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Molecular Dynamics Study of Carbon Diffusion in Cementite

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1. Introduction

Although cementite (Fe_3C) is a most important phase in steels, at the same time, there is very little known in regard to the fundamental properties of Fe_3C. This lack of information is largely a result of this compound being metastable with respect to its decomposition products: C-saturated ferrite or austenite (depending on temperature) and graphite. It is very difficult to obtain 'pure' Fe_3C in the sizes and amounts necessary for many fundamental studies of its properties including investigation of its thermodynamics and diffusion behaviour. For example, conventional radiotracer diffusion experiments are essentially impossible and the measured chemical diffusivities show considerable error and lack information on their compositional dependence.

In the last few years, the role of diffusion in Fe_3C in the technologically important metal-dusting process has attracted considerable interest [1] but the above mentioned problems mean that revealing the mechanism of diffusion in Fe_3C from experiments will be especially difficult. The simulation method of molecular dynamics has now reached a level of maturity and reliability that it can very profitably be used to understand for the first time the mechanism of C diffusion in Fe_3C. This is the subject of this paper.

2. The model

The Fe_3C structure was simulated as a calculation box with periodic boundary conditions consisting of 10×10×10 simple orthorhombic unit cells with lattice parameters a=4.523 Å, b=5.089 Å and c=6.743 Å and 4 Fe atoms of type 1 (0.833, 0.040, 0.250; 0.167, 0.960, 0.750; 0.667, 0.540, 0.250; 0.333, 0.460, 0.750), 8 Fe atoms of type 2 (0.333, 0.175, 0.065; 0.667, 0.825, 0.935; 0.167, 0.675, 0.435; 0.833, 0.325, 0.565; 0.667, 0.825, 0.565; 0.333, 0.175, 0.435; 0.833, 0.325, 0.935; 0.167, 0.675, 0.065) and 4 C atoms (0.430, 0.870, 0.250; 0.570, 0.130, 0.750; 0.070, 0.370, 0.250; 0.930, 0.630, 0.750) per unit cell (the atomic positions are in units of the lattice parameters). Fe (1) and Fe (2) are two stoichiometrically different iron sites. Thus, this model contains 12000 Fe atoms and 4000 C atoms. The Fe-Fe interaction was described using the Johnson empirical pair–potential [2]. To describe the Fe-C pair interaction we used the potential proposed by Johnson, Dienes and Damask [3]. The use of the Johnson–Dienes–Damask potential together with the Johnson potential permits an adequate description of the behaviour of C interstitials in α-Fe and in martensite [3]. The structure and relative energy of Fe_3C [3] have also been investigated by means of these potentials. The situation with the weak C–C potential is more complicated. There is no agreed and detailed data about the preferred type of interaction for C–C pairs in Fe-C alloys. That is why as a first approximation we do not consider the direct interaction between C–C atoms. However, we prevent the situation when two C atoms occupy the same positions, and, in the present study for describing the C-C interaction, we chose a purely repulsive Born–Mayer potential with a cut–off radius of 1.5 Å which is much smaller than the distance between the first nearest neighbour carbon positions. To initiate the diffusion process, atoms were given initial velocities according to the Maxwell distribution at a given temperature, and an isothermal annealing procedure was performed in a temperature range of 1173–1373 K with a step of 50 K. The MD simulations consist of a numerical integration of the equations of atomic motion using a time step $\Delta t = 1.5\times10^{-15}$ s according to the Verlet algorithm. Periodically, the system was transferred to a state at $T = 0$ K where atoms occupied equilibrium positions in a local potential minima. This was done by making use of the static relaxation method. After this, the C movements that occurred were analyzed.

3. Results and discussion

It was found that C diffusion in Fe_3C is realized by means of interstitial sites, which form a base-centered orthorhombic sublattice in cementite with sublattice parameters $a_I=a$, $b_I=b$ and $c_I=0.5c$ and 2 sublattice points 0.0, 0.0, 0.0 and 0.5, 0.5, 0.0 in units of a_I, b_I and c_I or, in other words, 4 interstitial positions per Fe_3C unit cell 0.0, 0.0, 0.0; 0.5, 0.5, 0.0; 0.0, 0.0, 0.5 and 0.5, 0.5, 0.5 in units of a, b and c. It should be noted that the distance between the nearest neighbours interstitial sites in [110] and $[1\bar{1}0]$ directions (3.404 Å) is very close to the distance between the nearest neighbour interstitial sites in the [001] direction (3.372 Å). The interstitial sites are less energetically favourable for C atoms than their original positions. However, with an increase of temperature, because of the growth of entropy, some fraction of the C atoms occupies the interstitial sites and the corresponding same fraction of originally C positions becomes vacant. In effect, this is equivalent to the formation of Frenkel defects. In particular, at the highest temperature 1373 K in our computer simulation the 'equilibrium' fraction of C atoms on interstitial sites is ~ 0.22. We defined the three principal carbon diffusion coefficients D_x, D_y and D_z along the three orthogonal crystallographic axes x, y and z at each temperature at 'equilibrium' by making use of the Einstein equation and the mean square displacements of the C atoms. Then the Arrhenius parameters of C diffusion in Fe_3C along the three orthogonal crystallographic axes were determined. It was established that the fastest C diffusion is along the [001] z-direction, followed by the [100] x- and [010] y-direction. For example, at 1373 K we have that $D_x/D_z\approx0.73$ and $D_y/D_z\approx0.45$.

4. Conclusions

We have performed molecular dynamics simulations to investigate C diffusion in cementite. The assumption that C atoms can interact with each other only indirectly (via neighbouring Fe atoms) has been used. We have elucidated the interstitial mechanism of C diffusion in Fe_3C as well as determining the 'equilibrium' fraction of carbon atoms on interstitial sites and parameters of C diffusion in Fe_3C along the three orthogonal crystallographic axes.

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References

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