This study was intended to investigate the effects of basicity and oxygen partial pressure on the distribution behavior of Ni in the nickel smelting process using nickel oxide ore, the raw material of nickel, among natural ores. Experiments were conducted in a vertical tube furnace using Fe-Ni metal and FeO-MgO-SiO$_2$ ternary slag, which simulated the composition of natural ore. An equilibrium experiment was conducted to observe the distribution ratio of Ni, and thermodynamic data required for this experiment was calculated through Factsage. As a result, it was found that as the oxygen partial pressure increased, the Ni content in the slag increased linearly. The Ni content in the slag increased as the basicity moved away from 0.60.

Keywords: metal; slag; Factsage; basicity; MgO saturated zone; SiO$_2$ saturated zone

1. Introduction

In line with issues on global carbon neutrality, the secondary battery market, which uses eco-friendly electric energy instead of fossil fuels that unavoidably generate carbon, has been rapidly expanding in recent years [1-4]. In addition, nickel is used as a representative lithium-ion battery cathode active material and a raw material for stainless alloys, and as an element that cannot be replaced with other elements, demand for it is steadily increasing [5]. Nickel is generally obtained from nickel oxide ore or nickel sulphide. About 69% of nickel oxide ore and 31% of nickel sulfide ore distributed around the world, but 60% of nickel is actually produced from nickel sulfide ore and 40% from nickel oxide ore [6]. This is because nickel sulfide ore is easy to separate as a group due to its crystal structure, whereas nickel oxide ore contains goethite (FeO(OH)) containing adsorbed water, and since nickel is substituted in the lattice, group separation through physical separation is difficult and therefore it is hard to manufacture high-purity nickel [7,8] However, as the resources available for economical mining of nickel sulfide have been depleted in recent years, high-purity nickel production technology is required with nickel oxide ore. Therefore, to determine the optimal slag composition of the pyrometallurgical process of nickel oxide ore, the effect of oxygen partial pressure and basicity on the behavioral characteristics of Ni in FeO-MgO-SiO$_2$ slag was investigated in this study.
a MgO crucible and ZrO₂ crucible (outer diameter 55 mm, inner diameter 50 mm, height 70 mm) was used.

All samples in the experiment had 99.9% purity, and all samples were vacuum-packed to prevent oxidation after use to maintain reproducibility. In particular, for Fe, electrolytic iron (EF), which was not in powder form, was used and the samples requiring mixing were placed in a container with a diameter of 120 mm and mixed uniformly for 20 minutes at 50 rpm. Among the composition of the sample, metal : slag was fixed at 10 g:10 g during the experiment and Fe(EF) and Ni were used for molten metal, and FeO, MgO, and SiO₂ were used for slag.

Oxygen partial pressure was controlled by passing a CO/CO₂ mixed gas through a Mass Flow Controller (MFC). Below is a relational expression for this.

\[
\text{CO} + \frac{1}{2} \text{O}_2 = \text{CO}_2
\]

\[
\Delta G^0 = -28000 + 85.23 T \text{ J/mol}
\]

\[
\frac{P_{\text{CO}_2}}{P_{\text{CO}} \cdot (P_{\text{O}_2})^2} = K
\]

\[
\frac{1}{K} \cdot \frac{P^2_{\text{CO}_2}}{P^2_{\text{CO}} \cdot P_{\text{O}_2}} = P_{\text{O}_2}
\]

This study is an experiment to confirm the behavior of Ni through an equilibrium experiment between molten slag and metal. Therefore, there should be no reaction between the slag and the crucible that are initially injected. Below is the reaction between slag and crucible calculated through Factsage 8.2, a thermodynamic analysis program.

The reaction with the crucible was minimized using MgO crucible in the olivine saturated region (M/S 0.5-0.8) and ZrO₂ crucible in the SiO₂ saturated region (0.2-0.4). The slag also uses pre-melted slag manufactured by rapid cooling at 1550°C.

In the experiment for manufacturing the pre-melted slag, high-purity samples were evenly mixed, loaded into a crucible, and then heated to 1550°C, the temperature of this experiment. The furnace atmosphere was maintained at Ar and heated.
after purging Ar gas for 2 hours. After that, the slag is kept at the highest temperature until the target retention time, and quenching.

**TABLE 1** and **TABLE 2** show the composition of the input pre-melted slag and the composition of the pre-melted slag after manufacturing. There was little change in the component during the initial pre-melting process through the MgO crucible, but there was no additional elution of ZrO₂ during the manufacturing stage of the slag through the ZrO₂ crucible, but changes in basicity and FeO components occurred significantly, unlike the results of the thermodynamic calculation program. The reason is that the equilibrium state derived from the thermodynamic program calculates the state of the material that exhibits the most stable phase under the given conditions as a state function, but in the actual experiment, the reaction takes place through a specific reaction path. Therefore, in this equilibrium experiment, in order to match the composition content of slag to the level of **TABLE 1** in the Final Slag Composition of **TABLE 2**, additional small amounts of components were mixed. In this case, since most of the slag components have completed the melting reaction during the pre-melting process, unlike the initial pre-melted slag, the activity value of the components has been lowered. Therefore, it is judged that the additional reaction level will not have a significant effect on the results of the subsequent equilibrium experiment.

### 2.1. Distribution Behavior of Ni in Slag with Differential Oxygen Pressure

According to the content of FeO in the slag, the equilibrium oxygen partial pressure between Fe-FeO is controlled by the following relational equation (9). Therefore, in order to confirm the distribution behavior of Ni in the slag according to the oxygen partial pressure, an equilibrium distribution experiment was conducted by changing the content of FeO in the slag to 20, 30, 40, and 50 wt%. At this time, the oxygen partial pressure was calculated by the following relational equation (5) and the oxygen partial pressure was maintained by injecting a CO/CO₂ mixed gas. And the activity of Fe and FeO was calculated through Factsage.

\[
\text{FeO} = \text{Fe} + \frac{1}{2}\text{O}_2 \tag{6}
\]

\[
\Delta G° = -228,640 + 43.71T \quad \text{(J/mol)} \tag{7}
\]

\[
K = a\text{FeO}/a\text{Fe} \cdot (P_{O_2})^{1/2} = \exp(-\Delta G°/RT) \tag{8}
\]

\[
P_{O_2} = (a\text{Fe} \cdot K/a\text{FeO})^2 \tag{9}
\]

### 2.2. Distribution Behavior of Ni in Slag according to Slag Basicity

Next, we conducted an experiment to investigate the effect of basicity in slag on Ni behavior. The experiment was carried out through the previously manufactured PreMelt Slag. It was conducted at a temperature of 1550°C and the equilibrium oxygen partial pressure was controlled by the activity calculated through Factsage.
3. Results and discussion

3.1. Behavior of Ni in Slag under Partial Oxygen Pressure

Fig. 2 shows the Ni content in the slag according to the oxygen partial pressure. Prior to the experimental results, the behavior of Ni according to the oxygen partial pressure can be expressed by the following equation.

\[ \text{Ni} (l)_{\text{metal}} + \frac{n}{2} \text{O}_2 (g) \rightarrow \text{NiO} (l)_{\text{slag}} \]  \hspace{1cm} (10)

Therefore, if equation (1) is expressed as a formula for deriving the equilibrium constant,

\[ K_4 = \frac{a_{\text{NiO}}}{a_{\text{Ni}}} \cdot \frac{P^{n/2}}{P_{\text{O}_2}} = \frac{\gamma_{\text{NiO}} \cdot x_{\text{NiO}}}{\gamma_{\text{Ni}} \cdot x_{\text{Ni}}} \cdot \frac{1}{P_{\text{O}_2}^{n/2}} \]  \hspace{1cm} (11)

Here, \( K_4 \) is the equilibrium constant of equation (2), the activity of component \( i \) is expressed as \( a_i \), the oxygen partial pressure is expressed as \( P_{\text{O}_2} \), the mole fraction of component \( i \) is expressed as \( x_i \); and the activity coefficient of component \( i \) is expressed as \( \gamma_i \). The Ni distribution ratio between metal and slag can be expressed as.

\[ \log L_{\text{Ni}} = \log \frac{x_{\text{NiO}}}{x_{\text{Ni}}} = \frac{n}{2} \log P_{\text{O}_2} - \log \frac{\gamma_{\text{NiO}}}{\gamma_{\text{Ni}}} + \log K_3 \]  \hspace{1cm} (12)

Here, \( L_{\text{Ni}} \) represents the distribution ratio of Ni, and since nickel dissolved in slag is very small (less than 0.1 mass%), the activity coefficient \( \gamma_{\text{Ni}} \) can apply Henrian behavior characteristics. Looking at Equation (12) above, the equilibrium constant \( K \) is a function related to temperature and is expressed as a constant value at a specific temperature. Therefore, since the distribution ratio \( K \) value among the terms on the right side can be expressed as constants, it can be inferred that the distribution ratio \( L_{\text{Ni}} \) of nickel has a linear relationship with the oxygen partial pressure \( \log P_{\text{O}_2} \) under temperature conditions.

3.2. Results of testing the behavioral characteristics of Ni in slag according to basicity

The following Fig. 3 is the result of the distribution behavior experiment of Ni in slag according to the basicity.

Fig. 3 below represents the distribution ratio of Ni in the slag according to basicity. As a result, in the SiO\(_2\) saturated region (0.2-0.6), the nickel content in the slag tended to decrease as the basicity increased, and in the Olivine \((2\text{MgSiO}_3)\) saturated region, the nickel distribution ratio increased as the MgO content increased. In other words, the nickel distribution ratio was the lowest when the basicity was \((\text{wt.}\%\text{MgO})/(\text{wt.}\%\text{SiO}_2)\) about 0.6.

In this experiment, the component system of slag was composed of MgO-SiO\(_2\)-FeO, of which basic slag was divided into MgO and FeO, and acidic slag was divided into SiO\(_2\). However, Fe, which can have various electron valence ions in the actual process, is dissociated into slag in various forms such as Fe\(^{2+}\) and Fe\(^{3+}\), so FeO does not exist alone but is expressed as FeO, because it exists with Fe\(_2\)O\(_3\) and Fe\(_3\)O\(_4\). Therefore, in consideration of this, the basicity was fixed to MgO/SiO\(_2\).

At this time, the activity of oxygen ions in the Slag is assumed to be the activity of MgO according to the basicity in the slag. Through this, the dissolution behavior of nickel has an inflection point in accordance with the MgO component content. Since Ni in the slag is most stable to exist in the form of Ni\(^{2+}\), it was determined that the dissolution behavior of Ni in the molten slag takes place through the following two dissociation processes.

\[
\begin{align*}
(\text{Basic slag}) \text{Ni} + \frac{1}{2}\text{O}_2 + \text{O}^{2-} &= \text{NiO}_2 \quad (13) \\
(\text{Acidic slag}) \text{Ni} + \frac{1}{2}\text{O}_2 &= \text{Ni}^{2+} + \text{O}^{2-} \quad (14)
\end{align*}
\]

In addition, through Factsage 8.2, the activity of NiO in the slag according to the basicity \((\text{MgO/SiO}_2)\) at MgO-SiO\(_2\)-FeO system was shown. It is shown in Fig. 4, the activity of NiO was different from this experiment in the exact inflection point basicity, but it was found that it had an inflection point according to the basicity.
Therefore, in the MgO-SiO$_2$-FeO component system, the dissolution behavior of nickel in slag is judged to act as acidic slag in the olivine saturated area and as basic slag in the SiO$_2$ saturated area.

In particular, comparing the results of this experiment with Figs. 12 and 13 calculated in the thermodynamic calculation program, it can be seen that the inflection point of NiO activity is between the olivine saturation area and the SiO$_2$ saturation area. This shows that as SiO$_2$ or MgO components are saturated in slag, the dissolution behavior of Ni changes, and this behavior is oxides that have neither very large nor very small supply power of oxygen ions in a specific slag component system. These oxides perform basic slag behavior that supplies oxygen ions to maintain the neutrality of the slag, or on the contrary, acidic slag behavior that is intended to be simplified by receiving oxygen ions to cut the structure. Therefore, the dissolution behavior of Ni in slag is also judged to have such an amphoteric behavior in the MgO-SiO$_2$-FeO component system.

4. Conclusions

In this study, the effects of oxygen partial pressure and basicity on the Ni distribution ratio in the slag in a FeO-MgO-SiO$_2$ slag system were investigated to determine the optimal slag composition for nickel smelting in nickel oxide mines. As a result, it was found that the distribution ratio of nickel increased linearly as the oxygen partial pressure increased under the melting condition of 1550°C. In addition, since Fe in slag increases the oxygen partial pressure, it can be expected that the oxygen partial pressure will increase as the FeO content increases. In addition, the distribution ratio of Ni under the melting condition of 1550°C tended to decrease in the SiO$_2$ saturation zone and increased in the Olivine saturation zone.

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