Second moment approximation of tight-binding potential for γFe applicable up to 1700 K

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Abstract

The atomic potential of γFe has been constructed on the basis of the second-moment approximation of the tight-binding scheme potential. To apply this potential to molecular dynamics simulations at high temperatures up to about 1700 K, the cut-off distance has been set to the sixth neighbours and other parameters have been determined from fitting to physical properties of γFe such as the cohesive energy, vacancy formation energy, lattice constant, elastic constants and bulk modulus. This potential can also describe the temperature dependencies of the lattice constant and the specific heat at constant pressure and can simulate hypothetical melting of γFe.

1. Introduction

Iron and its alloys are materials essential to human activity due to the fact that they can provide a large variety of useful properties by heat treatment. These heat treatments often utilise phase transformations during the cooling process from the γ phase. It is prerequisite to have fundamental knowledge of structures and physical properties of γFe as well as αFe to optimise the heat treatments on the basis of dynamics of the phase transformations. Molecular dynamics (MD) simulation would be one of the most useful approaches to obtain such knowledge.

The application of MD to γFe requires an interatomic potential of γFe which is applicable up to a temperature as high as about 1700 K. With respect to interatomic potentials for transition metals, it has already been known:

(i) The potentials should contain many-body interaction [1–4].
(ii) The interaction should be operative over a long distance, in particular, for the application to simulation at high temperatures [5,6].

The most commonly applied potential models for transition metals include the embedded atom method (EAM) [1] and the second-moment approximation for tight-binding (TB-SMA) [5,6]. Potential parameters for these models should be determined empirically so that the models can reproduce experimental values such as cohesive energy, lattice constants, elastic constants and so forth. Both potential models consist of a pairwise function and a many-body function. Consequently, there is no essential difference between these two; however, the TB-SMA model has an advantage that it is simpler in the mathematical form.

On the basis of the above models, a few workers have proposed interatomic potentials for transition metals including γFe. Yang and Johnson [7], for example, have made an EAM model potential with the cut-off distance up to the second neighbours in the bcc and fcc lattices to simulate αFe and γFe, respectively. However, no physical property data for γFe have been used to determine the potential parameters, thereby bringing about inaccuracy in γFe simulation. On the other hand, Rosato [8] has reported a TB-SMA model potential for γFe with the cut-off distance limited up to the first neighbours; however, the thermodynamic data used for fitting have not been compared with experimental values and, furthermore, the data sources have not been cited. In contrast, Cleri and Rosato [6] have made TB-SMA model potentials for fcc metals such as Ni, Cu, Ag, Au and Pb with the cut-off distance up to the fifth...
neighbours, and have shown that the extension of cut-off distance is very effective for simulation at high temperatures. This suggests that a TB-SMA model potential for γFe should also be given a longer cut-off distance.

Thus, potential parameters for γFe have not been determined based upon physical property data of γFe in the previous work. This is because these data are difficult to determine experimentally since γFe is stable only at temperatures between 1184 and 1665 K. However, in actuality, there have been some values reported for vacancy formation energy [9–11] and elastic constants [12] of γFe. Consequently, potential parameters for γFe should be determined again using these values. Thus, the aim of the present work is to establish an interatomic potential for γFe in the fcc lattice, where the TB-SMA model is used due to the simplicity of its mathematical form.

2. Potential model for γFe

In the potential function of TB-SMA [6], the total cohesive energy $E_C$ at an atomic site $i$ is written as

$$E_C = -(E_R^i + E_B^i)$$

(1)

where $E_R^i$ is the repulsive energy term and $E_B^i$ is the band energy term. The repulsive and band energy terms are in turn expressed by the respective equations

$$E_R^i = \sum_j A \exp[-p\left(\frac{r_{ij}}{r_0} - 1\right)]$$

(2)

$$E_B^i = -\left\{ \sum_j \xi^2 \exp[-2q\left(\frac{r_{ij}}{r_0} - 1\right)] \right\}^{1/2}$$

(3)

where $r_{ij}$ represents the distance between atoms $i$ and $j$, $r_0$ is the interatomic distance between the nearest neighbours in the fcc lattice, $A$, $\xi$, $p$ and $q$ are free parameters. Values of these parameters should be determined in order to reproduce physical property values of γFe such as the vacancy formation energy [9–11], elastic constants [12], bulk modulus [12], lattice constants at 0 K and other temperatures [13], and cohesive energy. Values of the lattice constant at 0 K and the cohesive energy cannot be measured but can be estimated as below.

2.1. Cohesive energy of γFe [8]

The difference between the cohesive energies for αFe ($E_C^\alpha$) and γFe ($E_C^\gamma$) can be derived from the characteristic of a state function that its cyclic integral must be zero, as follows

$$E_C^\gamma - E_C^\alpha = \int_0^{T_{\text{m}}} C_{\gamma,T} \, dT + \int_0^{T_{\text{m}}} C_{\gamma,T} \, dT$$

(4)

where $C_{\gamma,T}$ and $C_{\gamma,T'}$ are the specific heats at constant pressure for αFe and γFe, respectively, $T_{\text{m}}$ is the temperature of the phase transformation αFe $\rightarrow$ γFe (1184 K) and $\Delta H_0$ is the enthalpy change associated with the transformation. Substituting data for $E_C^\alpha$, $C_{\gamma,T}$, $C_{\gamma,T'}$ and $\Delta H_0$ into Eq. (4) can lead to a value of $E_C^\gamma$, which has been reported as 4.26 eV by Rosato [8].

2.2. Lattice constant of γFe at 0 K

Values for the lattice constant of γFe are available only for high temperatures, and thus the value at 0 K is estimated from those at higher temperatures on the basis of the temperature dependencies of the linear thermal expansions for fcc metals. Fig. 1 shows linear thermal expansions for several fcc metals as functions of temperature ($T$), where the values are normalised, e.g. expansion (Δ$T$) by the sample length at 293 K ($l_{293}$) as $\Delta l_{293}$ [14], and temperature by the respective melting points ($T_m$) [15] as $T/T_m$. Fig. 1 includes data for γFe; values of $\Delta l_{293}$ for γFe have been plotted as $\Delta l_{293}$, where $\Delta l$ is the expansion in the lattice constant and $l_{293}$ is the lattice constant at 293 K. The value of $a_{293}$ has been estimated as 3.586 Å by extrapolation of lattice constants at high temperatures [13]. The hypothetical melting point for γFe has been defined as a temperature where the Gibbs energy for γFe is equal to that for liquid Fe and has been estimated as 1793 K using thermodynamic data [16], as shown in Fig. 2. Inspection of Fig. 1 shows that temperature coefficients of the linear thermal expansions for these metals are very small near 0 K and become larger as the temperature increases. The value of $\Delta l_{293}$ for γFe at 0 K is estimated as $-0.20\%$ on the basis of the temperature dependencies of the linear thermal expansions for other fcc metals, especially for Ni. Using the values of $\Delta l_{293}$ at 0 K and $a_{293}$ obtained, the lattice constant at 0 K can be derived as 3.579 Å, leading to the interatomic distance between the nearest neighbours at 0 K (2.530 Å), which is used as $r_0$ in Eqs. (2) and (3).

![Fig. 1. Thermal expansion for several fcc metals [14] as function of temperature normalised by respective melting points.](image-url)
Values of the cohesive energy and lattice constant obtained in the above are given in Table 1.

### Table 1

Experimental and calculated properties of γFe

| Property                  | Values used for fitting | Calculated |
|---------------------------|-------------------------|------------|
| Cohesive, $E_C$ (eV)      | 4.26                    |            |
| Lattice constant at 0 K, $a_0$ (Å) | 3.579                   |            |
| Vacancy formation energy $\gamma$, $E_j^\gamma$ (eV) | 1.50 [9–11]            |            |

#### Elastic constant

| Elastic constant | $C_{11}$ (GPa) | $C_{12}$ (GPa) | $C_{44}$ (GPa) | $B$ (GPa) |
|-----------------|----------------|----------------|----------------|-----------|
| $C_{11}$ (GPa)  | 154 ± 14 [12]  | 162            |                |           |
| $C_{12}$ (GPa)  | 122 ± 8 [12]   | 118            |                |           |
| $C_{44}$ (GPa)  | 77 ± 13 [12]   | 73             |                |           |
| Bulk modulus, $B$ (GPa) | 132 [12]         | 132            |                |           |

*The value of vacancy formation energy has been determined as an average of values reported in Refs. [9–11].

and $q$ were determined using the software Mathematica. Various sets of parameters $A$, $\xi$, $p$ and $q$ were prepared in this stage.

In the next stage, the most reliable values of the parameters were determined by investigating which set of parameters most accurately reproduced the values for the lattice constant, elastic constants and bulk modulus of γFe at 1428 K, when using MD simulation. The unit cell for this simulation contained 500 Fe atoms arranged at fcc lattice sites, to which cell the three-dimensionally periodic boundary condition was applied. The canonical ensemble approach was adopted, where constant temperature and pressure conditions were established using the Nosé technique [17,18] and the Parrinello–Rhaman technique [19,20], respectively. Equations of motion for atoms were integrated with a time interval of 1 fs using Gear’s fifth-order predictor–corrector algorithm [21]. MD simulation was carried out using the software ‘MASPHYC’ produced by Fujitsu Co. Ltd installed in Global Scientific Information and Computing Centre in the Tokyo Institute of Technology, to obtain data for positions and velocities of Fe atoms at 1428 K. From these data, the lattice parameter, elastic constants and bulk modulus were calculated and compared with the respective, reported values.

Various sets of parameters were determined by iteration of the above calculation, the most reliable potential parameters were obtained as $A = 0.11313$ eV, $\xi = 1.5534$ eV, $p = 11.948$ and $q = 2.7654$. MD calculation using these parameters produced values for the elastic constants and bulk modulus as given in Table 1. This table also summarises experimentally determined elastic constants and bulk modulus for γFe. Comparison between the experimental and calculated values indicates that the potential determined in the present work can reproduce the mechanical property values for γFe within experimental error. Table 2 gives elastic constants and bulk moduli for several fcc metals determined by experiments [22] and MD simulations; the latter were carried out using the TB-SMA.
potential by Cleri and Rosato [6]. For each metal, values in the upper line are determined by experiments and those in the lower line by MD, and it can be seen that these are in good agreement with each other. The agreement seen in Table 1 is as good as that in Table 2, which suggests that the potential parameters determined in the present work are reasonable.

4. Applicability of potential to other physical properties of $\gamma$Fe

To further confirm the validity of the potential determined in the previous section, MD simulations were carried out to derive (i) the lattice constant and (ii) specific heat at constant pressure as functions of temperature, (iii) the melting temperature and (iv) the vacancy formation energy at 0 K—this is recalculated to confirm the self-consistency of the potential—as below.

4.1. Lattice constants

Lattice constants were calculated for temperatures between 1223 and 1634 K at 1 atm using a unit cell containing 500 Fe atoms, where a NTP ensemble was applied. Fig. 3 shows the temperature dependence of lattice constant of $\gamma$Fe, where solid circles represent values calculated in the present work and open triangles represent values measured by Kohlhaas et al. [13]. The difference between these values is less than 0.2% and both are in very good agreement with each other.

Fig. 3 also includes values calculated using the EAM potential which has been reported by Yang and Johnson [7], which are represented by open circles. The EAM potential can describe the temperature dependence of the lattice constant. However, it can be seen that the values are much larger than the experimental values. Furthermore, in this simulation the $\gamma$Fe melts apparently at about 1500 K although real $\gamma$Fe exists in the state of solid at this temperature; consequently no lattice constant data at higher temperatures could be determined and shown in the figure.

4.2. Specific heat at constant pressure

The specific heat at constant pressure was obtained as the derivative of the enthalpy with respect to temperature. The results obtained in Section 4.1 gave the internal energy and volume per unit cell at each temperature, leading to the enthalpy per unit mass. The enthalpy was approximated to a quadratic function of temperature by the regression method.

Fig. 4 shows the specific heat at constant pressure for Fe as a function of temperature, where the solid line represents the specific heat for $\gamma$Fe derived from MD simulations and solid triangles represent recommended values for Fe in the solid and liquid states [16]. The calculated values are in fairly good agreement with the recommended values and describe the temperature dependence very well.

4.3. Melting temperature

The melting temperature was determined as a temperature where the internal energy changed discontinuously with a temperature rise. It is commonly known that MD simulation overestimates the melting temperature of a substance for the following reason. Melting starts at the surface in a real substance, i.e. the surface is very relevant to melting; however, simulation is carried out on a bulk model having no surfaces. To avoid this problem, simulation would be required on a model having surfaces such as a thin film model [23]. In this simulation, however, there is
a possibility of underestimating the melting temperature because a thin film model is subjected to surface melting, i.e. a phenomenon that the surface structure becomes liquid-like at temperatures lower than the melting point [24,25]. On the other hand, it has also been reported that surface melting does not occur in fcc metals having close-packed (111) surface [26,27]. In the present work, accordingly, a unit cell having the (111) surface was used for determining the melting temperature.

For this calculation, a unit cell consisting of 42 atomic layers was prepared: each layer contained 120 Fe atoms and vacuum regions were provided in the upper and lower parts of the unit cell. The dimensions of the unit cell were determined on the basis of the lattice constant at 1000 K. As a consequence of this, the surface model expresses a thin film of about 88 Å thickness and has two (111) surfaces. The unit cell at a required temperature was constructed on the basis of the structure at a temperature lower than the required temperature, where the dimensions of the unit cell were determined from the lattice constant for the required temperature. Using the unit cell, the position and velocity of each atom were calculated at constant temperatures between 1000 and 1800 K. The simulation was carried out for more than 300 ps and the internal energy was statistically averaged over the last 100 ps period to observe a discontinuous change in the internal energy.

Fig. 5 shows the temperature dependence of the internal energy per unit cell. The internal energy increases linearly with increasing temperature but displays a discontinuous change at a temperature between 1720 and 1730 K. This change suggests that the surface model melts around 1725 K. In fact, the structure calculated by MD was crystalline at 1720 K but liquid-like at 1730 K, as shown in Fig. 6. Accordingly, it is likely that the melting temperature of this model exists around 1725 K, and this value is comparable to the hypothetical melting point (1793 K) for γFe determined thermodynamically in Section 2.

4.4. Vacancy formation energy

The vacancy formation energy at 0 K was derived as the difference between internal energies for a unit cell containing 500 atoms and for that containing 499 atoms and one point defect. The calculated vacancy formation energy is 1.48 eV, and this value is smaller by about 1.3% than a value of 1.50 eV used for determination of the potential parameters, given in Table 1. This difference would be due to structural relaxation associated with vacancy formation and, thus, these values are in reasonable agreement with each other.

5. Conclusions

The potential of γFe has been constructed on the basis of the TB-SMA potential which is expressed by Eqs. (1)–(3). The potential with the cut-off distance up to the sixth neighbours and \( r_0 = 2.530 \) Å, \( \varepsilon = 0.11313 \) eV, \( \xi = 1.5534 \) eV, \( p = 11.948 \) and \( q = 2.7654 \) can reproduce well physical property values of γFe such as the cohesive energy, vacancy formation energy, lattice constant, elastic constants and bulk modulus. It can also describe the temperature dependencies of the lattice constant and the specific heat at constant pressure and can simulate...
hypothetical melting of γFe. The potential proposed in the present work can be applied at temperatures up to 1700 K.

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