Ab initio studies of the short-range atomic structure of liquid iron–carbon alloys

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ARTICLE INFO

ABSTRACT

In this work ab initio molecular dynamics simulation of liquid Fe–C system was carried out for different carbon concentrations (from 0 to 5 wt.% of C). Structures obtained by simulations were subjected to statistical analysis of geometry. The results indicate that short-range order of carbon atoms in liquid changes significantly with C concentration: from carbon solution in iron to cementite-like. It is also shown that nearest neighbors of C atoms at high concentrations form geometry similar to distorted prismatic sites in Fe_3C.

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1. Introduction

It can't be argued that Fe–C system is one of the most important materials for mankind in the past and in the present. So no wonder that during the last 50 years carbon solutions in iron have been extensively studied by numerous researchers in crystalline [1] and liquid phases [2,3], as well as in the form of nanoparticles (see e.g. [4]).

Chipman in his review [5] used published to date thermodynamic data to create comprehensive phase diagram for iron–carbon solutions. One of the key features appearing on the diagram is the presence of eutectic transformation $L \rightarrow \gamma + Fe_3C$ at 4.32 ± 0.03 wt.% of carbon with the formation of a metastable Fe_3C phase. This structure with 3:1 stoichiometry, named cementite, attracts significant amount of researchers' attention as it is the dominant carbide in steels at elevated temperatures [6], thus effectively determining their mechanical properties, and is believed to be the most abundant compound in Earth's inner core composition [3].

The structure of solid cementite was obtained by X-ray diffraction in [7]: it has an orthorhombic lattice with parameters $a = 4.523$ Å, $b = 5.089$ Å and $c = 6.743$ Å, and the symmetry corresponds to the space group *Pnma*. There are 16 atoms in the unit cell: 12 iron and 4 carbon. Iron atoms occupy two nonequivalent positions, which are firmly determined, while there are four possible nonequivalent positions for carbon placement in the iron lattice [8]. There it was shown also that energetically preferable structures for cementite are with carbon atoms situated in so called "normal prismatic" and "normal octahedral" pores.

But, the design of new materials with predetermined characteristics requires knowledge of the physical properties of the molten alloys, prior to solidification. One of the key conditions in the reliable management of metallurgical processes is clear understanding of the processes and reactions taking place in the structure of the melt. Obviously, liquid structure does not have any symmetry, either rotational or translational, as compared with crystalline solids, and that's why it is extremely difficult to study liquids using traditional X-ray or neutron diffraction methods. Although there have recently been published X-ray diffraction spectra for Fe–C melts [9], there exist objective difficulties in the experimental determination of short-range order and structure packing of carbon in the iron lattice, and because of that there are no direct experimental results on the positions of C in Fe in liquid phase.

In this work we present the results of ab initio molecular dynamics simulations of the atomic structure of iron–carbon solutions and discuss the changes in short-range atomic environment around carbon atoms in the melt.

2. Computational details

The theory standing behind ab initio molecular dynamical (AIMD) simulations is now widely known [10], so we don't have to give it in the present work. The main idea of the method is calculation of the total energy of a system and forces acting on the atoms of the system. Total energy is calculated by the self-consistent solving of Schrödinger equation and finding electron density of the system. Forces are used then to find evolution of the system in time by solving Newton's equations of motion.

The modeling of the structure of liquid Fe–C atomic clusters was done in the way AIMD is implemented in SIESTA software package [11]. This method is based on using non-local norm-conserving pseudopotentials generated by Troullier–Martins procedure [12]. In this work we utilize iron pseudopotential which was proposed by Izquierdo et al. in [13].

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The pseudopotential is generated employing the following set of valent orbitals and their radii (the number after orbital moment is the number of electrons on the orbital; in brackets the radius of the orbital in Bohr units is written): 3d7(2.00) 4s1(2.00) 4p0(2.00) 4f0(2.00). We used GGA in Perdew–Wang–Ernzerhof parameterization [14] as an approximation for exchange–correlation potential due to the known problem with LSDA not accounting for BCC as the ground state for crystalline iron. Non-linear corrections to the exchange–correlation terms proposed by Louie et al. [15] are also explicitly stated in the pseudopotential. These corrections represent substitution of a full core charge density into the pseudocore charge density, which, in its turn, is equal to the full core charge density outside the pseudocore radius and the spherical Bessel function j_0 inside the pseudocore. In [13] it is shown that the optimal pseudocore radius for iron is $0.7\ r_B$.

Another parameter accounting for the accuracy of self-consistent electron density calculations (and calculation time as well) is basis size, which is used for wave function expansion. Wave functions in SIESTA are expanded in products of radial functions, which depend on orbital quantum number, and spherical harmonics:

$$\phi_{lmn} = \phi_{ln}(r)Y_{lm}(r). \qquad (1)$$

In Eq. (1) one spherical harmonic with angular momentum lm can correspond to several radial functions with different orbital momenta ln and different cut-off radii [11]. The number of radial functions taken into account defines "quality" of the basis. In [13] it is shown that the using of "standard" DZP basis is enough to reproduce the parameters of crystalline iron structure with high degree of accuracy, and as a result we took this basis in the simulation process. The size of the basis was determined by cut-off energy $E_{cutoff} = 200$ Ry. All electronic structure calculations were done using one Γ-point in the Brillouin zone.

Temperature effects are taken into account in the AIMD simulation in the following way. First, temperature dependence of the melt's density is considered: the density of the model at each temperature is derived from the equation deduced on the basis of experimental data in [16]. The influence of temperature on the electronic subsystem is recognized by so called "electronic temperature" — parameter showing the smearing of Fermi distribution function with temperature. The biggest contribution to atomic dynamics is made by imposing a thermostat to the system. We carried out several modeling series using different canonical ensembles — NVT classical ensemble, where temperature was kept up using the Nosé–Hoover thermostat [17], and NPT canonical ensemble which was used to find equilibrium density of the system. For NPT simulations, Parrinello–Rahman barostat [18] was imposed to the system.

In this work we simulated the molecular dynamics of 6 supercells with different carbon contents. The compositions used for calculations, as well as densities taken from [16], are presented in Table 1. Initial atomic configurations for MD simulations were prepared using the following algorithm. First, we took ideal supercell of 200 atoms of iron and carbon, divided proportionally according to carbon concentration, in BCC state. Then, we introduced random atomic distortion with a mean amplitude of 10% of interatomic distance, which corresponds to Lindemann crystal melting criterion [19]. Third, we relaxed resulting configurations using conjugate gradients numerical scheme until atomic forces became less

than 0.2 eV/Å. After the relaxation atomic configurations were subjected to an AIMD run for a time interval of several ps. One time step in our simulation was 1 fs.

3. Results

Due to small atomic number of carbon its relative scattering factor is approximately 50 times smaller than that of iron atoms (see [9]). Hence, there are no direct experimental data on the positions of C in the iron lattice, and transitions in Fe–C structure are associated only with changes in the interference curves. Unlike the experiment, structure simulations can provide the researcher with direct description of the structure of a multi-component melt (if the simulation cell is large enough). The structure can be described in terms of either partial structure factors, or partial radial distribution functions. The partial radial distribution functions (PRDFs) for iron–carbon alloys, along with the data for pure iron, are presented in Fig. 1. It could be seen that for Fe–Fe and Fe–C pairs with the increase of C concentration PRDFs do not change considerably. Moreover, Fe–Fe PRDF for all examined carbon concentrations nearly coincides with both calculated RDF for pure iron and the data obtained by X-ray diffraction at 1833 K [20] up to the second minimum (Fig. 1(a)). Thus, unlike solid, where carbon atoms form interstitial solutions (imposing elastic stress on iron atoms), we assume that carbon admixture to iron in liquid state does not influence iron substructure in the melt.

The statistics for $g_{C-C}(r)$ at small carbon quantities is poor due to considerably small amount of time steps and the number of C–C pairs
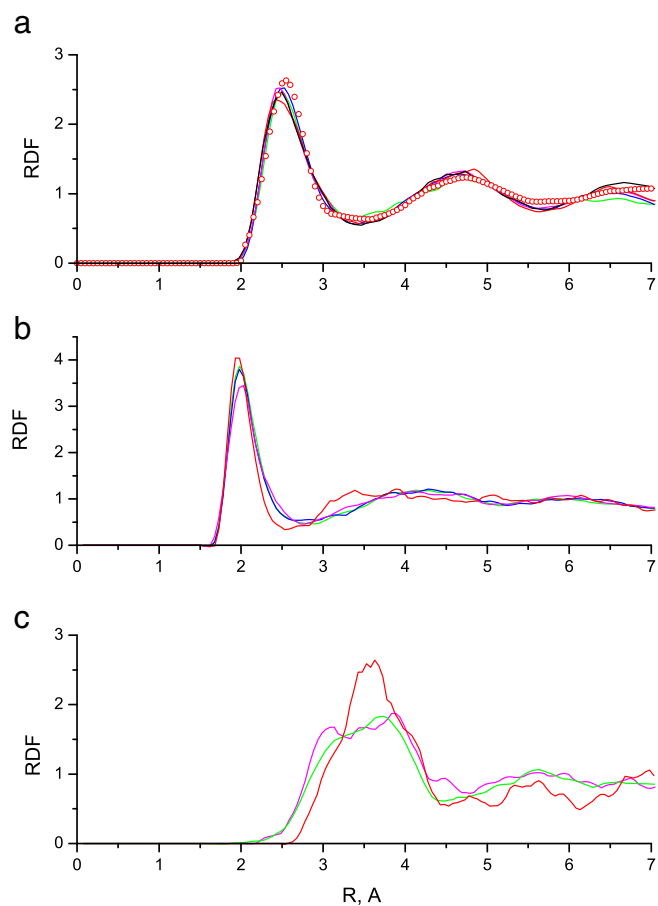

Fig. 1. Partial radial distribution functions for FeC alloys at different concentrations: (a) — Fe–Fe; (b) — Fe–C; (c) — C–C. Black line — pure Fe; red — 1 wt.%; magenta — 2 wt.%; blue — 3 wt.%; green — 4 wt.% of carbon. Red circles — experimental data for pure Fe [20].

Table 1
Composition and density of supercells used in the calculations.

C content (at.%)	C content (wt.%)	Density [16]
2	0.44	7.059
4.5	1.02	7.017
8.5	1.99	6.947
12.5	3.02	6.873
16	3.99	6.803
19.5	5.02	6.728