ON THE SOLUBILITY OF OXIDES IN LIQUID ALLOYS CONTAINING TITANIUM

D. C. Hu
Amron Company
Waukesha, Wisconsin 53186

W. W. Liang
Materials Department
University of Wisconsin-Milwaukee
Milwaukee, Wisconsin 53201

E. S. McCormick
AMOCO Research Center
Naperville, Illinois 60540

Abstract

Solubility curves, $x_0^{\text{M-Ti}}$ vs $x_{\text{Ti}}$, representing the saturation of an alloy, M-Ti-0, with a particular oxide phase, Ti $\text{O}_p$, were calculated. The solute interactions model predicted the oxygen solubility reasonably well for Fe-Ti-0 alloys at low Ti contents of less than a few wt pct. It was found that the Wagner model with the correlation of Chiang and Chang provides a good correlation both at low and at high concentration of Ti up to 30 wt pct. The present approach requires only binary data on M-0, Ti-0 and M-Ti systems to obtain the ternary system, M-Ti-0. The Fe-Ti-0, Ni-Ti-0 and Co-Ti-0 systems were evaluated.

Introduction

The oxygen solubility data of Fe-Ti-0 system saturated with oxides has clearly indicated that there is a minimum of 0.002 to 0.004 wt pct in the presence of 0.1 to 1.0 wt pct Ti [1,2]. (Figure 1.) The position of such minima may be predicted by the available first-order Gibbs energy interaction parameter data [3-6]. Very recently, St. Pierre [7] pointed out that a maximum point may also be established mathematically on the solubility curve at higher deoxidizer contents when the second-order Gibbs energy interaction parameters are considered. It must be pointed out that the first-order and second-order Gibbs energy interaction models are valid only at low concentration of alloying elements [6-8].
The objectives of the present paper are (1) to extend St. Pierre's treatment [7] using the Wagner model [9] and the correlation proposed by Chiang and Chang [10], (2) to evaluate the present approach with the available data of Fe-Ti-0 system and (3) to predict the oxygen solubility curve for Ni-Ti-0 and Co-Ti-0 alloys saturated with various oxides of titanium.

Theoretical Models

A. Solute Interactions

Deoxidation equilibria in liquid M-Ti-0 alloys can be represented by the following equation:

\[ \text{Ti}_0 (s) = p\text{Ti} \text{(i.d.)} + qO \text{(i.d.)} \]

(1)

where \( p \) and \( q \) are stoichiometric coefficients, \( \text{Ti} \) (i.d.) and \( O \) (i.d.) are titanium and oxygen in solution (infinite dilution as reference state) respectively and \( \text{Ti}_0 O_q(s) \) is the deoxidation product. Accordingly, the equilibrium solubility curve can be obtained by the following equation:

\[ p\ln x_{\text{Ti}} + q\ln x_O = \ln K(1) + \ln y_{\text{Ti}} - \ln y_O \]

(2)

where \( K(1) \) is the equilibrium constant of Eq. (1), and \( \ln y_O \) and \( \ln y_{\text{Ti}} \) can be approximated in terms of the first-order and second-order Gibbs energy interaction parameters by Eqs. (3) and (4).

\[ \ln y_O = \ln y_O^0 + \varepsilon_{0O} x_O + \varepsilon_{0\text{Ti}} x_{\text{Ti}} + \rho_{02} x_{\text{Ti}}^2 + \rho_{01} x_{\text{Ti}} x_O \]

(3)

\[ \ln y_{\text{Ti}} = \ln y_{\text{Ti}}^0 + \varepsilon_{\text{Ti}O} x_{\text{Ti}} + \varepsilon_{\text{Ti}0} x_O + \rho_{21} x_{\text{Ti}}^2 + \rho_{1} x_{\text{Ti}} x_O + \rho_{01} x_{\text{Ti}} x_O \]

(4)

At infinite dilute solution as reference state for Ti and O in solution \( \ln y_O^0 \) and \( \ln y_{\text{Ti}}^0 \) are zero. \( \varepsilon_j, \ldots, \rho_{(j,k)} \), etc. in Eq. (3) and (4) are in accordance with the definition by Lupis and Elliott [8]. Using the available solute interaction parameters tabulated by Sigworth and Elliott [11] which are given in Table 1, and the thermodynamic data from Tables 2 and 3, the equilibrium solubility curve for \( \text{Ti}_2 O_3(s) \) in liquid Fe-Ti-0 alloys can be calculated, as shown in Fig. 1. As expected, there is no maximum in the solubility curve when only first-order Gibbs energy interaction parameters (i.e., \( \varepsilon_i, \varepsilon_{ij} \), etc.) are used in Eqs. (2), (3) and (4). When the second-order terms are included, the maximum point follows the minimum point on the
solubility curve resulting from the two significant roots obtained in the quadratic equation given by St. Pierre [7]. Based on the experimental data of Hadley and Derge [1] and Fruehan [2], the solute interaction model does not work at higher concentration of Ti. The sharp decrease in oxygen content after the maxima (i.e., from Eqs. (2) (3) and (4) with second-order Gibbs energy interaction parameters) appears to have no physical meaning at higher Ti content (i.e., greater than 8 wt pct).

Table 1. First-order and Second-order Gibbs Energy Interaction Parameters in Liquid Fe-Ti-O Alloys at 1873 K [11]

<table>
<thead>
<tr>
<th></th>
<th>First-order</th>
<th>Second-order</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon_{Ti}^{0} )</td>
<td>-118</td>
<td>Ti ( \rho_{Ti} = 500 )</td>
</tr>
<tr>
<td>( \varepsilon_{0}^{0} )</td>
<td>0</td>
<td>Ti ( \rho_{0} = -9.0 )</td>
</tr>
<tr>
<td>( \varepsilon_{Ti}^{0} )</td>
<td>-12.5</td>
<td>Ti ( \rho_{Ti} = -1.4 )</td>
</tr>
<tr>
<td>( \varepsilon_{Ti}^{0} )</td>
<td>2.7</td>
<td></td>
</tr>
</tbody>
</table>

\( \rho_{Ti}, \rho_{0}, \) and \( \rho_{Ti,0} \) are set equal to zero.

B. The Wagner Model

Recently, Wagner proposed a theoretical model with one adjustable parameter, \( h \), to describe the effect of alloying elements on the activity coefficients of oxygen in binary liquid A-B alloys [9]. The dissolved oxygen atoms, which obey Henry's Law, occupy quasi-interstitial sites with a coordination number of \( Z = 6 \). It is also assumed that the solvation energy exhibits parabolic dependence on the number of atoms A and B in the solvation shell of oxygen atoms. Accordingly, Wagner obtained the following equation,

\[
\ln \gamma_{0} = -\ln \left\{ \sum_{i=0}^{Z} \frac{Z!}{i!(Z-i)!} \left[ \frac{1}{Z} \gamma_{0}^{A}(A) \right]^{i-1} \left[ \frac{1}{Z} \gamma_{0}^{B}(B) \right] \exp \left\{ \frac{(Z-i)i}{2RT} - h \right\} \right\} (5)
\]

where \( \gamma_{0}, \gamma_{0}^{A}(A), \gamma_{0}^{B}(B) \) are the activity coefficients of O in alloy \( A_{1-x}B_{x} \), in pure A and in pure B respectively, Z is the coordination number, R is the gas constant, T is the absolute temperature, x is the mole fraction of B in the alloy and \( h \) is the adjustable energy parameter.
Based on the empirical correlation proposed by Chiang and Chang [10], the Wagner's h parameter may be estimated by the following equation,

$$h = \frac{2\Omega}{k^2} + 0.09 \left\{ \Omega \left( \frac{V_B}{V_A} \right)^2 + 0.04 RT \left[ \ln \gamma_0^A - \ln \gamma_0^B \right] \right\}$$  \hspace{1cm} (6)

where $\Omega$ is $\Delta H/(1-x)$ where $\Delta H$ is the enthalpy of formation of $A_{1-x}B_x$ alloy and $V_B$, $V_A$ are the valences of pure A and B according to Pauling [12]. It must be noted that both $\gamma_0^A$ and $\gamma_0^B$ are needed for the Wagner model and for the prediction of Wagner's h parameter. Recently, Chang and Hu [17] tabulated most of the available data on $\gamma_0^M$. They also estimated some values of $\gamma_0^M$ (i.e., M = Al, Cr, Mn, Mo, Nb, Si and Ti) where experimental data were not available.

The binary liquid alloys are assumed regular unless otherwise stated. The regular solution parameters, $\Delta H/R$, are also tabulated by Chang and Hu [17] for most of the binary systems. If experimental data are not available, the enthalpy of formation of the binary liquid alloys can be obtained using the model of Miedema et al. [13, 14].

In the present study, metal A is Fe, Co or Ni and metal B is Ti. At dilute solution of oxygen, the effect of oxygen may be neglected. However, at high concentration of Ti, the dissolved oxygen content can be significant. Therefore, a correction factor is included to account for the effect of dissolved oxygen on the activity coefficient of B in the liquid alloys as follows,

$$\ln \gamma_B = \frac{\Omega}{RT} (1-x)^2 + \epsilon_{AB}^0 x$$  \hspace{1cm} (7)

where $\epsilon_{AB}^0$ is defined as $\frac{\delta \ln \gamma_B}{\delta x}^0_{T, P, x}$, $\epsilon_{AB}$ becomes $\epsilon_B^0$ when $x \rightarrow 0$.

However, when $x \rightarrow 1.0$, the activity coefficient of B is almost unity. Assuming $\ln \gamma_B$ has no significant dependence on the dissolved oxygen, then $\epsilon_{AB}^0$ becomes 0 as $x \rightarrow 1.0$. Using linear interpolation between pure A and pure B, we have

$$\epsilon_{AB}^0 = \epsilon_B^0 (1-x) = \epsilon_A^0 (1-x)$$  \hspace{1cm} (8)

It has been shown that Wagner model also predicts the first-order Gibbs energy interaction parameters reasonably well by Eq. (9) [17].

$$\epsilon_0^B = \left( \frac{\delta \ln \gamma_0}{\delta x} \right)_{x \rightarrow 0} = Z \left\{ 1 - \left( \frac{\gamma_0^A}{\gamma_0^B} \right) \right\} \frac{1}{2} \exp \left[ \frac{(z-1)}{2RT} h \right]$$  \hspace{1cm} (9)
Substituting Eqs. (5), (6), (7), (8) and (9) into Eq. (2) and using the appropriate thermodynamic data from Tables 2, 3, and 4, the equilibrium solubility curve for Ti₂O₃(s) in liquid Fe-Ti-O alloys can be calculated as shown in Fig. 1. At low concentration of Ti (i.e., less than 1 wt pct Ti), the calculated curve is the same as those obtained by the first-order and second-order Gibbs energy interaction parameters. The minimum point shifted slightly to the lower right. The calculated line does not have a maximum point contrary to the result obtained using the first-order and the second-order interaction parameters as shown in Fig. 1. Similar conclusions can be obtained for the Fe-Al-O system [18]. The present approach gives an acceptable correlation at high concentration of Ti up to 30 wt pct.

| Table 2. Standard Gibbs Energies of Formation of Compounds at Temperature of 700 to 2000 K. |
|---------------------------------|---------------------------------|-----|
| Compounds*                     | \( \Delta G_f^0 = A + B T \), J/mole | Ref. |
| TiO (β)                        | -551,900 + 97.07 T                | 15  |
| TiO₂ (rutile)                  | -958,600 + 186.61 T               | 15  |
| Ti₂O₃ (s)                      | -1,535,600 + 274.97 T             | 15  |
| Ti₃O₅ (β)                      | -2,484,200 + 444.76 T             | 15  |
| Ti₄O₇ (s)                      | -3,452,100 + 635.55 T             | 15  |
| FeTiO₃ (β)                     | -1,172,200 + 210.16 T**           | 16  |

*Reference States: Fe(ℓ), Ti(ℓ) and O₂(g) at 1.0 atm.
**At temperature of 1600 to 1900 K.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Systems</td>
<td>( \Delta G_f^0(Metal) ), J/g-atom</td>
<td>T, K</td>
</tr>
<tr>
<td>Ti-O*</td>
<td>-385,000 (± 13,000)</td>
<td>1873</td>
</tr>
<tr>
<td>Fe-O</td>
<td>-115,585 - 14.414 T (± 1300)</td>
<td>1823-1973</td>
</tr>
<tr>
<td>Ni-O</td>
<td>- 79,470 - 4.393 T (± 1700)</td>
<td>1773-1973</td>
</tr>
<tr>
<td>Co-O</td>
<td>- 65,615 - 16.736 T (± 2100)</td>
<td>1823-1973</td>
</tr>
</tbody>
</table>

*Supercooled liquid titanium
Table 4. Regular Solution Parameters (\(\Omega\)) For Binary Liquid Alloys of Titanium

<table>
<thead>
<tr>
<th>Systems</th>
<th>(\Omega), J/g-mole</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Ti</td>
<td>-75,400</td>
<td>17</td>
</tr>
<tr>
<td>Ni-Ti</td>
<td>-152,700</td>
<td>17</td>
</tr>
<tr>
<td>Co-Ti</td>
<td>-154,800</td>
<td>17</td>
</tr>
</tbody>
</table>

Metal-Titanium-Oxygen Alloys

A. The Fe-Ti-O Alloys

The early work of Wentrup and Hieber [19] indicated that the minimum oxygen content in Fe-Ti-O alloys at 1873 K range from 0.09 to 0.9 wt pct Ti. At very low titanium contents 2FeO•TiO\(_2\), FeO•TiO\(_2\) and TiO\(_2\) were obtained. With residual titanium contents greater than 0.2%, Ti\(_2\)O\(_3\) was formed. X-ray diffraction work by Evans and Sloman [20] agreed in general with the findings of Wentrup and Hieber [19], but reported the existence of Ti\(_3\)O\(_5\) as a deoxidation product in the range near 0.1 wt pct Ti. Hadley and Derge [1] determined the oxygen solubility and identified the equilibrium oxide phases. They concluded that oxide phases were liquid FeO•TiO\(_2\) up to 0.05 wt pct Ti, TiO\(_2\) containing FeO from 0.05 to 1 wt pct Ti, Ti\(_2\)O\(_3\) from 1 to 5 wt pct Ti and TiO for higher titanium contents. The oxygen solubility reached a minimum of 0.002 to 0.004 wt pct in the presence of 0.1 to 1.0 wt pct Ti. Chino et al. [12] carried out a similar investigation in which they identified the oxide phase to be Ti\(_3\)O\(_5\) for alloys containing 0.001 to 0.2 wt pct Ti, Ti\(_3\)O\(_5\) from 0.2 to 2.0 wt pct Ti and TiO at higher concentrations of Ti. Kojima et al. [22] also found that Ti\(_3\)O\(_5\) was formed when Ti contents were from 0.001 to 0.4 wt pct and Ti\(_2\)O\(_3\) from 0.4 to 2.0 wt pct. Recently, Fruehan [2] measured directly the activity of oxygen in Fe-Ti-O melts at 1873 K up to 12.5 wt pct Ti using ZrO\(_2\) (CaO) and ThO\(_2\) (Y\(_2\)O\(_3\)) solid electrolytes. The presence of an oxide was confirmed visually, without any structural analysis. He concluded that the solubility of oxygen in liquid iron is decreased to a minimum of 0.004 wt pct at 0.9 wt pct of Ti. Yavoyskiy et al. [23] reported that the oxide phase were Ti\(_3\)O\(_5\) from 0.08 to 0.18 wt pct Ti, Ti\(_2\)O\(_3\) from 0.24 to 3.6 wt pct Ti and TiO with Ti contents greater than 5.0 wt pct. They observed a minima between 0.1 to 0.8 wt pct Ti. Hence, various forms of deoxidation products can be obtained depending on the Ti concentrations in the liquid alloys and the experimental conditions.
Depending on the oxygen-titanium ratio, five stable forms of titanium oxides, namely, TiO, Ti$_2$O$_3$, Ti$_3$O$_5$, Ti$_4$O$_7$, and TiO$_2$ [15] are found. At 1873 K the ternary oxide, FeTiO$_3$ (i.e., ilmenite) is stable in liquid form. Using the thermodynamic data of various oxides and binary metal-oxygen and metal-metal systems from Tables 2, 3 and 4, one can evaluate all possible solubility curves saturated with various oxides of titanium including the ternary oxide as shown in Fig. 2. The calculated curves, which are superimposed, predict that FeTiO$_3$(I) will form when Ti contents are less than 3 ppm Ti, TiO$_2$ from 3 to 5 ppm Ti, Ti$_4$O$_7$ from 5 to 30 ppm Ti, Ti$_3$O$_5$ from $5 \times 10^{-3}$ to 0.66 wt pct Ti, Ti$_2$O$_3$ from 0.66 to 12.6 wt pct Ti, and TiO for higher Ti contents. For comparison, the solubility minima obtained from the solute interaction model and the present study are given in Table 5.

### Table 5. Comparison of the Minima Obtained in Fe-Ti-O Alloys

<table>
<thead>
<tr>
<th>Oxide Phase</th>
<th>First-order Interaction Parameter wt pct Ti</th>
<th>First-order Interaction Parameter wt pct O</th>
<th>This Study wt pct Ti</th>
<th>This Study wt pct O</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO (B)</td>
<td>0.743</td>
<td>5.01 x $10^{-3}$</td>
<td>1.362</td>
<td>3.73 x $10^{-3}$</td>
</tr>
<tr>
<td>Ti$_2$O$_3$ (s)</td>
<td>0.492</td>
<td>1.32 x $10^{-3}$</td>
<td>0.682</td>
<td>1.16 x $10^{-3}$</td>
</tr>
<tr>
<td>Ti$_3$O$_5$ (B)</td>
<td>0.443</td>
<td>1.29 x $10^{-3}$</td>
<td>0.590</td>
<td>1.16 x $10^{-3}$</td>
</tr>
<tr>
<td>Ti$_4$O$_7$ (s)</td>
<td>0.421</td>
<td>1.51 x $10^{-3}$</td>
<td>0.542</td>
<td>1.36 x $10^{-3}$</td>
</tr>
<tr>
<td>FeTiO$_3$ (B)</td>
<td>0.245</td>
<td>8.4 x $10^{-3}$</td>
<td>0.271</td>
<td>8.24 x $10^{-3}$</td>
</tr>
</tbody>
</table>

Fig. 3 compares all the available experimental data with the calculated solubility curves of various oxides. The data of Wentrup and Hieber [19] (Fig. 3-a) are a factor of 2 to 4 higher than those calculated by Eqs. (2), (5), (6), (7), (8) and (9), except one point at 10 wt pct Ti which is a factor of 2 lower than the calculated values. As shown in Fig. 3-b, very good agreement is obtained between the data of Hadley and Derge [1] and the calculated curves, especially at the high concentration of titanium. The data of Chino et al. [21] at low concentration of Ti (i.e., < 0.1 wt pct) is a factor of two lower than the calculated values (Fig. 3-c). The differences may have resulted from the systematic error using the conductivity method. Good agreement is obtained between the data of Kojima et al. [22] (Fig. 3-d) except those at very low concentration of Ti (i.e., less than 100 ppm Ti). The uncertainties in analyzing the Ti contents at low levels may have contributed to the differences. The data of Fruehan [2] shows good agreement at high concentration of titanium greater than 2 wt pct (Fig. 3-e). The data of Yavoyskiy et al. [23] (Fig. 3-f) does not agree with the calculated values. The discrepancy may have resulted from using MgO as the solid electrolyte for oxygen activity measurements [24]. The form of oxides observed in the experiments also depends on the experimental conditions which determine the nucleation process for the formation of various deoxidation products. In
view of the experimental difficulties and the uncertainties in oxygen analysis at low levels, the agreement between the experimental data and the calculated values is very good.

It must be pointed out that the present approach does not require any experimental data in the ternary system (i.e., A-B-0) such as the first-order and second-order Gibbs energy parameters. Only binary data from M-0, Ti-0 and M-Ti systems as given in Tables 2, 3, and 4 are needed. Sensitivity analysis of various input data indicate that ±10% uncertainties in the regular solution parameter have no significant effect on the solubility curves. However, ±10% uncertainties in $\ln y_{O}$ shifted the minimum slightly lower to the right when a 10% increment was made and vice versa [18]. The prediction remains within the same order of magnitude. In view of the experimental difficulties and the resources and manpower involved to conduct these experiments, the present approach can be used conveniently as a first order approximation when there are no experimental data available on the solubility of oxides in liquid M-Ti-0 alloys.

B. The Ni-Ti-0 Alloys

There are no experimental data on the solubility of oxides in Ni-Ti-0 melts, except that of Sigworth and Elliott [25] who estimated $\varepsilon_{0}^{Ti} = \varepsilon_{0}^{Ti} = -86$ from the oxygen solubility measurements in Ni-Cr-Ti alloys [26]. Using the thermodynamic data of titanium oxides, Ni-0 and Ni-Ti systems from Tables 2, 3 and 4, similar deoxidation curves saturated with various oxides of titanium can be obtained as shown in Fig. 4. The calculated minima for various oxides are given in Table 6. It indicates that TiO(s) will not form when Ti is less than 20 wt pct. However, TiO(s) may be stable at higher oxygen content greater than 0.3 wt pct and higher Ti contents.

<table>
<thead>
<tr>
<th>Oxide Phase</th>
<th>Ni-Ti-0 System</th>
<th>Co-Ti-0 System</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt pct Ti</td>
<td>wt pct O</td>
</tr>
<tr>
<td>TiO (β)</td>
<td>1.30</td>
<td>0.012</td>
</tr>
<tr>
<td>Ti$<em>{2}$O$</em>{3}$ (s)</td>
<td>0.74</td>
<td>7.6 x 10$^{-4}$</td>
</tr>
<tr>
<td>Ti$<em>{3}$O$</em>{5}$ (β)</td>
<td>0.65</td>
<td>5.5 x 10$^{-4}$</td>
</tr>
<tr>
<td>Ti$<em>{4}$O$</em>{7}$ (s)</td>
<td>0.72</td>
<td>5.6 x 10$^{-4}$</td>
</tr>
<tr>
<td>TiO$_{2}$ (rutile)</td>
<td>0.52</td>
<td>6.73 x 10$^{-3}$</td>
</tr>
</tbody>
</table>
C. The Co-Ti-O Alloys

There is practically no information on the Co-Ti-O system. For a first approximation on the solubility of oxides in Co-Ti-O alloys, one can use the thermodynamic data given in Table 2, 3 and 4 to calculate the solubility curves. Fig. 6 shows the calculated curves for various oxides of titanium. The overall features are similar to Ni-Ti-O system except that the minimum oxygen content at about 1 wt pct Ti is a factor of two higher than those in Ni-Ti-O melts, as can be seen in Table 6.

Conclusions

It has been shown with the Fe-Ti-O system that the present approach using the Wagner equation and the correlation proposed by Chiang and Chang provides a good correlation both at low and at high concentration of Ti, up to 30 wt pct. The present approach requires only binary data on M-O, Ti-O and M-Ti systems to obtain the solubility curves of oxides in liquid M-Ti-O alloys. The calculated curves for Ni-Ti-O and Co-Ti-O systems can be used as a first approximation in process evaluation and process design before any experimental data are available.

Acknowledgement

The authors are grateful to Professor Y.A. Chang for his interest and support in this work.

References


**Fig. 1.** Solubility curves for Ti$_2$O$_3$ (s) in Fe-Ti-O alloys at 1873 K. The dashed lines are calculated from solute interaction parameters [5, 7] and the full line from Wagner model [9] and the correlation of Chiang and Chang [10].

**Fig. 2.** The solubility curves calculated using Wagner model [9] and the correlation of Chiang and Chang [10] for TiO (β), A, Ti$_2$O$_3$ (s), B, Ti$_3$O$_5$ (β), C, Ti$_4$O$_7$ (s), D, TiO$_2$ (s), E, and FeTiO$_3$ (β), F, in Fe-Ti-0 alloys at 1873 K.
Fig. 3. Comparison of experimental data of (a) Wentrup and Hieber [19], (b) Hadley and Derge [1], (c) Chino et al [21] (d) Kojima et al [22], (e) Fruehan [2] and (f) Yavoyskiy et al [23] with the calculated solubility curves for TiO (B), A, Ti$_2$O$_3$ (s), B, Ti$_3$O$_5$ (B), C, Ti$_4$O$_7$ (s), D, TiO$_2$ (s), E and FeTiO$_3$ (F), F, in Fe-Ti-O alloys at 1873 K.
Fig. 4. The solubility curves calculated using Wagner model [9] and the correlation of Chiang and Chang [10] for TiO (\(\beta\)), A, Ti\(_2\)O\(_3\) (s), B, Ti\(_3\)O\(_5\) (\(\beta\)), C, Ti\(_4\)O\(_7\) (s), D, and TiO\(_2\) (s), E, in Ni-Ti-O alloys at 1873 K.

Fig. 5. The solubility curves calculated using Wagner model [9] and the correlation of Chiang and Chang [10] for TiO (\(\beta\)), A, Ti\(_2\)O\(_3\) (s), B, Ti\(_3\)O\(_5\) (\(\beta\)), C, Ti\(_4\)O\(_7\) (s), D, and TiO\(_2\) (s), E, in Co-Ti-O alloys at 1873 K.