Research Article

Thermodynamic and Elastic Properties of Interstitial Alloy FeC with BCC Structure at Zero Pressure

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The analytic expressions for the thermodynamic and elastic quantities such as the mean nearest neighbor distance, the free energy, the isothermal compressibility, the thermal expansion coefficient, the heat capacities at constant volume and at constant pressure, the Young modulus, the bulk modulus, the rigidity modulus, and the elastic constants of binary interstitial alloy with body-centered cubic (BCC) structure, and the small concentration of interstitial atoms (below 5%) are derived by the statistical moment method. The theoretical results are applied to interstitial alloy FeC in the interval of temperature from 100 to 1000 K and in the interval of interstitial atom concentration from 0 to 5%. In special cases, we obtain the thermodynamic quantities of main metal Fe with BCC structure. Our calculated results for some thermodynamic and elastic quantities of main metal Fe and alloy FeC are compared with experiments.

1. Introduction

Thermodynamic and elastic properties of metals and interstitial alloys are specially interested by many theoretical and experimental researchers [1–21]. For example, in [1, 2] the equilibrium vacancy concentration in bcc substitution and interstitial alloys is calculated taking into account thermal redistribution of the interstitial component in different types of interstices. The conditions where this effect gives rise to a decrease or increase in vacancy concentration are formulated. Coatings based on interstitial alloys of transition metals have acquired a wide application range. However, interest in synthesizing coatings from new materials with requisite service properties is limited by the scarceness of data on their melting temperature. In [3], Andryushechkin and Karpman considered the calculation of melting temperature for interstitial alloys of transition metals with hydrogen, deuterium, and oxygen. Special attention is given to the formation of interstitial superstructures, stepwise processes of disordering and property changes attributed to order–disorder. Four groups of interstitial alloys are considered: (1) TO, ZrO, and HfO; (2) VO; (3) VH and VD; and (4) TaH and TaD. Characteristic features of the phase transformations in each group and each system are presented and discussed in comparison with others. In [14], Philibert presents the Morse potential and the Finnis-Sinclair for alloys FeH and FeC. In [15], a type of empirical potential for alloy FeC is developed in calculating defects with high energy. Structural, elastic, and thermal properties of alloy FeC are studied by using the modified embedded atom method (MEAM) in [16].

In this paper, we build the thermodynamic and elastic theory for binary interstitial alloy with bcc structure by the
statistical moment method (SMM) [8–10] and apply the obtained theoretical results to alloy FeC.

2. Content

2.1. Thermodynamic Quantities. The model of interstitial alloy AB with BCC structure in this paper is the same model of interstitial alloy AC in our previous paper [9]. That means in this model, the main atoms A are in body center and peaks of cubic unit cell and the interstitial atoms B are in face centers of cubic unit cell. The cohesive energy $u_0$ and the crystal parameters $k$, $\gamma_1$, $\gamma_2$, and $\gamma$ for atoms B, A1 (atom A in body center), and A2 (atom A in peaks) in the approximation of three coordination spheres are determined analogously as for atoms C, A1, and A2 in [9]. Note that in the expressions of these quantities there are the cohesive energy and the crystal parameters of atoms A in clean metal A in the approximation of two coordination sphere [8].

The equation of state for interstitial alloy AB with BCC structure at temperature $T$ and pressure $P$ is written in the following form:

$$PV = -r_1(\frac{1}{6} \frac{\partial u_0}{\partial r_1} + \theta x \coth x \frac{1}{2k} \frac{\partial k}{\partial r_1}).$$

(1)

At 0 K and zero pressure, this equation has the following form:

$$0 = -r_1(\frac{1}{6} \frac{\partial u_0}{\partial r_1} + \frac{\hbar \omega_0}{4k} \frac{\partial k}{\partial r_1}).$$

(2)

If we know the form of interaction potential $\varphi_{i0}$, equation (2) permits us to determine the nearest neighbor distance $r_{1X}(0, 0) (X = B, A, A_1, A_2)$ at 0 K and zero pressure. After knowing that, we can calculate crystal parameters $k_X(0, 0), \gamma_{1X}(0, 0), \gamma_{2X}(0, 0), \gamma_X(0, 0)$ at 0 K and zero pressure. After that, we can calculate the displacements [8–10].

$$y_{0X}(0, T) = \sqrt{\frac{2y_X(0, 0)\theta^2}{3k_X^2(0, 0)}} A_X(0, T),$$

(3)

where $A_X(0, T)$ is determined as in [9]. From that, we derive the nearest neighbor distance $r_{1X}(0, T)$ at temperature $T$ and zero pressure:

$$r_{1B}(0, T) = r_{1B}(0, 0) + y_{1B}(0, T), r_{1A}(0, 0)$$

$$= r_{1A}(0, 0) + y_{1A}(0, 0),$$

$$r_{1A_1}(0, T) = r_{1B}(0, T), r_{1A_2}(0, T) = r_{1A}(0, 0) + y_{1B}(0, T).$$

(4)

Then, we calculate the mean nearest neighbor distance in interstitial alloy AB by the expressions as follows [8–10]:

$$r_{1A}(0, T) = r_{1A}(0, 0) + y(0, T),$$

$$r_{1A}(0, 0) = (1 - c_B)r_{1A}(0, 0) + c_B r_{1A}(0, 0), r_{1A}(0, 0)$$

$$= \sqrt{3} r_{1B}(0, 0),$$

$$y(0, T) = (1 - 7c_B)y_A(0, T) + c_B y_B(0, T)$$

$$+ 2c_B y_{A_1}(0, T) + 4c_B y_{A_2}(0, T),$$

(5)

where $r_{1A}(0, T) = \alpha_{AB}(0, T)$ is the mean nearest neighbor distance between atoms A in interstitial alloy AB at zero pressure and temperature $T$, $r_{1A}(0, 0)$ is the mean nearest neighbor distance between atoms A in interstitial alloy AB at zero pressure, 0 K, $r_{1A}(0, 0)$ is the nearest neighbor distance between atoms A in clean metal A at zero pressure, 0 K, $r_{1A}(0, 0)$ is the nearest neighbor distance between atoms A in the zone containing the interstitial atom B at zero pressure and 0 K, and $c_B$ is the concentration of interstitial atoms B.

The free energy of alloy AB with BCC structure and the condition $c_B \ll c_A$ has the following form:

$$\psi_{AB} = (1 - 7c_B)\psi_A + c_B \psi_B + 2c_B \psi_{A_1} + 4c_B \psi_{A_2} - TS,$$

$$\psi_X = \frac{1}{2} N \cdot u_{0X} + \psi_{0X} + 3N \frac{\theta^2}{k_X^2} \theta X \frac{X^2}{3} \left( \frac{1}{X} \right)$$

$$+ \frac{2\theta^2}{k_X^2} \left[ \frac{4}{3} \frac{X^2}{X} \frac{X}{1 + X} \right] 2(\frac{X^2}{X} + 2\psi_{1X}X_2X)$$

$$- \left[ 1 + \frac{X}{2} \right] \left[ 1 + \frac{X}{2} \right],$$

$$\psi_{0X} = 3N \theta \left[ X + \ln \left( 1 - e^{-2X} \right) \right], X_X = x_X \coth x_X,$$

(6)

where $\psi_X$ is the free energy of atom X, $\psi_{AB}$ is the free energy of interstitial alloy AB, $S_X$ is the configuration entropy of interstitial alloy AB.

The isothermal compressibility of interstitial alloy AB has the following form:

$$\chi_{TAB} = \frac{(a_{AB}/a_{0AB})^3}{\sqrt{3/4a_{AB}^2/3N(\partial^2\psi_{AB}/\partial a_{AB}^2)}},$$

$$\left( \frac{\partial^2 \psi_{AB}}{\partial a_{AB}^2} \right)_T = (1 - 7c_B)\left( \frac{\partial^2 \psi_A}{\partial a_{1A}^2} \right)_T + c_B \left( \frac{\partial^2 \psi_B}{\partial a_{1B}^2} \right)_T$$

$$+ 2c_B \left( \frac{\partial^2 \psi_{A_1}}{\partial a_{1A_1}^2} \right)_T + 4c_B \left( \frac{\partial^2 \psi_{A_2}}{\partial a_{1A_2}^2} \right)_T,$$

$$\frac{1}{2N} \left( \frac{\partial^2 \psi_X}{\partial a_{1X}^2} \right)_T = \frac{1}{6} \frac{\partial^2 u_{0X}}{\partial a^2_{1X}} + \frac{\hbar \omega_X}{4k_X} \left[ \frac{\partial^2 k_{1X}}{\partial a_{1X}^2} - \frac{1}{2k_X} \left( \frac{\partial k_{1X}}{\partial a_{1X}} \right)^2 \right].$$

(7)
The thermal expansion coefficient of interstitial alloy AB has the following form:

\[
\alpha_{T_{AB}} = -\frac{k_{B}a_{T_{AB}}}{3} \left( \frac{a_{0_{AB}}}{a_{AB}} \right)^2 \frac{a_{AB}}{3V_{AB}} \frac{\partial^2 \psi_{AB}}{\partial \theta \partial a_{AB}} V_{AB} = N\rho_{AB} = N \frac{4a_{AB}^3}{3\sqrt{3}},
\]

\[
\frac{\partial^2 \psi_{AB}}{\partial \theta \partial a_{AB}} \approx (1 - 7c_{B}) \frac{\partial^2 \psi_{A}}{\partial \theta \partial r_{1A}} + c_{B} \frac{\partial^2 \psi_{B}}{\partial \theta \partial r_{1B}} + 2c_{B} \frac{\partial^2 \psi_{A}}{\partial \theta \partial r_{1A}} + 4c_{B} \frac{\partial^2 \psi_{A}}{\partial \theta \partial r_{1A}},
\]

\[
\frac{1}{3N} \frac{\partial^2 \psi_{X}}{\partial \theta \partial r_{1X}} = \frac{1}{2k_{X}} \frac{\partial k_{X} Y_{1X}^2}{\partial r_{1X}} + \frac{2\theta^2}{k_{X}} \left[ \frac{\partial k_{X}}{\partial r_{1X}} \right] Y_{X} + \frac{2Y_{2X}}{k_{X}} \frac{\partial k_{X}}{\partial r_{1X}} \left( \frac{\partial Y_{2X}}{\partial r_{1X}} - \frac{\partial k_{X}}{\partial r_{1X}} \right)
\]

\[
Y_{X} = \frac{x_{X}}{\sinh x_{X}}.
\]

The heat capacity at constant volume of interstitial alloy AB is determined by

\[
C_{V_{AB}} = (1 - 7c_{B})C_{V_{A}} + c_{B}C_{V_{B}} + 2c_{B}C_{V_{A}},
\]

\[
C_{V_{X}} = 3Nk_{B} \left\{ \frac{Y_{1X}^2}{2} + \frac{2\theta^2}{k_{X}} \left[ \frac{\partial Y_{1X}}{3} X_{X} Y_{X}^2 \right] \right. \]

\[
+ \frac{2Y_{2X}}{3} \left( 1 + Y_{X}^2 \right) - Y_{2X} \left( Y_{X}^4 + 2X_{X}^4 Y_{X}^2 \right) \right\}.
\]

The heat capacity at constant pressure of interstitial alloy AB is determined by

\[
C_{P_{AB}} = C_{V_{AB}} + \frac{9TV_{AB} a_{T_{AB}}^2}{\chi_{T_{AB}}}.
\]

2.2. Elastic Quantities. The Young modulus of alloy AB with BCC structure at temperature T and zero pressure is determined as the one of alloy AC at P = 0 in [9].

The bulk modulus of alloy AB has the following form:

\[
K_{AB} = \frac{E_{AB}}{3(1 - 2\nu_{A})}.
\]

The rigidity modulus of alloy AB at temperature T and zero pressure is as follows:

\[
G_{AB} = \frac{E_{AB}}{2(1 + \nu_{A})}.
\]

The elastic constants of alloy AB at temperature T and zero pressure are as follows:

\[
\begin{align*}
C_{11_{AB}} &= \frac{E_{AB}(1 - \nu_{A})}{(1 + \nu_{A})(1 - 2\nu_{A})}, \\
C_{12_{AB}} &= \frac{E_{AB}\nu_{A}}{(1 + \nu_{A})(1 - 2\nu_{A})}, \\
C_{44_{AB}} &= \frac{E_{AB}}{2(1 + \nu_{A})}.
\end{align*}
\]

The Poisson ratio of alloy AB is as follows:

\[
\nu_{AB} = c_{A}\nu_{A} + c_{B}\nu_{B} \approx \nu_{A},
\]

where \(\nu_{A}\) and \(\nu_{B}\), respectively, are the Poisson ratio of materials A and B and are determined from the experimental data.

2.3. Numerical Results for Interstitial Alloy FeC. For pure metal Fe, we use the m–n potential that the m–n potential parameters between atoms Fe-Fe were given in [12]. For alloy FeC, we use the Finnis-Sinclair potential as follows:

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

\[
\rho(r) = t_{1}(r-R_{1})^2 + t_{2}(r-R_{1})^3 \quad (r < R_{1}),
\]

\[
\phi(r) = (r-R_{2})^2(k_{1} + k_{2}r + k_{3}r^2) \quad (r < R_{2}).
\]

where the Finnis-Sinclair potential parameters between atoms Fe-C are as shown in Table 1.

Our numerical results for the thermal expansion coefficient and the heat capacity at constant pressure, the Young modulus, the bulk modulus, the rigidity modulus and the elastic constants of alloy FeC are summarized in tables from Tables 2–5 and are described by figures from...
Table 1: The Finnis–Sinclair potential parameters between atoms Fe-C [15].

<table>
<thead>
<tr>
<th>A (eV)</th>
<th>$R_1$ (Å)</th>
<th>$t_1$ (Å$^{-2}$)</th>
<th>$t_2$ (Å$^{-3}$)</th>
<th>$R_2$ (Å)</th>
<th>$k_1$ (eV(Å)$^{-2}$)</th>
<th>$k_2$ (eV(Å)$^{-3}$)</th>
<th>$k_3$ (eV(Å)$^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.958787</td>
<td>2.545937</td>
<td>10.024001</td>
<td>1.638980</td>
<td>2.468801</td>
<td>8.972488</td>
<td>-4.086410</td>
<td>1.483233</td>
</tr>
</tbody>
</table>

Table 2: Dependence of thermal expansion coefficient on temperature for Fe.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>500</th>
<th>700</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_T$ ($10^{-6}$K$^{-1}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This paper</td>
<td>5.71</td>
<td>10.93</td>
<td>12.77</td>
<td>14.64</td>
<td>16.15</td>
<td>18.66</td>
</tr>
<tr>
<td>EXPT [11]</td>
<td>5.6</td>
<td>10.0</td>
<td>11.7</td>
<td>14.3</td>
<td>16.3</td>
<td>19.2</td>
</tr>
</tbody>
</table>

Table 3: Dependence of heat capacity at constant pressure on temperature for Fe.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_p$ (J/mol.K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>This paper</td>
<td>10.68</td>
<td>20.13</td>
<td>22.92</td>
<td>24.13</td>
<td>24.77</td>
</tr>
</tbody>
</table>

Table 4: The dependence of Young modulus E ($10^{10}$ Pa) for alloy FeC with $c_C = 0.2\%$ from the SMM and alloy FeC with $c_C \leq 0.3\%$ from EXPT [17].

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>73</th>
<th>144</th>
<th>200</th>
<th>294</th>
<th>422</th>
<th>533</th>
<th>589</th>
<th>644</th>
<th>700</th>
<th>811</th>
<th>866</th>
</tr>
</thead>
</table>

Table 5: The dependence of Young modulus E ($10^{10}$ Pa) for alloy FeC with $c_C = 0.4\%$ from the SMM and alloy FeC with $c_C \geq 0.3\%$ from EXPT [17].

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>73</th>
<th>144</th>
<th>200</th>
<th>294</th>
<th>422</th>
<th>533</th>
<th>589</th>
<th>644</th>
<th>700</th>
<th>811</th>
<th>866</th>
<th>922</th>
</tr>
</thead>
</table>

Figure 1: $\alpha_T (T)$ for FeC at $P = 0$, $c_C = 0$, 1, 2, and 4%.

Figure 2: $\alpha_T (c_C)$ for FeC at $P = 0$, $T = 100$, 300, 500, and 700 K.
Figures 1–12. When the concentration $c_C \rightarrow 0$, we obtain thermodynamic quantities of Fe. Our calculated results shown in Tables 2–4 and Figures 5, 6, 11, and 12 are in rather good agreement with experiments (the obtained deviations are smaller than 15%).

For alloy FeC at the same temperature when the concentration of interstitial atoms increases, the thermal expansion coefficient $\alpha_T$ and the heat capacity at constant pressure $C_P$ decrease. For example, for FeC at $T=1000$ K when $c_C$ increases from 0 to 5%, $\alpha_T$ decreases from 18.66 $\times$ 10$^{-6}$ K$^{-1}$ to 12.95 $\times$ 10$^{-6}$ K$^{-1}$, and $C_P$ decreases from 26.67 to 25.59 J/(mol K).

For alloy FeC at the same concentration of interstitial atoms when temperature increases, the thermal expansion coefficient $\alpha_T$ and the heat capacity at constant pressure $C_P$ increase. For example, for FeC at $c_C=5\%$ when $T$ increases from 100 to 1000 K, $\alpha_T$ increases from 3.23 $\times$ 10$^{-6}$ to 12.95 $\times$ 10$^{-6}$ K$^{-1}$, and $C_P$ increases from 9.26 to 25.59 J/(mol K).

For alloy FeC at the same temperature when the concentration of interstitial atoms increases, the elastic moduli $E$, $G$, $K$, and the elastic constants $C_{11}$, $C_{12}$, $C_{44}$ decrease. For example, for FeC at $T=1000$ K when $c_C$ increases from 0 to 5%, $E$ decreases from $12.28 \times 10^{10}$ to $10.39 \times 10^{10}$ Pa, $G$ decreases from $4.87 \times 10^{10}$ to $4.12 \times 10^{10}$ Pa, $K$ decreases from $8.53 \times 10^{10}$ to $7.21 \times 10^{10}$ Pa, $C_{11}$ decreases from $15.02 \times 10^{10}$ to $12.71 \times 10^{10}$ Pa, $C_{12}$ decreases from $5.28 \times 10^{10}$ to $4.40 \times 10^{10}$ Pa. **Figure 3:** $C_P(T)$ for FeC at $P=0$, $c_C=0$, 1, 3, and 5%.

**Figure 4:** $C_P(c_C)$ for FeC at $P=0$, $T=100$, 200, 300, and 500 K.

**Figure 5:** $\alpha_T(T)$ for Fe at $P=0$ from the SMM and the experimental data [11].

**Figure 6:** $C_P(T)$ for Fe at $P=0$ from the SMM and the experimental data [11].
For alloy FeC at the same concentration of interstitial atoms when temperature increases, the elastic moduli $E$, $G$, and $K$, and the elastic constants $C_{11}$, $C_{12}$, and $C_{44}$ also decrease. For example, for FeC at $c_C = 5\%$ when $T$ increases from 100 to 1000 K, $E$ decreases from $19.39 \times 10^{10}$ to $10.39 \times 10^{10}$ Pa, $G$ decreases from $7.69 \times 10^{10}$ to $4.12 \times 10^{10}$ Pa, $K$ decreases from $13.47 \times 10^{10}$ to $7.21 \times 10^{10}$ Pa, $C_{11}$ decreases from $23.72 \times 10^{10}$ to $12.71 \times 10^{10}$ Pa, $C_{12}$ decreases from $8.33 \times 10^{10}$ to $4.46 \times 10^{10}$ Pa, and $C_{44}$ decreases from $7.69 \times 10^{10}$ to $4.12 \times 10^{10}$ Pa.

The calculated values from the SMM for the Young modulus $E$ in Tables 4 and 5 and Figures 11 and 12 and therefore other elastic quantities, such as the elastic moduli $G$ and $K$, the elastic constants $C_{11}$, $C_{12}$, and $C_{44}$ of alloy FeC, are in good agreement with experiments. The nearest neighbor distance, the elastic moduli $E$, $G$, and $K$, the elastic constants $C_{11}$, $C_{12}$, and $C_{44}$, and the isothermal elastic modulus $B_T$ of main metal Fe at $P = 0$, $T = 300$ K according to the SMM, the other calculation [21] and experiments [18–20] are given in [9]. Our obtained deviations are smaller than 15%.
3. Conclusion

From the SMM, using the minimum condition of cohesive energies and the method of three coordination spheres, we find the mean nearest neighbor distance, the free energy, the isothermal compressibility, the thermal expansion coefficient, the heat capacities at constant volume and at constant pressure, the Young modulus, the bulk modulus, the rigidity modulus, and the elastic constants of binary interstitial alloy with BCC structure with very small concentration of interstitial atoms. At zero concentration of interstitial atoms, thermodynamic and elastic quantities of interstitial alloy become ones of main metal in alloy. The theoretical results are applied to interstitial alloy FeC. Our calculated results for the nearest neighbor distance, the elastic moduli, the elastic constants, and the isothermal elastic modulus at 300 K, the thermal expansion coefficient in the range from 100 to 1000 K and the heat capacity at constant pressure in the range from 100 to about 450 K of main metal Fe, the Young modulus, the bulk modulus, the rigidity modulus, and the elastic constants of alloy FeC with \( c_C = 0.2\% \) and \( c_C = 0.4\% \) are in rather good agreement with experiments.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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References


