Oxidation of Molten Nickel and Cobalt Sulfides

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An amount of 100 mg of nickel or cobalt sulfide was put in a slender alumina tube of 3 mm ID and 25 mm length and oxidized at 1473 K in a mixed O2–Ar gas stream. Sulfur atomic fraction, xS, was 0.30 to 0.40 for nickel sulfide and 0.40 to 0.446 for cobalt sulfide. When the xS was lower, the NiO or CoO layer was formed on the melt surface without the evolution of SO2 gas and the growth rate of the oxide layer was controlled initially by gas diffusion and subsequently by cation diffusion through the oxide layer. When the xS was higher, the desulfurization took place which resulted in lowering of sulfur potential of the melt. When the $p_{SO_2}$ in equilibrium with the melt and the oxide becomes lower than the atmospheric pressure, the formation of oxide starts to occur. The xS-value at the transition from desulfurization to the oxide formation was 0.30 to 0.33 for nickel sulfide and 0.41 to 0.43 for cobalt sulfide.

(Received August 5, 1987)

Keywords: oxidation, nickel sulfide, cobalt sulfide, molten sulfide, desulfurization, gas diffusion, oxide formation, parabolic rate constant, cation diffusion

I. Introduction

Several attempts have been made to produce metallic nickel from nickel sulfide and oxide. For instance, the direct conversion of molten nickel sulfide to metallic nickel at higher temperature has been already commercially operated(1). Fukunaka and Toguri(2) investigated the oxidation of molten nickel sulfide by use of levitation technique and reported that desulfurization of the melt was controlled by gas film mass transfer and that the oxidation of evaporated nickel took place in the latter stage of oxidation because of extremely high temperature. On the other hand, the possibility of the formation of metallic nickel by the mutual reaction between molten nickel sulfide and solid nickel oxide under a reduced pressure was suggested by Prasad and Jena(3), and Yokoyama, Tozawa and Yazawa(4). However, the reaction mechanism was very much complicated. It is our thought that the mechanism of the oxidation of molten sulfide

by gaseous oxygen is of basic importance for understanding the reaction mechanism of a more complicated system.

Cobalt is found, on the other hand, to associate frequently with nickel sulfide ore and the oxidation behavior of cobalt is also important in the sulfide smelting process.

The present work was intended to study the progress of the oxidation of molten nickel and cobalt sulfides as a first step of investigation. All experiments were carried out at 1473 K. The oxidation of a mixture of molten nickel and cobalt sulfides and a more complicated system at higher temperature will be reported elsewhere.

II. Experimental

1. Sample preparation

Nickel and cobalt sulfides were prepared from nickel or cobalt powder of 99.9% purity and distilled sulfur of 99.99% purity. Weighed mixtures of nickel and sulfur, and of cobalt and sulfur were heated in evacuated quartz tubes at 520 K for 86 ks and at 1470 K for 3.6 ks. They were subsequently quenched in cold water. The atomic fraction of sulfur, xS, of nickel sulfide was chosen at 0.30, 0.35 and
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0.40, while that of cobalt sulfide was 0.400, 0.430 and 0.446. These compositions of the sulfides were chosen so that the sulfur pressure over the sulfide melt at 1473 K was low and the amount of sulfur evaporated during the heating of the sample to the experimental temperature of 1473 K in Ar gas stream could be neglected.

2. Experimental procedure

The experimental apparatus and the procedure were described in the previous paper(5). A quartz tube of 30 mm ID and 900 mm length was used for the reaction tube. An amount of 100 mg of nickel or cobalt sulfide was put in a slender alumina tube of 3 mm ID and 25 mm length, and it was placed in a quartz basket and hung from a Shimadzu automatic microbalance, RMB-50, in a uniform temperature zone of the furnace by a quartz fiber of 0.5 mm diameter. It was heated in an Ar gas stream at a flow rate of $1 \times 10^{-5} \text{ m}^3 \cdot \text{s}^{-1}$. The furnace temperature was measured by a Pt-Pt13%Rh thermocouple placed just below the sample. The depth of molten sulfide in the alumina tube was about 3 mm. When the furnace temperature attained 1473 K, the Ar gas stream was switched to an O$_2$-Ar gas mixture at the same flow rate and the oxidation was started.

The mass change of the sample during the oxidation was continuously measured by the microbalance and the SO$_2$ concentration in the exit gas from the reaction tube was also continuously measured by a Shimadzu infrared gas analyser, URA-2S.

By the use of a slender alumina tube, the rate of gaseous diffusion between the open end of alumina tube and the surface of molten sulfide could be calculated theoretically and it was feasible to follow precisely the progress of reaction.

III. Results and Discussion

1. Mass change and evolution of SO$_2$ gas

Mass change during the oxidation of nickel sulfide of $x_S=0.30$ are shown in Fig. 1. When the oxygen partial pressure was higher than 20 kPa, the sample mass increased from the start of oxidation and no SO$_2$ gas was evolved. At $p_{O_2}=10$ kPa, on the other hand, the sample mass increased slightly which was followed by a decrease and again increased in the subsequent stage of oxidation, and the evolution of SO$_2$ gas was observed only during the duration of mass decrease.

When the $x_S$ was 0.35 and 0.40, as shown in Figs. 2 and 3, the sample mass decreased linearly with time and an appreciable amount of SO$_2$ gas was evolved in the earlier stage of oxidation. The rate of mass decrease was higher at a higher oxygen partial pressure. Subsequently, the evolution of SO$_2$ gas ceased and the sample mass increased. The broken lines shown in these figures are the calculated values described later.

Similar results were also obtained in the oxidation of cobalt sulfide though the sulfur atomic fraction was higher than that of nickel sulfide. At $x_S=0.400$, the sample mass increased from the start of oxidation without the evolution of SO$_2$ gas, and the sample mass decreased followed by an increase at higher $x_S$ of 0.430 and 0.446. However, the sample mass slightly increased in the initial stage even at higher $x_S$ as seen in Figs. 5 and 6, which was not observed in the oxidation of nickel sulfide.

2. Reaction of mass increase

A scanning electron micrograph of a section of the nickel sulfide sample of $x_S=0.30$ oxidiz-
As seen in this photograph, a dense NiO layer of about 20 μm thickness was formed on the melt surface and two phases of Ni$_3$S$_2$ and a small amount of Ni were found in the inner sulfide from X-ray diffraction analysis. Metallic nickel might be precipitated on cooling the sample.

In the oxidation of this sample, mass increase was observed without the evolution of SO$_2$ gas as described above. From these observations, the following reaction can be considered:

$$\text{Ni(in melt)} + \frac{1}{2} \text{O}_2 \rightarrow \text{NiO(s)}.$$  \hspace{1cm} (1)

The solubility of oxygen in molten nickel sulfide is thought to be not so high though no precise data are available. An unstable mass change observed in the initial stage of oxidation at $p_{\text{O}_2} = 10$ kPa will be discussed later.
Figure 8 shows a section of the cobalt sulfide sample of \( x_s = 0.400 \) oxidized for 4.8 ks at \( p_{O_2} = 30 \) kPa. The formation of a dense CoO layer of about 150 \( \mu \)m thickness is also observed on the sample surface, and the inner sulfide is composed of Co\(_9\)S\(_8\) and a small amount of metallic cobalt. Mass increase shown in Fig. 4 might be due to the following reaction:

\[
\text{Co(in melt)} + \frac{1}{2} \text{O}_2 = \text{CoO(s)}. \tag{2}
\]

Oxygen gas must diffuse from the open end of alumina tube to the surface of the sample for the reactions (1) and (2) to take place. The rate of oxygen diffusion through stagnant Ar is represented by

\[
N_{O_2} = \frac{cD_{O_2-Ar}}{L} \ln \left( \frac{1-y_{O_2(L)}}{1-y_{O_2(O)}} \right) \tag{3}
\]

and mass increase due to the reactions (1) and (2) is expressed by the following equation when the overall rate of reaction is controlled by gas diffusion.

\[
\frac{d\Delta m}{dt} = \frac{\pi}{4} d^2 N_{O_2} M_{O_2}. \tag{4}
\]

Binary gas diffusion coefficient, \( D_{O_2-Ar} \), was estimated from an empirical equation obtained by Ajersch and Toguri\(^6\) as \( 3.21 \times 10^{-4} \) m\(^2\) s\(^{-1}\). The oxygen mole fraction at the open end of alumina tube, \( y_{O_2(O)} \), was the same as in the mixed \( O_2-Ar \) gas stream and that at the gas/melt interface, \( y_{O_2(L)} \), was taken as zero. The mass increase calculated from eq. (4) are shown in Figs. 1 and 4 by broken lines. As seen in these figures, the rapid mass increase in the initial 100 s of oxidation is of gas diffusion control. The thickness of the oxide layer formed in this duration was estimated from the amount of mass increase as about 4 \( \mu \)m for NiO and about 10 \( \mu \)m for CoO.

The rate of mass increase was lowered in the subsequent stage. Square of mass increase was plotted against the reaction time in Fig. 9 for nickel sulfide of \( x_s = 0.30 \). For the oxidation at \( p_{O_2} = 10 \) kPa, the mass gain above the minimum mass at the reaction time 0.5 ks was plotted. As seen in this figure, measured points can be divided roughly into three periods. The initial 0.1 to 0.2 ks is of gas diffusion control as described above. In the latter stage after a period of about 3 ks had elapsed, diffusional processes through the oxide layer is thought to be controlling step for the growth of oxide layer, and the intermediate duration from 0.1 to 3 ks might be of transition from gas diffusion control to the control by the diffusional
process in the solid oxide layer. Similar plot was obtained also for the oxidation of cobalt sulfide of $x_S=0.400$.

In order to verify the above presumptions, the growth rate of the oxide layer was examined. The parabolic rate constants, $K_p$, was obtained from the slope of straight lines in the latter stage of oxidation in Fig. 9 and the results shown in Table 1 were obtained. The surface of molten nickel and cobalt sulfides in the alumina tube was found to be slightly convex upwards and surface area of molten sulfide, $A$, used in the calculation of parabolic rate constant was estimated by

$$A = \pi (r^2 + h^2)$$

where $r$ is radius of alumina tube and $h$ is height of convexed surface. Parabolic rate constant is related to rational rate constant, $K_r$, by

$$K_r = \frac{2K_p}{2M \rho_{MO}} \frac{M}{M_0}$$

Table 1 Parabolic rate constant and self-diffusion coefficient in the oxide. (1473 K)

| Melt | Oxide | $p_{O_2}$ kPa | $K_p$ g$^2$ m$^{-4}$ s$^{-1}$ | $D_{M0}^{*}D_{Co}^{*}$ m$^2$ s$^{-1}$ |
|------|-------|---------------|-----------------|------------------|
| Ni-S | NiO   | 10            | 0.66            | $2.2 \times 10^{-14}$ |
|      |       | 20            | 1.30            | $4.1 \times 10^{-14}$ |
|      |       | 30            | 1.43            | $4.4 \times 10^{-14}$ |
| Co-S | CoO   | 10            | 8.8             | $2.7 \times 10^{-13}$ |
|      |       | 20            | 25.0            | $7.3 \times 10^{-13}$ |
|      |       | 30            | 27.0            | $7.7 \times 10^{-13}$ |

where $M$ is Ni or Co, and $z_0$ is the valence of oxygen ions. Furthermore, self-diffusion coefficient of cations can be obtained from the following equation assuming that the diffusion coefficient of oxygen is much smaller than that of cations:

$$D_{M0}^{*} = \frac{K_r}{2c_0 \ln \left( \frac{a_0^e}{a_0^e} \right)}$$

where $c_0$ is oxygen concentration in the oxide, and $a_0^e$ and $a_0^e$ are oxygen activities at the sulfide melt/oxide and the oxide/gas interfaces, respectively.

The $a_0^e$-value was taken as the square root of oxygen partial pressure in the $O_2$-$Ar$ gas mixture divided by 101.3 kPa. The $a_0^e$-value at the molten nickel sulfide/NiO interface was estimated as follows. The equilibrium constant for the reaction:

$$\text{Ni(l)} + \frac{1}{2} \text{O}_2 = \text{NiO(s)}$$

is calculated as $8.78 \times 10^2$ at 1473 K from thermodynamic data(7)(8). The standard state for nickel is supercooled liquid nickel. Then, the $a_0^e(=p_{O2}^{1/2})$ is obtained by

$$a_0^e = \frac{a_{NiO}}{8.78 \times 10^2 a_{Ni}}$$

The nickel activity, $a_{Ni}$, has been reported as 0.58(9) at $x_S=0.30$. Taking $a_{NiO}$ as unity, the $a_0^e$ obtained was $1.96 \times 10^{-4}$.

The $a_0^e$ at the molten cobalt sulfide/CoO interface was also calculated in the same way as 5.29 $\times 10^{-5}$. The activity of cobalt relative to supercooled liquid cobalt was obtained as 0.38 at $x_S=0.40$ from the Gibbs-Duhem equation by using the reported sulfur pressure over the cobalt sulfide melt(10)(11).

Self-diffusion coefficient of Ni and Co calculated from eq. (7) increased with oxygen partial pressure in $O_2$-$Ar$ gas mixture as shown in Table 1. The $p_{O2}$ dependence of diffusion coefficient was also reported by Mrowec et al. (12). From the reported cation-diffusion coefficient in the oxide, $D_{Ni0}^{*}$ and $D_{Co}^{*}$ at $p_{O2}=20$ kPa and 1473 K were estimated as $2.8 \times 10^{-14}$ and $1.1 \times 10^{-12}$ m$^2$ s$^{-1}$, respectively. Diffusion coefficients listed in Table 1 might
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involve several kinds of error, including error in the measurement of mass change of the sample because of a very small amount of mass increase of only a few milligrams and that in the estimation of thermodynamic quantities used in the calculation of diffusion coefficient. However, the diffusion coefficients obtained in the present work are rather close to the reported data, indicating that the overall rate of reactions (1) and (2) in the later stage of oxidation is controlled by the cation diffusion in the oxide layer.

3. Reaction of mass decrease

In the oxidation of nickel sulfide of \( x_5 = 0.35 \) and 0.40, the sample mass decreased from the start of oxidation as shown in Figs. 2 and 3. Figure 10 shows a scanning electron micrograph of a section of the nickel sulfide sample of \( x_5 = 0.40 \) oxidized for 0.9 ks at \( p_{O_2} = 20 \text{kPa} \), which duration of the oxidation is about a half way in the duration of mass decrease as seen from Fig. 3. From this photograph and X-ray diffraction analysis, \( \text{Ni}_3\text{S}_2 \) and \( \text{Ni} \) were observed and no oxide was detected in the oxidized sample. Therefore, the reaction of mass decrease might be a desulfurization which is written as

\[
\text{S(in melt)} + O_2 = \text{SO}_2. \tag{10}
\]

During the progress of this reaction, counter diffusion of \( O_2 \) and \( \text{SO}_2 \) must take place between the open end of alumina tube and the melt surface. Assuming that the overall rate of desulfurization is controlled by this diffusional process, the rate of mass decrease of the sample can be calculated as follows.

The equimolar counter diffusion of \( O_2 \) and \( \text{SO}_2 \) through stagnant \( \text{Ar} \) is to be considered: that is,

\[
N_{\text{SO}_2} = -N_{O_2} \quad \text{and} \quad N_{\text{Ar}} = 0. \tag{11}
\]

From the Stefan-Maxwell equation \(14\)

\[
\frac{dy_j}{dz} = \sum_{j=1}^a \left[ \frac{1}{c D_l_j} \left( y_j N_j - y_j N_i \right) \right], \tag{12}
\]

the following expression is obtained under the conditions of eq. (11) and \( y_{O_2} = 0 \) at the melt surface.

\[
\frac{S_1}{S_2} y_{\text{Ar}(O)} \left[ 1 - \exp \left( -\frac{LS_2}{c} N_{O_2} \right) \right] = -\frac{LN_{O_2}}{c D_{\text{SO}_2-O_2}} + y_{O_2(O)} \tag{13}
\]

where

\[
S_1 = \frac{1}{D_{\text{SO}_2-O_2}} - \frac{1}{D_{O_2-\text{Ar}}}
\]

and

\[
S_2 = \frac{1}{D_{\text{SO}_2-\text{Ar}}} - \frac{1}{D_{O_2-\text{Ar}}}. \tag{14}
\]

This equation can be solved numerically by Newton’s method for the flux of oxygen, \( N_{O_2} \). Diffusivities \( D_{\text{SO}_2-O_2} \) and \( D_{\text{SO}_2-\text{Ar}} \) were estimated from the Chen-Othmer equation \(15\), and \( D_{O_2-\text{Ar}} \) was taken as \( 3.21 \times 10^{-4} \text{ m}^2 \cdot \text{s}^{-1} \) because this value was obtained by similar experiments to the present work and might be accurate for the present purpose.

The rate of mass decrease of the sample is expressed by using \( N_{O_2} \) thus obtained:

\[
\frac{d\Delta m}{dt} = -\frac{\pi}{4} d_i^2 M_8 N_{O_2}. \tag{14}
\]

The calculated results are shown in Figs. 2 and 3 by broken lines of \( k = 1 \), where \( k = -N_{O_2}/N_{\text{SO}_2} \). As seen in these figures, the calculated results are in good agreement with

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Fig. 10 Scanning electron micrograph of nickel sulfide oxidized for 0.9 ks at \( p_{O_2} = 20 \text{kPa} \). (Initial \( x_5 = 0.40 \))
the observations. Thus, it can be concluded that the rate of interfacial reaction is much higher and the overall rate of reaction (10) is controlled by the gaseous diffusion in the alumina tube. The broken lines of $k=7/4$ shown in Figs. 2 and 3 are for the reaction:

$$2\text{Ni}_3\text{S}_2 + 7\text{O}_2 = 6\text{NiO} + 4\text{SO}_2$$

which were indicated for comparison with reaction (10).

On the other hand, a slight mass increase was observed at the start of oxidation of cobalt sulfide of $x_S=0.430$ and 0.446 as shown in Figs. 5 and 6 and the subsequent mass decrease was not linear with time. The rate of mass decrease calculated from eqs. (13) and (14) was higher than the measurements as shown in Fig. 11. However, the rate of mass decrease calculated from the observed amount of evolved SO$_2$ gas assuming reaction (10) is rather close to the measurement as shown by dotted and dashed lines in this figure, which indicates that the reaction during the course of mass decrease is substantially desulfurization described by reaction (10). Though the reason for disagreement between the measurement and the calculation based on eqs. (13) and (14) is not known, a possible account is that a very small amount of CoO is formed at the start of oxidation, which corresponds to a slight mass increase observed, and it partly prevents the diffusion of gaseous species.

### 4. Transition from mass decrease to mass increase

As shown in Figs. 2, 3, 5 and 6, the sample mass decreased due to desulfurization, which was followed by an increase. The evolution of SO$_2$ gas also ceased. The mass increase in the latter stage of oxidation is due to the formation of NiO and CoO as described in section 2. Melt compositions at minimum mass calculated from the amount of mass decrease are listed in Table 2. The $x_S$ at minimum mass does not depend on the initial composition of the sample but slightly varies with oxygen partial pressure.

Transition from the reaction of mass decrease to that of mass increase might be due to the lowering of sulfur potential of the melt. From eqs. (1) and (2) and

$$\text{S}_2 + 2\text{O}_2 = 2\text{SO}_2,$$

the following equations are obtained:

$$\text{Ni}(l) + \frac{1}{2} \text{SO}_2 = \text{NiO}(s) + \frac{1}{4} \text{S}_2$$

$$\text{Co}(l) + \frac{1}{2} \text{SO}_2 = \text{CoO}(s) + \frac{1}{4} \text{S}_2.$$

The equilibrium constants for reactions (17) and (18) are 0.256 and 1.45 at 1473 K, respectively$^{(7)(8)(16)}$. The standard states for Ni and Co are supercooled liquid metal. The equilibrium sulfur pressure over the melt and activities of

| Table 2 | Melt compositions at minimum mass. |
|----------|-----------------------------------|
| Melt     | Initial $x_S$ | $p_{O_2}/kPa$ | $x_S$ at minimum mass |
| Ni-S     | 0.35          | 0.1            | 0.301                  |
|          | 0.40          | 0.1            | 0.304                  |
|          | 0.35          | 0.2            | 0.318                  |
|          | 0.40          | 0.2            | 0.318                  |
|          | 0.35          | 0.3            | 0.327                  |
|          | 0.40          | 0.3            | 0.339                  |
| Co-S     | 0.430         | 0.1            | 0.411                  |
|          | 0.446         | 0.1            | 0.418                  |
|          | 0.430         | 0.2            | 0.422                  |
|          | 0.446         | 0.2            | 0.421                  |
|          | 0.430         | 0.3            | 0.425                  |
|          | 0.446         | 0.3            | 0.426                  |

![Fig. 11 Comparison of measured and calculated mass decreases. (Cobalt sulfide of $x_S=0.446$)](image-url)
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Nickel and cobalt were estimated at different compositions of the melt from the reported data\(^{(9)-(11)}\). The \(p_{SO_2}\) in equilibrium with the melt and the oxide was calculated by taking activities of NiO and CoO as unity and the results were shown in Fig. 12 by solid and broken lines. The \(x_S\)-values at minimum mass listed in Table 2 were also illustrated in this figure.

It can be said from the above calculations that the desulfurization takes place when the sulfur potential of the melt is higher and the formation of nickel and cobalt oxides starts to occur when the \(p_{SO_2}\) becomes lower than the atmospheric pressure. The \(x_S\) at minimum mass increases slightly with the oxygen partial pressure. This might be due to the difference in the rate of the oxide formation.

On the other hand, an unstable behavior of mass change was observed in the initial stage of oxidation of nickel sulfide sample of \(x_S=0.30\) at \(p_{O_2}=10\) kPa as shown in Fig. 1. This might be due to that the initial \(x_S\) of this sample was very close to that at minimum mass as seen from Fig. 12.

**IV. Summary**

In the oxidation of molten nickel and cobalt sulfides, desulfurization takes place when the sulfur potential of the melt is higher. The reaction rate at the melt/gas interface is much higher and the overall rate of desulfurization is controlled by the gaseous diffusion.

When the \(SO_2\) partial pressure in equilibrium with the sulfide melt and nickel or cobalt oxide was lowered below the atmospheric pressure due to the desulfurization, the formation of the oxide layer starts to occur on the melt surface and the evolution of \(SO_2\) gas ceased. Although the \(x_S\) of the melt at which the transition from desulfurization to the oxide formation occurred was different between nickel and cobalt sulfides: 0.30 to 0.33 for nickel sulfide and 0.41 to 0.43 for cobalt sulfide, the equilibrium \(SO_2\) partial pressure at these compositions was almost the same for both sulfides. Furthermore, the \(x_S\) at which transition occurs increases slightly with the oxygen partial pressure in the gas stream because of increasing rate of the oxide formation.

The growth rate of the oxide layer was initially controlled by the gaseous diffusion until the thickness of the oxide layer attains to 4 \(\mu\)m for NiO and 10 \(\mu\)m for CoO. Subsequently, the controlling step moved to the cation diffusion through the oxide layer.

**Acknowledgment**

The authors express their hearty thanks to Associate Professor T. Oishi, Kyoto University, for his valuable discussion.

**Nomenclature**

\(a_i\): activity of species \(i\) (\(i=\text{Ni and NiO}\))

\(a_O\): oxygen activity at sulfide/oxide interface

\(a_O^0\): oxygen activity at oxide/gas interface

\(c\): total concentration of gas phase [\(\text{mol} \cdot \text{m}^{-3}\)]

\(c_O\): oxygen concentration in oxide [\(\text{mol} \cdot \text{m}^{-3}\)]

\(d_i\): inner diameter of alumina tube [\(\text{m}\)]

\(D_{-j}\): binary diffusion coefficient \((i, j=\text{O}_2, \text{SO}_2\) and Ar)[\(\text{m}^2 \cdot \text{s}^{-1}\)]

\(D_i^*\): self-diffusion coefficient of species \(i\) \((i=\text{Ni and Co})[\text{m}^2 \cdot \text{s}^{-1}]\)

\(k\): \(-N_{O_2}/N_{SO_2}\)

\(K_p\): parabolic rate constant [\(\text{g}^2 \cdot \text{m}^{-4} \cdot \text{s}^{-1}\)]

\(K_r\): rational rate constant [equiv \cdot \text{m}^{-1} \cdot \text{s}^{-1}]\]

\(L\): distance from open end of tube to melt surface [\(\text{m}\)]

\(\Delta m\): mass change [\(\text{g}\)]

\(M_i\): molar mass of species \(i\) \((i=\text{O, S, NiO and CoO})[\text{g} \cdot \text{mol}^{-1}]\)
$N_i$: flux of species $i$ ($i=O_2, SO_2 \text{ and } Ar$) \[\text{[mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}]\]

$p_{O_2}$: oxygen partial pressure [kPa]

$x_S$: sulfur atomic fraction

$t$: time [s]

$y_i$: mole fraction of species $i$ ($i=O_2$ and Ar)

$z$: distance [m]

$\rho_i$: density of species $i$ ($i=\text{NiO and CoO}$) \[\text{[g} \cdot \text{m}^{-3}]\]

subscript

(O): open end of alumina tube

(L): melt surface

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