



A molecular-dynamics study on carbon diffusion in face-centered cubic iron



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ABSTRACT

Molecular-dynamics calculations targeted at the diffusion of carbon in γ -iron were performed using the Modified Embedded Atom Method (MEAM) interatomic potential by Lee. The diffusion coefficients were calculated at different temperatures and carbon concentrations. A temperature-dependence of the diffusion coefficient according to the Arrhenius law was assumed. By doing so, activation energies as well as pre-exponential factors for different carbon concentrations were derived from the diffusion coefficients and compared to experimental values. Good agreement was reached for the activation energies while the calculated pre-exponential factors differ from experimental values.

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1. Introduction

Understanding dynamical processes on an atomistic or molecular level and their influence on mechanical properties is vital to the design of new steel materials. If we consider the importance of Fe–C solid solutions in steel technology, the dynamical behavior of carbon in solid iron is of particular interest.

On the aforementioned atomistic or molecular level, dynamical processes can be effectively studied by atomistic simulation techniques such as molecular dynamics or Monte Carlo simulations. In order to describe the atomic interactions most accurately, quantum–mechanical methods should be the preferred choice. The study of dynamical processes, however, involves the simulation of many hundreds or rather thousands of atoms on a timescale of picoseconds to nanoseconds. Due to their computational complexity, quantum–mechanical methods are currently not suited for this kind of simulations taking into account the presently available computational resources. Thus, semi-empirical potentials have to be developed. A common way to model metallic systems is the so-called Embedded Atom Method (EAM) [1] that is similar, at least to some degree, to Density-Functional-Theory, and which describes the total energy of a system by the sum of a pair-wise

interaction function and an embedding function representing the energy of an atom embedded in the background electron density. Originally developed by Daw and Baskes, EAM was extended to the Modified Embedded Atom Method (MEAM) [2] by Baskes through including angular-dependent terms in the embedding function. In this way the same functional form of the potential can be used for a wide range of materials from metallic systems to covalently bonded silicon [3] or carbon [4]. For more details on the method, we refer to literature [5]. MEAM potentials have been published for a number of pure elements [6,7] as well as binary [8,9] and ternary [10] alloys including the Fe–C [11] binary alloy. Nonetheless, potentials for some systems of specific importance for steel materials, e.g., Fe–Mn–C or Fe–Al–C, are not yet available.

Because it makes up the basis of mass transport, diffusion is particularly important among the processes governing dynamical behavior on a molecular level. Indeed, the diffusion of carbon in ferritic and austenitic iron has been experimentally investigated for many decades [12–19], and diffusion coefficients are available for a wide range of conditions and carbon concentrations. Nonetheless, studying the atomistic mechanism of diffusion experimentally is difficult. Hence, simulation techniques can help as the movement of every atom can be tracked individually instead of statistically. Tapasa et al. have studied the diffusion of carbon atoms in α -iron by molecular-dynamics simulations using semi-empirical interatomic potentials [20]. The Fe–Fe interaction was described by an EAM potential while a pair potential was used

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for the Fe–C interaction. The activation energy as well as the pre-exponential factor of the diffusion of one carbon atom in a bcc iron matrix were obtained in good agreement with experiments and static *ab initio* calculations. Diffusion of carbon in bcc- and fcc-iron has also been studied by Rosato using Tight-Binding Second-Moment-Approximation (TB-SMA) potentials for both the Fe–Fe and Fe–C interaction [21]. In addition to static calculations of migration energies, some molecular-dynamics simulations were performed to study the diffusion path of carbon. No diffusion coefficients were reported, and carbon–carbon interactions were disregarded. We note that a carbon atom in an fcc-iron host is most stable in an octahedral position. Thus, diffusion can be seen as a number of subsequent jumps between adjacent octahedral sites. The currently available data suggest that diffusion takes place by direct jumps along the $\langle 110 \rangle$ direction such that the tetrahedral position is not visited as an intermediate state [11]. These direct jumps of the migrating carbon atoms take place through the edges of the edge-sharing iron octahedra.

Most of the computational research that has so far been done on the Fe–C binary alloy has focused on the bcc phase of iron. The scope of this work, however, is to study the diffusion of carbon in fcc iron. In what follows, diffusion coefficients are calculated from molecular-dynamics simulations for a range of temperatures and carbon concentrations and are compared to experimental data [14,18,19,22]. According to the Einstein relation, the diffusion coefficient is linked to the mean-squared displacement of the diffusing atoms by:

$$\langle R^2(t) \rangle = 6Dt, \quad (1)$$

where D is the diffusion coefficient, t the time and $\langle R^2(t) \rangle$ denotes the ensemble average of the squared displacement at time t , the mean-squared displacement (MSD) [23]. In other words, the diffusion coefficient is proportional to the slope of the MSD curve versus time and can thus be obtained by molecular-dynamics simulations. A number of empirical formulas to describe the dependence of the diffusion coefficient on temperature and carbon concentration have been proposed, all based on experimental results, and these formulas usually have an Arrhenius-type shape. According to the latter law, the temperature dependence of the diffusion coefficient can be described by:

$$D(T) = D_0 \times e^{-\frac{E_A}{RT}}, \quad (2)$$

where $D(T)$ denotes the diffusion coefficient at temperature T , D_0 the pre-exponential factor and E_A the activation energy of diffusion. Therefore, the diffusion rate can be characterized by the activation energy E_A and a pre-exponential factor D_0 . The pre-exponential factor is sometimes interpreted as a frequency factor, i.e., being proportional to the number of attempted jumps over a period of time. In the limit of infinite temperature, every attempted jump is successful such that the diffusion coefficient is equal to the pre-exponential factor.

Given the calculated diffusion coefficients at different temperatures, the activation energies and pre-exponential factors are determined for each simulated carbon concentration. These values are then compared to activation energies and pre-exponential factors from Arrhenius-type empirical formulas published in literatures [14,22].

In order to describe the interatomic interaction, the 2NN MEAM potential by Lee is used [11] which includes first- and second-nearest-neighbor interactions (hence 2NN). To our knowledge this potential originally published in 2006 has only been applied in a handful of studies [24,25]. The ability of the potential to describe diffusion correctly would pave the way for applying it to further studying the dynamical behavior of carbon in γ -iron.

2. Computational methods

All simulations were performed using the LAMMPS [26] molecular-dynamics code. The 2NN Modified Embedded Atom Method (MEAM) potential for the Fe–C system by Lee [11] was used as interatomic potential. Periodic boundary conditions were applied to all three dimensions. The simulation box was filled with Fe atoms on the respective fcc lattice sites. Carbon atoms were added, randomly distributed among the octahedral sites of the fcc lattice. Initial velocities were assigned corresponding to an initial temperature of 50 K. Subsequently, the systems were heated to and equilibrated at the desired temperatures. Productive simulations were carried out for 10 ns with a timestep of 1 fs. The mean-squared displacement (MSD) of all carbon atoms in the simulation box with respect to their positions in the equilibrated systems was recorded every timestep. All simulations were performed under zero pressure. Both temperature and pressure were controlled by means of weak coupling [27] during equilibration. For the productive simulations, a Nose–Hoover thermostat and barostat were employed. A relaxation time of 0.1 ps was used for the thermostats. The barostats had a relaxation time of 1 ps.

3. Results and discussion

In order to make sure that this study on carbon diffusion arrived at reasonable quantities, the influence of the size of the simulation box was investigated first. In the interest of lowering the computational burden, a small simulation box, i.e., a small number of atoms, is generally preferable. Any impact of the box size on the results, however, must be excluded or at least reduced to a tolerable level. Various diffusion simulations were performed for a carbon concentration of 1.1 wt% at a temperature of 1300 K with simulation boxes containing 4000 ($10 \times 10 \times 10$ cells), 13,500 ($15 \times 15 \times 15$) and 32,000 ($20 \times 20 \times 20$) iron atoms. The MSD curves for the carbon atoms were compared with each other, as given in Fig. 1 (top). Fluctuations from perfect linearity are expected to increase with decreasing box size as the number of carbon atoms is lowered. While the curve for the $10 \times 10 \times 10$ supercell shows quite some fluctuation, the curves for the $15 \times 15 \times 15$ and $20 \times 20 \times 20$ cells are almost linear and fairly similar to each other. As a consequence, the extension from 13,500 to 32,000 iron atoms has only a negligible impact such that size effects appear to be vanishingly small for these box sizes. Thus, all further simulations were performed with 13,500 iron atoms in a $15 \times 15 \times 15$ fcc supercell.

Carbon diffusion was studied for carbon concentrations of 0.6, 1.1 and 1.4 wt%, corresponding to 351, 702 and 984 carbon atoms accordingly. MSD curves were simulated for each carbon concentration at different temperatures. According to Eq. (1) the corresponding diffusion coefficient is proportional to the slope of the MSD curve versus simulation time. The comparison of the MSD curves for different carbon concentrations at a temperature of 1300 K (Fig. 1, bottom) shows an increase in the rate of diffusion with increasing carbon concentration. This observation is in accordance with experimental data.

By using the Arrhenius equation, the activation energy of diffusion as well as the frequency factor were obtained from the temperature dependence of the diffusion coefficient. For this purpose, the logarithms of the calculated diffusion coefficients were plotted versus $1/k_B T$ (Fig. 2). According to the Arrhenius equation, the activation energy and frequency factor correspond to the slope and the intercept of the resulting curve:

$$\ln(D) = -E_A \frac{1}{k_B T} + \ln(D_0) \quad (3)$$

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