Theoretical Calculation and Analysis of Coherent Interfacial Energy between B1-Type Carbides and FCC Iron Matrix

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Abstract. The valence electron structures (VES) of unit cells of the FCC iron matrix (γ) and B1-type carbides (ξ) in γ-Fe-M-C alloy systems (M=Nb, Ti, and V) were calculated using the empirical electron theory of solids and molecules (EET). Based on the results, the coherent interfacial energy between B1-type carbides and FCC iron matrix in γ-Fe-M-C alloy system was calculated and analyzed by combining EET and the discrete lattice plane-nearest neighbor broken bond (DLP-NNBB) method with covalent bond energy. The results showed that the solid solution strengthening effect was produced by the solute phase boundary segregation of the alloy elements at the γ/ξ interface, which enhanced the covalent bond network. The Nb alloy system had the largest segregation effect in γ-Fe-M-C alloy system. Moreover, the γ/ξ interfacial energy varies with different alloy elements over the range of 0.4-1.3 J/m², and the γ-Fe-Nb-C alloy system has the largest coherent interfacial energy. The proposed theoretical method is consistent with the theoretical values calculated using other models, as well as empirical values. This indicates that the method proposed in this work is feasible for providing theoretical analysis and guidance.

1. Introduction

The precipitated phase of B1 type carbides is crucial for controlling the microstructure properties of alloy steel. For example, the particles of the precipitated phase can inhibit the growth of recrystallized grains through the pinning effect, which affects grain refinement. Moreover, they can promote the decomposition of austenite as preferential nucleation points [1]. These effects are related to the interfacial energy of B1 carbides and FCC iron matrix. The interfacial energy reflects the thermodynamic stability of the two-phase interface, and significantly affects the nucleation and growth processes of the precipitated phase. Thus, it is an important factor influencing the precipitation. An accurate understanding of the interfacial energy between B1 carbides and FCC iron matrix is required in order to study nucleation precipitation and precipitation strengthening problems for alloy steels, which are important research directions.

It is not possible to directly measure the interfacial energy of B1 type carbides with a coherent or semi-coherent relationship because the sizes of their precipitated phases are very small (only 2-10 nm on average) [2]. This limitation poses challenges for the study of the above problems. Therefore, several...
new theoretical calculation methods for interfacial energy have been proposed. Becker assumed that the formation of the interface was completed by breaking the nearest neighbor bonds between atoms, followed by formation of new bonds between the unpaired elements, while the components on both sides of the interface remained uniform. Moreover, the author presented a method to calculate the coherent interfacial energy between two random phases using the nearest neighbor broken bond (NNBB) model [3]. Cahn and Hilliard proposed a continuous model to calculate the coherent interfacial energy considering the energy gradient, i.e. the concentration distribution, in the interfacial region [4]. Further, Lee and Aaronson presented a discrete lattice plane (DLP) model based on previous studies to analyze the coherent interfacial energy of the FCC/FCC binary system [5]. Subsequently, a general calculation method for the number of nearest neighbor broken bonds was introduced [6-8]. The DLP model was subsequently applied to a wider range of alloy systems, such as binary displacement systems [9, 10], ternary displacement systems [11], and displacement-gap systems [1, 12]. However, all the above models have the same fundamental limitation, i.e., they can only be applied to alloy systems having positive heat of mixing. Otherwise, the concentration gradient in the interfacial region would be unstable and cannot be calculated using the thermodynamic theory [3, 12]. Moreover, the bond energy calculation is limited by the constant of regular solution, which can be challenging to measure accurately for carbonatites due to factors such as experimental conditions and magnetic moments [1, 3].

The empirical electron theory of solids and molecules (EET) has been widely used since its introduction [13, 14]. For instance, Fu combined the EET analysis method with the dangling bond analysis method to calculate the surface energy of pure metals [15]. Liu studied the relationship between the valence electron structures (VES) of TiB and TiB2 and the hardening of borided layer of TC4 alloy [16]. Furthermore, Yang calculated the magnetic moments of Fe3W3C and Ni3Mo3C using EET analysis method [17]. In a related work, Lin combined the EET method with the self-consistent bond distance difference method to determine the initial concentration of non-thermal phases in titanium alloys [18]. Recently, Wang used the EET method to model the spallation strength [19], while Li used EET analysis to study adiabatic shear fracture properties [20]. In this study, the EET model is combined with the DLP-NNBB model to theoretically calculate and analyze the coherent interfacial energy of B1 carbides and FCC iron matrix. The concentration of alloy elements was shown to change the bond distance and bond energy in the interfacial region. Furthermore, the dependence on regular solution constants in the original model can be entirely avoided and the application scope of the DLP-NNBB model can be further extended through the proposed model. Moreover, the proposed model could achieve a scale connection to the microscopic interface of the alloy at the electronic level, which can provide theoretical guidance for alloy modification.

2. Cell Structure Model

2.1. Cell structure model

According to literature [1, 2], the positional relationship between B1 type carbides and FCC iron matrix to form a coherent or semi-coherent interface is the cube-cube one, i.e. \((100)_\gamma // (100)_\gamma\). Only the \(\gamma\)-Fe/MC interface is a calculated example in this work. The iron matrix has a \(\gamma\)-Fe crystal cell structure, and the secondary phase has a MC crystal cell structure. The crystal structure for the interfacial region is approximated by a \(\gamma\)-Fe-C-M crystal cell structure by varying the lattice constant [5, 21].
Figure 1(a) shows the $\gamma$-Fe crystal cell structure model, with $A_1$ type structure. There are four Fe atoms in each cell, and the lattice parameter $a_0 = 0.35602$ nm at room temperature (25°C). Figure 1(b) shows the $\gamma$-Fe-C-M crystal cell model, where M atom corresponds to Fe$^e$ atom. This model is based on the repulsion of M atom produced by dummy electron pair in the atom-hybrid state of Fe$^e$ atom, and the need for covalent electrons by C atom [13]. Since Fe$^e$ is replaced by M, the lattice constant of the $\gamma$-Fe-C-M crystal cell changes with M, making it difficult to analyse the bond distance. In such cases, the lattice constant of the $\gamma$-Fe-C crystal cell is used as the lattice constant of $\gamma$-Fe-C-M crystal cell, as the change in bond distance after the replacement of M is reflected by the changes in the hybridization states of Fe$^e$, Fe$^i$, M and C. According to the literature [22], the lattice parameter $a_\sigma$ in the interfacial region is determined by:

$$a_\sigma = \left( a_c + a_\xi / \sqrt{2} \right) / 2$$

$$a_c = \frac{1}{4} \left( 5 - \frac{100}{A_c} \right) a_0 + \frac{1}{4} \left( \frac{100}{A_c} - 1 \right) a$$

Where, $a_c$ and $a_\xi$ are the lattice parameters of the $\gamma$-Fe-C-M crystal cell and the precipitated phase of the MC crystal cell, respectively. Specifically, $a_\sigma = 0.35750 + 0.00451(C-0.44)$, and $a_0 = 0.35602$ nm. $C$ is the weight percentage of carbon in steel; $A_c$ is the atomic percentage of carbon.

Figure 1(c) shows the MC crystal cell structure model. All the MC carbides (M for Nb, V, or Ti) have NaCl-B1 type structure, and their lattice parameters are NbC: 0.44702 nm, VC: 0.41600 nm, and TiC: 0.43274 nm, respectively, at room temperature (25°C).

Assuming the lattice parameter at room temperature (25°C) to be $a_1$, and using the formula of the expansion coefficient, the lattice parameter $a$ at temperature $T$ can be given by:

$$a = a_1 [1 + b(T - 25)]$$

where, $b$ is the linear expansion coefficient, and its approximate value is $14.2 \times 10^{-6}/$°C for alloy steel from 20°C to 1200°C [23].

2.2. Bond network distribution
For the ternary Fe-M-C alloy system, no Bain strain, such as a martensitic transformation, occurs during the formation of the coherent interface. This is because the FCC iron matrix lattice and B1-type carbide lattice have the same crystalline form, which is different from the precipitate interface in the bcc iron matrix. Additionally, there is a large gap between the next-nearest neighbor and the nearest neighbor, and the extremely weak interaction between the next-nearest neighbor atoms can be ignored [1,12]. This is consistent with the valence electron distribution of a large number of crystal structures in previous
reports [13-15, 24]. Therefore, only the nearest neighbors will be considered in this work. The covalent bond name $D_{\text{co}}$, experimental bond distance $D_{\text{exp}}$, and equivalent bond number $I$ of the crystal structure for each cell can be obtained from Fig. 1. The bond distributions for the nearest neighbor bond for each cell are summarized in Tables 1-3.

### Table 1. Valence electron structures (VES) of crystal cells in Fe-Nb-C alloy system (C=0.2)

| Bond       | $I_a$ | $n_a$ | $D_{\text{exp}}$/nm | $\sigma_n$/nm | $\Delta D$/nm |
|------------|-------|-------|---------------------|----------------|--------------|
| Fe—Fe      | 12    | 0.32990 | 0.25390            | 0.25792        | 0.00402      |

Interfacial region $\sigma$ cell Fe$^\text{Fe} = \text{Fe}^\text{Fe}$: $\sigma = \text{B18}$, $n_e = 6$, $R(I)^{18} = 0.10810$nm; C: $\sigma = 6$, $n_e = 4.0000$, $R(I)^c = 0.07630$nm;

Nb: $\sigma = \text{B18}$, $n_e = 5$, $R(I)^{18} = 0.11098$nm; $\beta = 0.0710$nm

| Bond       | $I_a$ | $n_a$ | $D_{\text{exp}}$/nm | $\sigma_n$/nm | $\Delta D$/nm |
|------------|-------|-------|---------------------|----------------|--------------|
| Fe—Nb      | 8     | 0.37986 | 0.26153            | 0.26443        | 0.00290      |
| Fe—C       | 8     | 1.44840 | 0.18493            | 0.18783        | 0.00290      |
| Nb—C       | 4     | 1.59020 | 0.18493            | 0.18783        | 0.00290      |

Secondary phase $\xi$ cell Nb: $\sigma = \text{B4}$, $n_e = 4.1262$, $R(I)^{14} = 0.13068$nm; $C: \sigma = 4$, $n_e = 3.6638$, $R(I)^c = 0.07630$nm; $\beta = 0.0600$nm

| Bond       | $I_a$ | $n_a$ | $D_{\text{exp}}$/nm | $\sigma_n$/nm | $\Delta D$/nm |
|------------|-------|-------|---------------------|----------------|--------------|
| Nb—C       | 12    | 0.52485 | 0.22543            | 0.22569        | 0.00026      |
| Nb—Nb      | 12    | 0.14414 | 0.31881            | 0.31907        | 0.00026      |

### Table 2. Valence electron structures (VES) of crystal cells in Fe-Ti-C alloy system (C=0.2)

| Bond       | $I_a$ | $n_a$ | $D_{\text{exp}}$/nm | $\sigma_n$/nm | $\Delta D$/nm |
|------------|-------|-------|---------------------|----------------|--------------|
| Fe—Fe      | 12    | 0.32990 | 0.25390            | 0.25792        | 0.00402      |

Interfacial region $\sigma$ cell Fe$^\text{Fe} = \text{Fe}^\text{Fe}$: $\sigma = \text{B17}$, $n_e = 5.9718$, $R(I)^{17} = 0.10833$nm; Fe$^\text{Fe}$: $\sigma = \text{B18}$, $n_e = 6$, $R(I)^c = 0.10810$nm; C: $\sigma = 6$, $n_e = 4.0000$, $R(I)^c = 0.07630$nm;

Ti: $\sigma = \text{B18}$, $n_e = 4$, $R(I)^{18} = 0.10530$nm; $\beta = 0.0710$nm

| Bond       | $I_a$ | $n_a$ | $D_{\text{exp}}$/nm | $\sigma_n$/nm | $\Delta D$/nm |
|------------|-------|-------|---------------------|----------------|--------------|
| Fe—Ti      | 8     | 0.24819 | 0.26153            | 0.26457        | 0.00394      |
| Fe—C       | 8     | 1.12930 | 0.18493            | 0.18877        | 0.00394      |
| Ti—C       | 4     | 1.03127 | 0.18493            | 0.18877        | 0.00394      |

Secondary phase $\xi$ cell Ti: $\sigma = \text{B11}$, $n_e = 3.5900$, $R(I)^{11} = 0.11760$nm; $C: \sigma = 3$, $n_e = 2.3362$, $R(I)^c = 0.07630$nm; $\beta = 0.0600$nm

| Bond       | $I_a$ | $n_a$ | $D_{\text{exp}}$/nm | $\sigma_n$/nm | $\Delta D$/nm |
|------------|-------|-------|---------------------|----------------|--------------|
| Ti—C       | 12    | 0.42347 | 0.21823            | 0.21831        | 0.00008      |
| Ti—Ti      | 12    | 0.08372 | 0.30862            | 0.3087         | 0.00008      |
Table 3. Valence electron structures (VES) of crystal cells in Fe-V-C alloy system (C=0.2)

| Bond       | $I_α$ | $n_α$ | $D_{ma}$/nm | $\bar{r}_{ma}$/nm | $\Delta D$/nm |
|------------|-------|-------|-------------|-------------------|---------------|
| Fe—Fe      | 12    | 0.32990 | 0.25390     | 0.25792          | 0.00402       |
| Interfacial region σ cell Fe: $σ=B13$, $n_α^i=4.4610$, $R(1)^{i}=0.11220$nm; Fe: $σ=B17$, $n_α^j=5.9153$, $R(1)^{j}=0.10833$nm; C: $σ=6$, $n_α^k=4.0000$, $R(1)^{k}=0.07630$nm; V: $σ=C16$, $n_α^L=3.9705$, $R(1)^{L}=0.10633$nm; $β=0.0710$nm |
| Bond       | $I_α$ | $n_α$ | $D_{ma}$/nm | $\bar{r}_{ma}$/nm | $\Delta D$/nm |
| Fe—V       | 8     | 0.25775 | 0.26153     | 0.26484          | 0.00331       |
| Fe—C       | 8     | 1.00800 | 0.18493     | 0.18824          | 0.00331       |
| V—C        | 4     | 0.94469 | 0.18493     | 0.18824          | 0.00331       |
| Secondary phase ξ cell V: $σ=B7$, $n_α^l=2.4797$, $R(1)^{l}=0.14341$nm, C: $σ=5$, $n_α^m=3.9038$, $R(1)^{m}=0.07630$nm; $β=0.0600$nm |
| Bond       | $I_α$ | $n_α$ | $D_{ma}$/nm | $\bar{r}_{ma}$/nm | $\Delta D$/nm |
| V—C        | 12    | 0.51075 | 0.20979     | 0.20985          | 0.00006       |
| V—V        | 12    | 0.18436 | 0.29669     | 0.29675          | 0.00006       |

3. Calculation model

3.1. Cell valence electron structure calculation model

According to the EET of solids and molecules [13, 14], the covalent electrons are distributed on the bonds connecting the nearest neighbor, the next nearest neighbor, and the neighbor atoms. The number of covalent electrons on each bond and in the crystal cell can be determined by Eqs. (4) and (5), respectively:

$$D_{ma}^{α,ν} = R_u + R_v - β \log n_α$$  \hspace{1cm} (4)

$$k_1 n_u^α + k_2 n_v^α = \sum I_α n_α$$  \hspace{1cm} (5)

Where, the subscripts u and v denote the two atoms; α represents different bonds, and α = A, B,..., N, represents the bonds in the structure which cannot be ignored; R is the radius of atomic single bond; and β is a parameter depending on the value of the strongest bond in the studied molecule or crystal [14]. The terms $n_α$ and $D_{ma}^{α,ν}$ represent the number of covalent electron pairs and the distance of covalent bond on the α bond formed by different atoms u and v, respectively; $k_1$ and $k_2$ are the numbers of atoms u and v in the cell, respectively; $n_u^α$ and $n_v^α$ are the numbers of covalent electrons of atoms u and v, respectively; and $I_α$ is the number of equivalent bonds for bond α.

The structure of each cell was determined, and the lattice constants were obtained from the experimental results. Therefore, the $n_α$ equations can be established as:

$$n_α = \sum n_c / \sum I_α r_α$$  \hspace{1cm} (6)

The valence electron structures (VES) of the atoms in each cell of the Fe-M-C alloy system can be calculated one by one through solving Eqs. (4), Eqs. (5) and Eqs. (6) Simultaneously with the BLD criteria ($|ΔD_{ma}| = |\bar{D}_{ma} - D_{ma}| < 0.05$ Å). The calculated results of the valence electron structure of each cell are shown in Tables 1 to 3.
3.2. Interfacial energy calculation model

The bond energy $e_\alpha$ of covalent bonds formed by the same atoms in the crystal, without interstitial elements, can be expressed as [14]:

$$e_\alpha = b \times f \times n_\alpha / D_{na}$$  \hspace{1cm} (7)

Where, $f$ is the bonding ability of the covalent bond on bond $\alpha$, and is related to the element type and its hybridization state; and $b$ is the shielding factor of elements, which is given in a previous report [14].

Pauling introduced the concept of bonding ability based on the basic principles of quantum mechanics[25], and stated that the bonding ability of hybrid state atoms in solid molecules depends on two factors, namely, the state ($s$, $p$, $d$) before hybridization of valence electrons and the hybrid composition ($\alpha$, $\beta$, $\gamma$). Based on these, the formula was proposed for calculation of the bonding ability $f$ of the covalent bond. Yu considered the contribution of $d$ electron spin-orbital effect to the bonding ability, and included the $g$ factor [24]. Then, the bonding ability can be written as:

$$f = \sqrt{\alpha} + \sqrt{3\beta} + g\sqrt{5\gamma}$$  \hspace{1cm} (8)

where, the values of $g$ are 0, 1, 1.35, and 1.70, corresponding to 3, 4, 5, and 6 cycles respectively; $\alpha$, $\beta$ and $\gamma$ are the components of $s$, $p$ and $d$ orbitals in the hybrid orbital.

For heterogeneous atoms in interstitial element cells, Xu et al. [24] first derived the calculation formula of the bond energy $e_\alpha$ for the covalent bond formed by two different atoms $u$ and $v$, which can be written as:

$$e_\alpha = B \times F \times n_\alpha / D_{na}$$  \hspace{1cm} (9)

Where, $B$ and $F$ are the geometric averages of corresponding effects of two different atoms $u$ and $v$, respectively. That is, $B = (b_u \times b_v)^{1/2}$ and $F = (f_u \times f_v)^{1/2}$, where, $b$ and $f$ are the same as above.

According to previous studies [1, 12], the contribution of entropy to the interfacial energy is determined by the thickness of the interfacial region with changed compositions. In the ternary Fe-M-C alloy system, there is a large bond energy difference between Fe-I and Fe-M, whereas the thickness of the interface region ($\gamma/\xi$) between the precipitated phase $\zeta$ and the iron matrix $\gamma$ is very small. Therefore, the concentration gradient region is very narrow, indicating that the concentration of alloy elements in solid solution can be regarded as the same mole fraction in the 1 to $J$ plane and $J+1$ to $2J$ planes if $2J$ denotes the number of interfacial planes, respectively. That is,

$$\begin{cases} 
  y_{ij}^\gamma = y_i^\gamma, 1 \leq j \leq J \\
  y_{ij}^\xi = y_i^\xi, J + 1 \leq j \leq 2J 
\end{cases}$$  \hspace{1cm} (10)

Where, $i = 1, 2, 3$ represent the elements Fe, M, and I, respectively.

As the concentration gradient varies over a very narrow range, the contribution of entropy to the interfacial energy is negligible. It can be reasonably assumed that the interfacial energy is determined by the differences in the chemical compositions and structures between the iron matrix and the interfacial region. This is ultimately the differences in the cell valence electron structure in the calculation model. Therefore, the interfacial energy can be expressed as:
\[ \sigma = E_{\gamma/\xi} - \frac{1}{2}(E_{\gamma/\gamma} + E_{\xi/\xi}) \]  

(11)

where, \( E_{\gamma/\xi} \) is total binding energy of the \( \gamma/\xi \) interfacial region; \( E_{\gamma/\gamma} \) and \( E_{\xi/\xi} \) are the total binding energies of the iron matrix and the plane parallel to the interface in the precipitated phase, respectively.

For the ternary Fe-M-I alloy systems, \( E_{\gamma/\xi}, E_{\gamma/\gamma} \) and \( E_{\xi/\xi} \) can be expressed as follows:

\[ E_{\gamma/\xi} = n_s \sum_{i,k=1}^{2} Z e_{ik}^\gamma y_i^\gamma y_k^\xi + n_s^{'} \sum_{i=1}^{2} Z' e_{i3}^\gamma y_i^\gamma y_3^\xi \]  

(12)

\[ E_{\gamma/\gamma} = n_s \sum_{i,k=1}^{2} Z e_{ik}^\gamma y_i^\gamma y_k^\gamma \]  

(13)

\[ E_{\xi/\xi} = n_s \sum_{i,k=1}^{2} Z e_{ik}^\xi y_i^\xi y_k^\xi + (n_s + n_s^{'}) \sum_{i=1}^{2} Z' e_{i3}^\xi y_i^\xi y_3^\xi \]  

(14)

Where, \( n_s \) and \( n_s^{'} \) are the numbers of atomic positions per unit area of the atomic layer in the replacement sub lattice and the interstitial sub lattice, respectively; \( y_i^\gamma \) is the atomic percentage of the atom \( i \) in its sub lattice. \( i, k=1, 2, \) and \( 3 \) represent the elements of Fe, M, and C, respectively; \( e_{ij}^v \) is the bond energy between \( i \) and \( k \) atoms in \( v \); \( v=\gamma, \xi, v=\sigma \) represent the interfacial regions; \( Z \) and \( Z' \) are the total coordination numbers of the metal-metal atom and the metal-non-metal atom, respectively.

For the calculated example of \( \gamma \)-Fe/MC interface, \( y_i^\gamma =0, y_i^\xi =0, y_i^\sigma =0 \).

According to the DLP model proposed in literature [5], \( n_s \) and \( n_s^{'} \) can be determined by:

\[ n_s = \eta n_s d_{hkl} \]  

(15)

\[ n_s^{'} = \eta n_s^{'} d_{hkl} \]  

(16)

Where, \( h, k, \) and \( l \) are the interfacial crystal surface indices; \( d_{hkl} \) is the distance between the \( (h, k, l) \) parallel crystal planes; \( n_s = n_s^{'} = 2a_0^{'} \) is the number of replaced atom positions per unit volume; \( \eta \) is a constant reflecting the alloy element concentration distribution and crystal structure difference between the interfacial region and the base, which equals 0.05537 for FCC iron matrix.

\( d_{hkl} \) is determined by:

\[
\begin{align*}
  d_{hkl} &= \frac{1}{2}d', \text{if at least one of } h, k \text{ and } l \text{ is not even}, \\
  d_{hkl} &= d', \text{if } h, k \text{ and } l \text{ are all even},
\end{align*}
\]

(17)

Where, \( d' = a_0/|\vec{m}| \) and \( |\vec{m}| = \left( h^2 + k^2 + l^2 \right)^{1/2} \).
\[ Z = Z_1 + 2Z_\nu \]  

(18)

Where, \( Z \) is the total coordination number; \( Z_1 \) and \( Z_\nu \) are the coordination numbers in the parallel and vertical directions, respectively.

The above known parameters are substituted into Eqs. (12), (13) and (14) and then combined with Eq. (11). Consequently, the interfacial energy of the coherent interface between B1 carbides and FCC iron matrix can be given by:

\[ \sigma = n_s Z \Delta e + n_s' Z' \Delta e' \]  

(19)

Where, \( \Delta e = e_{12}^\sigma - e_{12}^{\xi} + e_{22}^{\xi} \), and \( \Delta e' = e_{13}^\sigma - e_{13}^{\xi}. \) The calculated bond energy data are presented in Table 4.

**Table 4.** Bond energies of crystal cells in Fe-M-C alloy system (C=0.2) (800°C)

|                 | Fe-Nb-C alloy system | Fe-V-C alloy system | Fe-Ti-C alloy system |
|-----------------|----------------------|---------------------|----------------------|
| \( \Delta e / \text{(KJ/mol)} \) | 32.15170              | 187.21130            | -5.42540             | 8.91430             | 154.88310             |
| \( \Delta e' / \text{(KJ/mol)} \) | -5.42540             | 98.65950             | 8.91430              | 154.88310            |

4. Results and Discussion

It can be seen from Tables 1, 2, and 3 that, after the precipitation of B1-type carbides, the number of covalent electron pairs of the C-M bond is significantly higher than most of other bonds in the \( \gamma/\xi \) interfacial region with the same amount of carbon. This results in the segregation of alloy elements and enhancement of the covalent bond, which accounts for the solid-solution strengthening effect of the alloy elements at the valence electron level. Furthermore, as shown in Fig. 2, the number of covalent electron pairs of the strongest C-M bonds \( n_s \) in the interfacial regions of Nb, Ti and V alloy systems are 1.59020, 1.03127 and 0.94469, respectively. This result indicates that Nb has the largest segregation effect.

**Figure 2.** Relationship between the number of covalent electron pairs of the strongest C-M bonds \( n_s \) and alloy element M.
Grain refinement improves both the strength and toughness of the steel. The particles of the precipitated phase hinder the grain boundary migration during the recrystallization process through the pinning of the grain boundary and the grain growth. Consequently, the matrix grains are refined and a strengthening effect is produced. The grain boundary migration rate \( v \) can be expressed by \( v = M (F_r - F_z) \) [26], where \( F_z \) is the pinning force of the particles of the precipitated phase on the grain boundary, which can be expressed by \( F_z = \pi r \sigma N_s \) [27], where \( \sigma \) is the interfacial energy. As seen from the two equations above, the greater the interfacial energy, the greater the pinning force of the particles of precipitated phase on the grain boundaries and the smaller grain boundary migration. Consequently, there is better refinement effect on the iron matrix grains, and the strengthening effect is greater. Figure 3 shows the relationship between interfacial energy calculated by our model and different alloy elements. It can be seen that the \( \gamma \)-Fe-Nb-C alloy has the largest interfacial energy. Therefore, the effect of Nb on the grain refinement is the greatest, which is consistent with the conclusion in previous work [28]. Furthermore, the \( \gamma/\xi \) interfacial energy varies with different alloy elements over the range of 0.4-1.3 J/m², which is consistent with the theoretical values of 0.2-1.0 J/m² [12] and the empirical values of 0.3-1.5 J/m² [29]. Thus, the grain refinement effect of alloy elements can be understood at the valence electron level of alloy atoms.

Figure 3. Relationship between \( \gamma/\xi \) coherent interfacial energy and alloy element M.

5. Conclusion
This study calculated and analyzed the interfacial energy between B1 type carbides and FCC iron matrix in three Fe-M-C alloy systems using a theoretical method that combines EET with a DLP-NNBB model. The main conclusions of this work are as follows:

(1) The C-M bonds have significantly higher number of covalent electron pairs than most of other bonds in the interfacial region. This results in the segregation of alloy elements and the enhancement of the covalent bond, which accounts for the solid solution strengthening effect of the alloy elements at the electronic level. The number of covalent electron pairs of the strongest C-M bonds in the interfacial region is Nb alloy system, indicating that the Nb alloy system showed the largest segregation.

(2) The \( \gamma/\xi \) interfacial energy varies with different alloy elements over the range of 0.4-1.3 J/m², and the \( \gamma \)-Fe-Nb-C alloy system has the largest coherent interfacial energy. Therefore, the particles of the precipitated phase of B1 type carbides in \( \gamma \)-Fe-Nb-C alloy have the best grain refinement effect. Thus, the grain refinement effect of alloy elements can be understood at the valence electron level of the alloy atoms in the \( \gamma \)-Fe-Nb-C alloy system.

(3) The proposed theoretical method is consistent with the theoretical values calculated using other models, as well as empirical values. This indicates that the method proposed in this work is feasible for providing theoretical analysis and guidance.
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