Molecular dynamics study of composition dependence of solid-liquid interfacial energy of Fe-Ni binary alloy

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Abstract. Interfacial properties strongly affect solidification microstructure of practical alloy materials. Therefore, it is essential to understand interfacial properties including composition dependence for target alloys. In this study, composition dependence of solid-liquid interfacial energy of Fe-Ni alloy is investigated by molecular dynamics simulations in conjunction with a capillary fluctuation method. The solid-liquid interfacial energy of Ni-rich composition taking FCC-solid phase is larger than that of Fe-rich composition taking BCC-solid phase. Moreover, solid-liquid interfacial energy has a high anisotropy at the composition with FCC-solid phase compared to the one with BCC-solid phase.

1. Introduction
It is well known that solid-liquid interfacial properties strongly affect solidification microstructure in practical production process of metallic materials [1, 2]. Therefore, it is essential to estimate solid-liquid interfacial properties precisely. In addition to many experimental approaches, in recent years, numerical approaches such as molecular dynamics (MD) simulations have contributed to the estimation of these properties. For example, there are many reports on solid-liquid interfacial energies of pure metals on the basis of the MD simulation in conjunction with a capillary fluctuation method [3-6] and a classical nucleation theory-based technique [7]. However, there are not so many reports on those of alloys till now since it is not straightforward to reproduce proper solute partition at the solid-liquid interface for alloy systems by the MD simulation with a given interatomic potential. At present, there are several reports focusing on this problem by a semi-grand canonical Monte-Carlo (SGCMC) technique [8-10], an atom swap technique in line with a Metropolis Monte-Carlo (MMC) simulation [11] and a direct monitoring of solute partition at the solid-liquid interface by a long-time MD simulation [11]. These techniques have contributed to the estimation of interfacial properties of various alloys [12-15]. Nevertheless, there are not so many reports on composition dependence of interfacial properties for alloy systems since it takes time and effort. To this end, composition dependence of solid-liquid interfacial energy of Fe-Ni binary alloy is investigated by MD simulations in conjunction with capillary fluctuation method in this study.

Here, Fe-Ni binary alloy is employed as a target alloy material since Fe-Ni alloy has an interesting feature from the scientific viewpoint that the stable solid phase changes from body-centered cubic (BCC) to face-centered cubic (FCC) with increasing Ni composition. Fe-Ni binary alloy is also important from the practical viewpoint since Fe-Ni alloy has unique properties such as a low coefficient of thermal expansion (known as invar alloy) and a large magnetic permeability (known as permalloy).
2. Methodology
The solid-liquid interfacial energy of Fe-Ni alloy is investigated by MD simulation in conjunction with a capillary fluctuation method [3]. Simulation methodology basically follows our previous study [14, 15]. MD simulations are performed by Large-scale Atomic/Molecular Massive Parallel Simulator (LAMMPS) [16]. An embedded atom method (EAM) potential fitted by Bonny et al. [17] is employed as the interatomic potential of Fe-Ni alloy. Parameter files of the EAM potential are employed from the database of NIST-IPR project [18] for the MD simulations by LAMMPS. Nose-Hoover thermostat and barostat [19, 20] are employed to control temperature and pressure in MD simulations. Visualization of simulation results and post-analyses are performed by the open visualization tool (OVITO) [21]. The polyhedral template matching (PTM) technique [22] is employed for classifying atoms in crystalline or liquid, which is suitable for the classification of atoms at high temperature. A root-mean-square deviation (RMSD) cutoff parameter of the PTM is set to 0.16.

3. Results and discussion

3.1. Equilibrium temperature for each composition
Prior to derivation of the solid-liquid interfacial energy, equilibrium temperatures at various Ni compositions, at which the solid-liquid interface does not move, are estimated for the potential employed in this study using a convergence temperature technique [23, 24]. Firstly, a solid FCC crystals of Fe-xat%Ni alloys (x = 15, 30, 40, 50, 60, 70, 80, 90 and 100 (i.e., pure Ni)) consisting of 100×25×25 unit cells (250,000 atoms) is annealed at 5000 K for 10 picoseconds (ps) with the number of atoms, volume and temperature (NVT)-constant ensemble to obtain liquid structures. For pure Fe and Fe-rich Fe-Cr alloy (5 at% and 10 at%), solid BCC crystal consisting of 100×25×25 unit cells (125,000 atoms) is employed. A solid crystal of same size and composition is connected with each liquid facing (100) plane at the interface. Then, energy minimization is performed to avoid the unexpected proximity of atoms at the solid-liquid interface. Prepared solid-liquid biphasic systems of various compositions are relaxed with the number of atoms, pressure and temperature (NPT)-constant ensemble to obtain liquid structures. For pure Fe and Fe-rich Fe-Cr alloy (5 at% and 10 at%), solid BCC crystal consisting of 100×25×25 unit cells (125,000 atoms) is employed. A solid crystal of same size and composition is connected with each liquid facing (100) plane at the interface. Then, energy minimization is performed to avoid the unexpected proximity of atoms at the solid-liquid interface. Prepared solid-liquid biphasic systems of various compositions are relaxed with the number of atoms, pressure and temperature (NPT)-constant ensemble to obtain liquid structures. For pure Fe and Fe-rich Fe-Cr alloy (5 at% and 10 at%), solid BCC crystal consisting of 100×25×25 unit cells (125,000 atoms) is employed. A solid crystal of same size and composition is connected with each liquid facing (100) plane at the interface. Then, energy minimization is performed to avoid the unexpected proximity of atoms at the solid-liquid interface. Prepared solid-liquid biphasic systems of various compositions are relaxed with the number of atoms, pressure and temperature (NPT)-constant ensemble to obtain liquid structures. For pure Fe and Fe-rich Fe-Cr alloy (5 at% and 10 at%), solid BCC crystal consisting of 100×25×25 unit cells (125,000 atoms) is employed. A solid crystal of same size and composition is connected with each liquid facing (100) plane at the interface. Then, energy minimization is performed to avoid the unexpected proximity of atoms at the solid-liquid interface. Prepared solid-liquid biphasic systems of various compositions are relaxed with the number of atoms, pressure and temperature (NPT)-constant ensemble to obtain liquid structures.

Table 1 shows estimated values of the equilibrium temperature of Fe-Ni binary alloy with various compositions for the EAM potential employed in this simulation. The solid FCC structure naturally transforms into bcc one during the relaxation for Fe-15at%Ni alloy. Therefore, we define threshold composition dividing FCC and BCC phases between 15 and 30at%Ni. Note that this value is higher than the value from experimental reports (around 5at%Ni) due to the characteristic of the EAM potential employed in this study [17]. There is almost no solute partition at the solid-liquid interface for all compositions, which basically agrees with the experimental feature.

3.2. Capillary fluctuation method
Next, solid-liquid interfacial energy of Fe-Ni binary alloy is derived by a capillary fluctuation method [3]. A quasi two-dimensional solid-liquid biphasic system is employed to obtain atomic configurations of solid-liquid interface for each composition, which is prepared as follows [14]. Firstly, a liquid structure is prepared by annealing a BCC (259,200 atoms in a cell of 514.8×11.44×514.8 Å³) for Fe-rich composition and an FCC crystal (345,744 atoms in a cell of 517.44×14.08×517.44 Å³) for Ni-rich composition at 5000 K at 10 ps with the number of atoms, volume and temperature (NVT)-constant ensemble, respectively. Then, a solid crystal of the same size is connected with the liquid facing (100) plane at the interface, respectively. The short side of the system is set to be [010] direction (noted as (100)[010] orientation hereafter). Figure 1 shows the snapshot of the atomic configuration of pure Ni with the (100) interface. In the same manner, biphasic systems with (110)[001] and (110)[1-10]
interfaces are prepared. Details of configuration of the biphasic system are listed in Table 2. Then, the energy minimization is performed for the combined structure to avoid unexpected proximity of atoms at the solid-liquid interface. All prepared biphasic systems are relaxed with the number of atoms, pressure and temperature (NPT)-constant ensemble for 100 ps at 0 Pa.

**Table 1.** Equilibrium temperature and stable solid structure at that temperature for Fe-Ni binary alloy with various compositions estimated with the EAM potential.

| Composition          | Solid Structure | $T_{eq}$ [K] |
|----------------------|-----------------|--------------|
| Pure Fe              | BCC             | 1768         |
| Fe-5at%Ni            | BCC             | 1751         |
| Fe-10at%Ni           | BCC             | 1740         |
| Fe-15at%Ni           | BCC             | 1722         |
| Fe-30at%Ni           | FCC             | 1726         |
| Fe-40at%Ni           | FCC             | 1724         |
| Fe-50at%Ni           | FCC             | 1743         |
| Fe-60at%Ni           | FCC             | 1749         |
| Fe-70at%Ni           | FCC             | 1740         |
| Fe-80at%Ni           | FCC             | 1719         |
| Fe-90at%Ni           | FCC             | 1681         |
| Pure Ni              | FCC             | 1627         |

**Figure 1.** Quasi 2D solid-liquid biphasic system of pure Ni with (100) interface.

**Table 2.** Size of simulation cells for three interface orientations.

| Orientation          | Number of Atoms | $W$ [Å] | $b$ [Å] |
|----------------------|-----------------|---------|---------|
| (100)[010]_{bcc}     | 518,400         | 514.8   | 11.44   |
| (100)[010]_{fcc}     | 691,488         | 517.44  | 14.08   |
| (110)[001]_{bcc}     | 516,128         | 513.671 | 11.44   |
| (110)[001]_{fcc}     | 692,224         | 517.715 | 14.08   |
| (110)[1-10]_{bcc}    | 548,640         | 514.8   | 12.134  |
| (110)[1-10]_{fcc}    | 733,824         | 517.44  | 14.9341 |
Figure 2. Snapshots of the solid-liquid interface for Fe-5at%Ni and Fe-90at%Ni. Blue, green and white atoms represent atoms with BCC, FCC and liquid configurations, which are defined by the polyhedral template matching (PTM) technique. The solid-liquid interface is drawn by the red curve.

Figure 2 shows the snapshots of the solid-liquid interface for Fe-5at%Ni and Fe-90at%Ni with (100)[010] orientation after 100 ps calculation. Position of the solid-liquid interface is drawn by the red curve, which is then extracted in the same manner of our previous simulations [14, 15]. Coordinates of the solid-liquid interface extracted from snapshots between 60 and 100 ps at 0.1 ps intervals (i.e., 401 snapshots) are used for capillary fluctuation method [3]. In the equilibrium solid-liquid biphasic system, solid-liquid interface is fluctuated in order to minimize the free energy. The interface stiffness can be estimated from the amplitude of the fluctuation of the solid-liquid interface on the basis of the following equation:

\[
\langle |A(k)|^2 \rangle = \frac{k_B T_{eq}}{bW^2k^2}
\]

where \( \bar{\gamma} \) is the solid-liquid interfacial stiffness, \( A(k) \) is the Fourier amplitude of the interface height profile, \( k \) is the wave number, \( k_B \) is Boltzmann’s constant and \( T_{eq} \) is the equilibrium temperature at which the solid-liquid interface does not move. \( b \) and \( W \) are the thickness and length of the interface, respectively. The brackets represent averages over the number of sampling times. Therefore, the interfacial stiffness can be estimated from the amplitude of the fluctuation spectrum of a quasi-one-dimensional interface. Here, interfacial stiffness of solid-liquid interfaces with (100)[010], (110)[001] and (110)[1-10] orientations is estimated. Then, solid-liquid interfacial energy is derived using the following relations [14, 25]:

\[
\bar{\gamma} = \gamma_0 \left(1 - \frac{18}{5} \epsilon_1 - \frac{80}{7} \epsilon_2 \right) \quad \text{(for (100)[010] orientation)}
\]

\[
\bar{\gamma} = \gamma_0 \left(1 + \frac{39}{10} \epsilon_1 + \frac{155}{14} \epsilon_2 \right) \quad \text{(for (110)[001] orientation)}
\]

\[
\bar{\gamma} = \gamma_0 \left(1 - \frac{21}{10} \epsilon_1 + \frac{365}{14} \epsilon_2 \right) \quad \text{(for (110)[1-10] orientation)}
\]

where \( \gamma_0 \) represents the average solid-liquid interfacial energy and \( \epsilon_1 \) and \( \epsilon_2 \) are the anisotropy parameters. Practically, \( \gamma_0, \epsilon_1 \) and \( \epsilon_2 \) are specifically obtained by assigning values of interfacial stiffness for three different orientations into equations (2), (3) and (4). These equations are derived from a low-order
expansion consistent with cubic symmetry [25]. Finally, the solid-liquid interfacial energy including its anisotropy can be derived from Fehlner and Vosko’s equation [25] expressed as:

$$\gamma = \gamma_0 \left[ 1 + \varepsilon_1 \left( \sum_{i=1}^{3} n_i^4 - \frac{3}{5} \right) + \varepsilon_2 \left( 3 \sum_{i=1}^{3} n_i^4 + 66n_1^2n_2^2n_3^2 - \frac{17}{7} \right) \right]$$  \hspace{1cm} (5)

where $n_i$ represent the orientation indices of the solid-liquid interface $(n_1, n_2, n_3)$. The solid-liquid interfacial energy of (100), (110) and (111) orientations are derived by assigning $\gamma_0$, $\varepsilon_1$ and $\varepsilon_2$ into equation (5). These calculations are performed three times for each configuration using different initial configurations of liquid atoms.

3.3. Solid-liquid interfacial energy of Fe-Ni alloy

Figure 3 shows average solid-liquid interfacial energy as a function of Ni composition for Fe-Ni binary alloy. Error bar represents standard deviation of three calculations. As a whole, solid-liquid interfacial energy at Ni-rich composition taking an FCC solid structure is larger than the one at Fe-rich composition taking a BCC solid structure. This agrees with a general trend of the relationship in the solid-liquid interfacial energy of pure metals between FCC and BCC [4]. In the FCC solid region, solid-liquid interfacial energy basically increases with increasing Ni composition until about 50at%Ni and becomes almost constant with some fluctuation at more than 50at%Ni. On the other hand, solid-liquid interfacial energy basically decreases with increasing Ni composition at the BCC solid region. Figure 4 represents anisotropy parameters $\varepsilon_1$ and $\varepsilon_2$ as a function of Ni composition. It is confirmed that $\varepsilon_1$ in the FCC solid region is larger than that in the BCC solid regions. As a result, the solid-liquid interface for Ni-rich composition with FCC solid structure has a strong anisotropy than that for Fe-rich composition with BCC solid structure. This agrees with previous reports on the comparison of the anisotropy in the solid-liquid interfacial energy between FCC and BCC metals [6].

Figure 3. Average solid-liquid interfacial energy, $\gamma_0$ of Fe-Ni alloy as a function of Ni composition. Error bar represents standard deviations of three calculations.
Figure 4. Anisotropy parameters, $\varepsilon_1$, $\varepsilon_2$ for Fe-Ni alloy as a function of Ni composition. Error bar represents standard deviations of three calculations.

Figure 5 shows the solid-liquid interfacial energy of (100), (110) and (111) orientations as a function of Ni composition. It is confirmed that there is a clear tendency, $\gamma_{(100)} > \gamma_{(110)} > \gamma_{(111)}$ at all compositions regardless of its solid structure. This tendency also agrees with previous reports both for FCC and BCC crystals [4, 12, 14]. The difference in the solid-liquid interface among three different orientations becomes larger at Ni-rich composition with FCC solid structure compared to that at Fe-rich composition with BCC solid structure since anisotropy parameters for the former composition is larger than that for the latter composition as shown in figure 4.

4. Conclusions
In this study, solid-liquid interfacial energy of Fe-Ni binary alloy is investigated by MD simulations in conjunction with the capillary fluctuation method. It is revealed that the solid-liquid interfacial energy of Ni-rich composition taking FCC-solid phase is larger than that of Fe-rich composition taking BCC-solid phase. Moreover, the solid-liquid interfacial energy has a higher anisotropy in the FCC solid region than in the BCC solid region. On the other hand, there is a same tendency, $\gamma_{(100)} > \gamma_{(110)} > \gamma_{(111)}$ at all compositions regardless of its solid structure. It is significant in this study to reveal composition dependence of solid-liquid interfacial energy of Fe-Ni alloy, which has a different stable phase of solid depending on the composition. Utilizing this methodology, solid-liquid interfacial energy for many other alloys with various stable solid phase will be examined in the next step.
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