The melting temperature of BCC perfect ternary alloy FeCrC under pressure

C D Tran\(^1\), G Coman\(^2\), H Q Nguyen\(^1\), H T Nguyen\(^3\) and V Q Dinh\(^1\)

\(^1\) Hanoi National University of Education, Hanoi, Vietnam
\(^2\) “Dunarea de Jos” University of Galati, Romania
\(^3\) University of Transport and Communications, Hanoi, Vietnam

Email: nthoaly@utc.edu.vn

Abstract. The analytic expressions of the mean nearest neighbour distance, the free energy, the absolute stabilizing temperature of alloy state and the melting temperature for substitution alloy AB with interstitial atom C and body-centered cubic structure under pressure are derived by the statistical moment method. The theoretical results are applied to alloy FeCrC. Our calculated results are compared with other calculations and experimental data.

1. Introduction
Iron-based alloys are of fundamental importance in the development of science and technology due to their valuable mechanical and thermodynamic properties [1, 2]. Notably, the FeCrC alloy is a prominent physical system that attracts the attention of many researchers [3]. The FeCrC alloy is known as the basis for tool steels and stainless steels, so it is widely used in many industries. Besides, iron and its alloys are believed to be the main components of the Earth’s core, so the information about their phase diagrams is of central importance for geophysics and planet physics [4].

Although the FeCrC alloy has been experimentally and theoretically investigated many times, our knowledge about its melting is still incomplete. On the theoretical side, Molecular Dynamic (MD) simulation and ab initio calculation are evaluated as two main methods to study the melting properties of the crystal. However, the increasing of alloying elements will lead to expensive computational cost and significant deviation from experiments in many cases. For example, in [5], the coexisting phases approach has been used to calculate melting phase diagrams of several Fe-C interaction potentials, such as Embedded Atom Method (EAM) potential [6, 7] and Analytic Bond Order (ABO) potential [8]. However, these obtained results are not consistent with Experimental Data (EXPT), and more work is required to solve this problem. To get a whole physical picture of the relationship between alloying elements and thermodynamic properties of the crystal, we often use the Calculation of Phase Diagram (CALPHAD) method [9]. However, using the CALPHAD method requires great support from experiments and the combination of many calculation software. Furthermore, the CALPHAD method mainly provides only melting information at zero pressure. As a result, building a general melting theory is a never-ending story but inspiring in modern physics.

For the reasons above, in this paper, we will determine the melting point of the FeCrC alloy with Body-Centered Cubic (BCC) structure by using the Statistical Moment Method (SMM). Nguyen Tang and Vu Van Hung introduced the SMM from the 1990s [10], and its melting theory is based on the condition of absolute stability for the crystalline state as
\[
\left( \frac{\partial P}{\partial v} \right)_{T,T_S} = 0
\]  

(1)

where \( P \) is the hydrostatic pressure, \( v \) is the atomic volume, and \( T_S \) is the critical temperature. The condition (1) corresponds to the infinite value of the isothermal compressibility, so the critical temperature \( T_S \) is just indeed a theoretical hypothesis. In the previous study of SMM theory [11, 12], the authors proved that the critical temperature \( T_S \) is close to the melting temperature \( T_m \) at the same physical conditions, so we can find \( T_m \) from \( T_S \) by using a simple correction. By following this path, we can easily obtain the melting curves of metals and binary alloys with only using the solid phase. It is the first time the SMM is expanded to investigate the melting of BCC perfect ternary alloy.

2. Method

The model of the ternary ABC alloy with BCC structure is shown in figure 1, where A is the main atom, B is the substitutational atom and C is the interstitial atom. For simplicity, we assume that the atom C only interacts with the main atoms A which are closest to it (A\(_1\) and A\(_2\)). The analytic expressions for the cohesive energy \( u_{0_X} \) and the alloying parameters \( k_X, \omega_X, \gamma_X, \gamma_{2X}, \gamma_X \) for the atom X (X = A, B, C, A\(_1\), A\(_2\)) were determined in our previous works [13]. The atomic concentration \( c_X \) satisfy the following condition

\[
c_A = 1 - c_B - 7c_C, \quad c_A = 2c_C, \quad c_{A_1} = 4c_C
\]  

(2)

Figure 1. The model of the ternary ABC alloy with BCC structure.

The nearest neighbor distance \( a_X(P,0) \) for atom X can be derived by solving the following equation

\[
Pv_X = -a_X \left( \frac{1}{6} \frac{\partial u_{0_X}}{\partial a_X} + \frac{\hbar \omega_X}{4k_X} \frac{\partial k_X}{\partial a_X} \right)
\]  

(3)

where \( v_X \) is the atomic volume. Then, the average atomic displacement \( y_X(P,T) \) is given by

\[
y_X(P,T) = \left( \frac{2\gamma_X(P,0)\theta^2}{3k_X(P,0)} - A_X(P,0) \right)
\]  

(4)

where \( \theta = k_{B}T \), \( k_{B} \) is the Boltzmann constant and \( A_X(P,0) \) was defined as in Ref. [14].

After that, the nearest neighbour distance \( a_X(P,T) \) for atom X at pressure \( P \) and temperature \( T \) is determined by
\[ a_A(P,T) = a_A(P,0) + y_A(P,T) \quad (5a) \]
\[ a_B(P,T) = a_B(P,0) + y_B(P,T) \quad (5b) \]
\[ a_C(P,T) = a_C(P,0) + y_A(P,T) \quad (5c) \]
\[ a_A(P,T) \approx a_C(P,T) \quad (5d) \]
\[ a_A(P,T) = a_B(P,0) + y_C(P,T) \quad (5e) \]

and we can calculate the mean nearest neighbour distance \( a_{ABC} \) between two main atoms A in the ternary ABC alloy as follows:

\[ a_{ABC} = \frac{(1-c_B)B_{AC}a_{AC} + c_BB_{AB}a_B}{(1-c_B)B_{AC} + c_BB_{AB}} \quad (6a) \]
\[ a_{AC}(P,T) = a_{AC}(P,0) + y_{AC}(P,T) \quad (6b) \]
\[ a_{AC}(P,0) = (1-c_C)a_A(P,0) + c_C\sqrt{3}a_C(P,0) \quad (6c) \]
\[ y_{AC}(P,T) = (1-7c_C)y_A(P,T) + c_Cy_C(P,T) + 2c_Cy_A(P,T) + 4c_Cy_A(P,T) \quad (6d) \]

where \( B_{AC} \) is the isothermal bulk modulus of the interstitial AC alloy and \( B_B \) is the isothermal bulk modulus of the pure metal B [13].

The equation of state of the ternary ABC alloy with BCC structure has the form

\[ P = \frac{a_{ABC}}{6\nu_{ABC}} \sum_x c_x \left( \frac{\partial u_{ox}}{\partial a_x} \right) + \frac{3\gamma_G}{\nu_{ABC}} \frac{\partial \mu}{\partial a} \]

where \( \gamma \) is known as the Gruneisen parameter

\[ \gamma_G = -\frac{a_{ABC}}{6} \sum_x c_x \frac{\partial k_x}{\partial a_x} \frac{h\omega_x}{2\theta} \frac{\coth \left( \frac{h\omega_x}{2\theta} \right)}{2\theta} \]

By combining equations (1), (7), (8) we have

\[ T_s = \frac{2P_{ABC} + a_{ABC}^2}{6} \sum_x c_x \frac{\partial^2 u_{ox}}{\partial a_x^2} \frac{h\omega_{ABC}^2}{4} \sum_x c_x \omega_x \frac{1}{k_x} \left[ \frac{1}{2k_x} \frac{\partial k_x}{\partial a_x} \right] \]

Solving equation (9) will give us the value of the critical temperature \( T_s \). Because \( T_s \) is close to \( T_m \) at the same physical condition, so we have \( a_m = a_{ABC}(P,T_m) \approx a_S = a_{ABC}(P,T_s) \) and \( T_m \) can be expanded in term of \( a_m - a_S \) as

\[ T_m \approx T_s + \frac{a_m - a_S}{k_B/\gamma_G(P,T_s)} \left\{ P_{ABC}(P,T_s) \frac{a_S}{a_S} + \sum_x c_x \left[ \frac{\partial u_{ox}}{\partial a_x} \right]_{T=T_s} + a_S \left[ \frac{\partial^2 u_{ox}}{\partial a_x^2} \right]_{T=T_s} \right\} \]

### Reference

[13]
In 1939, Born [15] proposed that the melting initiates when the shear modulus vanishes and the crystal loses its ability to resist shear, so the melting curve of crystal under pressure can be given in the form [16]

\[ T_m(P) = T_m(0) \left( \frac{G(P)}{G(0)} \right)^{\frac{1}{b}} \left( \frac{B_f(P)}{B_f(0)} \right) \]

where \( G(P) \) and \( G(0) \) are the shear moduli at pressure \( P \) and zero pressure, respectively, \( B_f(0) \) is the isothermal bulk modulus at zero pressure, \( b = \left( \frac{dB_f(P)}{dP} \right)_{P=0} \), \( B_f(P) \) is the isothermal bulk modulus at pressure \( P \).

3. Numerical results

For the Fe-Fe and Cr-Cr interactions, we use the Mie-Lennard-Jones pair potential as

\[ \varphi = \frac{D}{n-m} \left[ m \left( \frac{r_0}{r} \right)^n - n \left( \frac{r_0}{r} \right)^m \right] \]

where \( D \) is the dissociation energy, \( r_0 \) is the equilibrium value of \( r \), \( m \) and \( n \) are taken empirically [17]. To describe the Fe-C interaction, we use the Finnis-Sinclair potential as follows

\[ U = -A \sqrt{\sum_i \rho(r_i)} + \frac{1}{2} \sum_{i<j} \phi(r_{ij}) \]

where \( \rho(r_{ij}) \) is the embedded potential and \( \phi(r_{ij}) \) is the pair potential introduced in Ref. [6].

Firstly, we will check a limited case when \( c_C, c_C \to 0 \). Figure 2 shows the melting curve of the pure Fe metal obtained from the SMM correspond well with EXPT [18-21]. In the surveyed range, the differences are lower than 3 %. The melting temperature of the pure Fe metal is known as the increasing function of pressure. Specifically, when pressure increases from 0 to 5 GPa, the melting temperature of the pure Fe metal also increases from 1800 to 1990 K. The average melting slope \( \frac{\Delta T_m}{\Delta P} \) is about 38 K.GPa\(^{-1}\) from the SMM and about 35 K.GPa\(^{-1}\) from EXPT [21].

Figure 2. \( T_m(P) \) for Fe obtained from the SMM and EXPT [18-21].
Figure 3 shows the effects of the interstitial atom C (figure 3a) and the substitutional atom Cr (figure 3b) on the melting temperature of Fe at zero pressure. We recognize that the melting temperature of the FeC alloy decreases rapidly with increasing atomic concentration of C. The average melting slope \( \frac{\Delta T_m}{\Delta c_C} \) shown in figure 3a is about \(-125\) K.(%)\(^{-1}\) from the SMM and about \(-112.5\) K.(%)\(^{-1}\) from EXPT [22]. This value is rather high due to the substantial deformation of crystal structure when C is added into the lattice of the Fe metal [22]. Conversely, figure 3b shows that the melting temperature of the FeCr alloy does not change much when the atomic concentration of Cr ranges from 0 to 55%. It is clear to see that Fe and Cr approximately have the same atomic mass, the same interaction distance and the same dissociation energy [17], so the cohesive energy is almost unaffected by replacing Fe with Cr. However, the melting curve of the FeCr alloy at zero pressure has an extraordinary form. It has a minimum point at \( c_{Cr} = 21\% \), and the value of the corresponding melting temperature is about 1769 K from the SMM, about 1782 K from the CALPHAD method [23] and about 1783 K from EXPT [24]. We notice that the deviation between EXPT [24] and the SMM’s results for the melting temperature of the FeCr alloy becomes higher at Cr-rich side. The maximum error can be up to 10 \% in the case of the pure Cr metal. The explanation for this result is that Cr melts at very high temperature, so the point defects including vacancies will have a significant influence on the physical properties of the crystal, while in this paper we only apply the SMM melting theory to the perfect model.

![Figure 3](image-url)

**Figure 3.** \( T_m(c_C) \) for FeC (figure 3a) and \( T_m(c_{Cr}) \) for FeCr (figure 3b) obtained from the SMM are consistent with the CALPHAD’s results [23] and EXPT [22, 24].

Next, we consider how the melting temperature of the FeCrC alloy depends on the weight percent of C at a few given weight percents of Cr (figure 4). At zero pressure, the maximum deviation between SMM’s results and CALPHAD’s results [9] for the melting temperature of the FeCrC alloy is lower than 1.5\%. At \( w_{Cr} = 13\% \) (figure 4a), the average melting slopes \( \frac{\Delta T_m}{\Delta w_C} \) calculated by the SMM and the CALPHAD [9] are about \(-550\) K.(%)\(^{-1}\) and \(-515\) K.(%)\(^{-1}\), respectively. At \( w_{Cr} = 17\% \) (figure 4b), the average melting slopes \( \frac{\Delta T_m}{\Delta w_C} \) calculated by the SMM and the CALPHAD [9] method are about \(-620\) K.(%)\(^{-1}\) and \(-604\) K.(%)\(^{-1}\), respectively. Our numerical results are qualitatively and quantitatively consistent with CALPHAD's calculations [9]. However, the most exciting thing here is the expansion of maximum carbon solubility in the BCC Fe. In reality, when we substitute Cr for Fe, the crystal lattice is stretched a bit [1], so adding carbon to steel is easier to do.
Figure 4. $T_m(w_C)$ for FeCrC at $w_{Cr} = 13\%$ (figure 4a) and $w_{Cr} = 17\%$ (figure 4b) obtained from the SMM correspond well with CALPHAD’ results [9].

Similar to the main metal Fe, when pressure increases, the melting temperature of the FeCrC alloy also increases (figure 5). For example, in the range of pressure from 0 to 5 GPa, the melting temperature of Fe$_{82.95\%}$Cr$_{17\%}$C$_{0.05\%}$ increases from 1742 to 1926 K, the melting temperature of Fe$_{82.85\%}$Cr$_{17\%}$C$_{0.15\%}$ increases from 1680 to 1851 K, the melting temperature of Fe$_{82.75\%}$Cr$_{17\%}$C$_{0.25\%}$ increases from 1618 to 1776 K. Although the weight percent of C is very small, it has a significant contribution to the melting properties of the FeCrC system. It is an essential feature of the interstitial atoms that engineers need to pay close attention. Based on the presented results above, we believe that the melting curves of the FeCrC alloy shown in figure 5 have very high accuracy.

Figure 5. $T_m(P)$ of the FeCrC alloy obtained from the SMM..

4. Conclusion

By using the statistical moment method, we built the melting theory for the ternary ABC alloy with a body-centered cubic structure. The theoretical results have been performed for the FeCrC alloy in the interval of pressure from 0 to 5 GPa. Our numerical results correspond well with experiments and other calculations without large computational programs. These obtained results proved the effectiveness of the statistical moment method when studying on the melting properties of the crystal.
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