Solubility of Oxygen in Molten Ni–Cr Alloys in Equilibrium with Silicate Slag System Containing Cr Oxide

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A study has been carried out to measure the solubility of oxygen in a molten Ni–Cr alloy contained in a MgO crucible in equilibrium with CaO–SiO2–MgO–Cr2O3 system slag. It was found that oxygen content increased with increasing Cr content in the range between 2 and 40 mass%.

According to SEM observation along with EDS analysis, the oxide phases in the slag consisted of MgO-Cr2O3 crystals and CaO–SiO2–MgO silicate phases. In the crucible close to the surface in contact with the molten alloy and the slag, almost pure MgO phases were observed in addition to the above two phases. Therefore, it was confirmed that soluble oxygen in the molten Ni–Cr alloy was supplied by decomposition of the MgO-Cr2O3 phase as MgO-Cr2O3(s) = MgO(s) + 2Cr + 3O. Consequently, thermodynamic analysis led to the interaction coefficient of $e_{\text{CrO}}^{\text{NiO}} = -0.162 \pm 0.012$ (Cr: 2–5 mass% in reference to Ni) and $-0.044 \pm 0.001$ (Cr: 5–40 mass% in reference to Ni-5%Cr) available in molten Ni.

KEY WORDS: Ni–Cr alloy; interaction coefficient; oxygen; slag; crucible; deoxidation.

1. Introduction

Ni–Cr system alloys are known as one of the basic systems of Ni-based superalloys. These alloys have excellent corrosion resistance and heat resistance. Therefore, the alloys are applied for severe environments of highly corrosive environments and high temperatures. Refining has to be appropriately processed to remove impurities such as sulfur and oxygen to show the performance of the alloys as much as possible. In this view, it has been expected to estimate the results after some reactions such as deoxidation and desulfurization. However, it is generally recognized that the available thermodynamic data in the Ni-based alloys are still insufficient compared with Fe-based alloys. Therefore, it has been required to obtain those data available in molten Ni as a solvent.

As for Ni–Cr alloys, work has been carried out by some researchers. Janke et al. measured oxygen solubility in equilibrium with Cr2O3 phase in Ni–Cr alloys by EMF method. They determined the value of $e_{\text{CrO}}^{\text{NiO}}$ as $-0.231 + 0.009$ (mass% Cr) expressed by the first and second order interaction coefficients. Katayama et al. also carried out the experiments quite similar to those by Janke. They measured oxygen potential in the molten Ni–Cr alloys leading to activity of Cr in molten Ni in reference to Raoult’s law. Ishii et al. carried out the experiments to understand Si deoxidation equilibrium of a molten Ni–Cr alloy contained in a silica crucible, by which the value of $e_{\text{CrO}}^{\text{NiO}}$ was determined as $-0.171$. It should be mentioned that Si and O contents were measured in the relatively wide range between 2 and 19 mass%. But, the experimental data in the range of Cr content over 5 mass% were neglected. This reason was owing to the uncertainty to determine the effect of Si on Cr corresponding to the interaction coefficient of $e_{\text{CrO}}^{\text{NiO}}$ as discussed in their report.

Industrially, Ni-based superalloys typically contain Cr of 5 to 25 mass%. However, it is not too much to mention that the thermodynamic data available in molten Ni are insufficient to estimate the terminal content of some elements as a result of some chemical reactions.

Therefore, this study aims at clarifying the interaction coefficient of $e_{\text{CrO}}^{\text{NiO}}$ in the relatively wide range available for the actual alloy systems, through the measurement of oxygen solubility in equilibrium with the top slag. This value is quite important to estimate the deoxidation equilibrium either with Si or Al.

Firstly, oxygen contents were measured by the experiments, where molten Ni- 2–40 mass% Cr alloys contained in the MgO crucibles were in equilibrium with CaO–SiO2–MgO–Cr2O3 quaternary system slag. Thereafter, the oxide phases in the slag and the MgO crucible were observed by SEM along with the analysis by EDS. Finally the reaction governing the whole system was determined, by which the value of $e_{\text{CrO}}^{\text{NiO}}$ was obtained in the Cr content range from 2 to 40 mass%.

2. Experimental

2.1. Procedure

300 grams of Ni–Cr alloy, contained in a MgO crucible ($\varnothing 50 \text{ mm} \times \varnothing 70 \text{ mm} \times 90 \text{ mmH}$), was placed in a vertical furnace as illustrated in Fig. 1. In this study, MgO crucible was applied for the experiments because MgO based refrac-

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tories are usually used for the lining of the furnaces and the ladles in practice.

The purities of Ni and Cr were confirmed to be higher than 99.99 mass%. Cr contents were selected as 2, 3.5, 5, 10, 23 and 40 mass%. The raw materials of Ni and Cr was heated up to the aimed temperature of 1550°C under an Ar gas atmosphere. Ar gas was flown at a rate of 1 L/minute. After attaining 1550°C, the alloy was kept for 30 minutes to homogenize the temperature. This was followed by stirring the melt with a silica rod to thoroughly homogenize the molten alloy. Thereafter, the first sample was taken by the following way. The silicon rubber cap of the top lid was taken off and a silica tubing, inside which it was evacuated, was inserted to the melt to suck up the molten alloy.

Thereafter, 40 grams of the mixture of CaO–SiO₂–MgO–Cr₂O₃ oxide powder was added onto the molten alloy from the top of the furnace, at which it was defined as time zero. The pure reagents of each oxide were uniformly mixed before the experiments. Usually pre-melting is done to create mother slags. But, it was difficult to pre-melt for the present system because Cr₂O₃ is easily reduced.

For the slag compositions, it should be noted that the basicity defined as the mass ratio of (mass% CaO)/(mass% SiO₂) was fixed as 1 and that MgO was fixed as 10 mass%. The Cr₂O₃ concentrations were also fixed as 20 mass% so as for Cr₂O₃ to be saturated. After the addition of the top slag, the molten Ni–Cr alloy was sampled at 10, 30, 60, and 90 minutes by a silica tube, as described above, to analyze oxygen contents. For the Ni-40 mass% Cr alloy, the samples at 120 and 180 were further taken. Analysis of oxygen was conducted by an inert gas fusion method (Horiba; EMGA 530).

2.2. Analysis of Oxide Phases

The slags after the experiments were collected to observe the oxide phases. In addition to the slags, the crucibles after the experiments were observed to understand how they reacted with the slags. The slags and crucibles were mounted, polished up to 1 μm diamond paste and finally coated by Au. Au coating allows the samples to be observed by SEM (Scanning Electron Microscope; HITACHI S-3500N) equipped with EDS (Energy Dispersive X-ray Spectrometry; HORIBA EMAX-7000).

The oxides were quantitatively analyzed along with mapping the components. For the quantitative analysis, the area as wide as possible was analyzed depending on each phase to take data as average as possible. Further, three positions each phase were analyzed to have as representative composition as possible in addition to the area analyses. XRD (X-ray diffraction) was also carried out for some of the slags to identify the crystalline phase from the view point of structure.

3. Results and Discussion

3.1. Variation of Oxygen Content as Time

Figure 2 shows the variation of oxygen content as time. As can be seen, oxygen content increases as time. The lines are drawn so as to pass through the plots intermediately. Oxygen content for the Ni-40 mass% Cr alloy attained the constant value of 480 ppm after 90 minutes while the others attained the constant values after 60 minutes. It is clearly realized that oxygen content increases with increasing Cr content. This tendency is more clearly seen in Figure 3, where the attained oxygen contents are plotted against Cr content. The attained values, at 90 minute for 2 to 23 mass% Cr and at 180 minute for 40 mass% Cr, are considered as the oxygen contents in equilibrium with the oxide phase containing Cr oxide. Hereinafter, these values are taken as the values for analysis.

3.2. Observation of Oxide Phases

It is quite important to understand what oxide phase determines oxygen content in the Ni–Cr alloys. In this view, the slags and the crucibles after the experiments were observed carefully.
3.2.1. Slag

Figures 4(a) and 4(b) show the SEM image and the element distribution analyzed by EDS after the experiment of the Ni-23 mass% Cr alloy, respectively. The same pictures for the experiment of the Ni-40 mass% Cr alloy are shown in Figs. 5(a) and 5(b). It is obvious that the phases consisting of Mg–Cr–O and Ca–Si–Mg–O are observed in both figures. The phase of Mg–Cr–O was identified as MgO·Cr2O3 crystal by XRD analysis. In Table 1, the average values of the quantitative analyses are shown indicating that MgO·Cr2O3 phase contains negligibly small amount of CaO and SiO2. This is considered to be caused by the probable measurement error. This fact also supports that the phase of Mg–Cr–O is MgO·Cr2O3 crystal.

On the other hand, the phase of Ca–Si–Mg–O is considered to be CaO–SiO2–MgO silicate system containing a small amount of Cr oxide. The basicity, corresponding to the mass ratio of (mass% CaO)/(mass% SiO2) in the CaO–SiO2–MgO silicate melt, is over 3, though the initial blend was adjusted to 1. This reason is not surely understood but SiO2 might be absorbed by the crucible during the experiment.

According to this observation, the oxide phase containing Cr oxide is recognized as MgO·Cr2O3 crystal with MgO enriched, compared with stoichiometric MgO·Cr2O3 as realized in Table 1. It is presumed that MgO has been enriched due to decomposition of Cr2O3 in the MgO·Cr2O3 crystal by which oxygen is supplied to the molten alloy. This mechanism will be described later in detail with showing

![Fig. 3. Attained oxygen content plotted against Cr content.](image-url)

![Fig. 4. SEM image (a) and element distribution (b) of the slag for the experiment with Ni-23%Cr alloy. (Online version in color.)](image-url)
the governing reactions.

3.2.2. Crucible

Figures 6(a) to 6(e) show the cross-sectional views of the crucible after the experiment of the Ni-40 mass% Cr alloy as a typical example. These figures sequentially indicate the illustration of the position, where the sample was taken, in Fig. 6(a), the cross-sectional appearance in Fig. 6(b), the SEM image in Fig. 6(c) and the magnified images of the molten alloy side close to the surface in Fig. 6(d) and crucible side in Fig. 6(e). Furthermore, Fig. 7 shows the element distribution of the cross section of the crucible after the experiment.

The position with the darker color was observed at the position closer to the surface than in the crucible side as can be seen in Fig. 6(b). The SEM image of the position with the darker color is shown in Fig. 6(c). The magnified image close to the surface of Fig. 6(d) corresponds to the result shown in Fig. 7. It can be understood that the oxide consists of the three phases including MgO, MgO·Cr_2O_3 and CaO–SiO_2–MgO phases. It was probable that the partially molten slag firstly eroded the MgO crucible causing the reaction to form these three phases.

The quantitative analysis results provided in Table 1 show that the molar ratio of Mg:Cr for the composition of MgO·Cr_2O_3 indicates almost 1:2. This fact also supports that this phase is stoichiometrically the MgO·Cr_2O_3 crystal. It is also important to note that the MgO phase is almost pure oxide. The MgO content is as high as 92.9 mass% and this phase merely contains 3.6 mass% CaO along with 2.9 mass% Cr_2O_3, which could be CrO owing to probable

| Table 1. Quantitative analysis of the phases observed in the slag phase and the MgO crucible (mass%). |
|----------------------------------|----------|-------|-------|-------|
| Phase                           | MgO      | CaO   | SiO_2 | Cr_2O_3 |
| Slag MgO·Cr_2O_3                | 34.2     | 0.8   | 0.6   | 64.4   |
| Slag MgO                        | n/d      | n/d   | n/d   | n/d    |
| Slag CaO–SiO_2–MgO              | 15.3     | 62.1  | 16.8  | 5.8    |
| Crucible MgO·Cr_2O_3            | 21.9     | 0.7   | 0.3   | 77.1   |
| Crucible MgO                    | 95.8     | 2.5   | 0.1   | n/d    |
| Crucible CaO–SiO_2–MgO          | 12.1     | 38.6  | 48.2  | 1.1    |

Table 1. Quantitative analysis of the phases observed in the slag phase and the MgO crucible (mass%).

n/d denotes not detected.
Fig. 6. Cross sectional views of the crucible for the experiment with Ni-40%Cr alloy, showing an illustration (a), cross sectional appearance (b), SEM image (c) and magnified images of molten alloy side close to the surface (d) and crucible side (e). (Online version in color.)

Fig. 7. Element distribution of the cross section of the crucible for the experiment with Ni-40%Cr alloy, which corresponds to Fig. 6.
The substitution of Cr\(^{2+}\) with the cation site of Mg\(^{2+}\). In Table 1, the composition inside the crucible is also shown for comparison. As realized, the MgO phase contains 2.5 mass% CaO. This means that the difference of the MgO phase at the surface is only 2.9 mass% Cr\(_2\)O\(_3\).

The basicity of the CaO–SiO\(_2\)–MgO silicate phase is 0.8 that is lower than 1, even though the initial blend ratio was adjusted to 1. This can be compensated by the basicity of CaO–SiO\(_2\)–MgO phase in the slag which is over 3. This may show that SiO\(_2\) might be absorbed by the crucible. According to this observation, the oxide phase containing Cr oxide was identified as the MgO–Cr\(_2\)O\(_3\) crystal the same as in the slags.

It is very important to confirm if Cr atoms contained in MgO–Cr\(_2\)O\(_3\) crystal are trivalent in the determination of the oxide phase in equilibrium with oxygen in the Ni–Cr alloy. Thus, further analysis has been conducted as follows.

Morita \textit{et al}.\(^7\) measured the solubility of MgO–Cr\(_2\)O\(_3\) in MgO–Al\(_2\)O\(_3\)–SiO\(_2\)–CaO slag using molten Ni–Cr alloys at 1600°C under reducing conditions. Their work showed the oxygen partial pressure dependence of Cr\(^{2+}\)/Cr\(^{3+}\) in MgO–SiO\(_2\)–CrO\(_x\) melts saturated by 2MgO·SiO\(_2\). The composition of the silicate phase is not totally the same as that of our study but said to be similar to ours. Therefore, it is very meaningful to estimate the Cr\(^{2+}\)/Cr\(^{3+}\) ratio referring to their study because the entire system is also similar to the present study.

Dissolution reaction of oxygen gas into molten Ni is expressed as follows:

\[
\frac{1}{2} \text{O}_2(g) = \text{O} \quad \text{................................(1)}
\]

Here, the standard state of activity of the element in molten Ni is taken as an infinite dilute solution with mass% as the unit. The equilibrium constant \(K^0\) of the above reaction is provided as:

\[
\log K = \frac{-4160}{T} - 0.37 \quad \text{................................(2)}
\]

where \(T\) is absolute temperature (K). As described earlier, oxygen contents were measured in the range between 0.0028 and 0.048 mass%. Therefore, oxygen partial pressures in equilibrium with the dissolved oxygen has been calculated as \(\log P_{O_2} = -8.9 \sim -6.4\). According to the work by Morita,\(^7\) the value of \(\log (\text{Cr}^{2+}/\text{Cr}^{3+})\) is around −1.5 in this oxygen partial pressure range implying that Cr\(^{2+}/\text{Cr}^{3+}\) ratio is 0.03 in this study. This result shows that Cr\(^{3+}\) is dominant by 33 times in comparison to Cr\(^{2+}\) in this crystal.

### 3.3. Governing Reaction to Determine Oxygen Content

The above analyses and results have determined the governing reaction to supply oxygen into the molten Ni–Cr alloys as follows:

\[
\text{MgO} \cdot \text{Cr}_2\text{O}_3(s) = \text{MgO}(s) + 2\text{Cr} + 3\text{O} \quad \text{................................(3)}
\]

The standard state of the oxide is taken as a pure solid, while the standard state of activity of the element in molten Ni is taken as an infinite dilute solution with mass% as the unit. The equilibrium constant of the above reaction is expressed using activity of the components as follows:

\[
\log K_{(3)} = \frac{\log \sigma_{\text{MgO}} \cdot \sigma_{\text{Cr}}^2 \cdot \sigma_{\text{O}}^3}{\sigma_{\text{MgO}} \cdot \sigma_{\text{Cr}}^2 \cdot \sigma_{\text{O}}^3} = \log \sigma_{\text{MgO}} + 2\log \sigma_{\text{Cr}} + 3\log \sigma_{\text{O}} - \log \sigma_{\text{MgO}} \cdot \sigma_{\text{Cr}} \cdot \sigma_{\text{O}} \quad \text{................................(4)}
\]

In this equation, activity of MgO can be approximated as unity because MgO content has been analyzed to be as high as 92.9 mass%. Activity of MgO–Cr\(_2\)O\(_3\) can be also taken as unity because the above results show that the MgO–Cr\(_2\)O\(_3\) crystal is a stoichiometric compound. Using the interaction coefficients between Cr and O in molten Ni, Eq. (4) can be written as follows:

\[
\log K_{(3)} = 2(\varepsilon_{(\text{ONi})}^{\text{Cr}} [\%\text{O}] + \log [\%\text{Cr}]) + 3(\varepsilon_{(\text{ONi})}^{\text{Cr}} [\%\text{Cr}] + \log [\%\text{O}]) \quad \text{................................(5)}
\]

The term of \(\varepsilon_{(\text{ONi})}^{\text{Cr}} [\%\text{O}]\) can be negligibly small because the oxygen content in this study is 0.048 mass% at highest. Then, the following relation is obtained finally:

\[
\log [\%\text{O}] + \frac{2}{3} \log [\%\text{Cr}] = -\varepsilon_{(\text{ONi})}^{\text{Cr}} [\%\text{Cr}] + \frac{1}{3} \log K_{(3)} \quad \text{................................(6)}
\]

Taking the term of \(\log [\%\text{O}] + \frac{2}{3} \log [\%\text{Cr}]\) at the left hand side on the vertical axis while Cr content on the horizontal axis, the slope gives \(-\varepsilon_{(\text{ONi})}^{\text{Cr}}\) while the intercept gives the value of \(\frac{1}{3} \log K_{(3)}\). As shown in Fig. 8, oxygen content linearly increases with increasing Cr content in the two regions of 2 to 5 mass% and 5 to 40 mass% because a clear inflection point is apparent at 5 mass%. Least squares method gives us the values of \(\varepsilon_{(\text{ONi})}^{\text{Cr}}\) and \(\log K_{(3)}\) with the coefficient of determination \(R^2\) along with the standard error as follows:

#### a) \(\varepsilon_{(\text{ONi})}^{\text{Cr}} = -0.162 \pm 0.012\), in reference to Ni

\[\log K_{(3)} = -7.96 \quad \text{in the Cr range of 2 – 5 mass% at 1550°C,} \]

\[R^2 = 0.988\]

#### b) \(\varepsilon_{(\text{ONi})}^{\text{Cr}} = -0.044 \pm 0.001\), in reference to Ni-5%-Cr

\[\log K_{(3)} = -6.01 \quad \text{in the Cr range of 5 – 40 mass% at 1550°C,} \]

\[R^2 = 0.996\]

![Fig. 8. Relation between log[O]+2/3log[Cr] and Cr content.](image-url)
The first and second order interaction coefficients \( e_{\text{CrNi}} \) and \( e_{\text{CrNi}}^1 \) are usually proposed when interaction coefficient varies with the content of \( j \) element. It is also possible to derive the first and second order interaction coefficients with connecting all the plots by one smooth curved line. The results are obtained with the quadratic approximation with the coefficient of determination \( R^2 \) along with the standard error as follows:

c) \( e_{\text{CrNi}}^{Cr} = -0.088 \pm 0.010, e_{\text{CrNi}}^{Cr} = 0.0009 \pm 0.0004, \)
\[ \log K_{(3)} = -7.22 \text{ in the Cr range of } 2 - 40 \text{ mass% at } 1550^\circ \text{C}, \]
\[ R^2 = 0.971 \]

As realized, a) and b) are with the higher accuracy when comparing the above three \( R^2 \) values of a), b) and c). In addition, the present study primarily aims at clarifying the value of \( e_{\text{CrNi}}^{Cr} \) in the Cr range higher than 5 mass%. Thus, the target is b) \( e_{\text{CrNi}}^{Cr} = -0.044 \pm 0.001 \), as found to be very low in the standard error. Therefore, the authors would propose the interaction coefficients as a) and b).

It is difficult to understand why the clear inflection point appears at 5 mass% Cr at this moment. The authors presume that a probable reason lies in the characteristic of activity of Cr in molten Ni–Cr alloy system.

Figures 9(a) and 9(b) show activity of Cr in molten Ni–Cr alloy obtained by Katayama et al.\(^5\) in the entire range and that in the molar fraction range of Cr lower than 0.2, respectively. It is obvious at every temperature that activity of Cr is closer to ideal solution in the lower fraction range while it deviates more negatively at the higher range. In fact, around 5 mass% Cr is seen to be the inflection point. This implies that self-interaction coefficient of Cr atoms corresponding to \( e_{\text{CrNi}}^{Cr} \) might be taken into account. In other words, \( e_{\text{CrNi}}^{Cr} \) may be involved in the coefficient in the Cr range higher than 5 mass% obtained in this study. This value has never been on discussion in the previous studies neither by Janke et al.\(^2\) and Ishii et al.\(^6\) Hence, this opinion is not beyond assumption so that it should be a future work to clarify this behavior.

Using the above values of a) and b), the interaction coefficient of \( e_{\text{CrNi}}^{Cr} \) can be calculated. It can be assured if the assumption to ignore the term of \( e_{\text{CrO}\text{Ni}}^{O} \) is correct. The coefficient is calculated as \( e_{\text{CrNi}}^{Cr} = -0.536 \) and \(-0.153 \) in the ranges of Cr content of 2–5 mass% and 5–40 mass%, respectively. As stated earlier, the oxygen contents analyzed are in the range between 0.0028 and 0.048 mass% showing that this term has not affected the treatment of Eq. (6). It is concluded that the assumption to ignore the term of \( e_{\text{CrO}\text{Ni}}^{O} \) makes sense, which does not affect the interaction coefficient of \( e_{\text{CrNi}}^{Cr} \).

The experimental data by Katayama et al.\(^5\) are plotted in Fig. 8. They measured oxygen content in molten Ni–Cr alloy in equilibrium with Cr\(_2\)O\(_3\) by EMF method. The governing reaction is expressed as follows:

\[ \text{Cr}_2\text{O}_3 (s) = 2\text{Cr} + 3\text{O} \] \hspace{1cm} \text{(7)}

\[ \log K_{(7)} = \log \frac{a_2^2 - a_0}{a_{\text{Cr2O3}}} = 2\log a_\text{Cr} + 3\log a_0 - \log a_{\text{Cr2O3}} \] \hspace{1cm} \text{(8)}

Here, activity of Cr\(_2\)O\(_3\) can be taken as unity resulting in the equation same as Eq. (4), which finally provides the equation formula same as Eq. (6). Their experiments were carried out up to 47 mass% Cr. It can be seen that oxygen content linearly increases with increasing Cr content same as this study. Least squares method gives us the following values:

d) \( e_{\text{CrNi}}^{Cr} = -0.046, \)
\[ \log K_{(7)} = -5.38 \text{ in the Cr range of } 9 - 47 \text{ mass% at } 1560^\circ \text{C} \]

It is evident that our value of \(-0.046 \) obtained in the range of 5–40 mass% is in good agreement with the value of \(-0.046 \). This fact also implies that the entire system including oxygen content has surely attained equilibrium. On the other hand, \( \log K_{(7)} = -6.01 \) obtained in this study is lower than \( \log K_{(7)} = -5.38 \). It is considered that this is caused by the difference of the governing reactions of Eqs. (3) and (7).

3.4. Verification of Interaction Coefficient of \( e_{\text{CrNi}}^{Cr} \)

Ishii and Ban-ya\(^6\) carried out the deoxidation experiments of Ni–Cr alloys with Si. They obtained the activity
coefficients of O and Si against Cr as shown in Fig. 10. They compared with the data by Janke

\[ \log f_{\text{Si}}^{(\text{Cr})} = 0 \text{ leading to } \log f_{\text{Si}}^{(\text{Cr})} = 0.035 \text{ obtained by this difference was much larger than they expected as well as the corresponding value of } \epsilon_{\text{SiCr}}^{(\text{Cr})} = -0.0003 \text{ in molten Fe as the solvent.} \]

Accounting for the above discussion, the present authors have once attempted to approximate the corresponding interaction coefficient as \( \epsilon_{\text{SiCr}}^{(\text{Cr})} = 0 \), with which the slope becomes smaller with increasing Cr content. The present authors think that the slope significantly changes between 5 and 9 mass\%.

Hence, the following values were obtained as for Table 2

\begin{align*}
\text{e)} \quad & \epsilon_{\text{ONi}}^{(\text{Cr})} = -0.160 \text{ in the Cr range up to 5 mass\% in } 1550-1650^\circ C, \text{ in reference to Ni} \\
\text{f)} \quad & \epsilon_{\text{ONi}}^{(\text{Cr})} = -0.040 \text{ in the Cr range from 9 to 19 mass\% in } 1550-1650^\circ C, \text{ in reference to Ni-9\%-Cr} \\
\end{align*}

As realized, these values well agree not only with ours but also with that at high Cr range by Katayama.\(^5\) The values between 5 and 9 mass\% is not able to be shown here because of no data in this Cr range. The interaction coefficients \( \epsilon_{\text{ONi}}^{(\text{Cr})} \) are summarized in Table 2. It is clearly understood that the present values are consistent with the others. It would be very meaningful to discuss the reason why the difference had occurred between the two data in Fig. 10. They conducted the same experiments with Ni-Mo and Ni-W alloy systems.\(^6\) In these two systems, they mentioned in the paper that the interaction between Si and Cr was not seen implying that the interaction coefficients of \( \epsilon_{\text{SiCr}}^{(\text{Mo})} \) and \( \epsilon_{\text{SiCr}}^{(\text{W})} \) were presumed to be zero.

It is worthy to note that they did not observe the crucible surface. Thus, it is estimated that Cr in the Ni-Cr alloy might have reacted with the silica crucible. If this had really taken place, reaction resulted in the difficulty to treat the activity of the equilibrium oxide phase, which then could not be taken as unity. Indeed, it is quite important to observe the oxide phase in equilibrium to correctly determine the governing reaction.

3.5. Thermodynamic Consideration

Availability of the value of \( \epsilon_{\text{ONi}}^{(\text{Cr})} \) obtained in this study should be assessed. Al deoxidation equilibrium\(^9\) in molten Ni is considered as an example. The reaction is written as follows:

\[ \text{Al}_2\text{O}_3(s) = 2\text{Al} + 3\text{O} \quad \text{................. (9)} \]

The equilibrium constant of the above reaction is given as follows:

\[ \log K = \frac{-35200}{T} + 7.8 \quad \text{................. (10)} \]

\[ \log K_{(10)} = \log \frac{a_{\text{Al}}^2}{a_{\text{Al}_2\text{O}_3}} \quad \text{................. (11)} \]

In Table 3, the interaction coefficients\(^1,2,6,9,10\) are listed necessary for the above equation. The value in the brackets, available for the molten Fe, is used because of no reported value for the molten Ni. Meanwhile, activity of alumina was taken as 0.001\(^1\) assuming that the molten alloy was equilibrated with Al\(_2\)O\(_3\) in the molten slag of CaO-MgO-Al\(_2\)O\(_3\) system doubly saturated by CaO and MgO. Figure 11 shows the calculated result of the oxygen content in equilibrium with Al in a Ni-15 mass\%Cr alloy.

The lines were calculated with the interaction coefficient

![Fig. 10. Activity coefficients of O and Si with Cr, where Ishii conducted the experiments of Si deoxidation for Ni-Cr alloys and Janke measured oxygen solubility in Ni-Cr alloys in equilibrium with Cr\(_2\)O\(_3\) by an oxygen sensor. (Online version in color.)](image)

**Table 2.** Interaction coefficient obtained in this study in comparison with the previous results.

<table>
<thead>
<tr>
<th>Researcher</th>
<th>( \epsilon_{\text{ONi}}^{(\text{Cr})} ) (Cr range)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Low</td>
</tr>
<tr>
<td>This study</td>
<td>-0.162 (2–5%)</td>
</tr>
<tr>
<td>Katayama(^5)</td>
<td>-0.046 (9–47%)</td>
</tr>
<tr>
<td>Ishii(^6,8)</td>
<td>-0.160 (5%)</td>
</tr>
</tbody>
</table>

*\(^b\) after reassessment

**Table 3.** Interaction coefficients \( \epsilon_{ij}^{(\text{ONi})} \) applied for calculation.

<table>
<thead>
<tr>
<th>( i )</th>
<th>( j )</th>
<th>( \epsilon_{ij}^{(\text{ONi})} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>O</td>
<td>0.14(^9), 0(^5)</td>
</tr>
<tr>
<td>Cr</td>
<td>O</td>
<td>-0.84(^9), 0(^5)</td>
</tr>
</tbody>
</table>

\(^{10}\)
obtained in this study and the other two interaction coefficients.\(^2,6\) As can be seen, application of \(e_{O(Ni)}^{Cr} = -0.171\) shows unreasonably high oxygen content over 250 ppm. The oxygen content with application of \(e_{O(Ni)}^{Cr} = -0.096\) shows 20 ppm at lowest. It is not realistic as well because the condition assumed in this calculation is significantly a reducing condition. Applying our value of \(e_{O(Ni)}^{Cr} = -0.044\), the lowest attained oxygen content is 3 ppm. Oxygen content is in the range between 3 and 20 ppm in the range of Al content between 0.01 and 2 mass%. This result empirically fits the practical data. Therefore, the coefficient of \(e_{O(Ni)}^{Cr} = -0.044\) is the most consistent.

4. Conclusions

A study has been carried out to measure the solubility of oxygen in molten Ni–Cr alloy contained in MgO crucible in equilibrium with CaO–SiO\(_2\)–MgO–Cr\(_2\)O\(_3\) system slag. Further, the oxide phases in the slag and crucible were observed to clarify the governing reaction to determine oxygen content in the alloy. The following words summarize the present study.

1. It was found that oxygen content increased with increasing Cr content in the Cr content range between 2 and 40 mass%.

2. It was observed that the oxide phases in the slag consisted of MgO·Cr\(_2\)O\(_3\) crystals and CaO–SiO\(_2\)–MgO silicate phases. In the crucible close to the surface in contact with the molten metal and the slag, almost pure MgO phases were observed in addition to the above two phases.

3. Therefore, oxygen in the molten alloy was supplied by decomposition of the MgO·Cr\(_2\)O\(_3\) phases.

4. This result revealed that the reaction of MgO·Cr\(_2\)O\(_3\)(s) = MgO(s) + 2Cr + 3O determined oxygen content in the molten alloys.

5. Subsequent thermodynamic analysis led to the interaction coefficient of \(e_{O(Ni)}^{Cr}\) available in molten Ni as follows:

\[
e_{O(Ni)}^{Cr} = -0.162 \pm 0.012, \text{ Cr} : 2 – 5 \text{ mass%},
\]

in reference to Ni

\[
e_{O(Ni)}^{Cr} = -0.044 \pm 0.001, \text{ Cr} : 5 – 40 \text{ mass%},
\]

in reference to Ni-5%Cr

REFERENCES


