Melting of thin $\gamma$Fe–C films having (100), (110) and (111) surfaces in terms of molecular dynamics simulation

R. Kojima*, M. Susa

Department of Metallurgy and Ceramics Science, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

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Abstract

Structural changes associated with melting of thin $\gamma$Fe–C films having (100), (110) and (111) surfaces have been investigated by molecular dynamics simulation. Structures of thin film and bulk models of $\gamma$Fe containing about 0–4 at.-% C were calculated at constant temperatures between 1000 and 1800 K. The liquidus temperature for each thin film model decreased with increasing the C concentration. Comparison between the atomic number density distributions of Fe and C showed: (i) The atomic number density of C near the surface increases before the formation of liquid near the surface. (ii) This increase becomes more prominent as temperature rises. (iii) Melting of $\gamma$Fe–C alloy would be rate-controlled by diffusion of C from the solid phase to the solid–liquid interface. These findings suggest that the increase in the C concentration enhances atomic vibrations of Fe near the surface and promotes melting of Fe at lower temperatures. Furthermore, it has been concluded from Lindemann’s law of melting that surface melting occurs in $\gamma$Fe–C alloy having (110) surface more easily.

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1. Introduction

Nano-particles of a material melt at temperatures lower than its bulk due to the effect of surface. This has been predicted from thermodynamics in consideration of surface energy [1] but melting dynamics of nano-materials has not been investigated so far. However, such investigations have a possibility of proposing new processes of melting and joining for nano-structured materials at further lower temperatures than expected from thermodynamics. Apart from nano-materials processing, generally, melting is an important phase transition relevant to materials processing. Because of this, attempts have been made to investigate melting dynamics of metals. The first interest in melting is about the site where melting starts, which site is known to be surface. Furthermore, the empirical fact that melting of pure metals is not associated with superheating suggests that there is nucleation of liquid occurring on the surface at temperatures lower than the melting points [2].

This phenomenon is known as surface melting, which was firstly observed for Pb using the medium-energy ion scattering technique [3]. The surface-melting layer is essentially a solid phase because it has the structural periodicity of crystals; nevertheless, atoms in the surface-melting layer have large mean square displacements comparable to those of atoms in liquid, and thus this layer also seems close to liquid from the perspective of atomic movements [1]. Afterwards, surface melting was also observed for metals having lower melting points such as Ga [4] and Al [5]. Meanwhile, there has been little experimental work on metals having higher melting points such as transition metals due to experimental difficulty of high vapour pressures at the melting points.

Molecular dynamics (MD) simulation would be useful to systems on which it is very difficult to experiment. Actually, MD simulation has been applied to Pb [6], Al [7], Ni(110) [8] and Cu(110) [9], and could have successfully reproduced surface melting occurring in these metals. Furthermore, Kojima and Susa [10] have simulated surface melting of thin Cu film models having (100), (110) and (111) surfaces by MD and found that the (110) model surface-melts at...
a temperature lower than the others, which finding is consistent with those obtained in other fcc metals. However, there have been no reports about surface melting of alloys so far. Thus, the aim of the present work is to investigate melting dynamics of γFe–C alloy by MD to explore a possibility of surface melting being applied to nanomaterials processing.

2. MD simulation

MD simulation for the γFe–C system requires potentials between Fe atoms, between Fe and C atoms and between C atoms in γFe. The interaction between Fe atoms was expressed by the approximation of second-moment tight-binding scheme potential [11], and the interaction between Fe and C atoms was reported by Butler and Cohen [12], while the interaction between C atoms was not known. However, McLellan and Ko calculated the interaction between C atoms in the first neighbour in γFe (D3g) using a second-order statistical mechanical technique based upon cumulant expansions at temperatures between 1073 and 1673 K [13]. Using these data, in the present work, the atomic potential between C atoms was determined in the following procedure:

(i) The interaction energy between C atoms was plotted against the first neighbour distance of C atoms, where this distance is assumed to equal the first neighbour distance of Fe atoms.

(ii) The interaction energy plotted against distance was regressed to an exponential function of distance, which is typical of potential functions.

Consequently, the potential \( \Phi \) was obtained in the following mathematical form:

\[
\Phi(r) = 7.206 \times 10^6 \exp\left(-7.072r\right)
\]

where \( r \) represents the distance of C atoms in Å.

The software ‘MASPHYC’ produced by Fujitsu Co. Ltd was used for MD simulation. The canonical ensemble approach was applied to this simulation, where constant temperature and pressure conditions were established using the Nosé technique [14,15] and the Parrinello–Rhaman technique [16,17], respectively. Equations of motion for atoms were integrated with a time interval of 1 fs using Gear’s fifth-order predictor–corrector algorithm [18]. The three-dimensionally periodic boundary condition was applied to the unit cell.

Firstly, to confirm the reasonability of MD simulation, the lattice constants of γFe containing 0–6 at.% C were calculated at a pressure of 1 atm and temperatures between 500 and 1700 K by constant pressure MD. The unit cell used for this calculation was in the shape of a cube consisting of 5×5×5 fcc lattices, which cube contained 500 Fe atoms at lattice sites and 0–30 C atoms at interstitial sites.

Secondly, the structure near the surface of γFe was investigated: This simulation was carried out on thin film models of γFe–C alloy having (100), (110) and (111) surfaces at temperatures between 1000 and 1800 K by constant temperature MD. About 5000 Fe atoms were arranged in the unit cell in the shape of a rectangular parallelepiped of ca. 26×26×88 Å³ so as to have (100), (110) or (111) surface. The dimensions of the unit cell were determined from the lattice constant at 1000 K obtained from the simulation mentioned in the above paragraph. By adding vacuum regions above and below this unit cell, the unit cell for the thin film model was produced as shown in the previous work [10]. In addition, C atoms were arranged in the unit cells randomly so as to have 0, 2 or 4 at.% C concentration. The unit cell at the required temperature was constructed based upon 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.

MD simulation was conducted for more than 200 ps, and the internal energy was statistically averaged over the last 50 ps period. To investigate the structural and thermal properties, calculations were also made on the distribution of the number density of atoms (\( \rho(z) \)) [19] and the mean square amplitude of thermal vibration of each atom for 50 ps.

3. Results and discussion

3.1. Accuracy of MD simulation

Fig. 1 shows the dependence of the lattice constant of γFe on the C concentration, which is expressed as the number of C atoms in 100 Fe atoms. Solid and dashed lines represent values calculated in the present work and measured by Onink et al. [20], respectively. The calculated lattice constants increase with an increase in the C concentration and temperature; however,
3.2. Melting dynamics of thin γFe films

MD simulation showed: The thin film models melted completely at 1730 K for (111), at 1700 K for (100) and at 1690 K for (110), whereas there were solid phases still remaining at temperatures lower by about 10–15 K than the respective temperatures. This suggests that melting temperatures for the (111), (100) and (110) thin film models exist around 1725, 1690 and 1685 K, respectively. This dependence of the melting temperatures on the surface orientation of thin γFe films is the same as that of thin Cu films [10] and would be relevant to the ease with which atoms can move in each plane.

To know possible structural changes near the surface with an increase in temperature, attempts were made to investigate the displacement of atoms near the surface from MD outputs. Fig. 2 shows number density distributions \( \rho(z) \) for (a) (111) and (b) (110) thin film models at 1000 and 1600 K along the direction perpendicular to the surface. The origin on the abscissa is located at the centre of the unit cell and each arrow represents the initial surface layer at 1000 K. The peaks in the (111) and (110) thin film models correspond to (111) and (110) planes, respectively. Fig. 2(a) shows clear peaks both inside the film and near its surface at 1000 K. Also at 1600 K, peaks are still clear throughout the film but the height of the peaks is slightly lowered. These findings say that atoms move around lattice sites and that the magnitude in atomic movements is enhanced by a temperature rise throughout the film. In Fig. 2(b), peaks near the surface are clear at 1000 K but become much lower and broader than those inside at 1600 K, which indicates that the surface structure in the (110) model becomes disordered more easily than that in (111) by a temperature rise. Furthermore, it should be noted that there is an additional peak on the initial surface layer at 1600 K. This peak can be assigned to the presence of adatoms. These structurally disordered layers can be considered as the surface-melting layer.

On the other hand, Kojima and Susa [10] have focused on atomic movements in the surface-melting layer and estimated its thickness from Lindemann’s law of melting [21,22]. This law says that melting occurs when the mean square amplitude of atomic vibrations \( \langle u^2 \rangle \) exceeds a value calculated from the following:

\[
\langle u^2 \rangle = (\delta d)^2
\]  

(2)

where \( d \) is the nearest atomic distance at the melting point and \( \delta \) is a constant specified by element. Namely, if proper values of \( d \) and \( \delta \) are given, a value of \( \langle u^2 \rangle \) can be calculated from Eq. (2), and its comparison with values of \( \langle u^2 \rangle \) calculated from MD simulation shows whether the system under consideration melts or not. For γFe, however, values of \( d \) and \( \delta \) have not been reported yet because Fe melts via the δFe phase at 1 atm. Because of this, these values are derived from the results by MD simulation in the present work. Namely, the value of \( \langle u^2 \rangle \) at the melting point of γFe has been determined as 0.04876 Å\(^2\) from a value of \( \langle u^2 \rangle \) inside the (111) thin film model at its melting point (1725 K) because this model has the highest melting temperature. On the other hand, the nearest atomic distance \( d \) at 1725 K has been obtained as 2.6110 Å from the previous MD calculation. Using these values and Eq. (2), a value of \( \delta \) for γFe is obtained as 0.08457. This value will be used to derive the value of \( \langle u^2 \rangle \) as a criterion for melting of γFe–C alloy in the later section.

On the basis of the above discussion, it is likely that atomic layers of which \( \langle u^2 \rangle \) exceeds 0.04876 Å\(^2\) surface-melts and thereby the thickness of the surface-melting layer can be estimated [10]. Fig. 3 shows the temperature dependence of the surface-melting layer thickness \( l_n \) of the (100), (110) and (111) thin film models of γFe. The thickness increases with increasing temperature, and surface

![Fig. 2. Number density distribution for (a) (111) and (b) (110) thin γFe film models at 1000 and 1600 K along the direction perpendicular to the surface.](image-url)
melting occurs at 1200 K for (110) and (100) and at 1400 K for (111). The screened portion represents the temperature range where \( \gamma \)Fe exists at 1 atm in actuality; accordingly, surface melting would occur in \( \gamma \)Fe.

3.3. Melting dynamics of thin \( \gamma \)Fe–C alloy films

Fig. 4 shows melting temperatures for the thin \( \gamma \)Fe–C film models as functions of the C concentration, obtained in the same manner as those for pure \( \gamma \)Fe. These melting temperatures are considered to be the liquidus temperatures, because the thin film models were completely melted at these temperatures, whereas the solid phases still remained at temperatures lower by 5 K than the respective temperatures. The melting temperatures of the thin film models decrease with increasing the C concentration; however, the melting temperatures for the thin film models are lower by about 100 K than the liquidus temperatures on the phase diagram. This decrease would correspond to that predicted from thermodynamics in consideration of surface energy.

Fig. 5 shows number density distributions of Fe and C atoms for the (110) thin film model containing 4 at.% C at each temperature. Values of \( \rho(z) \) for C are expressed as those multiplied by five. The origin on the abscissa is located at the centre of the unit cell, and each arrow represents the surface layer at 1000 K. The peaks for Fe near the surface are lower than those inside at 1400 K and further decrease with increasing temperature. These findings say that atomic movements are stronger near the surface than the inside and are enhanced by a temperature rise. Furthermore, at 1560 K there are no distinct peaks near the surface, which indicates that there is a liquid phase formed near the surface, solid and liquid phases containing C coexisting at this stage. It should be noted that there are no C atoms on the surface of Fe: This positioning of C near the Fe surface is in very good agreement with that predicted from the magnitude of chemisorption energy of C onto \( \gamma \)Fe [23].

Inspection of Fig. 5 shows that the temperature rise increases the number density of C atoms near the surface and, as a result, the presence of C between Fe atoms weakens the attractive force between Fe atoms, which would cause the thin film models of \( \gamma \)Fe–C alloy to melt at temperatures lower than \( \gamma \)Fe. Accordingly, it is also likely that surface melting of \( \gamma \)Fe–C occurs at temperatures lower than pure \( \gamma \)Fe. To confirm this, the thickness of the surface-melting layer is...
estimated on the basis of Lindemann’s law given by Eq. (2) using a value of $\delta = 0.08457$, assuming that melting of γFe–C alloy is equivalent to melting of γFe.

Fig. 6 shows the temperature dependence of the melting layer thickness obtained for the (110) thin film model of γFe containing 4 at.% C. The surface-melting layer thickness increases with increasing temperature up to about 1450 K, above which the thickness change shows very wide fluctuation. This could be explained as follows: Above 1450 K the system does not undergo surface melting but melting. In the γFe–C system the formation of a liquid phase at the surface inevitably requires the diffusion of C to the vicinity of the surface because the liquid phase should contain a certain concentration of C to be equilibrated with its corresponding solid phase at a temperature. Further growth of the liquid layer requires more diffusion of C; however, it is difficult for MD simulation to supply constantly enough quantity of C for melting within its limited calculation time. Accordingly, the fluctuated change would be due to the diffusion control of C from the solid phase to the solid–liquid interface.

Fig. 7 shows the relation between the temperatures to form 5 Å thick surface-melting layers in equilibrium and the C concentration for the thin film models, along with the respective liquidus temperatures shown in Fig. 4. The temperatures to form 5 Å thick surface-melting layers decrease with an increase in the C concentration in all the models and are always lower than the corresponding liquidus temperatures. Comparison between the thin film models at the same temperature suggests that the (110) model has a thicker surface-melting layer. It can be concluded from Fig. 7 that the (110) thin film model surface-melts more easily, i.e. at temperatures lower than the others. Conventional thermodynamic discussion has not taken into account the existence of surface-melting layers and the difference between surface-melting temperatures in various surface orientations. Accordingly, there is a possibility of making γFe–C alloy being melted at temperatures lower than expected from thermodynamics, by effective utilisation of the surface-melting phenomenon.

Surface melting is also likely to be useful for joining of nano-materials at lower temperatures because its atomic diffusion characteristic is close to that of a liquid phase. Consequently, surface melting would work more effectively in the melting and joining processes for nano-particles as well as nano thin films, in addition to nano-structured objects, under optimised conditions of the dimensions and surface orientations of materials.

4. Conclusions

- Melting temperatures for the thin film models of γFe containing 0–4 at.% C are in the hierarchy (111) > (100) > (110), and these temperatures are lower by about 100 K than the corresponding liquidus temperatures on the Fe–C phase diagram. The liquidus temperature for each thin film model decreases with increasing the C concentration.
- Before the formation of liquid near the surface, the atomic number density of C increases near the surface and this increase enhances atomic vibrations of Fe around there, forming a surface-melting layer. The surface-melting layer becomes thicker as temperature rises, and promotes melting of the thin film models at lower temperatures. Surface melting occurs in γFe–C alloy having (110) surface more easily.
- Melting of γFe–C alloy would be rate-controlled by diffusion of C from the solid phase to the solid–liquid interface.
- The effective use of surface melting would help to design melting and joining processes for nano-structured materials at lower temperatures, under optimised conditions of the dimensions and surface orientations of materials.

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