Materials Science Forum, Vols 638-642 (2010) pages 3319-3324

First-principles calculations and the thermodynamics of Cementite

Jae Hoon Jang[1, a], In Gee Kim[1,b] and H.K.D.H. Bhadeshia[1,2,c]

[1]Graduate Institute of Ferrous Technology, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea

[2]Materials Science and Metallurgy, University of Cambridge, Cambridge CB2 3QZ, UK

[a]impurity@postech.ac.kr, [b]igkim@postech.ac.kr, [c]hkdb@postech.ac.kr

Keywords: Cementite, Silicon, Manganese, Fe_3C, Si_3C, Mn_3C, First-principles study.

Abstract. Thermodynamic data for the substitution of silicon and manganese in cementite have been estimated using first-principles methods in order to aid the design of steels where it is necessary to control the precipitation of this phase. The need for the calculations arises from the fact that for silicon the data cannot be measured experimentally; manganese is included in the analysis to allow a comparison with its known behaviour. The calculations for Fe_3C, $(Fe_{11}Si^{4c})C_4$, $(Fe_{11}Si^{8d})C_4$, $(Fe_{11}Mn^{4c})C_4$ and $(Fe_{11}Mn^{8d})C_4$ are based on the total energy all-electron full-potential linearized augmented plane-wave method within the generalized gradient approximation to density functional theory. The output includes the ground state lattice constants, atomic positions and bulk moduli. It is found that $(Fe_{11}Si^{4c})C_4$ and $(Fe_{11}Si^{8d})C_4$ have about 52 and 37 kJ greater formation energy when compared with a mole of unit cells of pure cementite, whereas the corresponding energy for $(Fe_{11}Mn^{4c})C_4$ and $(Fe_{11}Mn^{8d})C_4$ is less by about 5 kJ mol^{-1}. These results for manganese match closely with published trends and data; a similar comparison is not possible for silicon but we correctly predict that the solubility in cementite should be minimal.

Introduction

There is considerable excitement in the possibility of exploiting steel microstructures consisting of cementite-free bainitic ferrite embedded in austenite, because preliminary results show the potential for outstanding combinations of strength and toughness [1–13]. The bainitic ferrite has a body-centred cubic crystal structure (bcc) and that of austenite is face-centred cubic (fcc). The austentite phase is not usually stable at ambient temperature, but is made so by preventing cementite (Fe_3C) precipitation using silicon as an alloying element, to some extent manganese which works in a different way, by increasing the thermodynamic stability of austenite relative to that of ferrite.

The specific role of silicon in retarding cementite precipitation has been known for a in spite of the lack of thermodynamic data [14–26]. The question arises as to why it is necessary to deal with the thermodynamics of silicon in cementite given that its equilibrium solubility when in contact with ferrite or cementite is negligible. It turns out that when cementite forms at low temperatures, it is forced to inherit the solute content of the parent phase; thus, it traps silicon and hence its stability changes dramatically. Without thermodynamic data is it impossible to estimate the consequences of this process [27-29]. It is, hence, necessary to adapt a first-principles calculation method for obtaining thermodynamic data.

The purpose of this work was to derive the thermodynamic data for Mn and Si in cementite using first-principles calculations, in particular, by using the total-energy all-electron full-potential linearized augmented plane-wave (FLAPW) method [30,31] implemented in the QMD-FLAPW package.

Previous work

The crystal structure of cementite is orthorhombic with the space group *Pnma* and its experimental lattice constants are known as $a = 5.0896$ Å, $b = 6.7443$ Å and $c = 4.5248$ Å. In this unit cell there are four Fe atoms taking Fe(4c) positions, which are not equivalent to the Fe(8d) positions of the remaining eight Fe atoms, and four C atoms located at C(4c) positions [32,33].

A first-principles study on pure cementite using the linear muffin-tin orbital method has shown the calculated cohesive energy per atom was found to be 8.37 eV [34]. The calculated bulk modulus was found to be 235 GPa [35] and equilibrium lattice parameters, lattice positions, bulk modulus and formation energy of cementite has also been similarly estimated [36]. The substitution of silicon and chromium into cementite has previously been investigated; the 8d iron positions were found to be the favored sites for chromium according to the self-consistent full-potential technique [37]; the 8d iron positions were found to be the favored sites for the location of silicon [36].

Computational model and methods

The substituted Fe_3C system was simulated by an orthorhombic unit cell with the composition $(Fe_{11}Si)C_4$, $(Fe_{11}Mn)C_4$ where it is reasonable to assume that silicon and manganese substitute into the iron sites given that their because the atomic radii are similar to that of iron, and much larger than that of carbon [38]. The specific locations at the Fe(4c) and Fe(8d) sites are identified using superscripts: $(Fe_{11}Si^{4c})C_4$, $(Fe_{11}Si^{8d})C_4$, $(Fe_{11}Mn^{4c})C_4$ and $(Fe_{11}Mn^{8d})C_4$. The total energy calculations for the other positions of the same Wyckoff positions show essentially the same values within numerical error.

The Kohn-Sham equation was solved self-consistently in terms of the total energy all-electron full-potential linearized augmented plane-wave method [30,31] by using the generalized gradient approximation [39] for the exchange-correlation potential. The integrations over the three dimensional Brillouin zone were performed by the tetrahedron method over a 9×9×9 Monkhorst-Pack mesh, which corresponds to 125, 205 and 365 k-points inside the irreducible wedge of the Brillouin zone for Fe_3C, $(Fe_{11}M^{4c})C_4$ and $(Fe_{11}M^{8d})C_4$, respectively, where M stands for Si or Mn. The precision required was obtained by considering a plane-wave cutoff up to 21 Ry, which corresponds to about 1700 linearized augmented plane-waves per each k-point and spin. The wave functions, the charge densities, and the potential were expanded with $l \leq 8$ lattice harmonics inside each muffin-tin sphere with the radii of 2.04 a.u. for the Fe, Si, Mn atoms and 1.30 a.u. for the C atoms, respectively. The density and potential in the interstitial region were depicted by using a star-function cutoff at 340 Ry. Core electrons were treated fully relativistically, while valence states were calculated scalar relativistically, without considering spin-orbit coupling [40]. Self-consistency was assumed when the root-mean-square distances between the input and output total charges and spin densities were less than $1.0\text{x}10^{-5}$ electrons/a.u.^{3} All the lattice parameters and the internal atomic positions were relaxed.

Results and Discussion

Table 1 contains the energy minima of referenced elemental states and Table 2 gives the corresponding equilibrium lattice volumes, the formation energy and calculated bulk moduli of Fe_3C, $(Fe_{11}Si^{4c})C_4$, $(Fe_{11}Si^{8d})C_4$, $(Fe_{11}Mn^{4c})C_4$ and $(Fe_{11}Mn^{8d})C_4$ in their ferromagnetic states.
Both silicon and manganese substitution decrease the unit cell volume of pure cementite. Silicon has a larger effect when substituted in the 4c positions but effect of the two solutes on volume cannot be distinguished when the substitution is in the 8c positions.

The calculated bulk modulus of ferromagnetic cementite is 226.84 GPa agrees reasonably with a previous estimate of 235.13 GPa [35] where different precision criteria were used. The substitution of Si into the 4c and 8d sites increases the bulk moduli about 2.2% and 2.6%, respectively [36]. In contrast, the Mn at the 4c and 8d positions increases the bulk moduli by 4.5% and 3.3% respectively.

The formation energies were calculated as differences between the total energy of each phase and the sum of the energies of the stable state of elements forming this phase. The formation energy (ΔU) of each system is defined, with the integers l, m and n, at zero Kelvin, as follows,

$$\Delta U = E(\mathrm{Fe}_l\mathrm{M}_m\mathrm{C}_n) - l \times E(\mathrm{Fe}) - m \times E(\mathrm{M}) - n \times E(\mathrm{C}). \quad (1)$$

where $E(\mathrm{Fe}_l M_m \mathrm{C}_n)$, E(Fe), E(Si), E(Mn) and E(C) are the total energies of $\mathrm{Fe}_l M_m \mathrm{C}_n$, ferromagnetic bcc iron, diamond silicon, fcc manganese and graphite carbon, respectively, at the corresponding equilibrium lattice constants.

The formation energy of pure cementite is calculated to be about 21.5 kJ mol^{-1} which is 3.1 kJ mol^{-1} larger than the experimental value, 18.3 kJ mol^{-1} [41]. Those of $(\mathrm{Fe}_{11}\mathrm{Si}^{4c})\mathrm{C}_4$, $(\mathrm{Fe}_{11}\mathrm{Si}^{8d})\mathrm{C}_4$, $(\mathrm{Fe}_{11}\mathrm{Mn}^{4c})\mathrm{C}_4$ and $(\mathrm{Fe}_{11}\mathrm{Mn}^{8d})\mathrm{C}_4$ are calculated to be 138.1, 123.2, 81.7 and 81.1 kJ mol^{-1}, respectively. Thus silicon increases the formation energy whereas manganese has the opposite effect, consistent with the low solubility of silicon and high solubility of manganese in cementite.

element	volume(Å^3)	V/V_0	energy (kJ mol^{-1})	bulk modulus (GPa)	
				calculation	measurement
bcc Fe	11.36	0.97	−3340575.03	185.20	170
graphite C	8.89	1.01	−99997.13	37.69	33
diamond Si	20.46	0.99	−761219.33	88.52	100
bcc Mn	10.87	0.89	−3040972.35	283.72	-
fcc Mn	10.96	0.90	−3040979.39	292.23	-

Table 1: Calculated equilibrium atomic volumes, total energies, and bulk moduli of the reference materials of ferromagnetic bcc Fe, graphite C, diamond Si, bcc Mn and fcc Mn. The experimental bulk moduli of the pure elements as included for reference, V_0 is the experimental volumes per atom of the reference elements.

type	volume(Å^3)	V/V_0	ΔU (kJ mol^{-1})	bulk modulus(GPa)
$\mathrm{Fe}_3\mathrm{C}$	152.20	0.980	21.5(86.1)	226.84
$(\mathrm{Fe}_{11}\mathrm{Si}^{4c})\mathrm{C}_4$	151.44	0.975	138.1	221.83
$(\mathrm{Fe}_{11}\mathrm{Si}^{8d})\mathrm{C}_4$	151.97	0.978	123.2	221.00
$(\mathrm{Fe}_{11}\mathrm{Mn}^{4c})\mathrm{C}_4$	152.10	0.979	81.7	236.94
$(\mathrm{Fe}_{11}\mathrm{Mn}^{8d})\mathrm{C}_4$	151.96	0.978	81.1	234.33

Table 2: Equilibrium unit cell volume, formation energy, and bulk moduli in ferromagnetic cases, which are calculated using the third order polynomial fitting with V_0=155.31 Å^3, the experimental volume of $\mathrm{Fe}_3\mathrm{C}$. The energy is stated in units of kJ mol^{-1} of each formula unit, $\mathrm{Fe}_3\mathrm{C}$ has also the formation energy which is multiplied by four in parentheses to compare with $(\mathrm{Fe}_{11}M^{4c})\mathrm{C}_4$ and $(\mathrm{Fe}_{11}M^{8d})\mathrm{C}_4$. The reference states are ferromagnetic bcc Fe, graphite C, diamond Si and fcc Mn.

Table 3 contains the calculated results of equilibrium unit cell volume, formation energy per formula unit and the bulk moduli of the hypothetical $\mathrm{Fe}_3\mathrm{C}$, $\mathrm{Si}_3\mathrm{C}$ and $\mathrm{Mn}_3\mathrm{C}$ cementite. The calculated formation energies are 21.5, 256.4 and −52.7 kJ mol^{-1} for its calculated equilibrium lattice constants using the same optimization procedure with $\mathrm{Fe}_3\mathrm{C}$. The calculated formation energy of the $\mathrm{Si}_3\mathrm{C}$ and $\mathrm{Mn}_3\mathrm{C}$ over $\mathrm{Fe}_3\mathrm{C}$ agree reasonably with 250 kJ mol^{-1} and −40 kJ mol^{-1} usually assumed in thermodynamic calculations [41]. The formation energy of $\mathrm{Si}_3\mathrm{C}$ is one order larger than that of $\mathrm{Fe}_3\mathrm{C}$. The results of VASP also are contained in the Table 3 – there is a discrepancy with the FLAPW results for the manganese carbide. We attribute this difficulty to the fact that the former method does not treat the core-valence interactions properly.

type	volume(Å^3)	V/V_0	ΔU (kJ mol^{-1})		bulk modulus(GPa)
			VASP	FLAPW	

Fe_3C(FM)	152.20	0.980	18.8	21.5	226.84
Si_3C [37]	208.29	1.341	260.0	256.4	130.90
Mn_3C	147.60	0.950	−26.7	−52.7	329.34

Table 3: Equilibrium unit cell volume, formation energies, and bulk moduli which are calculated using the third order polynomial fitting with V_0=155.31 Å^3, the experimental volume of Fe_3C. The energy is stated in units of kJ mol^{-1} of each formula unit. Only Fe_3C is ferromagnetic state but the others are nonmagnetic cases. The formation energies from VASP are from Miyamoto's paper [41]. The referenced states are ferromagnetic bcc Fe, graphite C, diamond Si and fcc Mn.

Fig. 1 shows the dependency of formation energy at zero Kelvin with respect to silicon and manganese atomic concentration in cementite for the ferromagnetic Fe_3C, $(Fe_{11}Si^{4c})C_4$, $(Fe_{11}Si^{8d})C_4$, $(Fe_{11}Mn^{4c})C_4$, $(Fe_{11}Mn^{8d})C_4$ and nonmagnetic Si_3C, Mn_3C. It is clear to see that the formation energy behavior is nonlinear to the alloying concentrations in cementite.

Fig. 2 shows the equilibrium ternary phase diagram at 773 K using MTDATA with TCFE database and FLAPW calculation results. A free energy of cementite phase has been modified as substitutional solid solution $(Fe,Si)_3C$ and $(Fe,Mn)_3C$ using the same effect of temperature dependency with Fe_3C. The excess energy term has been modified using a regular solution model and using the FLAPW results of $(Fe_{11}M)C_4$ without temperature dependency.

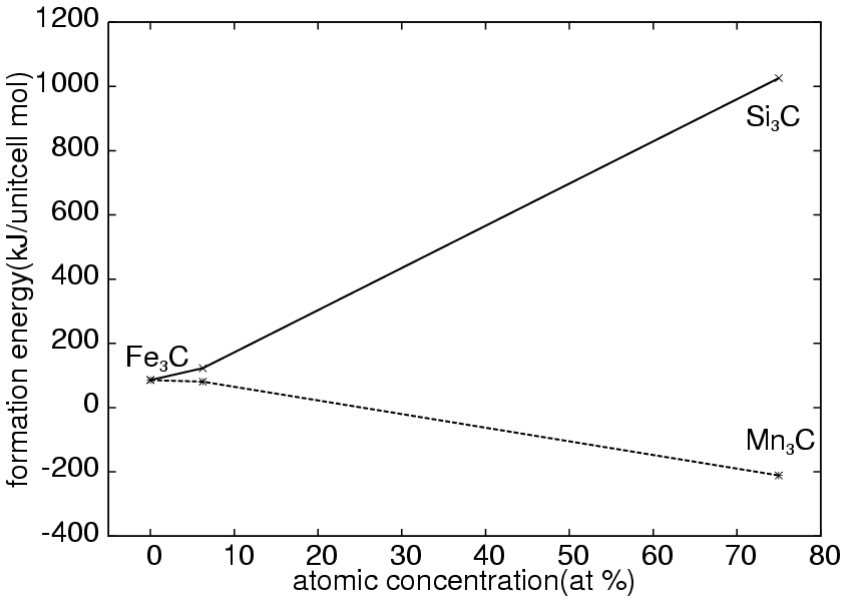

Figure 1: Calculated formation energy of one mole of unit cell with respect to alloying concentration in Fe_3C cementite. The selected data are chosen as the smallest formation energy from the corresponding atomic configurations. The lines are drawn as guides.

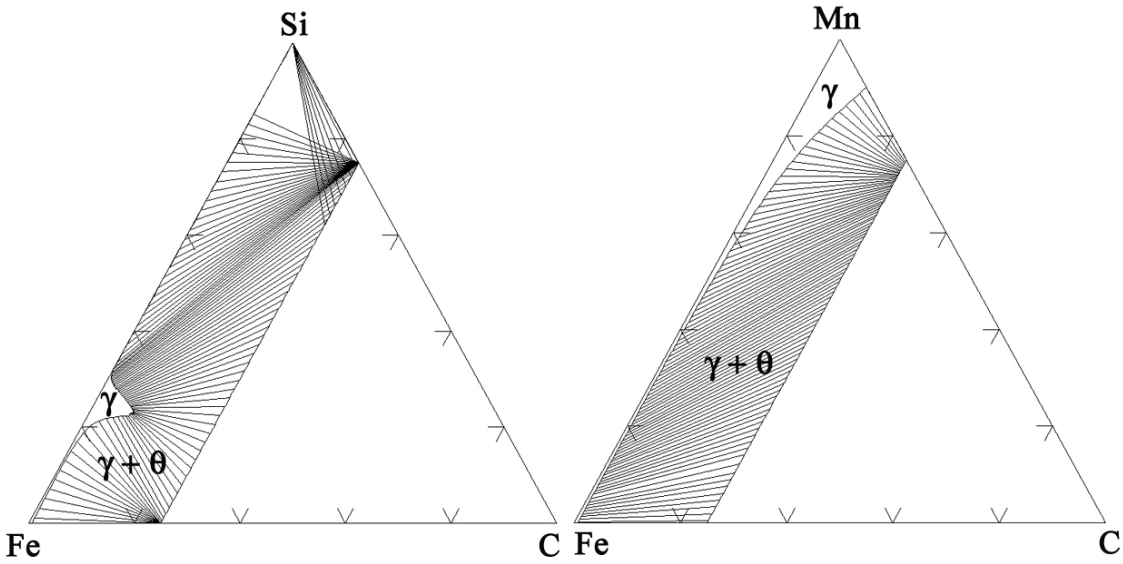

Figure 2: Equilibrium ternary phase diagrams of Fe-Si-C and Fe-Mn-C system at 773 K using FLAPW calculation results.

Summary

The formation energies of cementite in which silicon and manganese have been have been calculated using an ab initio method which considers not only the valence but also the core electrons. Consistent with previous work, the substitution of silicon into cementite is not favoured, but as expected from experiments, that of manganese is favoured.

Acknowledgements

The authors are grateful to Prof. Hae-Geon Lee for the provision of laboratory facilities at the Graduate Institute of Ferrous Technology (GIFT), POSTECH. We are also grateful to Hugh Davies of the NPL for his support of MTDATA.

References

[1] O. Matsumura, Y. Sakuma, H. Takechi, Trans. ISIJ 27 (1987) 570–579.

[2] O. Matsumura, Y. Sakuma, H. Takechi, Scripta Metall. 27 (1987) 1301– 1306.

[3] F.G. Caballero, H.K.D.H. Bhadeshia, K.J.A. Mawella, D.G. Jones, P. Brown, Mater. Sci. and Technology 17 (2001) 512–516.

[4] F.G. Caballero, H.K.D.H. Bhadeshia, K.J.A. Mawella, D.G. Jones, P. Brown, Mater. Sci. and Technology 17 (2001) 517–522.

[5] F.G. Caballero, H.K.D.H. Bhadeshia, K.J.A. Mawella, D.G. Jones, P. Brown, Mater. Sci. and Technology 18 (2002) 279–284.

[6] C. Garcia-Mateo, F.G. Caballero, H.K.D.H. Bhadeshia, ISIJ International 43 (2003) 1238–1243.

[7] C. Garcia-Mateo, F.G. Caballero, H.K.D.H. Bhadeshia, ISIJ International 43 (2003) 1821–1825.

[8] J.G. Speer, D.V. Edmonds, F.C. Rizzo, D.K. Matlock, Current Opinion in Solid State and Mater. Sci. 8 (2004) 219–237.

[9] F.G. Caballero, H.K.D.H. Bhadeshia, Current Opinion in Solid State and Mater. Sci. 8 (2004) 251–257

[10] P.J. Jacques, Current Opinion in Solid State and Mat. Sci. 8 (2004) 259– 265.

[11] Z.G. Yang, H.S. Fang, Current Opinion in Solid State and Mater. Sci. 9 (2005) 277–286.

[12] B. De Cooman, Current Opinion in Solid State and Mater. Sci. 8 (2004) 285–303.

[13] S. Chatterjee, M. Murugananth, H.K.D.H. Bhadeshia, Mater. Sci. and Technology 23 (2007) 819.

[14] E.C. Bain, Alloying Elements in Steel, American Society of Mater., Cleveland, Ohio, USA, 1939.

[15] A.G. Allten, P. Payson, Trans. of ASM 45 (1953) 498–532.

[16] W.S. Owen, Trans. of ASM 46 (1954) 812–829.

[17] S.J. Matas, R.F. Hehemann, TMS–AIME 221 (1961) 179–185.

[18] A.S. Keh, W.C. Leslie, *Structure and Properties of Engineering Materials, Materials Science Research, vol. 1*, Plenum Publishing, NY, USA, 1963.

[19] J. Deliry, Memoires Scientifiques de la Revue de Metallurgie 62 (1965) 527–550.

[20] J. Pomey, Memoires Scientifiques de la Revue de Metallurgie 63 (1966) 507– 532.

[21] J. Gordine, I. Codd, J. of the Iron and Steel Ins. 207 (1969) 461–467.

[22] R.F. Hehemann, *The bainite transformation, in: H.I. Aaronson, V.F. Zackay (Eds.), Phase Transformations*, 1970, pp. 397–432.

[23] R. Le-Houillier, G. Begin, A. Dube, Metall. Trans. 2 (1971) 2645–2653.

[24] G.W. Lorimer, R.M. Hobbs, N. Ridley, J. of the Iron and Steel Ins. 210 (1972) 757–764.

[25] B.J.P. Sandvik, Metall. Trans. 13A (1982) 777–787.

[26] B.J.P. Sandvik, Metall. & Mater. Transa. A 13A (1982) 789

[27] H.K.D.H. Bhadeshia, Mater. Sci. Forum 426–432 (2003) 35–42.

[28] G. Ghosh, G.B. Olson, Acta Mater. 50 (2002) 2099–2119.

[29] H. K. D. H. Bhadeshia, M. Lord, L. –E. Svensson, Trans. of JWRI 32 (2003) 43-52

[30] E. Wimmer, H. Krakauer, M. Weinert, A. J. Freeman, Phys. Rev. B 24 (1981) 864

[31] M. Weinert, E. Wimmer, A.J. Freeman, Phys. Rev. B 26 (1982) 4571–4578.

[32] E.J. Fasiska, G.A. Jeffrey, Acta Crystall. 19 (1965) 463–471.

[33] F.H. Herbstein, J. Smuts, Acta Crystall. 17 (1964) 1331–1332.

[34] J. Haglund, G. Grimvall, T. Jarlborg, Phys. Rev. B 44 (1991) 2914–2919.

[35] H.I. Faraoun, Y.D. Zhang, C. Esling, H. Aourag, J. of Appl. Phys. 99 (2006) 093508.

[36] J. H. Jang, I. G. Kim and H. K. D. H. Bhadeshia Computational Mater. Sci. 44 (2009) 1319-1326

[37] N.I. Medvedeva, L.E. Kar'kina, A.L. Ivanovskii, Phys. Solid State 48 (2006) 15–19.

[38] Information on http://www.webelemtns.com

[39] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865

[40] D. D. Koelling and B. N. Harmon, J. Phys. C : Solid St. Phys. 10 (1977) 3107.

[41] G. Miyamoto, J. C. Oh, K. Hono, T. Furuhara, T. Maki, Acta Mater. 55 (2007) 5027-5038