,20]. We used a method proposed by Bennett [21] which was then adapted to compute cluster free energies on a simple cubic lattice [22,23]. This so-called method of overlapping distributions permits evaluation of the free energy differences \(G_{n+1} - G_n\) with a high precision, by means of a Monte Carlo sampling of thermodynamic averages. We used the first and second nearest-neighbor pair energies determined in Ref. [16], taking into account the non-configurational entropy. We consider that a cluster is split into two parts as soon as these two parts are not linked by first nearest neighbors, to keep coherency with the convention used to identify clusters in AKMC simulations. In order to extrapolate at larger cluster sizes, the free energy difference can be fitted by the following expression [23]:

\[
G_n = bn + cn^{2/3} + dn^{1/3} + e + f \ln n, \tag{4}
\]

where the \(n\) and \(n^{2/3}\) terms are, respectively, the bulk and surface contributions, the \(n^{1/3}\) term corresponds to a line contribution, the constant term to a point contribution, and the logarithmic term accounts for the fact that the surface must close on itself [24]. Such a fit is necessary at small sizes, but we have observed that varying the lower bound \(n_{\text{min}}\) of the fit renders the \(c\) parameter stable for sizes larger than around \(n_{\text{min}} = 20\), whereas \(d\) and \(f\) tend to fluctuate correlatively around zero, the sum of their contribution being zero. Therefore it seems that a fit with only the surface term is sufficient in our case, as for small sizes \((n \leq 200)\) the exact values are given by the method of over-
lapping distributions. A convenient way to rewrite Eq. (4) is to group all the contributions, except the bulk one, into an interface free energy term \( \sigma_n \):

\[
G_n = bn + (9\pi)^{1/3}a^2\sigma_n n^{2/3}.
\] (5)

The emission rate is thus:

\[
x_{n+1} = \beta_n \exp[-(9\pi)^{1/3}a^2(\sigma_1 + \sigma_n n^{2/3} - \sigma_{n+1}(n+1)^{2/3})/kT],
\] (6)

or, equivalently:

\[
x_{n+1} = \beta_n C_1 \exp[-(9\pi)^{1/3}a^2(\sigma_n n^{2/3} - \sigma_{n+1}(n+1)^{2/3})/kT].
\] (7)

Values of \( \sigma_n \) for three different temperatures are shown in Fig. 1. Two temperatures (500 °C and 600 °C) were chosen to compare the precipitation kinetics with AKMC; the third one (100 °C) was to check the trend when the temperature tends towards 0 K. The asymptotic value of \( \sigma_n \) is given by \( \sigma_\infty = c/(9\pi)^{1/3}a^2 \). It is 402.4, 332.0 and 305.5 mJ m\(^{-2}\) at 100, 500 and 600 °C, respectively. These values can be compared with the one given by the Wulff construction at 0 K, which leads to clusters faceted along (110) planes. Using the same first and second nearest-neighbor pair energies as for the method of overlapping distributions, we obtain an interface energy equal to \( \sigma_\infty = 431.0 \) mJ m\(^{-2}\), which is consistent with the computations at higher temperatures. The interface free energy can also be compared with results obtained by the Cahn–Hilliard phase-field theory [25], which was used in a previous study of the precipitation of copper in iron [13]. Keeping the same mixing energy and non-configurational entropy as for the method of overlapping distributions, interface free energies are significantly higher (Fig. 1). We have confirmed that at 500 °C, for an atomic fraction of copper close to the solubility limit (around 0.08%), the equilibrium concentrations obtained in CD with our parametrization are in very good agreement with AKMC simulations, contrary to the Cahn–Hilliard theory (not shown). It should be noted that such comparisons could not be done for large cluster sizes, since such clusters are not found in AKMC simulations with 128\(^3\) atomic sites, due to the low copper concentration.

AKMC simulations, performed with the parameters of Ref. [16], have shown that clusters are highly mobile, due to the vacancy formation energy being much lower in bcc copper (~0.9 eV) than in bcc iron (~2.1 eV). In order to compare CD and AKMC in the simple case where only copper monomers are mobile, the AKMC parameters have been modified to avoid vacancy trapping in the precipitates. With the new parameters, the vacancy formation energy in pure bcc copper is increased to 2.6 eV, but the Fe–Cu thermodynamic parameters remain the same (especially the mixing energies and the interface energies). The vacancy concentration on copper monomers is reduced, but the copper diffusion in pure iron is kept constant \( D_1 = 3.56 \times 10^{-18} \) cm\(^2\) s\(^{-1}\) at 500 °C), by decreasing the copper migration energy. Given that vacancy trapping inside the precipitates is avoided, results have been obtained within reasonable computation times using systems with 256\(^3\) atomic sites. To compare the results, the density and mean radius of precipitates were computed by considering only clusters containing more than 10 copper atoms, in agreement with AKMC simulations.

The result is shown in Fig. 2 for an atomic fraction \( x_{Cu} = 1.34 \) at.\% at \( T = 500 \) °C. We have also plotted the precipitation kinetics obtained using a constant value of the interface free energy from \( n = 2 \), given by the Cahn–Hilliard theory. The interface free energy of the monomer, which is readily deduced from the mixing energy and the

![Fig. 1. Interface free energy \( \sigma_n \) (Eq. (5)) as a function of the number \( n \) of Cu atoms in the cluster, obtained by the method of overlapping distributions. The fit is performed from \( n = 20 \) to \( n = 200 \) with only the surface term in Eq. (4). Dashed lines refer to values given by the Cahn–Hilliard theory.](image)

![Fig. 2. Density of precipitates, mean radius and monomer concentration in AKMC and cluster dynamics, with \( x_{Cu} = 1.34 \) at.\% and \( T = 500 \) °C, when clusters are immobile. The initial monomer concentration is taken from AKMC. Two different models are tested: varying the interface energy, or with a constant value from \( n = 2 \) (Cahn–Hilliard theory). In the latter case, the value \( \sigma_1 \) is taken the same as in the other method, to obtain the same solubility limit.](image)
non-configurational entropy, is treated separately to ensure a proper solubility limit \( C_1 \) (Eq. (7)). A better agreement is obtained by the precise computation of the cluster free energies, but the kinetics given by CD is slower than AKMC, as already observed in Al\(_2\)Zr and Al\(_3\)Sc alloys [19]. Other simulations have been done at 600 °C and the agreement is of the same order. Two calculations at atomic fractions \( x_{\text{Cu}} = 0.7 \) at.% and \( x_{\text{Cu}} = 5 \) at.% have revealed that the discrepancy increases with the atomic fraction.

While discussing this point it must be recalled that we have used stationary diffusion to determine the capture coefficients, which is certainly acceptable at large times, during coarsening, but is questionable during nucleation and growth. Moreover, it has been shown recently that it is possible to improve CD simulations by correcting the cluster gas entropy [26], which is involved in the equilibrium concentrations and thus in the emission coefficients. However this correction is expected to be significant only in concentrated alloys and we have observed that the cluster size distributions are in very good agreement with the AKMC data, so it is likely that this will have a minor effect in our case. Another correction consists in taking into account the overlapping of the diffusion fields around each cluster [27,28,19]. This correction is essentially valid during the coarsening stage, because it is supposed that the solute is conserved in the matrix. In our case it appeared to lead to only a small correction to the kinetics.

3. Mobility of copper clusters

The introduction of cluster mobility in CD has been proposed by Binder [29,30]. The approach is the same as in Section 2, but the fluxes between non-adjacent classes also have to be considered: two clusters of sizes \( n, m \geq 1 \) can produce a cluster of size \( n + m \).

Considering that clusters are mobile only for \( n \leq n_m \), the evolution equation for all sizes is:

\[
\frac{\text{d}c_n}{\text{d}t} = \sum_{m=1}^{n-1} J_{n-m,m} - \sum_{m=1}^{n} J_{n-m,m} - \sum_{m>1} J_{n,m+m},
\]

(8)

where the flux \( J_{n-m,m} \) reads:

\[
J_{n-m,m} = \beta_{n,m} c_n c_m - \alpha_{n+m,m} c_{n+m},
\]

(9)

and where:

\[
\beta_{n,m} = 4\pi (r_n + r_m) D_m / \Omega
\]

(10)

\[
\alpha_{n,m,m} = \beta_{n,m} \exp[-(G_m + G_n - G_{n+m})/kT].
\]

(11)

The first term in the right-hand side of Eq. (8) accounts for the reaction \( (n-m) + (m) \leftrightarrow (n) \), assuming that at least \( (m) \) is mobile. It is noteworthy that in the definition of the flux \( J_{n-m,m} \) (Eq. (9)), only \( (m) \) is presumed to be mobile (Eq. (10)), so it is zero if \( (m) \) is immobile. This definition avoids ad hoc corrections of coefficients when \( n = m \). Indeed the total flux for the reaction \( (n-m) + (m) \leftrightarrow (n) \) is \( J_{n-m,n} + J_{m-n} \), if \( n-m \neq m \) (both fluxes are found in the first sum of Eq. (8)), and only \( J_{n-m} \) when \( n-m = m \). Therefore, if \( n-m \neq m \), the sum \( D_{n-m} + D_m \) appears in the total flux, otherwise only \( D_{n/2} \) is present. This \( 1/2 \) correction is to take account of the indistinguishability of the reactants. The second term in Eq. (8) relates to the reaction \( (n) + (m) \leftrightarrow (n+m) \) due to mobile \( (m) \) and the third term accounts for the same reaction but takes into account the mobility of \( (n) \), so all \( (m) \) must be considered.

The coefficients \( \beta_{n,m} \) and \( \alpha_{n+m,m} \) are defined in the same way as in Section 2, assuming stationary diffusion and infinitely fast reaction kinetics at the interface for \( \beta_{n,m} \) and imposing a zero flux between all classes at equilibrium for \( \alpha_{n+m,m} \). The hypothesis on the reaction kinetics at the interface seems well justified by AKMC simulations, where two clusters that react transform very rapidly into a single quasi-spherical cluster.

The only new parameters that are needed in CD are the cluster diffusion coefficients. Unfortunately, at the temperatures at which most experiments have been performed [10,3,31], it is difficult to estimate cluster mobility by AKMC, because clusters tend to dissociate. Therefore we used a very simple law (Fig. 3) that reproduces the main features observed at lower temperatures in AKMC. At small sizes, the increase of the mobility is approximated by an exponential variation. At larger sizes the decrease is due to the solute jumps at the interface which are responsible for the mobility of clusters [32,16].

The precipitation kinetics is shown in Fig. 4 for \( x_{\text{Cu}} = 1.34 \) at.%, at \( T = 500 \) °C. In order to be able to make comparisons with results from Section 2, we have represented the case when the clusters are not mobile. Due to numerical limitations, mobile clusters are not allowed to contain more than \( n = 1300 \) Cu atoms, which corresponds to a radius \( r_s = 1.5 \) nm. The representation is thus not shown when the mean radius is greater than this value.

The kinetics obtained with CD simulations is close to the experimental results. It shows that cluster mobility can account for the fast kinetics observed experimentally, keeping the Cu diffusivity of the same order as the Fe.
self-diffusivity. As already observed experimentally and in AKMC simulations, there are no marked growth and coarsening stages, contrary to CD simulations when only monomers are mobile. However, as observed when only monomers are mobile, the kinetics is too slow. Given the uncertainty on the mobility of clusters, this discrepancy is acceptable: by increasing the mobility of clusters by a factor of 2, the CD and the experimental curves coincide from $t \approx 6 \times 10^3$ s. Furthermore, as discussed in the previous section, one cannot rule out a role of the stationary diffusion approximation made in CD. The role of spatial correlations, neglected in CD, could be also important, especially at small times.

It is worth noting that the detailed balance imposed on each pair of classes leads to the emission of clusters of size $n > 1$. It can be reasonably envisaged that clusters of small size, such as dimers and trimers, may be emitted at sufficiently high temperature, since precipitates can exhibit small arms of a few copper atoms where the copper neighbors are less numerous. However, for a large cluster of size $n$, the splitting of this cluster in two equal parts is possible in the CD equations, whereas physically it must occur through a deformation of the cluster which is energetically not favorable. Even though the probability of such a splitting is low in CD, given the high energy barrier $G_n + G_m - G_{n+m}$, the validity of such a detailed balance may be discussed.

We have checked that suppressing the emission of clusters does not modify significantly the precipitation kinetics: it is a little faster than when the emission is taken into account and the maximum density of clusters is higher. This slight modification of the kinetics is only due to the emission of small clusters: adding the emission of clusters containing more than $n \approx 4$ atoms does not perceptibly change the evolution of the density of precipitates and the mean radius. The effect of the emission of clusters can be seen more precisely on cluster distributions. In Fig. 5 the cluster distribution is shown in both cases and compared with AKMC simulations for the same concentration of monomers $C_1$, approximately at times when the maximum density of precipitates is reached, to make the comparison clearer. The agreement is clearly better when emission of clusters is permitted, despite the crudeness of the emission model in CD. Such a comparison at the beginning of the nucleation process, at times corresponding to the same values of $C_1$, does not show such a good agreement between CD and AKMC. The density of larger clusters is significantly higher in AKMC than in CD, which indicates that the hypothesis used to determine the absorption and emission coefficients may not be fully valid at the onset of precipitation.

4. Conclusion

Cu precipitation in $\alpha$-Fe has been modeled by CD. The model has been first validated on AKMC results when only Cu monomers are mobile. The parametrization of such a model is relatively straightforward: provided the cluster free energies are precisely determined, CD gives results very similar to AKMC simulations.

The mobility of clusters, highlighted by recent AKMC simulations, has been introduced in the model. The results are in good agreement with experimental results at $T = 500$ °C for $x_{Cu} = 1.34$ at.%. This mobility accelerates the precipitation kinetics by several orders of magnitude, whereas the monomer’s diffusivity remains close to Fe self-diffusivity. Our simulations thus support a strong role of the cluster mobility in Cu precipitation when clusters are coherent with the matrix.

![Fig. 4. Density of precipitates and mean radius in AKMC and CD, with $x_{Cu} = 1.34$ at.% and $T = 500$ °C, when clusters are mobile. Previous CD simulations (see Section 2 and Fig. 2), with no cluster mobility, are also represented. The experimental results are those of Mathon et al. [3] and Kampmann and Wagner [10], both obtained by small-angle neutron scattering measurements. The number of atomic sites in the AKMC simulation is $64^3$. This moderate size is due to the strong trapping of vacancies inside copper precipitates, which is responsible for a significant increase in the computation time.](image1)

![Fig. 5. Cluster distribution obtained in AKMC and CD, with $x_{Cu} = 1.34$ at.% and $T = 500$ °C. The values are taken in each case near the maximum cluster density, for the same monomer concentration, so not necessarily at the same physical time. In CD, results without the emission of clusters are also shown.](image2)
It should be noted that the emission of clusters is permitted in our CD simulations. This emission model, which ensures a detailed balance for non-adjacent classes of clusters, is necessary to obtain cluster distributions in agreement with AKMC simulations. At $T = 500\,^\circ$C, the emission of clusters containing more than around four atoms does not change the precipitation kinetics. Indeed, the emission of large clusters is negligible due to the high energy barriers involved.

Strong assumptions of CD simulations are the stationary diffusion approximation and the absence of spatial correlations, which may be responsible for the discrepancies observed at short times with AKMC. Additional simulations using event-based kinetic Monte Carlo modeling, which does not rely on such assumptions, will be reported elsewhere to assess their validity.

Acknowledgment

T.J. wants to thank Bernard Legrand and Georges Martin for fruitful discussions.

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