The effect of Mn/Ni on thermodynamic properties of critical nucleus in Fe-Cu-Mn (Ni) ternary alloys

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ABSTRACT

The aging- or radiation-induced hardening of Cu/Mn/Ni precipitates in Fe alloys is one of property degradation mechanisms in structural materials in nuclear reactors. Experiments show that aging or radiation leads the formation of Cu-rich precipitates, and the addition of Mn or Ni elements enhances the precipitation kinetics. In this work, the phase-field model coupled with the constrained string method have been applied to investigate the thermodynamic properties of critical nuclei such as the minimum energy path of Cu/Mn/Ni precipitation in Fe-Cu-Mn and Fe-Cu-Ni ternary alloys. The chemical free energies used in the model are taken from CALPHAD. The simulation results show that the formation of Cu/Mn/Ni clusters needs to overcome an energy barrier, and the precipitate has a Core-Shell structure. The thermodynamic properties of the critical nucleus are influenced by temperature and Cu/Mn/Ni overall concentrations, which are in accordance with the simulation results as well as the experimental observations.

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1. Introduction

For most steels, the addition of Cu, Mn, and Ni has a positive effect on mechanical, corrosion and radiation resistance properties. However, the aging- or radiation-induced Cu/Mn/Ni precipitates not only cause the hardening [1], but also lead to significant materials toughness property degradation, especially in reactor pressure vessel (RPV) steels [2]. Potapovs et al. [3] suggested that radiation-induced Cu precipitation is one of the main causes of deterioration of RPV steel, because it increases the ductile brittle transition temperature (DBTT) of the RPV steel. In consideration of the cost and safety of neutron irradiation experiments, aging experiments of RPV model steels, such as Fe-Cu, Fe-Cu-Mn, and Fe-Cu-Ni alloys were often used to study the effect of precipitation on properties. Nogiwa et al. [4] studied Cu precipitation under different aging conditions in Fe–1Cu alloys. The three dimensional atom probe results showed that the average radius of the Cu clusters increases with aging time. Styman et al. [5] studied the segregation and precipitation of solute atoms after aging in RPV model steel. They claimed that Cu precipices have Core-Shell structure, i.e., Cu locates at the center of precipitates while Mn/Ni atoms segregate at the interface between the precipitate and matrix. Dieter et al. [6] also found the Core-Shell structure. Simulation results show that aging and radiation lead to Cu-rich segregation and clusters in Fe-Cu binary alloys [7], and the addition of Mn/Ni elements accelerates this segregation [8]. Three-dimensional atom probe analysis by Miller et al. [9–12] demonstrated that Mn atoms segregate at the interface region between Cu-rich clusters and the Fe matrix in irradiated RPV steels. Based on atomistic simulations, Seko et al. [13] suggested that Ni atoms also prefer segregating at the interface of Cu-rich clusters. These clusters result in material property degradation, such as embrittlement, hardening, and the
decrease of ductile to brittle transition temperatures, which will reduce the anti-radiation performance [14]. Therefore, it is necessary to understand the thermodynamic properties of Cu/Mn/Ni nucleation and phase separation to calculate the nucleation rates and introduce the correct critical nuclei in the phase-field modeling of neutron induced segregation simulations for predicting material property degradation and for designing advanced radiation resistant materials.

In our previous work, we investigate a model coupling both the constrained string method and phase field approach, to find the Cu critical clusters, nucleation energy barriers, and minimum energy paths in Fe-Cu binary alloys [15–17]. In this work, we improved and extended the model to Fe-Cu-Mn and Fe-Cu-Ni ternary systems. The description of the model is presented in section 2, including the phase field approach and the constrained string method, as well as the thermodynamic and kinetic properties. The simulation results and discussion are presented in section 3.

2. Description of the model

2.1. Phase field model

In this model, we used \( C_a (r, t) \), \( a = \text{Fe, Cu, Mn or Ni} \) to describe the concentrations of alloy elements, where \( t \) is the time and \( r = (r_1, r_2, r_3) \) is the spatial coordinate. The formation energy of vacancy is 2.1 eV [18], and its thermal equilibrium concentration is needed. Thanks to the work in Ref. [24], the diffusion coefficient of these elements in bcc Fe matrix by a vacancy mechanism can be obtained. We list these parameters of different temperatures in Table 2.

2.2. Chemical free energy

To solve the phase field equations (1) and (2) and predict the precipitation of Cu/Mn/Ni, we need the chemical free energies \( (G) \) of Fe-Cu-Mn and Fe-Cu-Ni ternary alloys. Fortunately, they have been extensively investigated. In the simulations the chemical free energies in Refs. [20, 21] were used. The detailed expressions are provided in the appendix. For a given temperature, the Chemical free energy can be plotted, as shown in Fig. 1.

2.3. Diffusion coefficient

According to equation (3), the diffusion coefficient of Fe/Cu/Mn/Ni is needed. Thanks to the work in Ref. [24], the diffusion coefficient of these elements in bcc Fe matrix by a vacancy mechanism can be obtained. We list these parameters of different temperatures in Table 2.

2.4. Constrained string method

For a conserved concentration field, the computation of critical nucleus and minimum energy path (MEP) is subject to the constraint \( g(C) \equiv \int f(C) dV = 0 \), with \( C_0 \) is the concentration for the homogenous state. Following the previous work [15], we applied the constrained string method [25] to compute the critical nucleus and the MEP on a constrained manifold, which has been successfully used for nucleation in solids [26, 27] and phase transformations [28].

The constrained string method is an extension of the string method [29] and has several equivalent formulations to deal with the constraints. Let \( \varphi(t) \) denote the string at the time \( t \) with the arc-length parametrization \( \gamma \in [0, 1] \), the constrained MEP satisfies:

\[
\langle \nabla E \rangle^\perp (\varphi^*) = 0, \text{ subject to } \varphi(0) = 0
\]
Then the constrained critical nucleus is the node with the highest energy along the constrained MEP since it is the maximum along the path direction and the minimum along the other directions.

One direct way is to apply the Lagrange multiplier method by introducing a Lagrange multiplier to the string dynamics in order to enforce the constraint [25]. Specifically, the constrained string method is to evolve the string according to Table 1

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>Avocado’s constant</td>
<td>$6.022 \times 10^{23}$ (atom/mol)</td>
</tr>
<tr>
<td>$A_0$</td>
<td>constant</td>
<td>$1.602 \times 10^{-19}$ (J/atom)</td>
</tr>
<tr>
<td>$\kappa_s$</td>
<td>interfacial energy coefficient</td>
<td>$1.0 \times 10^{-14}$ (J/atom)</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>550, 650, 773(K)</td>
</tr>
<tr>
<td>$E_{elas}(\epsilon)$</td>
<td>elastic energy density</td>
<td>See section 2.1</td>
</tr>
<tr>
<td>$Y$</td>
<td>Energy function of elastic stiffness</td>
<td>$2.14 \times 10^{11}$ (Pa)</td>
</tr>
<tr>
<td>$V_m$</td>
<td>molar volume</td>
<td>$7.09 \times 10^{-5}$ (m$^3$/mol)</td>
</tr>
<tr>
<td>$C_{\text{av}}$</td>
<td>average concentration of species $\alpha$</td>
<td>See section 3</td>
</tr>
<tr>
<td>$G$</td>
<td>chemical free energy density</td>
<td>See section 2.2</td>
</tr>
</tbody>
</table>

Fig. 1. Chemical free energy for different model alloys at 650 K. (a) Fe-Cu alloys; (b) Fe-Cu-Mn alloys, $C_{\text{Cu}}=C_{\text{Mn}}$; (c) Fe-Cu-Ni alloys, $C_{\text{Cu}}=C_{\text{Ni}}$.

Table 2

<table>
<thead>
<tr>
<th>Element</th>
<th>$D_n/m^2s^{-1}(550 K)$</th>
<th>$D_n/m^2s^{-1}(650 K)$</th>
<th>$D_n/m^2s^{-1}(773 K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>$7.2 \times 10^{-32}$</td>
<td>$4.2 \times 10^{-27}$</td>
<td>$6.3 \times 10^{-23}$</td>
</tr>
<tr>
<td>Cu</td>
<td>$5.0 \times 10^{-29}$</td>
<td>$7.9 \times 10^{-25}$</td>
<td>$3.9 \times 10^{-21}$</td>
</tr>
<tr>
<td>Mn</td>
<td>$1.9 \times 10^{-29}$</td>
<td>$4.3 \times 10^{-25}$</td>
<td>$2.8 \times 10^{-21}$</td>
</tr>
<tr>
<td>Ni</td>
<td>$9.9 \times 10^{-31}$</td>
<td>$4.6 \times 10^{-26}$</td>
<td>$5.8 \times 10^{-22}$</td>
</tr>
</tbody>
</table>

Then the constrained critical nucleus is the node with the highest energy along the constrained MEP since it is the maximum along the path direction and the minimum along the other directions.

One direct way is to apply the Lagrange multiplier method by introducing a Lagrange multiplier to the string dynamics in order to enforce the constraint [25]. Specifically, the constrained string method is to evolve the string according to
\[ \phi_t(\gamma, t) = -\nabla E(\phi) + \lambda \nabla g(\phi) + \tilde{\tau} \]

where \( \tilde{\tau} \) is the unit tangent vector to the string, i.e., \( \tilde{\tau} = \phi/|\phi| \). \( \lambda \) is the Lagrange multiplier for the constraint \( g(\phi) = 0 \) and \( \tilde{\tau} \) is the Lagrange multiplier to impose the equal arc-length constraint.

Another approach to implement the constrained string method is based on the augmented Lagrange multiplier method [26]. It considers a modified total energy involving two parameters \( \lambda \) and \( M \):

\[ E_1(\phi) = E(\phi) + \lambda \int (\phi - C_0) dx + M \left( \int (\phi - C_0) dx \right)^2 \]

Then we apply the string method to this modified energy to solve the string \( \phi \) and update the augmented Lagrange multiplier \( \lambda \). We iterate between these two steps until convergence.

Recently, we proposed an effective way to solve the constrained string method [15]. One advantage of such Cahn-Hilliard dynamics is satisfying the form of a conservation law so that it is no need to impose additional Lagrange multiplier. Thus, the Cahn-Hilliard type string method follows:

\[ \phi_t(\gamma, t) = -\nabla^2 E(\phi) + \lambda \tilde{\tau} \]

The detailed numerical algorithm is referred to [15].

3. Results and discussion

Experiments show that a Cu-rich cluster or precipitate in Fe has spherical shape [9,12]. According to the constrained spring method described in section 2.4, searching the minimum energy path needs simultaneously to run a set of phase field simulations which represent the evolution of nucleus on the string. In our simulations 120 nucleus images having different initial concentrations were considered on the string. Therefore, 3D simulation required huge computer resource and efficient parallel code. In this work, we focused on demonstrating the method and studying the effect of temperature and composition on thermodynamic properties of critical nucleus in ternary alloys, and performed the simulations in a two dimensional simulation cell of \( 128l_0 \times 128l_0 \) (\( l_0 = 0.2 \) nm) due to our limitation of computer resource. In the simulations, we prepared 120 simulation cells with the same overall concentrations of Fe, Cu and Mn/Ni, and a circular cluster/nucleus at the center of each simulation cell. The concentrations inside the cluster are different from each other which varies from overall concentrations to thermal equilibrium concentrations. These 120 initial concentration profiles or initial nuclei were assigned on the constrained string. For example, Fig. 2 shows 3 profiles of Cu concentrations of 120 concentration profiles on the initial string for Fe-3Cu-1Mn alloys. For simplicity, initial Mn concentrations were set up to be uniform, and equal to 1.0%. The concentration profiles on the initial string might affect the result, i.e., the minimum energy path and thermodynamic properties of critical nucleus. We investigated the influence of initial concentration profiles on MEP which is presented at the end of this section. The results demonstrated that the initial concentrations don’t affect the MEP and thermodynamic properties of the critical nucleus for the considered cases.

It is expected that the thermodynamic properties of critical nucleus may depend on the temperature and composition of alloys. In the simulations, we considered three different temperatures of 550 K, 650 K, and 773 K which are in the range of the RPV operation temperature, and two ternary alloys of Fe-xCu-1Mn and Fe-xCu-1Ni where Cu concentration of \( x \) was set to be 0.5%, 1.0%, 3.0% and 5.0%, respectively. For a given temperature (\( T \)), alloy and a set of initial concentration profiles on the string, the constrained string method can find the minimum energy path.

Fig. 3(a-c) shows the MEPs for Fe-3Cu-1Mn system at \( T = 550 \) K, 650 K and 773 K. The inserted figures show the distributions of Cu and Mn for the critical nucleus and the precipitate on the string. In the figure, x-axis represents the configurations (m) along the MEP. For instance, "m = 0" stands for the initial homogeneous configuration, "m = 120" represents the equilibrium precipitate configuration. The results for Fe-3Cu-1Ni system at \( T = 550 \) K, 650 K and 773 K are plotted in Fig. 4(a-c).

From these minimum energy paths shown in Figs. 3 and 4, it is found that the Cu-rich precipitate nucleation requires to overcome an energy barrier for considered the temperature and alloy compositions. The energy barrier values (eV) for different Cu concentrations and temperatures in Fe-Cu-Mn systems are listed in Table 3. It is found that the nucleation barrier strongly depends on the temperature and Cu concentration. The nucleation barrier

![Fig. 2: Cu concentration profiles at m = 1, 40, and 80 of 120 images on the initial string for Fe-3Cu-1Mn alloys.](image-url)
decreases with the decrease of temperatures and/or the increase of average Cu concentrations. The data in Table 3 also show there exists barrier free nucleation of Cu/Mn rich precipitates when the overall Cu concentration reaches to 5% for temperatures 550 K and 650 K.

Table 4 lists the energy barriers for Fe-xCu-1Ni system. The thermodynamic properties are similar with those of Fe-xCu-1Mn system. The nucleation barrier decreases with the decrease of temperatures and the increase of average Cu concentrations. Compared the results in Tables 3 and 4, it is found that the Cu/Ni nucleation barrier in Fe-xCu-1Ni system is higher than Cu/Mn nucleation barrier in Fe-xCu-1Mn system for the temperature and average Cu concentration of considered. The result indicates that Cu/Mn clustering in Fe-xCu-1Mn system is easier than Cu/Ni clustering in Fe-xCu-1Ni system.

We also simulated the effect of Ni concentration and temperature on nucleation barrier of Cu/Ni cluster in Fe-1Cu-xNi system. The results are listed in Table 5. We find that the nucleation barrier decreases as the temperature decreases and decreases as the average Ni concentration increases. The predicted composition dependence of nucleation barriers listed in Tables 3–5 demonstrate that the addition of Ni/Mn promotes the nucleation of Cu-rich precipitates. On the other hand, Hyde et al. [30] studied the effects of Ni concentrations on these Core-Shell structural clusters in both aging and irradiation conditions, and the results showed that high-Ni concentration promotes the formation of these clusters. Experiments also show that higher Ni concentration leads to higher density of the clusters after irradiation [31]. The simulation results are in agreement with experimental and previous simulation results [3–7,9,12,19,20,30–32].

The concentration profiles of critical nucleus and Cu-rich precipitate are also shown in Figs. 3–4. It is found that the distributions of Cu and Mn/Ni inside the critical nucleus are uniform, and the concentrations (for example, $C_{Cu} = 26.3\%$ and $C_{Ni} = 1.8\%$ for Fe-3Cu-1Ni at 773 K) is much smaller than the thermal equilibrium concentrations calculated by the free energies obtained from CALPHAD. It indicates that the Cu precipitate has non-classical nucleus, and is a solid solution phase. After the nucleation, the energy of the system decreases with the increases of Cu and Mn/Ni concentrations inside the precipitates. It is interesting to find that 1) the separation of Cu and Mn/Ni inside the precipitates decreases the energy of the system; and 2) a precipitate with a Core-Shell structure, where Cu has a thermal equilibrium concentration inside the precipitate and Mn/Ni has a higher concentration on the interface between the precipitate and the matrix, is thermodynamically stable.

The constrained spring method needs an initial set of nuclei which has different concentrations. In order to examine whether the initial condition affects the minimum energy path and the Core-Shell structure or not, we prepared another set of initial...
The simulation results for the different initial images shown in Figs. 2 and 5 will converge to the results shown in Fig. 3, resulting in a Core-Shell structure finally. The initial concentration profiles on the string doesn’t affect the MEP and the core structure. That is to say, the Core-Shell structure is independent of the initial concentrations of Cu-rich particles and the distribution of Mn/Ni on the string, just determined by the Chemical free energy.

The Core-Shell structure in Cu-rich precipitates has been observed in Refs. [9–12] and predicted in simulations [19,20]. If we assume that the Cu-rich precipitate growth follows the MEP we can explore the formation of core structure by examining the concentration profiles inside the critical nucleus and precipitate for Fe-3Cu-1Ni alloys at different temperatures. (a) 550 K (b) 650 K (c) 773 K.

### Table 3
Energy barrier (eV) for different Cu concentrations and temperatures in Fe-Cu-Mn alloys.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Fe-0.5Cu-1Mn</th>
<th>Fe-1Cu-1Mn</th>
<th>Fe-3Cu-1Mn</th>
<th>Fe-5Cu-1Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>1.9456</td>
<td>1.6384</td>
<td>0.6349</td>
<td>0</td>
</tr>
<tr>
<td>650</td>
<td>×</td>
<td>2.5805</td>
<td>1.4295</td>
<td>0</td>
</tr>
<tr>
<td>773</td>
<td>×</td>
<td>3.8380</td>
<td>2.8959</td>
<td>0.5693</td>
</tr>
</tbody>
</table>

### Table 4
Energy barrier (eV) for different Cu concentrations and temperatures in Fe-Cu-Ni alloys.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Fe-0.5Cu-1Ni</th>
<th>Fe-1Cu-1Ni</th>
<th>Fe-3Cu-1Ni</th>
<th>Fe-5Cu-1Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>2.5682</td>
<td>1.8883</td>
<td>0.6758</td>
<td>0</td>
</tr>
<tr>
<td>650</td>
<td>×</td>
<td>2.6337</td>
<td>1.5196</td>
<td>0.2212</td>
</tr>
<tr>
<td>773</td>
<td>×</td>
<td>4.3745</td>
<td>3.4570</td>
<td>0.7496</td>
</tr>
</tbody>
</table>

### Table 5
Energy barrier (eV) for different Ni concentrations and temperatures in Fe-Cu-Ni alloys.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>Fe-1Cu-0Ni</th>
<th>Fe-1Cu-0.5Ni</th>
<th>Fe-1Cu-1Ni</th>
<th>Fe-1Cu-3Ni</th>
<th>Fe-1Cu-5Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>2.1873</td>
<td>1.8928</td>
<td>1.8883</td>
<td>1.8836</td>
<td>1.8555</td>
</tr>
<tr>
<td>650</td>
<td>3.0065</td>
<td>2.6542</td>
<td>2.6337</td>
<td>2.6096</td>
<td>2.5710</td>
</tr>
<tr>
<td>773</td>
<td>5.2142</td>
<td>4.3909</td>
<td>4.3745</td>
<td>4.2624</td>
<td>4.1013</td>
</tr>
</tbody>
</table>

Fig. 4. MEP and concentration profiles inside the critical nucleus and precipitate for Fe-3Cu-1Ni alloys at different temperatures. (a) 550 K (b) 650 K (c) 773 K.

images on the string. Fig. 5 shows 3 images of Cu and Mn concentrations of 120 images on the initial string.

The simulation results for the different initial images shown in Figs. 2 and 5 will converge to the results shown in Fig. 3, resulting in a Core-Shell structure finally. The initial concentration profiles on the string doesn’t affect the MEP and the core structure. That is to say, the Core-Shell structure is independent of the initial concentrations of Cu-rich particles and the distribution of Mn/Ni on the string, just determined by the Chemical free energy.

The Core-Shell structure in Cu-rich precipitates has been observed in Refs. [9–12] and predicted in simulations [19,20]. If we assume that the Cu-rich precipitate growth follows the MEP we can explore the formation of core structure by examining the concentration profiles of nucleus on the MEP. For Fe-3Cu-1Ni at a temperature of 773 K, four concentration profiles marked by $A_1$, $A_2$, $A_3$, and $A_4$ along the minimum energy path are plotted in Fig. 6–7. $A_1$ is the homogeneous and initial image, in which Cu and Ni are uniform. $A_2$ is the critical nucleus, both Cu and Ni will segregate in the center of the cluster. The system has the highest energy with this critical nucleus of $A_2$. $A_3$ is an intermediate image, in which the Cu/Ni nucleus has higher concentrations of Cu and Ni than that inside the critical nucleus. $A_4$ is the stable image and has a core structure. Cu reaches the thermal equilibrium concentration while Ni segregates on the interface between the Cu-rich particle and the matrix. The Ni concentration in the center of the cluster of
A$_4$ is less than that of A$_3$. The results demonstrate that 1) a nucleus with solid solution phase has low nucleation barrier, and 2) the formation of core structure during precipitate growth minimizes the energy of the system.

4. Conclusions

In this work, a combined model of both constrained string method and phase field approach is successfully applied in predicting the thermodynamic properties of Cu/Mn/Ni clusters in Fe-Cu-Mn/Fe-Cu-Ni ternary alloys, including the nucleation energy barrier, minimum energy path, as well as the concentration profiles along the MEP.

A number of interesting results are obtained by analysing the MEP and concentration profiles inside the nuclei including:

1. The formation of Cu/Mn/Ni stable clusters needs to overcome an energy barrier;
2. The Cu/Mn/Ni nucleation barriers increase with the increase of the temperature or the decrease of Cu/Mn/Ni average concentrations.
3. The Cu-Mn or Cu-Ni precipitates has a Core-Shell structure.
4. The addition of Mn/Ni reduces the nucleation barrier, hence, promotes the nucleation of Cu rich precipitates.

These results are in good agreement with simulation results as well as experiment observations [3–7,9–12,19,20,30,31]. These thermodynamic properties are significant in introducing the correct critical nuclei in the phase-field modelling of neutron-induced segregation simulations for predicting material property degradation and for designing advanced radiation resistant materials.
Acknowledgement

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Appendix. Chemical free energy of Fe-Cu-Mn-Ni system

Due to the efforts made by many researchers, the analytical free energy density has now become available for the Fe-Cu-Mn-Ni system [19,20]. The chemical free energy density (Gibbs free energy) of bcc phase for Fe-Cu-Mn-Ni system with magnetic contribution is described as:

\[ G(C_{Cu}, T) = 0^G + E^G + m^G G + RT[\ln C_{Cu} + \ln C_{Fe} + \ln C_{Mn} + \ln C_{Ni}] \]

where \( 0^G \) is the ideal mixing Gibbs free energy and \( 0^G_i \) is the Gibbs free energy of pure element \( \alpha \) (\( \alpha = Fe, Cu, Mn, Ni \)) with bcc crystal structure in terms of temperature [33].

\[ 0^G_{Fe} = 0 \]

\[ 0^G_{Cu} = 4017 - 1.255T \]

\[ 0^G_{Mn} = -3235.3 + 127.85T - 23.77TlnT - 0.00744T^2 + 60000/T \]

\[ 0^G_{Ni} = 8715.084 - 3.556T \]

\( E^G \) is the excess free energy caused by the heat of mixing, and \( m^G G \) is the magnetic contribution to the Gibbs free energy. R and T are gas constant of \( R = 8.314 \) J/(mol K) and the absolute temperature (K), respectively.

\[ E^G = L_{Fe,Cu}C_{Cu}C_{Fe} + L_{Fe,Mn}C_{Mn}C_{Fe} + L_{Fe,Ni}C_{Ni}C_{Fe} + L_{Fe,Mn}C_{Cu}C_{Mn} + L_{Cu,Ni}C_{Cu}C_{Ni} + L_{Mn,Ni}C_{Mn}C_{Ni} + L_{Fe,Cu,Ni}C_{Cu,Ni}C_{Fe} + L_{Cu,Mn,Ni}C_{Cu,Mn}C_{Ni} + L_{Cu,Mn,Ni}C_{Cu}C_{Mn}C_{Ni} + L_{Fe,Cu,Ni}C_{Cu}C_{Fe}C_{Ni} \]

\[ m^G G = RT\ln(\beta^{\alpha} + 1)f(\tau) \]

where \( \tau = T/T_C \) is the relative temperature. The interaction parameters \( L_{Fe,Cu}, L_{Fe,Mn}, L_{Fe,Ni}, L_{Cu,Mn}, L_{Cu,Ni}, L_{Mn,Ni}, L_{Fe,Cu,Mn}, L_{Fe,Cu,Ni}, L_{Cu,Mn,Ni} \), the Curie temperature \( T_C \), and the atomic moment \( \beta^{\alpha} \) are available from the thermodynamic database of equilibrium phase diagrams and have been assessed by Miettinen [34]:

\[ L_{Cu,Fe} = 41033.0 - 6.022T \]

\[ L_{Fe,Mn} = -2759.0 + 1.237T \]

\[ L_{Fe,Ni} = -956.63 - 1.287T + (1789.03 - 1.929T)(C_{Fe} - C_{Ni}) \]
\[ L_{\text{Cu,Mn}} = 11190.0 - 6.0T - 9865.0(C_{\text{Cu}} - C_{\text{Mn}}) \]

\[ L_{\text{Cu,NI}} = 8366.0 - 2.802T \]

\[ L_{\text{Mn,NI}} = -51638.31 + 3.64T + 6276.0(C_{\text{Mn}} - C_{\text{NI}}) \]

\[ L_{\text{Fe,Cu, Mn}} = 30000.0 \]

\[ L_{\text{Fe,Mn,NI}} = L_{\text{Fe,Cu,Mn}} = L_{\text{Cu,Mn,NI}} = 0 \]

\[ T_c = 1043(1 - C_{\text{Cu}}) - 580C_{\text{Cu}} \]

\[ \beta^0 = 2.22C_{\text{Fe}} - 0.27C_{\text{Mn}} + 0.85C_{\text{Ni}} \]

The function of \( f(t) \) is given by Hillert and Jarl [35] as: For \( t \leq 1 \),

\[
f(t) = 1 - \frac{1}{D} \left( 79t^{-1}/140p + 474/497 \left( \frac{1}{p} - 1 \right) \times \left( t^{3.6} + t^{9/135} + t^{15/600} \right) \right)
\]

And for \( t > 1 \),

\[
f(t) = -\frac{1}{B} \left( t^{-5/10} + t^{-15/315} + t^{-25/1500} \right)
\]

\[ B = 518/1125 + 11692/15975 \left( \frac{1}{p} - 1 \right) \]

Here, \( p \) is a constant, and \( p = 0.4 \) for bcc Fe matrix.

References