Energetics for Interfaces between Group IV Transition Metal Carbides and bcc Iron

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An \textit{ab initio} study was carried out on interfacial energies and misfit strain energies at coherent interfaces between Fe (bcc structure) and MCs (NaCl structure, \(M=\text{Ti, Zr, Hf}\)). The interfacial energies at relaxed interfaces, Fe/TiC, Fe/ZrC and Fe/HfC, were 0.263, 0.153 and 0.271 J/m², respectively. The influence of bond energy was estimated using the discrete lattice plane/nearest neighbor broken bond model. It was found that the dependence of interfacial energy on the type of carbide was closely related to changes of the bond energies between Fe, M and C atoms before and after formation of the interfaces Fe/MC. The misfit strain energies in Fe/TiC, Fe/ZrC and Fe/HfC systems were 0.390, 1.692 and 1.408 eV per 16 atoms (Fe; 8 atoms and MC; 8 atoms). The misfit strain energy became larger when the difference in lattice parameters between the bulk Fe and the bulk MCs increased.

KEY WORDS: coherent interfacial energy; misfit strain energy; transition metals carbides; bcc iron; \textit{ab-initio} calculation.

1. Introduction

The strength of metals is determined by extrinsic obstacles (such as solute atoms, precipitates, and grain boundaries) which hinder or block the motion of dislocations. Control of the size distribution of precipitates such as carbides (MCs) and nitrides in steels is of prime importance for obtaining the desired mechanical properties (strength) of a metal. The size distribution of the precipitates is determined by nucleation, growth and coarsening rates, which depend on diffusion coefficients of precipitate components and on metal/precipitates interfacial energies. Precipitates also play an important role in microstructure control in steels. For example they are used as pinning particles which suppress grain growth. They can also inoculate austenite decomposition reactions acting as preferential nucleation sites of transformation. The plausibility of precipitates as pinning particles and transformation nucleation sites may depend on the iron/precipitate interfacial energy.

Unfortunately, there are no reliable experimental data on this energy due to the difficulty of measurement of solid/solid interfacial energy. The most general method used to obtain the interfacial energies is estimation of interfacial energy from experimental data of precipitate coarsening rate with the help of the Ostwald ripening law.\cite{1-7} Recently, the discrete lattice plane/nearest neighbor broken bond (DLP/NNBB) approach was also employed by Yang and Enomoto\cite{8} to calculate the energy of interfaces formed between ferrite (bcc Fe) and MCs or nitrides of Ti, V, Zr and Nb. The required bond energies in this approach were evaluated from the semi-empirical model of Boer et al.\cite{9}

Because of a lack of reliability in the estimation of interfacial energy by empirical and semi-empirical methods, the \textit{ab initio} method with a high physical accuracy has been recently used to calculate the interfacial energies. Hartford\cite{10} calculated the Fe/VN interfacial energy. Dudiy and Lundqvist\cite{11} and Christensen et al.\cite{12} calculated the Co/TiC, Co/TiN and Co/WC interfacial energies. Siegel et al.\cite{13} calculated the interfacial energy for Al/V, Al/VN, Al/CrN and Al/TiN systems. Dudiy and Lundqvist\cite{14} calculated the energy of interfaces formed between metals (Ti, Al, Ag, Cu and Au) and ceramics (TiC or TiN).

In the present study, interface atomic structures, coherent interfacial energies and misfit strain energies between bcc Fe and NaCl structured MCs of group IV transition metals (MCs, \(M=\text{Ti, Zr, Hf}\)) were calculated using the \textit{ab initio} method. The influence of atomic bond energies on the interfacial energies was estimated by using the DLP/NNBB method. The rippling phenomenon, which occurs after relaxation of the interface atomic structure, was explained in terms of bond energies.

2. Calculation Methods

2.1. \textit{Ab-initio} Calculation

In order to study atomic structures and energetics of the interfaces between ferromagnetic bcc Fe and MCs, we carried out \textit{ab initio} calculations using VASP package. These calculations are based on pseudopotential (Vanderbilt ultrasoft type), plane-wave and density functional theory (DFT).
as well as a generalized gradient approximation for the calculation of exchange-correlation potential developed by Perdew and Wang.\(^{16}\) As the interface contains a ferromagnetic phase, bcc Fe, spin-polarized calculation was carried out.

MCs precipitate in bcc Fe with NaCl structure. Due to the lattice mismatch, semicoherent interfaces form between bcc Fe and the MCs. NaCl-type MCs are reported to have the Baker-Nutting orientation relationship with bcc Fe. The semi-coherent interface contains more or less extensive nearly coherent regions that are bounded by a periodic network of misfit dislocations caused by a misfit between MCs and bcc Fe.

In the present calculation, we calculated coherent interfacial energy and misfit strain energy using a coherent interfacial approximation model as a first approximation for the real interface. Although MCs of transition metals have vacancies (less than 18\%) in the metalloid sublattice, perfect 1:1 stoichiometry was assumed to permit the use of smaller supercells. The interface was simulated by a periodic supercell with some layers of bcc-Fe and MCs (see Fig. 1). At the interface, a carbon atom lies directly under Fe atom. MCs and iron atoms are oriented according to Eq. (1). Total energies of Fe/MC were obtained for supercells with 16 and 32 atoms (see Fig. 1). Structural relaxation calculation was carried out with minimizing total energy. The volume and shape of supercell and positions of atoms were varied. Interfacial energy was calculated using the lattice constant obtained after the structural relaxation.\(^{16}\)

\[
\{001\}_{MC} \parallel \{110\}_{Fe}, \{110\}_{MC} \parallel \{100\}_{Fe} \cdots \cdots \cdots (1)
\]

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\[\gamma_{NNBB} = \left( e_{NaClFeC} - e_{NaClMC} \right) + \left( 4 e_{bccFeM} + e_{bceFeM} \right) - \left( 2 e_{bceFe,NN} + 0.5 e_{bceFe,2NN} \right) - 2 e_{bceMC,NN} \cdots \cdots (2)\]

where, \(e_{NaClFeC}\), \(e_{NaClMC}\), \(e_{bceMC}\), \(e_{bceFeM}\), \(e_{bceFe,NN}\) and \(e_{bceMC,NN}\) are Fe–C bond energy in NaCl type FeC, M–C bond energy in NaCl type MC, Fe–M bond energy in bcc FeM, Fe–Fe bond energy in bcc Fe and M–M bond energy in an fcc sub-lattice of MC respectively. Subscripts 1 and 2 in \(e_{bceFeM}\) represent Fe atoms in the first and second atomic layer from the interface. And subscripts 1NN and 2NN in \(e_{bceFe,NN}\) mean the interatomic distances of nearest and second nearest neighbor in bcc Fe lattice, respectively.

The first parenthesis term on the right hand side (RHS) of Eq. (2) is energy change when 2 M–C half bonds are broken and one Fe–C full bond is formed. The term in second parenthesis on the RHS of Eq. (2) is energy change when 5 half bonds in bcc Fe (4 nearest neighbor and a second nearest neighbor bonds) and 4 M–M half bonds in MC are broken and 5 Fe–M full bonds (4 nearest neighbor and a second nearest neighbor bonds) are formed. Bond energies in Eq. (2) can be calculated by the \textit{ab initio} method.\(^{16}\)

3. Results and Discussion

3.1. Lattice Constant and Bulk Moduli of Bulk Phase and Fe/MC System

Table 1 shows calculated lattice constants and bulk moduli for bcc metals (Fe, Ti, Zr, Hf) and MCs (TiC, ZrC, HfC) together with experimental ones reported in the literature.\(^{11,17–19}\) The calculated results for lattice constants agree well within less than 0.101 Å (2.8\%) deviation with the experimental values. The calculated results for bulk moduli agree with the experimental values within deviation less than 10 GPa except for the result of Fe. MCs have larger lattice constant than Fe. Among the lattice constants of MC, the lattice constant of ZrC is the largest. The lattice constant of HfC is slightly smaller than that of ZrC. The Gold Schmidt atomic radii of Ti, Zr and Hf are 1.47, 1.61 and 1.59 Å, respectively.\(^{17}\) The lattice constants of group IV carbides are larger than those of group V carbides owing to the larger lattice constants of pure metals as reported by Chung \textit{et al.}\(^{16}\) One can see that an MC with a larger radius of M atom has a larger lattice constant.

Table 2 shows lattice constants for Fe/MC systems. Because the bulk modulus of MC is larger than that of Fe, (in other words, MC is harder than Fe) the lattice constant of Fe/MC system should be closer to that of MC rather than that of Fe. Therefore, the value of \((a_{FeMC} - a_{Fe})/(a_{MC} - a_{Fe})\) lies between 0.79 and 0.82. This is because the strain of Fe/MC system should be closer to that of MC rather than that of Fe.
hard phase should be smaller than that of soft phase in order to minimize misfit strain energy. The bulk moduli of group IV metal carbides are smaller than those of group V metal carbides because of relatively small bulk moduli of group IV metals.16)

3.2. The Interface Structure of Fe/MC System

3.2.1. Rippling in MC Phases

Atomic structure around the Fe/MC interfaces becomes different from that in the bulk phases owing to the structural relaxation during the interface formation. As a result of rippling phenomena, the heights of M and C atoms become different within the same MC layer.

Table 3. Rippling parameters for Fe/MC interfaces calculated in present work and rippling parameters for MC surfaces taken from the other works.

| Fe/MC interface | MC surface |
|-----------------|------------|
| DFT (Present Work) | DFT | Experiment |
| $r_{\text{Int}}^{\text{DFT}}$, DFT | $r_{\text{Sur}}^{\text{DFT}}$, DFT | $r_{\text{Int}}^{\text{DFT}}$, DFT | $r_{\text{Sur}}^{\text{DFT}}$, DFT | $r_{\text{Sur}}^{\text{Exp}}$, DFT |
| TIC | 0.074 | 0.042 | 0.017 | 0.006 | 0.107 | 0.028 | 0.13 |
| ZrC | 0.031 | 0.040 | 0.010 | 0.304 | 0.027 | 0.026 | - |
| HfC | 0.015 | 0.052 | 0.008 | 0.002 | 0.15 | 0.057 | 0.11 |

In Table 3, $r_{\text{Sur}}^{\text{DFT}}$ and $r_{\text{Sur}}^{\text{Exp}}$ indicate $Z_c - Z_m$ (Å) in the $i$th layer from the surface and interface, respectively. $Z_c$ and $Z_m$ are the coordinates for the positions of atom C and M and they are normal to the surface or interface. They direct towards surface or interface from the inside of the MC phases.

The rippling of MC phase beneath Fe layer has positive values at all layers. Positive rippling means the C atoms move outwards and M atoms inwards. The rippling values, $r_{\text{Int}}^{\text{DFT}}$ at the first and second layers of MC have larger than those at the third and fourth layers. That is, the rippling occurs mainly in the first and second layers, and beyond those layers it diminishes rapidly.

On the other hand, the rippling parameter at the first layer of Fe/MC interfaces, $r_{\text{Int}}^{\text{DFT}}$ is smaller than the rippling parameter at the same layer of MCs free surfaces, $r_{\text{Sur}}^{\text{Exp}}$. Also, the value of $r_{\text{Int}}^{\text{DFT}}$ becomes smaller in a sequence of TiC, ZrC and HfC. This seems to be caused by the increase of the bond strength ratio between Fe–M and M–C in the same sequence. As a result, the M atom moves more towards the Fe atom (see Table 6 (C)/(B) ratio).

3.2.2. Bond Lengths at the Fe/MC Interface

Table 4 shows bond lengths at the Fe/MC interfaces.

Table 4. Fe–C and Fe–M bond lengths (Å) at Fe/MC interfaces.

| 32 atoms | Fe–M1 | Fe–M2 | Fe–M3 | Fe–M4 | Fe–M5 | Fe–M6 |
|----------|-------|-------|-------|-------|-------|-------|
| TIC      | 2.910 | 1.900 | 2.110 | 2.225 | 2.205 | 2.147 | 2.140 | 2.469 |
| ZrC      | 3.016 | 1.937 | 2.284 | 2.332 | 2.354 | 2.314 | 2.262 | 2.538 |
| HfC      | 2.988 | 1.937 | 2.284 | 2.332 | 2.354 | 2.314 | 2.262 | 2.538 |

* Difference between Fe–M1 bond lengths at rippled and unrippled interfaces
* Difference between the Fe–C bond lengths and the Fe–C bond length (2.020 Å) at bulk FeC
* Difference between MC bond lengths at the relaxed interfaces and the bulk MCs.
* Difference between the Fe–Fe bond lengths and the Fe–Fe bond length (2.477 Å) at bulk bcc FeC.

3.2.3. Bond Lengths at the Fe/MC Interface

Table 4 shows bond lengths at the Fe/MC interfaces. Subscripts 1, 2 mean the first and second atomic layers from the interface, respectively. Figure 2 shows a schematic atomic arrangement around the interface.

The $d_{\text{Fe1–C1}}$ bond lengths $d_{\text{Fe1–C1}}$ at the first layer in MC are equal to $[(d_{\text{Fe–MC}}/\sqrt{2})^2 + (r_{\text{Int}}^{\text{DFT}})^2]^{0.5}$. The $d_{\text{Fe1–C1}}$ is similar to the $a_{\text{Fe–MC}/\sqrt{2}}$ owing to the small value of rippling. Thus, the magnitude of variation of $d_{\text{Fe1–C1}}$ during the formation of interface, that is, $|d_{\text{Fe1–C1}} - a_{\text{Fe–MC}/\sqrt{2}}|$ (see parenthesis in the 8th column of Table 4) is similar to the magnitude of the variation of the lattice constant of MC, $|a_{\text{Fe–MC}} - a_{\text{MC}/\sqrt{2}}|$ (see the last column of Table 2). Fe1–C1 bond lengths $d_{\text{Fe1–C1}}$ at the interfaces are smaller than that of the bulk FeC.
Fe1–M1 bond lengths, $d_{\text{Fe1-M1}}$ are equal to $(a_{\text{Fe/M}}/\sqrt{2})+(d_{\text{Fe1-C1}}+r_{\text{DFT}}^{\text{Fe2}})^{1/2}$. Because of positive ripples $r_{\text{DFT}}^{\text{Fe2}}$, the values of $d_{\text{Fe1-M1}}$ are larger than those at unrippled interfaces (see parenthesis in 2nd column of Table 4). They are longer than the first nearest neighborhood distances for hypothetical bcc Fe–M lattices ($\sqrt{3}a_{\text{Fe/a}}/2$) (2.554 Å for bcc Fe–Ti, 2.733 Å for bcc Fe–Zr and 2.702 Å for bcc Fe–Hf), which are calculated by the ab initio method. This is mainly caused by the fact that the value of $d_{\text{Fe1-C1}}+r_{\text{DFT}}^{\text{Fe2}}$ is larger than $d_{\text{Fe2}}/2$. Fe1–Fe2 bond length is somewhat shorter than the value of bulk Fe ($\sqrt{3}a_{\text{Fe/a}}/2$) for the Fe/TiC system. They become somewhat longer than that of bulk Fe for Fe/ZrC and Fe/HfC systems.

Spacings ($z_{\text{Fe2}}-z_{\text{Fe1}}$) between the first and second Fe layers (1.234, 1.149 and 1.153 Å for Fe/TiC, Fe/ZrC and Fe/HfC, respectively) are smaller than spacing ($a_{\text{Fe/a}}/2$ = 1.43 Å) for the bcc Fe lattice. M1–Fe2 bond length $d_{\text{M1-Fe2}}$ is equal to ($z_{\text{Fe2}}-z_{\text{M1}}$)+($z_{\text{Fe1}}-z_{\text{Fe2}}$)=$d_{\text{Fe1-C1}}+r_{\text{DFT}}^{\text{Fe2}}$+$z_{\text{Fe2}}-z_{\text{Fe1}}$. Values of $z_{\text{Fe2}}-z_{\text{M1}}$ (1.973 Å, 1.962 Å and 1.953 Å for Fe/TiC, Fe/ZrC and Fe/HfC, respectively) are larger than the corresponding values for hypothetical bcc Fe–M lattices, $a_{\text{Fe/a}}/2$ (1.474 Å, 1.578 Å and 1.560 Å for Fe/TiC, Fe/ZrC and Fe/HfC, respectively). For the Fe/MC system, M2–C3 and M1–C2 bond lengths are shorter, C3–M3 and C1–M2 bond lengths are longer than those of bulk MCs.

### 3.3. Interfacial Energy and Misfit Strain Energy of Fe/MC System

#### 3.3.1. Interfacial Energy of Fe/MC System

Table 5 shows the calculated interfacial energies by the ab initio method for Fe/MC system. Interfacial energy lies between 0.153 and 0.271 J/m$^2$. According to the ab initio results,11,14 values of interfacial energy for Co/TiC, Cu/TiC, Al/TiC and Ti/TiC system are 0.20, 0.64, 0.21, −0.38 J/m$^2$, respectively. The interfacial energy between Co, whose atomic number is next to that of Fe, and TiC shows little bit smaller than that of Fe/TiC system (0.263 J/m$^2$) in the present work.

The interfacial energies are obtained experimentally from the growth or coarsening data by fitting to the proposed theories. The interfacial energies between group V transition metal carbides and Fe are well known and they are 0.26, 0.23 and 0.5 J/m$^2$ for Fe/NbC, Fe/NbN and Fe/VN system respectively.3,5,6 The only reported interfacial energy for group IV transition metal carbide/Fe is 0.2 J/m$^2$ for Fe/TiC system.7 As mentioned previously, experimentally obtained interfacial energies have uncertainties originated from too simple assumption adapted in theory as well as experiment errors. In spite of this, the calculated interfacial energy for Fe/TiC system in this study agrees very well with that of Gustafson.7

In order to understand the chemical bonding nature at the interfaces, DLP/NBBB model was adopted and the interfacial energies estimated by DLP/NBBB method were compared with those obtained from the ab initio methods. In DLP/NBBB model as shown in Eq. (2), it is assumed that the interfacial energy can be estimated by considering only the change of bond types and their energies before and after formation of the interface.

As a new interface is formed between Fe and MCs, the interfacial energy becomes smaller with increase in Fe–C and Fe–M bond strengths. Thus, a tendency of interfacial energy variation during the formation of the interfaces between Fe and MCs can be examined by comparison of bond energies expressed in Eq. (2) (see Table 6). Table 6 shows the bond energies and interfacial energies ($\gamma_{\text{NBBB}}$) estimated by the DLP/NBBB method.

The absolute value of Fe–C bond energy is 1.156 eV and the absolute value of M–C bond energies are 1.603, 1.613 and 1.656 eV for the Fe/TiC, Fe/ZrC and Fe/HfC systems respectively. That is, the M–C bonds are stronger than Fe–C bonds. With forming interface, M–C bonds change to Fe–C bonds. The energy accompanied by the change, (−(A)+(B)) in Table 6), increases in a sequence of Fe/TiC, Fe/ZrC and Fe/HfC. This implies that the interfacial energy of Fe/TiC is smallest if one considers only this energy change.

On the other hand, the absolute value of Fe–M and M–M bond energies ((C) and (D) in Table 6) increase in a sequence of Fe/TiC, Fe/ZrC and Fe/HfC. That is, the Fe–M bonds are stronger than M–M bonds. With forming interface, M–M and Fe–Fe bonds are broken and Fe–M bonds are newly formed. The energy accompanied by the change, (−(C)+(D)+(E) in Table 6), has negative values and Fe/ZrC and Fe/HfC systems have a smaller value than Fe/TiC system. If one considers both the terms in Eq. (2), interfacial energy of the Fe/ZrC system calculated by DLP/NBBB method is smallest and increases in a sequence of Fe/HfC and Fe/TiC systems as shown in Table 6.

Estimated interfacial energies by DLP/NBBB method were 0.275, 0.094 and 0.164 J/m$^2$ for Fe/TiC, Fe/ZrC and Fe/HfC systems.

### Table 5. Coherent interfacial and misfit strain energies of Fe/MC systems.

| System   | $\gamma_{\text{NBBB}}$ (J/m$^2$) | Misfit Strain Energy |
|----------|----------------------------------|----------------------|
|          | $\gamma_{\text{NBBB}}$ (J/m$^2$) | $\gamma_{\text{NBBB}}$ (J/m$^2$) |
| Fe/TiC   | 0.263                            | 0.390                |
| Fe/ZrC   | 0.153                            | 1.692                |
| Fe/HfC   | 0.271                            | 1.408                |

### Table 6. Interfacial energies of Fe/MC systems estimated by DLP/NBBB model.

| System | $\gamma_{\text{NBBB}}$ (J/m$^2$) | $\gamma_{\text{NBBB}}$ (J/m$^2$) |
|--------|----------------------------------|----------------------|
| Fe/TiC | 1.156                            | 3.712                |
| Fe/ZrC | 1.156                            | 4.215                |
| Fe/HfC | 1.156                            | 4.258                |
Fe/HfC systems, respectively. The interfacial energy of Fe/TiC interface calculated by DLP/NNBB method is similar to the value obtained from the *ab initio* calculation (see Table 5). On the other hand, $\gamma_{NNBB}$ is smaller than $\gamma_{ab\text{ initio}}$ in Fe/ZrC and Fe/HfC systems. Though the small difference between $\gamma_{NNBB}$ and $\gamma_{ab\text{ initio}}$ exists, the DLP/NNBB method is one of the reasonable approaches to estimate the interfacial energy when considering the nearest and second nearest neighbors simultaneously.

One can compare interfacial energies obtained in this study with previously reported result on group V transition metal carbides.\(^{16}\) As a new interface is formed between Fe and MCs, the energy change between M–C and Fe–C bonds in group IV transition metals are higher than that in group V metals. Also, group IV metals have higher energy change between M–M and Fe–M bonds compared with group V metals. Consequently, group IV transition metals have higher interfacial energies between Fe and MCs than group V metals.

It is known that MCs act as an effective nucleation site of ferrite during austenite to ferrite transformation and contribute to refining the grain size of ferrite. Zhang et al.\(^{27}\) reported that VN was most potential site of ferrite nucleation due to its lowest interfacial energy among VN, TiC, TiN and AlN phases. Furuhara\(^{28}\) also pointed out that V(CN) was favorable nucleation site of ferrite. It is useful to understand the nucleation and growth kinetics in phase transformation with the help of this and previous\(^{16}\) studies.

### 3.3.2. Misfit Strain Energy of Fe/MC Systems

Table 5 shows calculated misfit strain energies of Fe/MC systems, Fe phase and MC phases. Differences of misfit strain energies for Fe/MC systems and the summation of misfit strain energies for the Fe and MC phases are very small (0.044 eV/16 atom), thus the misfit strain energy of Fe/MC can be obtained from the calculation of the misfit strain energy for each phase followed by the summation. In the Fe/MC systems, misfit strain energies become larger in the sequence of TiC, HfC and ZrC. This is explained by Table 2 which shows that the misfit (\(a_{\text{Fe/MC}}/a_{\text{MC}}\)) is largest in ZrC (1.133) and it becomes smaller in the sequence of ZrC, HfC and TiC. The misfit strain energies in the Fe phase and MC phases show the same tendency as in Fe/MC systems, but the misfit strain energy in the Fe phase amounts to 76–84% of the total misfit strain energy because the soft Fe phase is strained more than harder MC phase.

### 4. Conclusions

From the *ab initio* calculation of coherent interfacial energies and misfit strain energies for Fe(bcc structure)/MCs(NaCl structure, M=Ti, Zr, Hf), the following results were drawn.

1. The rippling phenomena occur near the Fe/MC interface. It becomes weak in the sequence of TiC, ZrC and HfC.

2. Coherent interfacial energies calculated by the *ab initio* method were 0.263, 0.153, 0.271 J/m² for Fe/TiC, Fe/ZrC and Fe/HfC systems, respectively.

3. It was found from the DLP/NNBB model that energy is increased when the Fe–C bond is formed with breaking the M–C bond. This increase is largest in the Fe/HfC system. On the other hand, energy is decreased when the Fe–M bonds are formed with breaking the M–M and Fe–Fe bonds. This decrease is also largest in the Fe/HfC system.

4. Calculated misfit strain energies were 0.390, 1.692, 1.408 eV/16 atoms for Fe/TiC, Fe/ZrC and Fe/HfC systems, respectively.

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