Diffusion simulation of Cr-Fe bcc systems at atomic level using a random walk algorithm

I. San Sebastian¹, J. Aldazabal^{1,*}, C. Capdevila², C. Garcia-Mateo²

¹ CEIT and Tecnun (University of Navarra), Paseo Manuel de Lardizabal 15, 20018 San Sebastián, Spain

² MATERIALIA Research Group. Department of Physical Metallurgy, Centro Nacional de Investigaciones Metalúrgicas (CENIM-CSIC), Avda. Gregorio del Amo 8, 28040 Madrid, Spain

This paper proposes a model to simulate the diffusion of impurities in bcc atomic lattices. It works with three-dimensional volume divided in small cubic elements (voxels), containing more than one atomic cell each. Once the domain is discretized, impurities jump for one voxel to another according to certain probability that takes into account the composition and geometry of the target voxel.

In present work, model was applied to prismatic volume, and in order to deduce the relationship between the atomic jumping frequency and the temperature two different cases were studied. One consists of a Fe matrix with Cr impurities, and the other, is based on a Cr matrix with Fe impurities. Results obtained from these simulations were compared with profiles obtained by Dictra software.

Results for the atomic jumping frequencies were fitted to Arrhenius type equation, as shown in following expressions.

$$J_{Cr} = 3.396 \times 10^{18} \exp\left(\frac{-306421}{RT}\right)$$

$$J_{Fe} = 1.096 \times 10^{19} \exp\left(\frac{-411729}{RT}\right)$$

From these equations it is possible to obtain an activation energy for the atomic jumping phenomenon of ~ 306 and ~ 411 kJ/mol for the Fe-matrix and Cr-matrix systems respectively. These energies match the empirical measured values for the diffusion of Cr and Fe impurities, 250 and 407 kJ/mol respectively.

Results obtained in this work assure that the proposed model is suitable for simulating the three-dimensional diffusion of substitutional impurities in Cr and Fe bcc systems. It could be easily expanded to other bcc matrix systems.

1 Introduction Continuum theories assume that the chemical composition of materials changes smoothly in the volume [1]. A closer, and more realistic look reveals that the composition does not change so smoothly at the atomic level[2].

Single atoms jump randomly along the crystal lattice due to their thermal energy [3]. These random jumps create sporadic zones of the crystal with higher concentration of certain elements. These composition fluctuations are responsible for many phenomena, such as spinodal decom-

position, segregation, precipitation, Ostwald ripening,... [4–6].

During last decades, many analytical/continuum models were developed. In the last few years, the increase of computation power made very attractive the development of new models to simulate, study and understand phenomena that take place at the nanoscale [7]. This paper proposes a model based on the random walk algorithm [8] to simulate the diffusion of impurities in bcc systems at the atomic scale.

2 Model Description Proposed model works with 3D bcc systems, dividing the simulated domain in small cubic cells, called voxels. Once the domain is discretized, impurities could jump for one voxel to another according to certain probabilities. Model follows the position of individual atoms during the simulation.

2.1 Microstructure Discretization As previously mentioned, model works discretizing the microstructure in voxels, that could contain more than one atomic cell. The voxel must be cubic, and its size is a integer time lattice parameter, thus the number of cells contained within must be like $1^3, 2^3, 3^3, 4^3, \dots$

Each bcc crystallographic cell has some atoms that are shared by eight neighbour cells (vertex atoms), and a central one not shared by any other. From the logical point of view it is more interesting that atoms belong to a single cell. This could be obtained just by displacing voxels $[\frac{1}{4} \frac{1}{4} \frac{1}{4}]$, i.e. $\frac{1}{4}^{\text{th}}$ of the lattice parameter in the three crystallographic axes, as shown in figure 1 [5].

Figure 1 Top view of a bcc lattice where the dashed line delineate a 1-cell voxel. Dark sphere corresponds to atoms located in the $(0 \ 0 \ \frac{1}{2})$ plane.

The model knows the position of each atom during the simulation, via the cell that it belongs to. The composition of each voxel could be easily computed knowing the number of atoms located on it.

2.2 Model Steps To simulate composition evolution, atoms are chosen at random and swapped with one of their nearest neighbour. Following paragraphs will explain this process at more detail.

Proposed model only can handle two different kinds of atoms in the system. One type will be considered as a matrix and the other one will be considered as impurities, despite of its concentration, so to simulate the diffusion, only randomly chosen impurities will move.

In the process of jumping and swapping with one of its eight nearest neighbours the probability of each target is assumed to be identical, i.e. $1/8$. Atoms randomly chosen in the previous stage of the model will be moved according to this rule.

Even fulfilling this rule, it is possible to have a jump inside a voxel, with the source and the target in the same

voxel. This kind of jumps doesn't show any effect in voxels composition. These kind of jumps are referred as "internal" (J_{intern}).

There are three more possible kind of jumps, according to the target voxel; "face", "edge" and "vertex" (J_{face} , J_{edge} and J_{vertex} respectively).

Another phenomenon associated to the use of voxels, as defined in this paper, is that some nearest surrounding voxels never can be reached with a single jump. Table 1 shows the neighbours that can be reached by a single atomic jump. Despite of happening this phenomenon, model behaves isotropically. A set of simulations was performed to check it.

Table 1 Surrounding voxels that can be reached in a single atomic jump in bcc lattices.

Face (J_{face})	Edge (J_{edge})	Vertex (J_{vertex})
[100]	[110]	[111]
[$\bar{1}$ 00]	[101]	[$\bar{1}$ $\bar{1}$ $\bar{1}$]
[010]	[011]	
[0 $\bar{1}$ 0]	[0 $\bar{1}$ $\bar{1}$]	
[001]	[$\bar{1}$ $\bar{1}$ 0]	
[00 $\bar{1}$]	[$\bar{1}$ 0 $\bar{1}$]	

The bigger the voxels are, i.e. increasing the atomic cells contained, the more atoms could jump to a face neighbour voxel. The same happens with edge neighbours, but the number of atoms that could jump to a vertex neighbour will remain the same. Equation 1 shows the number of possible jumps according to the voxel size, in terms of lattice parameter (n), and target voxel.

$$\begin{aligned}
 J_{intern} &= 16n^3 - 24n^2 + 12n - 2 \\
 J_{face} &= 4n^2 - 4n + 1 \\
 J_{edge} &= 2n - 1 \\
 J_{vertex} &= 1 \\
 J_{total} &= J_{intern} + 6J_{face} + 6J_{edge} + 2J_{vertex}
 \end{aligned} \tag{1}$$

With these equations and Table 1 it is possible to know the number of jumps that will move atoms to a specific voxel. Also knowing the total number of possible jumps (J_{total}), it is easily obtained the probability of each type of jump. For each atom chosen in the previous step a jumping direction is randomly assigned according to these probabilities.

The jump will always happen, but it will be effective only if it produces a change in any voxel composition. If the target voxel is completely full of impurities, the jump will take place but it will be in-effective, because in that case, the model is swapping two atoms of the same specie. If the target cell is only occupied by matrix atoms, the jump will be always effective. The model assumes an effectiveness probability of jumps proportional to the atomic fraction of matrix on the target voxel. Jumps are randomly

identified as effective according to the previously mentioned probability. From a computational point of view, only effective atomic jump will take place.

2.3 Discretization Scale Proposed model can handle different size of volume elements, in terms of number of atomic cells containing, making it flexible. Different voxel dimensions could be used, depending on the phenomena to study. Even with different voxel sizes the model will keep its atomistic nature.

Small voxels will keep a lot of information about the spatial concentration fluctuations, but needs to work with a enormous number of voxels to simulate a tiny volume.

The use of bigger voxels implies smoother composition fluctuations, because the model only knows the average concentration on each volume element. This also saves computer memory because less voxels are needed to discretize the simulated system. As internal jumps (J_{intern}) are ineffective, and are not reproduced by the computational implementation of the model, bigger voxels involve a decrease in the number of jumps performed, resulting on faster simulations.

Two different executions were performed, using 2 and 4 cells per voxel, to see the differences in the results. The microstructure used consist of a $572 \times 1051 \times 1051$ nm prism with a cell size is $2.86 \text{ \AA}$. It was divided in two halves, one half contains pure matrix, and the other one contains 100 ppm of randomly located impurities. Simulated time for both, i.e. the number of atomic jumps, is the same. Simulations performed in this work were executed in a 24 Pentium IV@2.6GHz cluster with 24 GB of physical memory [9]. Table 2 shows time and memory needed to run each one of these examples.

Table 2 Time and memory needed to simulate the same microstructure using two different voxel sizes.

Voxel Size [cells]	Execution time [s]	Memory [GB]
2	3540	12.88
4	451	1.64

Figure 2 shows the composition profiles obtained for the two examples. It is clear that smaller voxels simulation keep the fluctuations more accurately than bigger ones, and as shown in table 2 the time needed to get these is about eight times longer.

3 Model Results Proposed model was applied to prismatic systems to study the relationship between the atomic jumping frequency and the temperature in two different systems. The first one that will be studied consists of a Fe matrix with Cr impurities and the second one of Cr matrix and Fe impurities.

Results obtained from simulations were compared with profiles obtained by Dictra software. This software is based on a numerical solution of the multicomponent diffusion equations.

Figure 2 Composition profiles obtained for the same $572 \times 1051 \times 1051$ nm microstructure using two discretization scales. On the top $5.72 \text{ \AA}$ per voxel (2 atomic cells), and on the bottom $11.44 \text{ \AA}$ (4 atomic cells).

Because Dictra simulations are one-dimensional [10], and in order to do the comparison, it is necessary to reduce the resulting three-dimensional microstructure to a single composition profile. This profile is obtained, along the simulated microstructure, by averaging the composition on one-voxel-thickness layers. The least square fitting method was used to decide when the simulation reaches the Dictra profile, i.e. the number of atomic jumps needed to match it.

Figure 3 compares concentration profiles obtained by the proposed model and by Dictra. This result was achieved for the Fe matrix case, after 3761 jumps/atom and using 2 cells per voxel. For pure Fe at 748 K the lattice parameter used was $2.86 \text{ \AA}$ [11]. Dictra results were calculated for a diffusion time of 3072 hours at 748 K for the same Fe-Cr system.

As shown in the figure, profile obtained by the model fits precisely with Dictra software profile.

The microstructure used to get the relation jumping-frequency/temperature, consists of a $572 \times 2950 \times 2950$ nm, lattice parameter for Cr and Fe matrix was fixed at $2.86 \text{ \AA}$. Studied temperatures range from 688 to 748 K (in 10 K steps).

3.1 Cr diffusion in a Fe matrix To simulate the diffusion of Cr the microstructure was divided in two parts.

Figure 3 Composition profiles obtained by the proposed model and by Dictra software for a Fe matrix containing initially 100 ppm of Cr on the right half of the system.

In the left one there are no Cr atoms and in the right one there are 100 ppm of Cr. As the diffusion of Cr in Fe- α is very slow, in the temperature range simulated, long time was required to smooth the initial step composition profile. Dictra simulation were calculated for this system using a diffusion time of 1.10×10^7 seconds.

Knowing the total number of jumps required by the model to match a Dictra profile, and knowing the conditions applied to this, it is possible to deduce the atomic jumping frequency for the simulated temperature. Figure 4 shows the relation obtained between the atomic jumping frequency and the temperature for the movement of Cr atoms in a Fe matrix.

Figure 4 Relation between atomic jumping frequency of Cr atoms, in a Fe bcc matrix, deduced for different temperatures.

These results were fitted to an Arrhenius type equation, as show in equation 2, allowing for the determination of the atomic jump activation energy as approximately 306 kJ/mol.

$$J_{Cr} = 3.396 \times 10^{18} \exp\left(\frac{-306421}{RT}\right) \quad (2)$$

This result is in agreement with the empirical value of Cr diffusion in Fe bcc, 250 kJ/mol[12,13].

3.2 Fe diffusion in a Cr matrix To study the diffusion of iron atoms in a pure Cr matrix at different temperatures a procedure analogous to the previous one was used. In this case, the microstructure has pure Cr in one half and 100 ppm of Fe in the other one. Simulated temperatures were the same, but as the macroscopic diffusivity of Fe in Cr is even smaller that in the case of Cr in Fe, the time used for Dictra simulations was 2.11×10^{14} seconds.

Figure 5 shows the relation obtained between atomic jumping frequency of iron atoms, in a Cr matrix, and temperature.

Figure 5 Atomic jump frequency of Fe in a pure bcc Cr matrix vs temperature.

Also in this case the results were fitted to an Arrhenius type equation, as show in equation 3. This determine a Fe atomic jump activation energy as approximately 411 kJ/mol[14,15].

$$J_{Fe} = 1.096 \times 10^{19} \exp\left(\frac{-411729}{RT}\right) \quad (3)$$

The numerical value, empirically measured, for the activation energy of diffusion of Fe in a Cr matrix is 407 kJ/mol, what is in good agreement with results.

Results obtained in this work assure that proposed model is suitable to simulate the three-dimensional diffusion of substitutional impurities in Cr and Fe bcc systems. It is easily expandable to other bcc matrix systems. This tool could help to study and understanding phenomena that take place at very small scales, like nucleation, segregation, . . . , keeping the random nature of diffusion at the atomic level.

4 Conclusions Proposed model is able to work at different scales keeping the atomic jumping nature of diffusion.

Obtained profiles match precisely Dictra/continuum results.

Computed atomic jumping frequencies adjust properly to Arrhenius type equations, matching predicted activation energies with empirical values.

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