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A Systematic Study on Iron Carbides from First-Principles

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Abstract. The formation enthalpy of a series of Fe-C carbides has been estimated using a first-principles approach. The Fe to C ratio dependence of the formation enthalpy is reasonable, but it is revealed that χ- and η-carbides require an extraordinary environment to be able to form. Furthermore, an addition of substitutional solutes other than Fe and C should promote other carbides with different crystal structures. The analysis suggests further studies to discover the critical concentrations of alloying which stimulate the other carbides to become more stable.

Introduction

There are many contemporary examples where advances in steel metallurgy are stifled by the lack of thermodynamic data for the carbide phases, and as resulting in the failure to understand and control their precipitation mechanisms. This is particularly so in the case of a certain class of steels which have led to dramatic developments in technologically vital contexts. Such alloys contain *carbide-free bainite*, i.e., an intimate mixture of fine ferrite plates with a body-centered cubic (bcc) crystal structure, embedded in a matrix of carbon-enriched austenite with a face-centered cubic (fcc) structure. This latter phase is not usually stable at ambient temperatures, but is made so by preventing cementite (Fe_3C) precipitation using silicon as an alloying addition to the steel. The austenite is then able to retain carbon in solid solution, enabling it to remain untransformed to room temperature.

The specific role of silicon, which is inherited the concentration of the parent phase, in suppressing cementite formation at low temperatures; since the solubility of silicon in cementite is negligibly small, the trapping of silicon is thought to dramatically reduce the driving force for precipitation.

However, it has not been possible to theoretically justify the mechanism by which the silicon acts, because thermodynamic data on silicon in cementite cannot be measured due to its incredibly low solubility in the carbide.

On a similar basis, the substitution of solutes other than carbon into the crystal structure of ε-carbide is uncharacterized. There also exists an array of other transition carbides of iron for which a detailed understanding is absent.

The purpose of the present work was to resolve these difficulties by applying calculations which do not require any inputs other than the crystal structure and the nature of the participating atoms. The data thus acquired have in some cases already been incorporated into thermodynamic databases which are used to conduct phase stability and kinetic calculations important in the efficient design of iron and its alloys.

Computation Methods

A series of (transition) carbides was considered, which generally appear during the tempering of martensite or the formation of bainite. They are, cementite (Fe_3C) in the orthorhombic structure, $Fe_{16}C_2$/$Fe_{16}C_4$ carbides in the Zener ordered body-centered tetragonal structures, and ε-carbide ($Fe_{2.4}C$) in the hexagonal structure. Some calculations were also done for Si, Al and Mn substitution of the Fe sites in the corresponding symmetric positions. In addition, the carbides that appear during tempering certain alloys at elevated temperatures, e.g., the κ-carbide ($AlFe_2MnC$) in the anti-Perovskite structure and $Cr_{23}C_6$ carbide with an Fe atom substitution in the Cr sites, were also examined.

In order to compare the thermodynamic properties of those systems, we calculated the formation enthalpy (ΔH). It is emphasized at the outset that this is an enthalpy change for the synthesis of carbides from the component elements, rather than a representation of energy changes during precipitation from a supersaturated matrix such as martensite. The work presented here might be better compared to experiments on mechanical alloying where carbides are prepared from their elemental constituents. Since the systems considered have different elemental contents, the enthalpy change is expressed in terms of the number of atoms involved in the synthesis, as follows. The individual carbides are optimized with respect to their lattice constants and internal atomic coordinates using first-principles calculations as well as their elemental structures for reference states. The total energy data obtained for those optimized structures are nothing more than the enthalpy, $H=U+pV$, where U is the internal energy directly calculated by the first-principles method, p is the external pressure, and V is the corresponding volume, at zero Kelvin and zero pressure. Suppose a ternary compound $X_lY_mZ_n$ made of the elements X, Y, and Z where l, m, and n are integers. ΔH is then calculated as follows:

$$\Delta H = \left(H\left(X_l Y_m Z_n\right) - lH(Z) - nH(Y) - mH(Z)\right)/(l + m + n). \tag{1}$$

The first-principles calculations are carried out in terms of density functional theory [1]. The Kohn-Sham equation [2] was solved in terms of the total-energy all-electron full-potential linearized augmented plane wave (FLAPW) method [3,4] implemented in the QMD-FLAPW package [5] within the generalized gradient approximation (GGA) [6] to density functional theory. More than 4.0 ($2\pi/a$) plane wave cutoffs were used to expand the linearized augmented plane wave (LAPW) basis set. Lattice harmonics inside each muffin-tin (MT) sphere were expanded within $l \leq 8$ ($l \leq 10$ for $Cr_{23}C_6$) were used for expanding the basis function, potential and density. The improved tetrahedron method [7] was used for integrations inside the Brillouin zone performed on the Monkhorst-Pack mesh [8]. All core electrons were calculated fully relativistically, while the valence states were treated scalar relativistically, without spin-orbit coupling [9]. The explicit orthogonalization (XO) scheme was involved to ensure the orthogonality between the core and valence states [10]. The chosen computational parameters satisfy the FLAPW convergence test [11]. Internal coordinates were relaxed by finding the force and energy minimum [12]. The optimized lattice parameters were found by fitting to either the equation of state [13] or to the 4th-order polynomial function [14].

Results and Discussion

Table 1 lists the calculated ΔH of the considered carbides. The huge ΔH values of χ- and η-carbides imply that they should only form in somewhat extraordinary cases, for example when their nucleation from a particular matrix is overwhelmingly favored by a low interfacial energy. As the

Fe to C ratio of the Fe-C system is increased, Δ*H* decreases until Fe/C equals 3, the cementite, and then there is dramatic increase at the Zener ordered $Fe_{16}C_4$ (Fe/C = 4), followed by greater stability at the Zener ordered $Fe_{16}C_2$ (Fe/C = 8), for which Δ*H* value is comparable to that of cementite.

The addition of impurities in the carbides does change the values of the pure carbides. It is clear to see that κ-carbide and $Cr_{23}C_6$ carbides are quite stable compared to the iron carbides. Note that the signs of Δ*H* of all the Fe-C system are positive, while those of κ-carbide and $Cr_{23}C_6$ carbide are negative. This fact implies that enough addition of alloying elements will stimulate alloy carbide to form.

It is also interesting to note that the change in Δ*H* values by an impurity atom substitution. The change is determined by element selection, which is usually inherited from the mother matrix. It will be interesting in future work to introduce a variety of solutes into the Fe-C system and re-examine the enthalpy changes.

Table 1Calculated formation enthalpy per atom-mole (Δ*H*) in units of kJ/atom-mol of the considered carbides. Δ*H* values with the substitution of an impurity atom into an M site are also given.

Carbide	Fe,M/C	Δ*H*	Δ*H* with the substitution by an impurity atom	Reference
Zener-ordered J-model $Fe_{16}C_2$	8	+5.80	-	[15]
Zener-ordered T-model $Fe_{16}C_2$	8	+5.78	-	
Zener-ordered J-model $Fe_{16}C_4$	4	+24.18	-	
Zener-ordered T-model $Fe_{16}C_4$	4	+23.98	-	
Cementite θ-Fe_3C	3	+5.38	+7.70 (Si) +4.53 (Al) +5.07 (Mn)	[16,17]
Hexagonal ε-Fe_3C	3	+5.13	+11.38 (Si)	[18]
Hägg carbide χ-Fe_5C_2	2.5 (=5/2)	+152.6	-	[19]
Hexagonal ε-$Fe_{2.4}C$	2.4 (=12/5)	+6.23	+9.08 (Si) +4.98 (Al) +4.40 (Mn)	[18]
Hexagonal ε-Fe_2C	2	+7.00	+20.33 (Si)	
Orthorhombic η-Fe_2C	2	+126.1	-	[19]
Anti-Perovskite κ-carbide Al(Fe_2Mn)C	4	−28.2 −27.9	- -	[20] [21]
Cubic $Cr_{23}C_6$ carbide	3.83	−8.61 −10.98 −8.75	−10.43 (Fe) - −10.65 (Fe)	[22] [23] [24]

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