Equilibrium between Ti and O in Molten Fe–Ni, Fe–Cr and Fe–Cr–Ni Alloys Equilibrated with ‘Ti$_3$O$_5$’ Solid Solution

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The Ti deoxidation equilibrium of Fe–Ni, Fe–Cr and Fe–Cr–Ni alloys saturated with ‘Ti$_3$O$_5$’ and Ti$_2$O$_3$ phase was clarified in previous researches. Solubility of Fe, Cr and/or Ni oxides in ‘Ti$_3$O$_5$’ phase equilibrated with liquid Fe–Ni, Fe–Cr and Fe–Cr–Ni alloys at 1823 K to 1923 K were measured by SEM–EDS. It was confirmed that the solubility of Fe, Cr and/or Ni oxide in ‘Ti$_3$O$_5$’ phase at low Ti content increase with decrease of Ti content in alloys. Titanium content that dissolution of Fe, Cr and/or Ni oxide into ‘Ti$_3$O$_5$’ phase becomes apparent increases with increase of Cr and/or Ni content of the alloys.

The activity of Ti deoxidation product, ‘Ti$_3$O$_5$’ phase, equilibrated with Fe–Ni, Fe–Cr and Fe–Cr–Ni alloys was also evaluated by Redlich-Kister type polynomial. Equilibrium between Ti and O at low Ti content of those alloys was analyzed using the activity of ‘Ti$_3$O$_5$’ phase.

KEY WORDS: Thermodynamics; Ti deoxidation equilibrium; Fe–Ni alloy; Fe–Cr alloy; Fe–Cr–Ni alloy; SEM EDS analysis; Redlich-Kister polynomial.

1. Introduction

Titanium has been used as a deoxidizer due to its strong affinity with oxygen. Reliable thermodynamic information on Ti deoxidation equilibrium is important for inclusion control in clean steel and its alloy production processes. In previous researches, equilibrium between Ti and O in molten Fe–Ni, Fe–Cr and Fe–Cr–Ni alloys at 1823 K to 1923 K were investigated to control the deoxidation products in these alloys.1,2) As the result, it was confirmed by EBSD distinction that Ti deoxidation product in molten Fe–Ni alloy was ‘Ti$_3$O$_5$’ and that in molten Fe–Cr and Fe–Cr–Ni alloys changed from Ti$_2$O$_3$ to ‘Ti$_3$O$_5$’ with decrease of Ti content in the alloys. Also, solubility of Fe, Cr and/or Ni in ‘Ti$_3$O$_5$’ phase were confirmed in low Ti content region in the alloys. It was assumed in previous reports1,2) that the activity of Ti$_3$O$_5$ was unity when the solubility of Fe, Cr and Ni oxides in ‘Ti$_3$O$_5$’ phase were lower than (X$_{Fe}$+X$_{Cr}$+X$_{Ni}$)/X$_{Ti}$(in ‘Ti$_3$O$_5$’ solid solution)=0.05. Only the experimental data that satisfy this condition were used for thermodynamic analysis by Redlich-Kister type polynomial.

Solubility of Fe oxide in ‘Ti$_3$O$_5$’ phase was reported by some researchers.3–7) Hadley and Derge3) analyzed metal-crucible interface by X-ray diffraction to determine the titanium deoxidation product. They confirmed substantial solution of iron oxide into titanium oxide layer. Suzuki and Sanbongi4) melted pure Fe in titanium oxide crucible and measured solubility of iron oxide in ‘Ti$_3$O$_5$’ phase by EPMA. They reported that solubility of iron oxide in ‘Ti$_3$O$_5$’ phase was less than 1.2 mass% when Ti content in pure Fe was between 0.013 and 0.25 mass%. Iwamoto et al.8) examined titanium oxides equilibrated with Fe–Ti alloy and confirmed solubility of iron oxide in ‘Ti$_3$O$_5$’ phase in low Ti concentration region. They estimated dissolution of iron oxide into ‘Ti$_3$O$_5$’ phase from ionic valance balance of transition metal Fe and Ti in ‘Ti$_3$O$_5$’ phase. More recently, Cha9) confirmed that iron oxide dissolved into ‘Ti$_3$O$_5$’ phase at low Ti content in Fe–Ti alloy at 1823 K to 1923 K by analyzing interface of metal/Ti$_3$O$_5$ crucible by SEM–EDS, and its solubility increase with decrease of Ti content in Fe–Ti alloy. They reported the decrease of Ti$_3$O$_5$ activity in oxide phase equilibrated with Fe–Ti alloy at low Ti content.

In previous work,1,2) the solubility of Fe, Cr and/or Ni oxides in ‘Ti$_3$O$_5$’ phase were determined at low Ti content in Fe–Ni, Fe–Cr and Fe–Cr–Ni alloys by EDS analysis. Dependence of alloy composition and temperature on solubility was evaluated in present work. The experimental results of titanium deoxidation of those alloys have been numerically analyzed by applying Redlich-Kister type polynomial to the excess Gibbs free energy change of mixing of Fe–Ni–Ti–O, Fe–Cr–Ti–O and Fe–Cr–Ni–Ti–O systems. The Ti$_3$O$_5$ activity in ‘Ti$_3$O$_5$’ solid solution equilibrated with Fe–Ni, Fe–Cr and Fe–Cr–Ni alloys at low Ti content was determined.

2. Experimental

Experimental method of titanium deoxidation are given previous report.1,2) Deoxidation of Fe–Ni, Fe–Cr and Fe–Cr–Ni alloys with titanium were carried out in a ‘Ti$_3$O$_5$’ crucible by induction furnace to fix the activity of titanium oxide and to avoid contamination of those alloys with the...
other crucible material. The samples were quenched by turning off the power of the furnace and impinging helium gas on the surface of the melt after the predetermined equilibrium time. Equilibrium time was 2 h, 1 h and 1.5 h for Fe–Ni,\(^1\) Fe–Cr\(^2\) and Fe–Cr–Ni\(^2\) alloys, respectively. The quenched sample was mounted and cut in order to analyze metal/crucible interface. Mounted sample was polished by abrasive paper of SiC and diamond paste. The composition at metal/crucible interface was analyzed by SEM–EDS in order to evaluate the solid solubility of Fe, Cr and Ni oxide in Ti oxide phase.

3. Experimental Results and Discussion

Results of titanium deoxidation experiments of molten Fe–Ni, Fe–Cr and Fe–Cr–Ni alloys\(^1,2\) are shown in Figs. 1 to 5 together with the results in pure Fe.\(^7,8\) Dependence of composition and temperature on titanium deoxidation equilibria in each alloy was evaluated and equilibrium relation between titanium and oxygen in titanium concentration region with unit activity of deoxidation product was analyzed by Redlich-Kister type polynomial in previous reports.\(^1,2\) Oxygen contents in each alloy were higher than those in pure Fe and oxygen contents increase with increasing temperature at constant titanium concentration in alloys. However, oxygen content at low titanium concentration deviates lower from the relation between titanium and oxygen extrapolated from high titanium region in Figs. 1 to 5. This was due to Fe, Cr and/or Ni oxides dissolution into ‘Ti\(_3\)O\(_5\)’ phase. Metal/crucible interface was analyzed by SEM–EDS in order to evaluate effect of alloying composition and temperature on the solubility of Fe, Cr and/or Ni in ‘Ti\(_3\)O\(_5\)’ phase. The dashed curves in solid solution region in Figs. 1 to 5 were derived from the Ti\(_3\)O\(_5\) activity determined afterwards.

Analyzed results at metal/crucible interface and distinguished deoxidation products in Fe–Ni, Fe–Cr and Fe–Cr–Ni alloys are listed in Tables 1 to 3. Titanium deoxidation product in Fe–Ni alloy was confirmed to be ‘Ti\(_3\)O\(_5\)’ and that...
of Fe–Cr and Fe–Cr–Ni alloy was changed from Ti2O3 to ‘Ti3O5’ with decrease of titanium content in these alloys. Analyzed results of ‘Ti3O5’ crucible interface with Fe–Ni alloy at 1823 K to 1923 K are shown in Fig. 6. Solubility of Fe and/or Ni oxide in ‘Ti3O5’ phase increases with decrease of titanium content in Fe–Ni alloy. It was confirmed from Figs. 7 and 8 that Fe, Cr and/or Ni oxides dissolves into “Ti3O5” phase at low Ti content in Fe–Cr and Fe–Cr–Ni alloys and its solubility increases with decrease of titanium and increase of Cr and Ni content in those alloys.

| Heat No. | Experimental Temperature | [mass% Ni] | [mass% Ti] | [mass% O] | (Fe+Ni)/Ti atomic ratio | Distinguished equilibrium oxides by EBSD analysis |
|----------|--------------------------|------------|------------|-----------|------------------------|-----------------------------------------------|
| D-1      | 1873 K                   | 19.0       | 0.0004     | 0.0089    | 0.039                  | ‘Ti3O5’                                      |
| D-2      | 19.3                     | 0.0008     | 0.0087     | 0.062     |                        |                                               |
| D-3      | 18.3                     | 0.0008     | 0.0191     | 0.026     |                        |                                               |
| D-4      | 21.7                     | 0.0009     | 0.0065     | 0.054     |                        |                                               |
| D-5      | 18.5                     | 0.0011     | 0.0135     | 0.055     |                        |                                               |
| D-6      | 19.7                     | 0.0013     | 0.0087     | 0.045     |                        |                                               |
| D-7      | 19.6                     | 0.0812     | 0.0021     | 0.027     |                        |                                               |
| D-8      | 18.7                     | 0.237      | 0.0015     | 0.029     |                        |                                               |
| D-9      | 17.7                     | 0.266      | 0.0009     | 0.033     |                        |                                               |
| E-1      | 37.2                     | 0.0014     | 0.0079     | 0.029     |                        |                                               |
| E-2      | 37.9                     | 0.0158     | 0.0038     | 0.063     |                        |                                               |
| E-3      | 39.4                     | 0.0813     | 0.0024     | 0.045     |                        |                                               |
| E-4      | 39.5                     | 0.31       | 0.0013     | 0.056     |                        |                                               |
| F-1      | 56.7                     | 0.0008     | 0.0114     | 0.021     |                        |                                               |
| F-2      | 57.5                     | 0.0089     | 0.0107     | 0.023     |                        |                                               |
| F-3      | 61.7                     | 0.0144     | 0.0051     | 0.05      |                        |                                               |
| F-4      | 60.8                     | 0.0166     | 0.0077     | 0.029     |                        |                                               |
| F-5      | 58.9                     | 0.183      | 0.0022     | 0.027     |                        |                                               |
| F-6      | 62.5                     | 0.26       | 0.0022     | 0.026     |                        |                                               |
| G-1      | 79.2                     | 0.0044     | 0.0072     | 0.029     |                        |                                               |
| G-2      | 84.8                     | 0.0165     | 0.006      | 0.123     |                        |                                               |
| G-3      | 75.9                     | 0.101      | 0.0017     | 0.013     |                        |                                               |
| G-4      | 74.1                     | 0.23       | 0.0018     | 0.022     |                        |                                               |
| G-5      | 78.7                     | 0.685      | 0.0014     | 0.022     |                        |                                               |
| H-1      | 99.9                     | 0.0546     | 0.0023     | 0.024     |                        |                                               |
| H-2      | 99.9                     | 0.075      | 0.0022     | 0.008     |                        |                                               |
| H-3      | 99.9                     | 0.128      | 0.0023     | 0.021     |                        |                                               |
| H-4      | 99.8                     | 0.182      | 0.0016     | 0.026     |                        |                                               |
| H-5      | 99.8                     | 0.217      | 0.0014     | 0.022     |                        |                                               |
| H-6      | 99.7                     | 0.348      | 0.0015     | 0.018     |                        |                                               |
| H-7      | 99.5                     | 0.459      | 0.0014     | 0.02      |                        |                                               |
| I-1      | 36.7                     | 0.0019     | 0.0055     | 0.081     |                        |                                               |
| I-2      | 36.2                     | 0.156      | 0.0013     | 0.06      |                        |                                               |
| I-3      | 39.3                     | 0.523      | 0.0012     | 0.022     |                        |                                               |
| J-1      | 99.9                     | 0.0499     | 0.0022     | 0.028     |                        |                                               |
| J-2      | 99.9                     | 0.111      | 0.0012     | 0.035     |                        |                                               |
| J-3      | 99.4                     | 0.57       | 0.0006     | 0.018     |                        |                                               |
| K-1      | 37.8                     | 0.0076     | 0.013      | 0.053     |                        |                                               |
| K-2      | 41.4                     | 0.214      | 0.0049     | 0.039     |                        |                                               |
| K-3      | 41.4                     | 0.373      | 0.0046     | 0.033     |                        |                                               |
| L-1      | 99.9                     | 0.106      | 0.0037     | 0.029     |                        |                                               |
| L-2      | 99.8                     | 0.247      | 0.0026     | 0.021     |                        |                                               |
| L-3      | 99.5                     | 0.547      | 0.0021     | 0.024     |                        |                                               |
At constant titanium content, dissolution of Fe, Cr and/or Ni oxide into ‘Ti3O5’ increases apparently with increase of Cr and/or Ni content. It was assumed in previous reports \(^1,2\) that the activity of Ti3O5 is unity when the solubility of Fe, Cr and Ni oxides in ‘Ti3O5’ phase was lower than \((X_{\text{Fe}}+X_{\text{Cr}}+X_{\text{Ni}}) / X_{\text{Ti}}\) (in Table 2.

### Table 2. Results of equilibration experiment using molten Fe–Cr alloy at 1823 K to 1923 K.

| Heat No. | Experimental Temperature | [mass% Cr] | [mass% Ti] | [mass% O] | (Fe+Cr)/Ti atomic ratio | Distinguished equilibrium oxides by EBSD analysis |
|----------|------------------------|------------|------------|-----------|------------------------|-----------------------------------------------|
|          |                        |            |            |           |                        |                                               |
| 1        | 1873 K                 | 20.6       | 0.0076     | 0.0127    | 0.148                  | ‘Ti3O5’ (Anovosite)                           |
| 2        |                        | 19.2       | 0.0403     | 0.0062    | 0.031                  |                                               |
| 3        |                        | 16.9       | 0.0627     | 0.0081    | 0.034                  |                                               |
| 4        |                        | 20.0       | 0.0645     | 0.006     | 0.075                  |                                               |
| 5        |                        | 18.6       | 0.0777     | 0.0033    | 0.060                  |                                               |
| 6        |                        | 18.6       | 0.157      | 0.0035    | 0.063                  |                                               |
| 7        |                        | 19.9       | 0.418      | 0.0023    | 0.019                  | ‘Ti3O5’ (Trigonal)                            |
| 8        |                        | 35.7       | 0.01      | 0.0311    | 0.184                  |                                               |
| 9        |                        | 34.9       | 0.0335     | 0.0121    | 0.011                  |                                               |
| 10       |                        | 39.6       | 0.035      | 0.0334    | 0.034                  |                                               |
| 11       |                        | 39.7       | 0.0437     | 0.0194    | 0.025                  |                                               |
| 12       |                        | 40.2       | 0.153      | 0.0071    | 0.013                  |                                               |
| 13       |                        | 41.0       | 0.389      | 0.0047    | 0.023                  |                                               |
| 14       | 1823 K                 | 22.0       | 0.0078     | 0.0052    | 0.567                  |                                               |
| 15       |                        | 21.8       | 0.0176     | 0.0042    | 0.109                  |                                               |
| 16       |                        | 19.1       | 0.0807     | 0.0024    | 0.060                  |                                               |
| 17       |                        | 21.8       | 0.028      | 0.0114    | 0.070                  |                                               |
| 18       |                        | 20.0       | 0.0064     | 0.0228    | 0.127                  |                                               |
| 19       |                        | 21.4       | 0.078      | 0.0116    | 0.077                  |                                               |

### Table 3. Results of equilibration experiment using molten Fe–Cr–Ni alloy at 1823 K to 1923 K.

| Heat No. | Experimental Temperature | [mass% Cr] | [mass% Ni] | [mass% Ti] | [mass% O] | (Fe+Cr+Ni)/Ti atomic ratio | Distinguished equilibrium oxides by EBSD analysis |
|----------|------------------------|------------|------------|------------|-----------|------------------------|-----------------------------------------------|
|          |                        |            |            |            |           |                        |                                               |
| 20       | 1873 K                 | 17.6       | 7.92       | 0.0028     | 0.0123    | 0.124                  | ‘Ti3O5’ (Anovosite)                           |
| 21       |                        | 16.4       | 8.08       | 0.0049     | 0.0194    | 0.445                  |                                               |
| 22       |                        | 19.0       | 10.48      | 0.007      | 0.0169    | 0.043                  |                                               |
| 23       |                        | 19.7       | 9.81       | 0.0506     | 0.0079    | 0.083                  |                                               |
| 24       |                        | 19.6       | 9.76       | 0.071      | 0.0064    | 0.063                  |                                               |
| 25       |                        | 14.3       | 7.34       | 0.0766     | 0.0052    | 0.072                  |                                               |
| 26       |                        | 17.5       | 12.58      | 0.0189     | 0.0054    | 0.033                  | ‘Ti3O5’ (Trigonal)                            |
| 27       |                        | 19.9       | 10.15      | 0.785      | 0.0019    | 0.038                  |                                               |
| 28       |                        | 38.7       | 19.76      | 0.0049     | 0.0350    | 0.192                  |                                               |
| 29       |                        | 34.5       | 20.23      | 0.0074     | 0.0550    | 0.195                  |                                               |
| 30       |                        | 38.8       | 18.69      | 0.0573     | 0.0175    | 0.118                  |                                               |
| 31       |                        | 38.9       | 19.39      | 0.241      | 0.0112    | 0.048                  |                                               |
| 32       |                        | 38.6       | 19.54      | 0.275      | 0.0074    | 0.025                  |                                               |
| 33       | 1823 K                 | 19.4       | 10.14      | 0.0895     | 0.0019    | 0.073                  | ‘Ti3O5’ (Anovosite)                           |
| 34       |                        | 16.2       | 8.39       | 0.0064     | 0.0103    | 0.044                  |                                               |
| 35       |                        | 19.0       | 9.98       | 0.0681     | 0.0030    | 0.051                  |                                               |
| 36       |                        | 16.8       | 8.36       | 0.0064     | 0.0150    | 0.098                  | ‘Ti3O5’ (Anovosite)                           |
| 37       |                        | 18.1       | 9.36       | 0.167      | 0.0137    | 0.053                  |                                               |
As mentioned before, oxygen content at low titanium concentration deviates lower from the relation between titanium and oxygen extrapolated from high titanium region in Figs. 1 to 5. Therefore, experimental data of high Fe, Cr and/or Ni oxides solubility in ‘TiO$_3$’ phase are used in the following for thermodynamic analysis in order to evaluate the activity of TiO$_3$ in ‘TiO$_3$’ solid solution equilibrated with the alloy in which titanium concentration was low.

In previous reports$^{1,2}$ numerical analysis was done in order to estimate deoxidation equilibrium relation between Ti and O in wide composition range of molten Fe–Ni, Fe–Cr and Fe–Cr–Ni alloys using Redlich-Kister type polynomial.

Pure liquid substances are chosen as a standard state for Fe, Ni, Cr and Ti. Hypothetical dissolved oxygen in the melt equilibrating with 101325 Pa (1 atm) oxygen gas is selected as the standard state$^{9–11}$ for oxygen.

Ti deoxidation reaction can be expressed at low Ti content by Eq. (1).

\[
\text{Ti}_2\text{O}_3(s) = 3\text{Ti} + 5\text{O} \quad \text{......... (1)}
\]

Choosing the standard state of Ti as pure liquid substance, Eq. (1) can be divided into Eqs. (2) and (3) as follows.

\[
\text{Ti}_2\text{O}_3(s) = 3\text{Ti} + \frac{5}{2}\text{O}_2(g) \quad \text{......... (2)}
\]

\[
\frac{5}{2}\text{O}_2(g) = 5\text{O} \quad \text{......... (3)}
\]

The Gibbs free energy change of Eq. (2) is identical to the summation of the minus value of Gibbs free energy change of TiO$_3$ formation ($\Delta G^0_{f,TiO_3}$) and the triple value of Gibbs free energy change of fusion of titanium ($3\Delta G^0_{fus,Ti}$). The Gibbs free energy change of Eq. (3) is zero due to chosen standard stage of oxygen as hypothetically dissolved state in the melt in equilibrium with 101325 Pa (1 atm) oxygen gas. As a result, the Gibbs free energy change of Eq. (1) is identical to that of Eq. (2).

The equilibrium constant, $K_{TiO_3}$, of Eq. (1) can be expressed as follows,

\[
\ln K_{TiO_3} = -\frac{(-\Delta G^0_{f,TiO_3} + 3\Delta G^0_{fus,Ti})}{RT}
= -\ln a_{TiO_3} + 3\ln a_{Ti} + 5\ln a_{O} + 3\ln X_Ti + 5\ln X_O
\quad \text{......... (4)}
\]

where, $\gamma$ and $X$ denote the Raoultian activity coefficient and mole fraction of component $i$, respectively. The Gibbs free energy change of TiO$_3$ formation ($\Delta G^0_{f,TiO_3}$) and Gibbs free energy change of fusion of titanium ($\Delta G^0_{fus,Ti}$) in Eq. (4) are taken from NIST–JANAF Thermochemical Tables.$^{12}$ The titanium oxide activity can be obtained from Eq. (4).

Pure stoichiometric solid TiO$_3$ was chosen as a standard state.

The excess free energy change of mixing in Fe–Cr–Ni–Ti–O system using Redlich-Kister type polynomial can be expressed as Eq. (5).
The term $\Omega_{ij}$ is binary interaction parameters of Redlich-Kister type polynomial between component $i$ and $j$. The interaction between four components and more were neglected in the present work. Also, ternary interaction in the Fe–Ni–Cr–Ti–O system except $\Omega_{FeCrNi}$ were assumed to be negligible due to low concentration of Ti and O. Literature values $^{1,2,6,7,11-13} \text{Fe–Ni–Cr–Ti–O}$ were used in the present work and are tabulated in Table 4.

The partial molar excess change of Ti and O in each alloy can be derived as following Eqs. (6) and (7), respectively.

\[
\Delta G_{ex}^{Ti} = RT \ln \gamma_{Ti} = \Delta G^{Ti} - X_{Ti} \frac{\partial \Delta G^{Ti}}{\partial X_{Ti}} - X_{O} \frac{\partial \Delta G^{Ti}}{\partial X_{O}} + (1 - X_{Ti}) \frac{\partial \Delta G^{Ti}}{\partial X_{O}} - X_{O} \frac{\partial \Delta G^{Ti}}{\partial X_{O}}
\]

\[
\Delta G_{ex}^{O} = RT \ln \gamma_{O} = \Delta G^{O} - X_{Ti} \frac{\partial \Delta G^{O}}{\partial X_{Ti}} - X_{O} \frac{\partial \Delta G^{O}}{\partial X_{O}} + (1 - X_{Ti}) \frac{\partial \Delta G^{O}}{\partial X_{O}} - X_{O} \frac{\partial \Delta G^{O}}{\partial X_{O}}
\]

Table 4. Interaction parameters used in this study.

| Literature | Values (J) |
|------------|------------|
| $^{5}$Lee | -17737+7.9965647 |
| $^{1}$Lee | 1331 |
| $^{4}$Lee | -1691+5.16227 |
| $^{10}$Lee | 1018+4.1466567 |
| $^{11}$Lee | -17360+5.1767 |
| $^{12}$Lee | 0 |
| $^{13}$Lee | -41540+142.47 |
| $^{14}$Lee | 298300+117.87 |
| $^{15}$Lee | 318+7.33187 |
| $^{16}$Lee | 1694+6.36967 |
| $^{17}$Lee | 365700+206.37 |
| $^{18}$Lee | 432900+208.87 |
| $^{19}$Lee | 52870+24.107 |
| $^{20}$Lee | -49820+234.77 |
| $^{21}$Lee | 424280+270.407 |
| $^{22}$Lee | -66338+313.157 |
| $^{23}$Miki and Hino | -10650+44.807 |
| $^{24}$Miki and Hino | 35500+15.927 |
| $^{25}$Miki and Hino | -118900+82.007 |
| $^{26}$Miettinen | 80000+507 |
| $^{27}$Miettinen | 130000+507 |
| $^{28}$Miettinen | 60000+507 |
inserting \( X_{Cr} = 0 \). Also, Fe–Cr–Ti–O system can be considered by inserting \( X_{Cr} = 0 \) into Eqs. (5) to (8).

The activity of \( Ti_3O_5 \) in ‘\( Ti_3O_5 \)’ solid solution equilibrated with Fe–Ni, Fe–Cr and Fe–Cr–Ni alloys at 1873 K was determined by substituting titanium deoxidation experimental results at low titanium content in Tables 1 to 3 into Eq. (8), and those results are shown in Fig. 9 and were utilized to determine the dashed curves in Figs. 1 to 5. The non-stoichiometric behavior of \( Ti_3O_5 \) was not taken into account due to lack of experimental results. Relation between Ti content in alloys and the \( Ti_3O_5 \) activity in the ‘\( Ti_3O_5 \)’ solid solution at 1823 K and 1923 K was assumed to be similar to the estimated results at 1873 K due to insufficient experimental data. Equilibrium between Ti and O in molten Fe–Ni, Fe–Cr and Fe–Cr–Ni alloys equilibrated with ‘\( Ti_3O_5 \)’ solid solution was clarified in the present work.

5. Conclusion

Interface of \( Ti_3O_5 \) crucible equilibrated with liquid Fe–Ni, Fe–Cr and Fe–Cr–Ni alloys at 1823 K to 1923 K were analyzed by SEM–EDS. Solubility of Fe, Cr and/or Ni oxide in ‘\( Ti_3O_5 \)’ phase was evaluated by EDS analysis result at the interface. Numerical analysis was conducted to estimate the relation between Ti and O in molten Fe–Ni, Fe–Cr and Fe–Cr–Ni alloy equilibrated with ‘\( Ti_3O_5 \)’ solid solution using the \( Ti_3O_5 \) activity in the ‘\( Ti_3O_5 \)’ solid solution determined by Redlich-Kister type polynomial. Equilibrium between Ti and O in molten Fe–Ni, Fe–Cr and Fe–Cr–Ni alloys equilibrated with ‘\( Ti_3O_5 \)’ solid solution was clarified in the present work.

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