

Calculations of stability of alloyed cementite from valence electron structure

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Abstract: Based on the empirical electronic theory of solids and molecules (EET), the actual model for unit cell of cementite (θ -Fe₃C) was built and the valence electron structures (VES) of cementite with specified site and a number of Fe atoms substituted by alloying atoms of M (M=Cr, V, W, Mo, Mn) were computed by statistical method. By defining P as the stability factor, the stability of alloyed cementite with different numbers and sites of Fe atoms substituted by M was calculated. Calculation results show that the density of lattice electrons, the symmetry of distribution of covalent electron pairs and bond energy have huge influence on the stability of alloyed cementite. It is more stable as M substitutes for Fe² than for Fe¹. The alloyed cementite is the most stable when Cr, Mo, W and V substitute for 2 atoms of Fe² at the sites of Nos. 2 and 3 (or No. 6 and No. 7). The stability of alloyed cementite decreases gradually as being substitutional doped by W, Cr, V, Mo and Mn.

Key words: valence electron structure; alloyed cementite; stability; density of lattice electrons; symmetry of bonds; bond energy

1 Introduction

Cementite (θ -Fe₃C), as an important phase that is also in the form of alloyed cementite in alloyed steels, affects steel properties since its stability would influence microstructures of alloyed steels. For example, cold working decreased the stability of cementite [1–3] and changed mechanical properties of alloyed steels, thus it is necessary to study the stability of alloyed cementite.

The investigation of cementite has been down to the atomic or even the electronic scale [4–8], and there are many reports about the valence electron structure (VES) of cementite. Based on the empirical electronic theory of solids and molecules (EET) [9], YU et al [10] calculated the VES of cementite and the calculation indicated that the bond strength of cementite is discontinuous along crystal axis b . It is this discontinuity that leads to the obvious brittleness. YE et al [11] then reported that structure along axis b in θ -Fe₃C can be divided into strong and weak bond layers and the strength of the bonds connecting strong and weak layers has huge influence on the shape of alloyed θ -Fe₃C during solidifying. HUANG et al [12] agreed that the bond

energy of the strongest bond can be used to testify stability of a phase by calculating binding energy [13], but unfortunately they did not consider the bond energy in different directions. LIU et al [14] calculated the VES of θ -Fe₃C and θ -(Fe, M)₃C by EET, and found that the strength of θ -Fe₃C was increased as Mn, V and Cr atoms substituted for Fe atoms at sites of 4c; however, the direction and variety of Fe atoms still are neglected in the report. MIN et al [15] discovered that the bond network of Al₂Ca has high bond energy and the differences of the bond strength between different crystal directions are not remarkable, which leads to the highest stability among the three structures studied. Above indicates that the stability of cementite is not dependent only on VES and the strongest bond energy, but also on the bond energy gap in different directions.

In addition to EET, there are many calculations on cementite structure and stability by first principle, in which the types of Fe substituted by alloy atoms are divided into Fe¹ and Fe². LV et al [16] analyzed the stability of θ -Fe₃C with 4 atoms of Fe¹ and 8 atoms of Fe² substituted by Cr or Mn atoms using first principle. The results indicated that Cr and Mn can enhance the

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strength of alloyed θ -Fe₃C. GAO et al [17] found the alloyed θ -Fe₃C with Cr substituting for Fe atoms at the site of 4c is more stable than that at the site of 8d. The stability of cementite doped with Co and Ni [18, 19], Ti and V [20] has been calculated, but they did not consider the influence of specified sites and numbers of Fe substituted by alloy atoms on the stability of cementite.

Cr, Mn, Mo, W and V are commonly used alloying elements in steel and they are doping preferable in cementite [21–23] and make cementite stable [24]. There are 4 atoms of Fe¹ (site of 4c) and 8 atoms of Fe² (site of 8d) in an unit cell of cementite; therefore, the type, number and site of the Fe atoms must be taken into consideration when substitutional alloying elements are added in cementite. However, up to now, the study on stability of cementite with specified number and site of Fe atoms replaced by alloying elements by VES calculations has not been found, which is essential for selecting the type and amount of alloying atoms.

In this work, the type (Fe¹, Fe²), number (1-4 or 1-8) and site (4c, 8d) of the Fe atoms are considered in calculation. Based on EET and parameter statistical method for VES [25], built the actual model for unit cell of cementite (AMUCC). The method of “statistics” is proposed to calculate VES of M (Cr, Mn, Mo, W, V) doped cementite. The AMUCC we built is easier than “average atom model” [9, 26, 27] to calculate the interaction between different atoms when Fe substituted by M. By analyzing crystal structure and bond energy calculation for cementite, a factor of P , which is used to judge the stability, is proposed. Variation law in stability of cementite with different types, numbers, sites of Fe substituted by M was analyzed and the mechanism of stability of cementite was interpreted.

2 Calculation method

The VES of cementite was computed according to the bond length difference (BLD) method [9] by MATLAB. The theoretical bond length, D_{n_α} , the number of covalent electron pairs, n_α , the BLD, $\Delta D_\alpha = |\tilde{D}_{n_\alpha} - D_{n_\alpha}|$ and bond energy, E_α , of covalent bonds that cannot be neglected were calculated. When $\Delta D_\alpha \leq 0.005$ nm, the theoretical bond length agrees with the experimental one in first order approximation; therefore, the chosen hybridization states of the atoms in alloyed cementite are their actual existing states. Lattice parameters of cementite (θ -Fe₃C) were selected to calculate the VES of alloyed cementite (θ -(M, Fe)₃C, M=Cr, V, W, Mo and Mn) and the variation of lattice parameters was realized by changing hybridization states of atoms in alloyed cementite.

For the multi-solutions of BLD method by EET,

statistical method was suggested to determine the number of covalent electron pairs n_α , i.e.,

$$\bar{n}_\alpha = \frac{\sum_i^{\sigma_N} n_{\alpha i} \cdot C_i}{\sigma_N}, C_i = \frac{1}{\sigma_N} \quad (1)$$

where \bar{n}_α is the statistical value of bond α ; σ_N is the number of probable states that meet $\Delta D_\alpha \leq 0.005$ nm. Then, the hybridization state whose VES is the closest to the statistical value was selected as the actual state of atoms in alloyed cementite, and the bond energy and density of lattice electrons were calculated out.

The space group of cementite (θ -Fe₃C) is $Pnma$ (No.62) with orthorhombic structure. A unit cell of cementite (UCC) shown in Fig. 1 has 4 molecules of Fe₃C, where 8 and 4 atoms of Fe are located at the sites of 8d and 4c, marked as Fe² and Fe¹, respectively and 4 atoms of C are in the interstices of UCC. The lattice parameters of UCC are $a=0.45144$ nm, $b=0.50787$ nm, $c=0.67297$ nm [14]. In calculation, the center UCC and 26 unit cells around it were considered. All atoms in the 27 unit cells have been numbered. The number of atoms in center UCC is shown in Table 1.

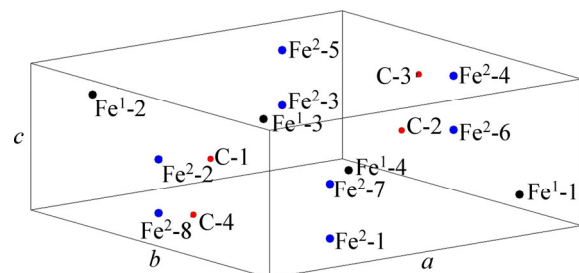


Fig. 1 Unit cell of θ -Fe₃C with all atoms numbered and positioned

The sites of bonding atoms can be shown by the designated numbers. Numbers 1 to 8 represent the atoms in the center UCC; numbers greater than 8 refer to atoms outside of the center UCC. For example, atom sites “2-3” and “6-7” mean that the two bonding atoms are inside the center UCC; “1-52” means that one atom is located at the site of 1 in the center UCC and the other atom is at the site of 52 inside the unit cells surrounding the center UCC. The atom sites of the top 12 bonds in UCC are illustrated in Table 2.

According to the number of covalent electron pairs n_α , the top 7 bond structures of cementite were drawn schematically in Fig. 2. Figure 2 shows that the structure along c direction in cementite can be divided into strong (C—Fe¹) and weak (Fe²—Fe²) bond layers. The numbers of covalent electron pairs are $n(\text{c—Fe}^1)=0.967131$ and $n(\text{Fe}^2\text{—Fe}^2)=0.202053$, respectively.

According to EET, the bond energy can be calculated through Eq. (2) for two identical atoms bondings:

Table 1 Coordinates and number of atoms in center unit cell of θ -Fe₃C

Type	Atom No.	Coordinate		
		<i>x</i> /(axis <i>a</i>)	<i>y</i> /(axis <i>b</i>)	<i>z</i> /(axis <i>c</i>)
Fe ¹	1	0.833	0.040	0.250
	2	0.167	0.960	0.750
	3	0.333	0.460	0.750
	4	0.667	0.540	0.250
Fe ²	1	0.333	0.183	0.065
	2	0.167	0.683	0.435
	3	0.667	0.817	0.565
	4	0.833	0.317	0.935
	5	0.667	0.817	0.935
	6	0.833	0.317	0.565
	7	0.333	0.183	0.435
	8	0.167	0.683	0.065
C	1	0.470	0.860	0.250
	2	0.530	0.140	0.750
	3	0.970	0.640	0.750
	4	0.030	0.360	0.250

$$E_a = b \cdot f \cdot \frac{n_a}{Dn_a} \quad (2)$$

where *b* is the shielding factor of the electron to nuclear charge [9, 25] and its value was listed in Table 3; *a* is the bond order; *n_a* is the number of covalent electron pairs of bond *a*; *f* is the bond-forming ability of covalent electrons for bond *a* and can be calculated by

$$f = \sqrt{\alpha_s} + \sqrt{3 \cdot \beta_p} + g \cdot \sqrt{5 \cdot \gamma_d} \quad (3)$$

where *g* represents the contribution of spin orbit coupling

Table 2 Sites of atoms in unit cell of θ -Fe₃C

No.	Bond name	<i>D_{n_a}</i> /nm	Atom site
1	Fe ¹ —C	0.185260	1-16, 2-19, 3-2, 4-1
2	Fe ¹ —C	0.187647	1-5, 2-10, 3-19, 4-16
3	Fe ² —C	0.205649	1-4, 2-1, 3-3, 4-2, 5-3, 6-2, 7-4, 8-1
4	Fe ² —C	0.215023	1-5, 2-4, 3-10, 4-3, 5-10, 6-3, 7-5, 8-4
5	Fe ² —C	0.230920	1-26, 2-19, 3-1, 5-21, 6-16, 7-2
6	Fe ² —Fe ²	0.248999	1-7, 2-8, 3-5, 4-6
7	Fe ² —Fe ²	0.251465	1-52, 2-3, 2-35, 3-26, 4-41, 5-48, 6-7, 6-31, 7-38, 8-53
8	Fe ¹ —Fe ²	0.251755	1-11, 2-23, 3-2, 3-48, 4-6, 4-52
9	Fe ¹ —Fe ²	0.254418	1-6, 1-52, 2-2, 2-48, 3-7, 3-41, 4-3, 4-53
10	Fe ² —Fe ²	0.254834	2-38, 3-23, 6-26, 7-11
11	Fe ¹ —Fe ¹	0.264762	1-4, 1-8, 2-3, 2-11, 3-6, 3-24, 4-9
12	Fe ² —Fe ²	0.264762	1-8, 1-16, 2-7, 2-23, 3-6, 3-22, 4-5, 4-13, 5-20, 6-11, 7-10, 8-17

effect of d electron to the bonding ability and it equals 1, 1.35 and 1.70 [9, 12] for elements in the 4th, 5th and 6th periods of the periodic table, respectively; *α_s*, *β_p*, *γ_d* are given as

$$\begin{cases} \alpha_s = \frac{n_s}{n_T} = (l\tau C_h + l'\tau' C_t) / n \\ \beta_p = \frac{n_p}{n_T} = (mC_h + m' C_t) / n \\ \gamma_d = \frac{n_d}{n_T} = (nC_h + n' C_t) / n \end{cases} \quad (4)$$

where *n_s*, *n_p* and *n_d* represent the valence electrons of s, p, d orbits, respectively; *l*, *m*, *n*, *l'*, *m'*, *n'* denote the valence electron numbers of s, p, d orbits for h and t state, respectively.

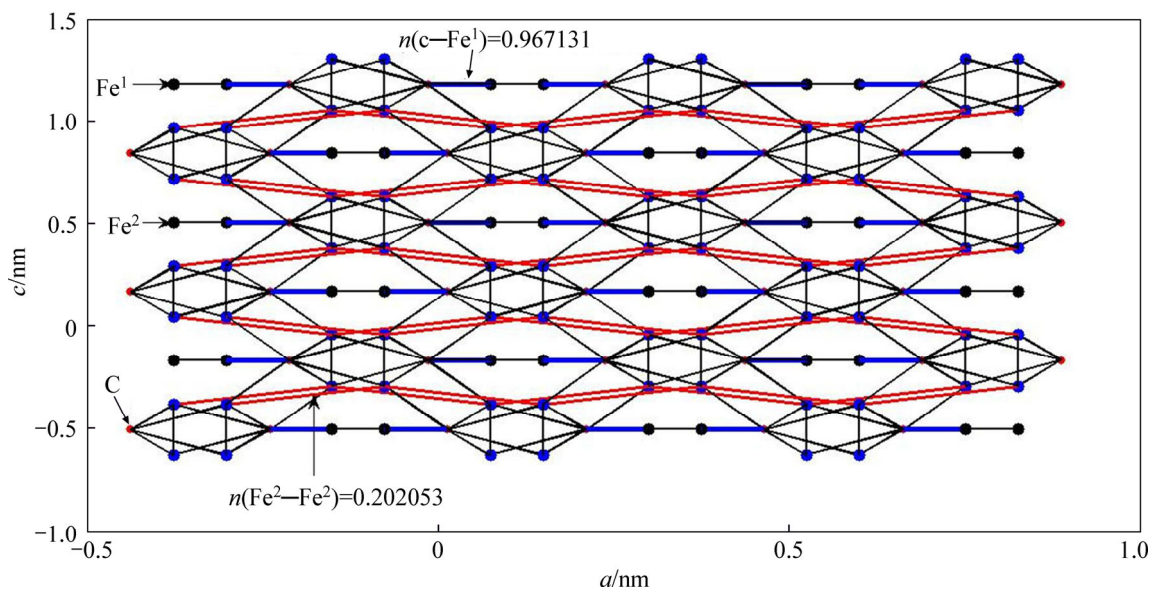


Fig. 2 Main bonds of θ -Fe₃C on *ac* plane

Table 3 Shielding factor of electron to nuclear charge

$b(\text{C})/$ (kJ·nm·mol ⁻¹)	$b(\text{Fe})/$ (kJ·nm·mol ⁻¹)	$b(\text{Cr})/$ (kJ·nm·mol ⁻¹)	$b(\text{Mn})/$ (kJ·nm·mol ⁻¹)
13.76972	15.69750	19.14329	11.89205
$b(\text{Mo})/$ (kJ·nm·mol ⁻¹)	$b(\text{W})/$ (kJ·nm·mol ⁻¹)	$b(\text{V})/$ (kJ·nm·mol ⁻¹)	
19.14329	19.14329	19.14329	

$\tau(\tau')=1$ while the valence electrons of s orbit for h(t) state are covalent electrons; otherwise, $\tau(\tau')=0$. $C_{h\sigma}$ and $C_{t\sigma}$ represent the components of h and t states at hybrid level, respectively. The value of $C_{h\sigma}$ and $C_{t\sigma}$ can be calculated with the use of k formula in EET [9]. n_T represents the total valence electron number, which can be calculated as

$$n_T = (1+m+n)C_{h\sigma} + (l'+m'+n')C_{t\sigma} \quad (5)$$

where D_{n_α} denotes the theoretical bond length of the α th type of covalent bond, which can be calculated as

$$D_{n_\alpha} = R_u(l) + R_v(l) - \beta \lg n_\alpha \quad (6)$$

where $R_u(l)$ and $R_v(l)$ represent the single-bond radius of u and v atoms.

When the two atoms of the bond consisted are not the same, the bond energy can be calculated as

$$E_a = \bar{B}_\alpha \cdot \bar{F}_\alpha \cdot \frac{n_a}{D_{n_a}} \quad (7)$$

The \bar{B}_α and \bar{F}_α can be calculated as

$$\bar{B}_\alpha = \sqrt{b_u \times b_v} \quad (8)$$

$$\bar{F}_\alpha = \frac{f_u + f_v}{2} \quad (9)$$

In EET, the “average atom model” is usually used to solve solid solution problem. This model considers the atoms in a crystal doped with alloy atoms the “mixed atoms”, i.e. linearly fixed atoms by the original crystal atoms and alloying atoms. This model cannot distinguish the relative sites of atoms in a crystal. In actual crystal units of alloyed cementite, the properties of alloyed cementite would be different as M substitutes Fe atoms at different sites. For example, there are 28 situations according to permutation and combination when M substitutes 2 atoms of Fe² since there are 8 atoms of Fe² in cementite crystal units. The “average atom model” regard the 28 kinds of structures the same, that's to say, the ‘average atom model’ neglected the influence of the replaced sites by M in alloyed cementite. In order to clearly understand the properties of cementite with different sites, types and numbers of Fe substituted by M, the ‘actual crystal model’ is proposed, considering the environment change around every atom. In this calculation, the VES of cementite with different sites, types and numbers of Fe substituted by M was calculated,

by which the stability of alloyed cementite was determined.

3 Calculation results

The difference in VES of alloyed cementite is not remarkable when one Fe¹ or Fe² is substituted by M at different sites, but this could be obvious when two or more Fe atoms are substituted by M since the relative location of Fe has great influence on VES. For example, the designated numbers of the bonding atoms forming Fe²—Fe² whose bond length is 0.251465 nm are shown in Table 2. When 2 atoms of Fe² located at the sites of Nos. 2 and 3 (or Nos. 6 and 7) in center UCC are replaced, there will form the bond of M—M, which is much stronger than Fe²—Fe². The bond energy values of M—M, Fe²—M and Fe²—Fe² decrease in turn. As for Mn, the bond energy decreases in order of Fe²—Mn, Mn—Mn and Fe²—Fe² since the shielding factor of the electron to nuclear charge is smaller (Table 3). If the 2 atoms of Fe² substituted by M are not located at the sites of Nos. 2 and 3 (or Nos. 6 and 7) at the same time, it would form the bond of Fe²—M. Therefore, the relative locations of Fe substituted by M must be considered in alloyed cementite.

When 2 atoms of Fe² located at the sites of Nos. 2 and 3 (or Nos. 6 and 7) in center UCC are substituted by M, the differences between strong and weak bond layers reach the minimum. The VES values of alloyed cementite with different numbers of Fe substituted are listed in Tables 4–14. The “total” in tables means the atoms of Fe¹ or Fe² in 27 UCCs (1 center UCC plus 26 UCCs surrounding the center one) are completely substituted by M. Bonds A and B represent the strongest bonds in strong and weak bond layers, respectively. Bond B is the bond of Fe²—M when one atom of Fe² is substituted by M (M=Cr, Mn, Mo and W), the rest of bond B is M—M. As for M=Mn element, the bond B is the bond of Fe²—Mn.

Table 4 VES of cementite

C	Fe ¹	Fe ²	n_A
6	A11	A11	0.9671
n_B	$E_A/(\text{kJ}\cdot\text{mol}^{-1})$	$E_B/(\text{kJ}\cdot\text{mol}^{-1})$	$\sum n_i$
0.3110	187.3549	57.8407	14.3412

Bond A: C—Fe¹; Bond B: Fe²—Fe².

4 Results discussion

According to EET, lattice electrons can move through the interstitials of a crystal unconstrainedly. When crystals were subjected to forces, lattice electrons move to the weak zones in crystal and help atoms bond

Table 5 VES of cementite with Fe¹ substituted by Cr

Substituted number of Fe ¹	C	Fe ¹	Fe ²	Cr	n_A	n_B	$E_A/(\text{kJ}\cdot\text{mol}^{-1})$	$E_B/(\text{kJ}\cdot\text{mol}^{-1})$	Σn_i
1	6	A11	A11	A10	1.24365	0.28961	338.4063	53.8651	13.8536
2	6	A10	A12	A10	1.23188	0.25809	335.20303	47.95625	12.2946
3	6	A9	A13	A11	1.268256	0.22866	342.91546	42.42438	10.221
4	5	A10	A14	A10	1.30154	0.21215	354.1516	39.27811	8.2668
Total	3	—	A16	A6	1.133386	0.291563	310.756	53.603782	6.316

Bond A: C—Cr; Bond B: Fe²—Fe².**Table 6** VES of cementite with Fe² substituted by Cr

Substituted number of Fe ²	C	Fe ¹	Fe ²	Cr	n_A	n_B	$E_A/(\text{kJ}\cdot\text{mol}^{-1})$	$E_B/(\text{kJ}\cdot\text{mol}^{-1})$	Σn_i
1	4	A11	A12	A9	0.94938	0.390606	183.88289	102.41684	14.2151
2	4	A11	A13	A9	0.93548	0.54738	181.191	202.5261	12.8527
3	5	A11	A13	A9	0.880774	0.515372	170.62351	190.68218	11.9142
4	4	A13	A13	A8	0.843419	0.434599	163.1579	166.09852	13.2712
5	4	A14	A13	A8	0.795704	0.43834	153.76621	167.52831	12.8595
6	5	A14	A12	A6	0.748953	0.385422	144.75625	148.28371	13.3560
7	5	A14	A10	A6	0.729173	0.357506	140.56823	137.54336	13.9848
8	4	A14	A9	A7	0.719512	0.346594	139.04244	132.91634	14.4424
total	6	A12	—	A6	0.776229	0.352342	150.3009	135.55685	16.5000

Bond A: C—Fe¹; Bond B: Cr—Cr/Cr—Fe².**Table 7** VES of cementite with Fe¹ substituted by Mn

Substituted number of Fe ¹	C	Fe ¹	Fe ²	Mn	n_A	n_B	$E_A/(\text{kJ}\cdot\text{mol}^{-1})$	$E_B/(\text{kJ}\cdot\text{mol}^{-1})$	Σn_i
1	4	A11	A11	A11	0.94585	0.304144	183.1991	56.567961	15.0701
2	4	A11	A11	A11	0.950484	0.305634	184.0967	56.845123	14.4542
3	6	A10	A10	A11	0.936797	0.317997	181.50738	59.16331	13.9038
4	5	A11	A10	A11	0.96557	0.320511	150.74664	59.631163	12.2624
total	6	—	A12	A11	0.984175	0.363589	153.65316	67.559451	10.6544

Bond A: C—Fe¹; Bond B: Fe²—Fe².**Table 8** VES of cementite with Fe² substituted by Mn

Substituted number of Fe ²	C	Fe ¹	Fe ²	Mn	n_A	n_B	$E_A/(\text{kJ}\cdot\text{mol}^{-1})$	$E_B/(\text{kJ}\cdot\text{mol}^{-1})$	Σn_i
1	4	A12	A11	A11	0.931544	0.340924	180.34188	51.102077	14.4585
2	4	A11	A11	A10	0.928206	0.324413	179.781656	48.622928	14.4806
3	4	A11	A11	A11	0.931471	0.323344	180.414133	48.467073	13.8383
4	5	A11	A11	A11	0.930119	0.322875	180.182584	48.396716	12.2624
5	6	A10	A10	A11	0.926723	0.321696	179.555511	48.22767	12.3586
6	1	A12	A11	A12	0.984071	0.307431	177.32243	45.923429	16.143
7	1	A12	A11	A12	1.003646	0.313546	180.84963	46.836911	15.2119
8	1	A12	A11	A12	1.019003	0.318344	183.616818	47.553565	14.2808
Total	6	A11	—	A9	0.898765	0.38897	174.11083	46.762218	10.5588

Bond A: C—Fe¹; Bond B: Mn—Fe².

Table 9 VES of cementite with Fe¹ substituted by Mo

Substituted number of Fe ¹	C	Fe ¹	Fe ²	Mo	n_A	n_B	$E_A/(kJ \cdot mol^{-1})$	$E_B/(kJ \cdot mol^{-1})$	Σn_i
1	3	A13	A13	A5	1.273457	0.272218	294.291175	50.505228	17.0049
2	1	A13	A14	A5	1.296627	0.242504	283.363611	44.898084	16.6742
3	6	A11	A12	A5	1.134114	0.272631	266.330174	50.658329	11.7695
4	4	A11	A12	A5	1.075563	0.258556	230.756658	48.042996	12.6648
Total	4	—	A13	A6	0.946857	0.334384	200.144540	62.038955	10.474

Bond A: C—Mo; Bond B: Fe²—Fe².**Table 10** VES of cementite with Fe² substituted by Mo

Substituted number of Fe ²	C	Fe ¹	Fe ²	Mo	n_A	n_B	$E_A/(kJ \cdot mol^{-1})$	$E_B/(kJ \cdot mol^{-1})$	Σn_i
1	4	A10	A11	A4	0.911953	0.406104	176.693745	91.767744	16.1438
2	4	A12	A12	A5	0.914157	0.448828	176.975854	122.670473	13.258
3	5	A11	A12	A5	0.900515	0.419365	174.447727	114.617901	12.613
4	4	A12	A12	A6	0.893292	0.327986	172.93634	88.803896	11.8268
5	6	A11	A11	A6	0.88221	0.307239	170.903712	83.186494	11.0462
6	4	A12	A11	A7	0.900423	0.252749	174.317026	67.353543	9.9588
7	4	A12	A11	A7	0.89158	0.250266	172.604921	66.692011	9.1062
8	4	A11	A11	A7	0.889933	0.236942	172.368697	63.141269	8.8652
Total	4	A10	—	A7	1.015323	0.256075	196.686484	68.240012	9.492

Bond A: C—Fe¹; Bond B: Mo—Mo/Mo—Fe².**Table 11** VES of cementite with Fe¹ substituted by W

Substituted number of Fe ¹	C	Fe ¹	Fe ²	W	n_A	n_B	$E_A/(kJ \cdot mol^{-1})$	$E_B/(kJ \cdot mol^{-1})$	Σn_i
1	3	A13	A13	A5	1.374069	0.26762	344.451219	49.652146	17.0049
2	3	A12	A14	A5	1.371839	0.233768	343.892130	43.280597	15.6676
3	3	A11	A14	A5	1.276531	0.217527	320.000457	40.273707	15.5239
4	4	A10	A13	A5	1.20339	0.234378	280.059972	43.484646	11.312
Total	5	—	A14	A6	1.068366	0.319261	271.467844	59.109074	7.966

Bond A: C—W; Bond B: Fe²—Fe².**Table 12** VES of cementite with Fe² substituted by W

Substituted number of Fe ²	C	Fe ¹	Fe ²	W	n_A	n_B	$E_A/(kJ \cdot mol^{-1})$	$E_B/(kJ \cdot mol^{-1})$	Σn_i
1	3	A13	A13	A5	0.93437	0.396845	177.906494	96.936292	17.0049
2	4	A12	A13	A5	0.948035	0.560697	183.534282	180.318719	12.2434
3	6	A11	A12	A5	0.871442	0.488861	168.817795	157.216242	12.2282
4	5	A12	A12	A6	0.857289	0.397813	165.994321	127.297230	10.8668
5	4	A13	A12	A7	0.869902	0.342241	168.28105	108.349136	9.6763
6	4	A13	A11	A7	0.80962	0.318525	156.619578	100.840801	9.2824
7	4	A13	A11	A7	0.790327	0.310935	152.887495	98.437869	8.4298
8	4	A13	A11	A7	0.768749	0.302445	148.713208	95.750220	7.5772
Total	4	—	A11	A7	0.884373	0.311205	171.291792	98.523535	7.5772

Bond A: C—Fe¹; Bond B: W—W/W—Fe².

Table 13 VES of cementite with Fe¹ substituted by V

Substituted number of Fe ¹	C	Fe ¹	Fe ²	V	n _A	n _B	E _A /(kJ·mol ⁻¹)	E _B /(kJ·mol ⁻¹)	Σn _i
1	1	A13	A14	A10	1.652697	0.244097	329.589044	45.192968	17.2156
2	4	A12	A14	A10	1.612251	0.238123	345.436518	44.086981	11.185
3	4	A13	A14	A11	1.420619	0.23997	304.694002	44.428845	10.5695
4	6	A11	A12	A11	1.141889	0.247923	244.956473	46.067302	12.224
Total	4	—	A14	A14	1.025503	0.343399	219.834587	63.578075	9.2992

Bond A: C—V; Bond B: Fe²—Fe².

Table 14 VES of cementite with Fe² substituted by V

Substituted number of Fe ²	C	Fe ¹	Fe ²	V	n _A	n _B	E _A /(kJ·mol ⁻¹)	E _B /(kJ·mol ⁻¹)	Σn _i
1	5	A11	A12	A9	0.926079	0.489576	179.399968	100.45198	13.8007
2	4	A12	A13	A10	0.900886	0.70925	174.406578	161.42104	13.0712
3	4	A13	A13	A12	0.882862	0.544107	170.788085	124.10875	12.0428
4	5	A12	A12	A13	0.870648	0.399841	168.581076	91.197687	11.8496
5	4	A12	A11	A14	0.877023	0.324108	169.786752	73.841042	12.2459
6	4	A12	A11	A15	0.8706	0.303885	168.543443	69.203614	11.442
7	6	A11	A10	A15	0.869708	0.287943	168.481965	65.573129	10.2601
8	4	A12	A10	A16	0.904711	0.268347	175.147111	61.011933	9.3176
Total	4	—	A11	A14	0.92742	0.325086	179.629521	74.063801	10.5488

Bond A: C—Fe¹; Bond B: V—V/V—Fe².

together temporarily so as to adjust the uniformity of VES here and enable crystals to deform successively. Thus, the lattice electrons stand for metallicity for intermetallic compounds and can be related to plasticity [9, 28, 29]. The crystal with good plasticity can keep the original structure easily when external environment changed, that is to say, it is beneficial to self-stability. The density of lattice electron ρ_V¹ [28, 29] is:

$$\rho_V^1 = \frac{\sum n_i}{V} \tag{10}$$

where Σn_i represents the sum of all lattice electrons in a crystal structure; V is the volume of crystal unit cell.

The symmetry of bond strength has influence on the stability of crystal [28]. The symmetry of bond strength S can be expressed by

$$S = \frac{E^{\min}}{E^{\max}} \tag{11}$$

where E^{min} and E^{max} represent the bond energy of the weakest and strongest bonds in crystal, respectively. When the crystal has good symmetry, its deformation would be more uniform as being subjected to external forces. Otherwise, defects will be formed in the weak zones and lead to instability of crystal. Because of the remarkable discontinuity along c axis of cementite, the factor S is equal to the ratio of the strongest energy bond

from the weak and strong bonds (Fig. 2) in this calculation.

The greater the bond-forming ability, the harder the damaging to the crystal is, and the more stable the crystal structure is. Bond-forming ability of unit volume crystal F_V [28–30] is expressed by

$$F_V = \frac{\sum n_\alpha \cdot I_\alpha \cdot F_\alpha}{V} \tag{12}$$

where V is the volume of crystal cell for cementite; F_α is the bond-forming ability of electron in bond α; I_α and n_α are the equivalent bond number and the number of covalent electron pairs of bond α, respectively. Because of remarkable difference of cementite in strong and weak bond layers, the geometrical mean Q [31] of the strongest bond energy in strong and weak bond layers was selected to describe the stability of bond strength for cementite with Fe¹ and Fe² replaced by M. Considering the formula of bond energy including n_α and F_α factors, Q is defined as

$$Q = (E_A^m \cdot E_B^n)^{1/(m+n)} \tag{13}$$

where m and n represent the numbers of bonds A and B in crystal cell for cementite, respectively; E_A and E_B are bond energy of the strongest bonds in strong and weak bond layers, respectively.

Taking density of lattice, symmetry of bond strength and bond energy into consideration, the factor of stability,

P , can be defined as

$$P = \rho_V^1 \cdot S \cdot Q$$

(14)

Calculation results of density of lattice electron, Q and S factors are listed in Tables 15 and 16.

For θ -Fe₃C, the $\sum n_i = 14.3412$, $Q = 73.1678$ kJ/mol

Table 15 Q and S factors of alloyed cementite with Fe¹ substituted by M

Substituted by Cr			Substituted by Mn			Substituted by Mo		
Number of Fe ¹ substituted by Cr	$Q/$ (kJ·mol ⁻¹)	S	Number of Fe ¹ substituted by Mn	$Q/$ (kJ·mol ⁻¹)	S	Number of Fe ¹ substituted by Mo	$Q/$ (kJ·mol ⁻¹)	S
1	60.0145	0.1591729	1	68.1009	0.3087786	1	56.0225	0.171617
2	59.5216	0.1430663	2	64.7738	0.3087786	2	55.0972	0.158447
3	59.0087	0.1237167	3	63.1961	0.3259554	3	65.8350	0.190209
4	60.9759	0.1109076	4	71.7841	0.3955721	4	65.7559	0.208198
Total	76.1799	0.1724948	Total	79.6264	0.439688	Total	78.4152	0.309971

Substituted by W			Substituted by V		
Number of Fe ¹ substituted by W	$Q/$ (kJ·mol ⁻¹)	S	Number of Fe ¹ substituted by V	$Q/$ (kJ·mol ⁻¹)	S
1	55.6442	0.144149	1	50.7960	0.1371191
2	54.4888	0.125855	2	55.4179	0.1276269
3	55.8660	0.125855	3	60.2139	0.1458146
4	63.1130	0.155269	4	64.3475	0.1880632
Total	80.1802	0.217739	Total	81.4826	0.2892087

Table 16 Q and S factors of alloyed cementite with Fe² substituted by M

Substituted by Cr			Substituted by Mn			Substituted by Mo		
Number of Fe ² substituted by Cr	$Q/$ (kJ·mol ⁻¹)	S	Number of Fe ² substituted by Mn	$Q/$ (kJ·mol ⁻¹)	S	Number of Fe ² substituted by Mo	$Q/$ (kJ·mol ⁻¹)	S
1	151.2927	0.556968	1	118.4524	0.2833622	1	142.0291	0.519360
2	188.0405	0.894655	2	116.2637	0.2704554	2	156.6232	0.693148
3	177.0636	0.894806	3	93.5101	0.2686434	3	151.6565	0.657033
4	164.1323	0.982296	4	86.8056	0.2685982	4	138.4846	0.513506
5	160.4998	0.917852	5	81.5938	0.2685948	5	119.2346	0.486745
6	146.5094	0.976211	6	72.0461	0.2589826	6	108.3553	0.386385
7	139.0476	0.978481	7	68.9010	0.2589826	7	107.2910	0.386385
8	135.9449	0.955941	8	66.6600	0.2589826	8	104.3244	0.366315
Total	138.3852	0.901903	Total	60.8249	0.2685773	Total	84.3308	0.346948

Substituted by W			Substituted by V		
Number of Fe ² substituted by W	$Q/$ (kJ·mol ⁻¹)	S	Number of Fe ² substituted by V	$Q/$ (kJ·mol ⁻¹)	S
1	145.3082	0.544872	1	147.8658	0.5599331
2	182.4561	0.982480	2	169.9660	0.9255445
3	164.8585	0.931278	3	153.5462	0.7266827
4	151.9387	0.766877	4	137.3622	0.5409723
5	135.0300	0.643858	5	111.9698	0.4349046
6	125.6728	0.643858	6	107.9991	0.4105981
7	122.6781	0.643858	7	105.1089	0.3891997
8	119.3286	0.643858	8	103.3734	0.3483468
Total	110.0473	0.575180	Total	88.4220	0.4123142

and $S=E_B/E_A=0.3087$. What should be noted particularly is that $S=E_A/E_B$ when 2–6 atoms of Fe^2 are substituted by Cr; in other cases, $S=E_B/E_A$. Calculation results of P , the stability factor of alloyed cementite, are shown in Figs. 3 and Fig. 4.

Comparison of Figs. 3 and 4 shows that factor P of alloyed cementite with Fe^2 substituted by M is one order of magnitude larger than cementite with Fe^1 substituted and it is also larger than that of $\theta-Fe_3C$. This means that M will substitute for Fe^2 when it is doped in cementite, which is in agreement with the results calculated by first principle [16, 20, 32]. The alloyed cementite is most stable when 2 atoms of Fe^2 (located at the sites of Nos. 2 and 3 or Nos. 6 and 7) are substituted by M, and the stability of alloyed cementite decreases in order of W, Cr, V, Mo, Mn.

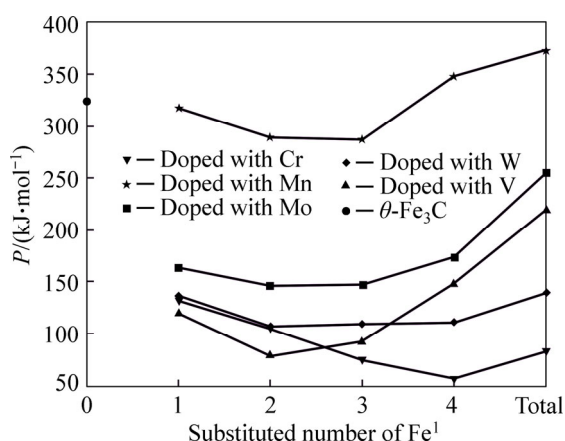


Fig. 3 Factor P of alloyed cementite with Fe^1 substituted by M

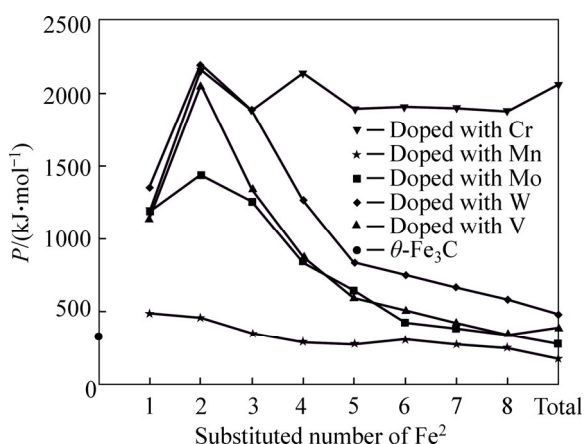


Fig. 4 Factor P of alloyed cementite with Fe^2 substituted by M

With the number of substituted atoms increasing, the density of lattice electrons of alloyed cementite with Fe^1 substituted by V, Mo, W increases first and then decreases. The density of lattice electron gradually decreases when cementite is doped with Cr. Compared with $\theta-Fe_3C$, factor S decreases by about 50% when one atom of Fe^1 is substituted by V, Mo, W and Cr, and S increases with increasing substituted atoms but not

greater than that of $\theta-Fe_3C$. This means that the addition of alloyed elements increases the difference between strong and weak bond layers, meanwhile, the Q is smaller than that of $\theta-Fe_3C$, thus factor P is not greater than that of $\theta-Fe_3C$, namely the stability of alloyed cementite decreases when V, Mo, W and Cr substitute Fe^1 . The density of lattice electron of alloyed cementite with Fe^1 substituted by Mn decreases gradually; S and Q are close to that of $\theta-Fe_3C$ and they slightly increase with increment of substituted atoms number. The variation of stability is not remarkable when Fe^1 is substituted by Mn.

The S significantly increases when Fe^2 is substituted by Cr, V, Mo and W, which means that the difference between strong and weak bond layers decreases and S and Q reach the maximum when 2 atoms of Fe^2 are substituted. Though the density of lattice electron decreases, the favorable bond strength and symmetry lead to signification improvement of P and result in enhancement of stability of alloyed cementite. As Fe^2 is substituted by Mn, the P decreases slightly with increasing substituted atoms, thus the stability of alloyed cementite decreases gradually when 2 atoms of Fe^2 are substituted with W, Cr, V, Mo and Mn. On the other hand, the density of lattice electron and symmetry of bond strength are related to plasticity, so the plasticity of alloyed cementite would be better than that of $\theta-Fe_3C$ when 2 atoms of Fe^2 are substituted by Cr, V, W and Mo, and decreases in order of V, W, Cr, Mo, Mn. The stress–strain curves of alloyed cementite doped with Cr and Mn, measured by UMEMOTO [33, 34], showed that the plasticity values of $(Fe_{0.8}Cr_{0.2})_3C$ and $(Fe_{0.8}Mn_{0.2})_3C$ were both greater than that of $\theta-Fe_3C$, which is in agreement with our calculations. Calculations in this work indicate that the most probable chemical formula of alloyed cementite is $\theta-(Fe_{2.5}M_{0.5})C$. According to the stability variation of cementite doped with Cr and Mn, the Cr and Mn could have a larger solid solubility than other alloyed elements.

Based on EET, the variation of P can be explained from the perspective of electron. The bond of Fe^2-M forms when one Fe^2 is substituted by M and the electron number on this bond is greater than that of the original bond of Fe^2-Fe^2 in cementite, so the bond energy of Fe^2-M is greater than that of Fe^2-Fe^2 , strengthening the weak bond layers in cementite. The bonds of Fe^2-M and $M-M$ gradually form when the number of M is increased. For elements Cr, V, W and Mo, the bond energy of $M-M$ is greater than that of Fe^2-M except for Mn, namely the bond energy of Fe^2-M is greater than $M-M$. The variation of equivalent bond number of $M-M$ and Fe^2-M is different when the number of alloyed atoms increasing. Table 17 shows that the increasement of equivalent bond number of Fe^2-M is

Table 17 Variation in equivalent bond number of M—M and Fe²—M with Fe² substituted by M

Bond name	Substituted number of Fe ² in center UCC								Total
	1	2	3	4	5	6	7	8	
Fe ² —M	1	1	2	2.5	3	4	5	6	—
M—M	—	0.5	0.5	0.5	1	1	1	1	4

faster. The ratio of equivalent bond number of M—M to Fe²—M reaches the maximum when 2 atoms of Fe² located at the sites of No. 2 and No. 3 (or No. 6 and No. 7) are substituted by M, the number of covalent electron pairs on M—M bond reaches the maximum and factors S and Q reach the maximum, thus P reaches the maximum when cementite is doped with Cr, V, Mo and W. Further increasing the number of M, the number of Fe²—M increases quickly, which leads to the reduction of covalent electron pairs on the M—M, bond energy decreasing, hybridization states varying, lattice electrons decreasing, factors S and Q decreasing; therefore, the stability of alloyed cementite decreases.

After Cr and Mn are doped in cementite, the variation of P is different from that after Mo, W and V are doped (Fig. 4). Alloyed cementite still has high stability even more atoms of Fe² are substituted by Cr atoms due to the strong strengthening effect of Cr. The strength of Cr-doped weak bond layers is greater than the original strong bond layers, i.e. $E_B > E_A$. Even though the covalent electron number on bond Cr—Cr decreases which leads to decrease of factor Q , the factor S increases, so factor P still maintains a high value and keeps high stability of alloyed cementite. Because the shielding factor of the electron to nuclear charge of Mn element is smaller than other alloyed elements, the strongest bond on weak bond layer is Fe²—Mn. With increasing number of Mn in cementite, the number of covalent electron pairs on Fe²—Mn decreases and bond energy decreasing results in less strengthening effect on weak bond layers. The decrease in S and P leads to the low stability of alloyed cementite doped with Mn. The stability increases slightly when the substituted numbers of Mn is 6, 7 and 8 due to the increase of the lattice electron number.

5 Conclusions

1) The VES has huge influence on stability of alloyed cementite. The higher the symmetry distribution of covalent electron pairs, the larger the number of lattice electron and the greater the bond energy, the more stable the alloyed cementite.

2) The stability of alloyed cementite with Fe² substituted is higher than that with Fe¹ substituted from

VES calculation. The alloyed cementite is the most stable as Cr, V, W and Mo substitute 2 atoms of Fe² at the sites of Nos. 2 and 3 (or Nos. 6 and 7). The stability of alloyed cementite decreases in order of W, Cr, V, Mo and Mn.

3) The VES values of the alloyed cementite with Cr, V, W and Mo becomes homogeneous after Fe² atoms are substituted, and stability of alloyed cementite is strengthened due to the enhancement of weak bond layers. The effect of Mn on the stability of alloyed cementite is not obvious after atoms of Fe² are substituted.

4) The most probable chemical formula of alloyed cementite is θ -(Fe_{2.5}M_{0.5})C since the stability of alloyed cementite is the most stable as atoms of M replace 2 atoms of Fe² at the site of 8d. Cr and Mn could have a larger solid solubility than other alloyed elements.

References

- [1] WONG J N, CHUL M B, SEI J O, KWON S J. Effect of interlamellar spacing on cementite dissolution during wire drawing of pearlitic steel wires [J]. Scripta Materialia, 2000, 42(5): 457–463.
- [2] HONO K, OHNUMA M, MUEYAMA M, NISHIDA S, YOSHIE A, TAKAHASHI T. Cementite decomposition in heavily drawn pearlitic steel wire [J]. Scripta Materialia, 2001, 44(6): 977–983.
- [3] CHAE J Y, JANG J H, ZHANG G H, KIM K H, LEE J S, BHADESHIA H K D H, SUH D W. Dilatometric analysis of cementite dissolution in hypereutectoid steels containing Cr [J]. Scripta Materialia, 2011, 65(3): 245–248.
- [4] LANGUILLAUME J, KAPELSKI G, BAUDELET B. Cementite dissolution in heavily cold drawn pearlitic steel wires [J]. Acta Materialia, 1997, 45(3): 1201–1212.
- [5] DANOIX F, JULIEN D, SAUVAGE X, COPREAUX J. Direct evidence of cementite dissolution in drawn pearlitic steels observed by tomographic atom probe [J]. Materials Science and Engineering A, 1998, 250(1): 8–13.
- [6] ZHOU C T, XIAO B, FENG J, XING J D, XIE X J, CHEN Y H, ZHOU R. First principles study on the elastic properties and electronic structures of (Fe, Cr)3C [J]. Computational Materials Science, 2009, 45(4): 986–992.
- [7] LI Zhi-lin, LIU Zhi-lin, LIU Wei-dong. Valence electron structure of cementite phase and its interface and the tempering phenomenon [J]. Science in China Series E: Technological Sciences, 2002, 45(3): 282–289.
- [8] WUN C C J, EMILY A C. Structure and stability of Fe3C-cementite surfaces from first principles [J]. Surface Science, 2003, 530(1): 88–100.
- [9] ZHANG Rui-lin. The empirical electron theory of solids and molecules [M]. Changchun: Jilin Science and Technology Press, 1993: 287–290. (in Chinese)
- [10] YU Rui-huang, ZHANG Rui-lin, ZHENG Wei-tao, HU An-guang. Valence structure and property of cementite [J]. Chinese Science Bulletin, 1993, 38(7): 665–667. (in Chinese)
- [11] YE Yi-fu, FAN Tong-xiang, SHANG Yu-xia, CHEN Zong-min. The different coefficient of bonding force between intrastatal and interlamination of M3C type cementite [J]. Science in China Series E: Technological Sciences, 1997, 27(4): 300–303. (in Chinese)
- [12] HUANG Lian, GAO Kun-yuan, WEN Sen-ping, HUANG hui, WANG Wei, NIE Zuo-ren. Valence electron structure analysis of

- equilibrium and metastable phases of Al3M(M=Ti, Zr, Hf) [J]. *Acta Metallurgica Sinica*, 2012, 48(4): 492–501. (in Chinese)
- [13] XU Wan-dong, ZHANG Rui-lin, YU Rui-huang. The bonding energy calculation of transition metal compound [J]. *Science in China Series A: Mathematics*, 1988(3): 323–330. (in Chinese)
- [14] LIU Zhi-lin, LI Zhi-lin, LIU Wan-dong. Calculation of the valence electron structures of alloying cementite and its biphas interface [J]. *Science in China Series E: Technological Sciences*, 2001, 44(5): 542–552.
- [15] MIN Xue-guang, SUN Yang-shan, XUE Feng, DU Wen-wen, WU Deng-yun. Analysis of valence electron structures (VES) of intermetallic compounds containing calcium in Mg–Al-based alloys [J]. *Materials Chemistry and Physics*, 2003, 78(1): 88–93.
- [16] LV Z Q, FU W T, SUN S H, BAI X H, GAO Y, WANG Z H. First-principles study on the electronic structure, magnetic properties and phase stability of alloyed cementite with Cr or Mn [J]. *Journal of Magnetism and Magnetic Materials*, 2011, 33: 915–919.
- [17] GAO Y, LV Z Q, SUN S H, QU M G, SHI Z P, ZHANG R H, FU W T. First principles study on surface structure and stability of alloyed cementite doped with Cr [J]. *Materials Letters*, 2013, 100: 170–172.
- [18] WANG C X, LV Z Q, FU W T, LI Y, SUN S H, WANG B. Electronic properties, magnetic properties and phase stability of alloyed cementite (Fe,M)₃C (M=Co,Ni) from density-functional theory calculations [J]. *Solid State Sciences*, 2011, 13: 1658–1663.
- [19] GAO Y, WANG B, GUO M W, LV Z Q, SUN S H, ZHANG R H, FU W T. First-principles study on surface structural, magnetic and electronic properties of alloyed cementite with Co or Ni [J]. *Computational Materials Science*, 2014, 85: 154–158.
- [20] WANG B W, XIE Y P, ZHAO S J, LI J, HU L J. Density functional theory study of the influence of Ti and V partitioning to cementite in ferritic steels [J]. *Physica Status Solidi B: Basic Solid State Physics*, 2014, 251: 950–957.
- [21] UMEMOTO M, LIU Z G, MASUYAMA K, TSUCHIYA K. Influence of alloy additions on production and properties of bulk cementite [J]. *Scripta Materialia*, 2001, 45(3): 391–397.
- [22] LIU Qing-dong, CHU Yu-liang, WANG Ze-min, LIU Wen-qin, ZHOU Bang-xing. 3D atom probe characterization of alloying elements partitioning cementite of Nb-V Microalloying steel [J]. *Acta Metallurgica Sinica*, 2008, 44(11): 1281–1285.
- [23] DUNLOP G L, CARLSSON C J, FRIMODIG G. Precipitation of VC in ferrite and pearlite during direct transformation of a medium carbon microalloyed steel [J]. *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science*, 1978, 9(2): 261–266.
- [24] SHEIN I R, MEDVEDEVA N I, IVANOVSKII A L. Electronic structure and magnetic properties of Fe3C with 3d and 4d impurities [J]. *Physica Status Solidi B: Basic Solid State Physics*, 2007, 244(6): 1971–1981.
- [25] LIU Zhi-lin, LIN Cheng. Statistics of alloy electronic structure parameter and calculation of mechanics performance [M]. Beijing: Metallurgical Industry Press. 2008: 20–22. (in Chinese)
- [26] LI Jing-ping, MENG Song-he, HAN Jie-cai, ZHANG Xin-hong, LUO Xiao-guang. Valence electron structure and properties of the ZrC_{1-x}N_x solid solution [J]. *Rare Metal Materials and Engineering*, 2008, 37(6): 980–983. (in Chinese)
- [27] PENG Ke, YI Mao-zhong, RAN Li-ping, GE Yi-cheng. Valence electron structure and properties of (Mo_{1-x}W_x)Si₂ solid solutions [J]. *Rare Metal Materials and Engineering*, 2010, 39(3): 414–416. (in Chinese)
- [28] JIANG Shu-ying, LI Shi-chun. Valence electron structures and properties of Al-Ce compounds [J]. *Rare Metal Materials and Engineering*, 2013, 42(S2): 397–400. (in Chinese)
- [29] JIANG Shu-ying, LI Shi-chun. Effect of valence electron structure of La-Al compounds on aluminum alloy properties [J]. *Transactions of Materials and Heat Treatment*, 2013, 34(7): 31–35. (in Chinese)
- [30] SU Juan-hua, JIANG Tao, REN Feng-zhang. Effect of Cr on electron structure and properties of copper [J]. *Transactions of Materials and Heat Treatment*, 2012, 33(4): 152–155. (in Chinese)
- [31] LUO Xiao-guang, LI Jing-ping, HU Ping, DONG Shan-liang. Empirical electron theory model for calculating hardness of Covalent crystals [J]. *Chinese Science Bulletin*, 2010, 55(19): 1957–1962. (in Chinese)
- [32] CHAITANYA K A, MARCEL H F S. First-principles prediction of partitioning of alloying elements between cementite and ferrite [J]. *Acta Materialia*, 2010, 58(19): 6276–6281.
- [33] UMEMOTO M, LIU Z G, MASUYAMA K, TSUCHIYA K. Influence of alloy additions on production and properties of bulk cementite [J]. *Scripta Materialia*, 2001, 45(4): 391–397.
- [34] UMEMOTO M, TODAKA Y, TAKAHASHI T, LI P, TOKUMIYA R, TSUCHIYA K. Characterization of bulk cementite produced by mechanical alloying and spark plasma sintering [J]. *Journal of Metastable and Nanocrystalline Materials*, 2003, 15: 607–614.

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