Oxidation of Mixed Nickel-Iron Sulfide*

By Teruo Tanabe**, Makoto Ogawa***, Zenjiro Asaki** and Yoshio Kondo**

Dense plates of mixed Ni–Fe sulfide of a composition Ni$_3$S$_2$–3 mass% FeS were oxidized in a mixed O$_2$–N$_2$ gas stream at 923, 973 and 1023 K. The oxygen partial pressure was maintained at 2.02 × 10$^4$ Pa. The sample mass increased during the oxidation and the rate of mass gain was higher than in the oxidation of Ni$_3$S$_2$. A very small amount of SO$_2$ gas was evolved in the initial few hundred seconds and no SO$_2$ gas was evolved thereafter during the oxidation for 72 ks. SEM observation, EPMA and powder X-ray diffraction revealed that a multi-layered oxide film of Fe$_2$O$_3$, Fe$_3$O$_4$ and Ni$_x$Fe$_{3-x}$O$_4$ was formed on the sulfide surface.

At the initial stage of oxidation, a thin layer of Fe oxide was rapidly formed, and the rate was controlled by the diffusion of Fe in the inner sulfide core. The activation energy was 190 kJ·mol$^{-1}$. At the subsequent stage of oxidation, the layers of Fe oxide and Ni$_x$Fe$_{3-x}$O$_4$ grew in accordance with the parabolic rate law. The growth rate of Fe oxide was controlled by the diffusion of Fe through the oxide layer with the activation energy of 127 kJ·mol$^{-1}$. The chemical diffusion coefficient of Ni in the Ni$_x$Fe$_{3-x}$O$_4$ layer was estimated at $10^{-16}$ to $10^{-17}$ m$^2$·s$^{-1}$. The Ni concentration in Ni$_x$Fe$_{3-x}$O$_4$ increased with the reaction time until the composition attained NiFe$_2$O$_4$. Thereafter, NiO was formed between the sulfide and NiFe$_2$O$_4$ in the oxidation at 1023 K.

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I. Introduction

The oxidation of mixed sulfide of metals is an important reaction in the nonferrous metallurgical processes. Some of the present authors studied the mechanism and the rate of oxidation of mixed Cu–Fe sulfide composed of bornite (Cu$_4$FeS$_4$) and troilite (FeS), and reported that iron was preferentially oxidized without evolution of SO$_2$ gas at the earlier stage of oxidation and a duplex oxide layer composed of Fe$_3$O$_4$ and Fe$_2$O$_3$ was formed on the sulfide surface.(1)(2) In the oxidation of mixed Ni–Co sulfide of a composition of Ni$_3$S$_2$–10 mass% Co$_2$S$_6$,(3) on the other hand, mixed Ni–Co oxide, (Ni, Co)O, was formed at the earlier stage of oxidation and subsequently Co$_3$O$_4$ was formed on the outer surface of (Ni, Co)O layer. Both (Ni, Co)O and Co$_3$O$_4$ layers grew in accordance with the parabolic rate law. No evolution of SO$_2$ gas was observed for the whole duration of oxidation experiment. The authors also studied the oxidation kinetics of Fe$_{1-x}$S$^{(6)}$ and Ni$_{1±x}$S$^{(5)}$, and reported that the cations diffused in the sulfide toward the outer surface and oxidized to form a dense oxide layer without the evolution of SO$_2$ gas when the sulfur activity of the sulfide was lower. The observation that no SO$_2$ gas was evolved in the oxidation of mixed Cu–Fe and Ni–Co sulfides was also due to the lower sulfur activity. In succession to the above works, it is intended in the present work to study the oxidation of mixed Ni–Fe sulfide.

In the nickel flash smelter, sulfide concentrate containing pentlandite and flux is fed to the top of the reaction shaft with preheated air, and matte and slag are formed in the settler. Kullerud$^{(6)}$ reported that pentlandite (Ni$_{4.5}$Fe$_{4.5}$S$_8$) was dissociated at 883 ± 2 K to form pyrrhotite containing nickel ([Fe, Ni]$_{1-x}$S) and heazlewoodite containing iron ([Ni, Fe]$_{3-x}$S$_2$). It is thought that the smelting reactions in the furnace include thermal decom-
position of pentlandite, oxidation of decomposed sulfides, and fusion. The elucidation of oxidation of mixed Ni–Fe sulfide is thought to be important for the analysis of the smelting process.

When a pellet of powder of mixed sulfide is used, the overall rate of oxidation might be markedly affected by gas phase mass transfer. Then, dense plates of the mixed sulfide were oxidized in this work to make the study of oxidation mechanism feasible.

II. Experimental

1. Sample preparation

A mixed Ni–Fe sulfide of a composition of Ni$_3$S$_2$–3 mass% FeS was oxidized in the present work. The isotherm of the system Ni–Fe–S at 973 K is shown in Fig. 1. The composition of this mixed sulfide is denoted by an open circle in this figure. It was prepared by heating the mixture of synthesized FeS and Ni$_3$S$_2$ in an evacuated quartz tube.

FeS and Ni$_3$S$_2$ were synthesized by heating the mixture of iron and sulfur and that of nickel and sulfur, respectively. Distilled sulfur of 99.999% purity and iron and nickel powder of 99.99% purity were used. FeS was obtained by heating the mixture of the stoichiometric composition in an evacuated quartz tube at 1173 K for 18 ks and by quenching in water.

To obtain Ni$_3$S$_2$, a mixture of nickel and sulfur was heated in an evacuated quartz tube at 1173 K for 18 ks. The obtained lump of Ni$_3$S$_2$ was crushed, again heated in vacuum at 1373 K for 18 ks to homogenize the composition and subjected to subsequent heating at 973 K for 36 ks at which temperature solid Ni$_3$S$_2$ was stable.

Both FeS and Ni$_3$S$_2$ obtained were mixed and melted in an evacuated quartz tube at 1223 K for 18 ks, and then it was maintained at 973 K for 36 ks and quenched in water. The obtained lump of mixed Ni–Fe sulfide was cut into rectangular plates 7 mm long, 8 mm wide and 1.5 mm thick.

An X-ray diffraction pattern of the sulfide sample thus obtained showed the existence of only Ni$_3$S$_2$ and was slightly deviated from a diffraction pattern of pure Ni$_3$S$_2$ due to iron sulfide contained. A very small amount of a second phase of troilite, FeS, was observed in the SEM observation, but it could not be detected in the powder X-ray diffraction because of a very small amount. It may have been formed at lower temperature, and it is thought that the sulfide sample consists of a phase of Ni$_3$S$_2$ containing iron sulfide at the experimental temperatures from 923 to 1023 K.

2. Experimental procedure

The experimental apparatus and procedure were described in a previous paper(1). A plate of mixed sulfide was placed on a platinum net and suspended from a Shimadzu automatic microbalance, RMB–50 V. After the sample attained a predetermined temperature in N$_2$ gas stream of a flow rate of $1.67 \times 10^{-5}$ m$^3$ s$^{-1}$, the oxidation was started by switching N$_2$ gas to mixed O$_2$–N$_2$ gas of the same flow rate, whose oxygen partial pressure was $2.02 \times 10^4$ Pa. The oxidation experiments were carried out at 923, 973 and 1023 K. The time variation of sample mass and SO$_2$ concentration in the exit gas was continuously measured during the oxidation. The latter was measured by a Shimadzu gas analyser, URA–2S. The microscopic and SEM observations were made on the partly oxidized samples. The oxidation products were identified by powder X-ray diffraction, and the concentration of each element in the oxide was
III. Results and Discussion

1. Progress of oxidation

The time variation of the mass of samples is shown in Fig. 2. The mass increases rapidly in the initial 1 ks of oxidation, and then the rate of mass gain was lowered. The experimental results obtained from the oxidation of Ni$_3$S$_2$ plate were also plotted in the same figure for comparison. It is seen that the mass gain was markedly raised due to the addition of a small amount of FeS in Ni$_3$S$_2$. A similar phenomenon was observed in the oxidation of mixed Ni–Co sulfide(3).

A very small amount of SO$_2$ gas was evolved in the initial 0.1 to 0.2 ks of oxidation, and no SO$_2$ gas was detected thereafter for the duration of 36 ks.

As described later, a dense oxide layer was formed on the sample surface due to the oxidation of the sulfide sample. From these observations, the following progress of oxidation can be considered. Oxygen gas is in direct contact with the sulfide at the start of oxidation, and the evolution of SO$_2$ gas in the initial duration of 0.1 to 0.2 ks might be due to the oxidation of the sulfide surface. Once a dense oxide layer is formed on the sulfide surface, it grows without the evolution of SO$_2$ gas. A similar phenomenon was observed in the oxidation of iron sulfide reported in a previous paper(4) and the following mechanism can be supposed: Cations diffuse from the interior of the sulfide to the sulfide/oxide interface and, furthermore, through the oxide layer to its surface where the cations are oxidized. Sulfur is concentrated in the sulfide due to the progress of this type of oxidation, and it is expected that the oxidation which is accompanied by the evolution of SO$_2$ gas takes place when the sulfur activity of the sulfide is raised enough high.

2. Structure and composition of oxide

SEM photographs of the cross section of samples oxidized for 36 ks at 923, 973 and 1023 K are demonstrated in Fig. 3. As seen in the figure, a duplex oxide layer is formed: The
grain size of crystals in the inner layer is relatively small, and the outer layer is composed of crystals grown unidirectionally toward the surface.

EPMA patterns of Ni, Fe and S along the cross section of the same samples are illustrated in Fig. 4. It is seen that the outer and inner layers are Fe oxide and mixed Ni–Fe oxide, respectively, and that the Ni concentration in the mixed Ni–Fe oxide is raised at higher temperature. Both Fe$_2$O$_4$ and a small amount of Fe$_3$O$_4$ were identified by powder X-ray diffraction from the oxide layer.

The oxide layer often peeled, when the samples were cut to pieces for the analysis of EPMA and X-ray diffraction. Figure 5(a) shows a SEM photograph of the surface of sample oxidized at 1023 K for 36 ks. As seen in this photograph, most of the outer oxide layer peeled and the mixed Ni–Fe oxide layer remained on the sample surface. The framed area of the photograph(a) is enlarged in Fig. 5(b). In this figure, Fe oxide and mixed Ni–Fe oxide are seen in the lower-right and upper-left part of the photograph, respectively. A further enlarged photograph of the mixed Ni–Fe oxide is shown in Fig. 5(c). Figure 6 shows a fractured edge of the sample shown in Fig. 5: The mixed Ni–Fe oxide peels and the inner sulﬁde is exposed. Many small pits and few large voids were

![Fig. 4 EPMA patterns of Ni, Fe and S along a cross section of samples oxidized for 36 ks: (a) 923 K, (b) 973 K and (c) 1023 K.](image1)

![Fig. 5 SEM photograph of a sample oxidized at 1023 K for 36 ks. (a) Sample surface where oxide film is partly spalled, (b) enlargement of framed area shown in (a) and (c) surface of Ni–Fe oxide.](image2)
A diffraction pattern was obtained from the edge near the sulfide/oxide interface of the fractured sample shown in Fig. 6. It is demonstrated in Fig. 7. The diffraction pattern (a) represents a reciprocal lattice of NiO near the sulfide/oxide interface. The pattern (b) was obtained from the oxide at a short distance from the interface and shows the oxide to be \( \text{Ni}_{0.53}\text{Fe}_{2.43}\text{O}_4 \). It is indicated that a very thin NiO layer was formed between the sulfide and mixed Ni-Fe oxide, though the formation of this layer was not detected by EPMA. Mixed Ni-Fe oxide of a spinel type is usually expressed as \( \text{Ni}_{x}\text{Fe}_{3-x}\text{O}_4 \)(8).

EPMA patterns of Ni, Fe, S and O along a cross section of the sample oxidized at 1023 K for 72 ks is illustrated in Fig. 8. It is seen that an appreciable amount of NiO has been formed between sulfide and mixed Ni-Fe oxide.
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during a long duration of oxidation. At lower
temperatures of 923 and 973 K, however, the
formation of NiO was not observed even after
72 ks of the oxidation.

It can be said from the above observations
that the multi-layered oxide composed of
Fe₂O₃, Fe₃O₄ and NiₓFe₃₋ₓO₄ is formed on the
sample surface and that NiO layer is also
formed between NiₓFe₃₋ₓO₄ and sulfide at
higher temperature.

3. Mass gain in the initial 0.1 ks of
oxidation

As mentioned in III-1., the sample mass
increased rapidly in the first 1 ks of oxidation
and it was plotted against the square root
of time in Fig. 9. It is seen that the sample
mass increases in accordance with the par-
abolic rate law and that the rate of mass gain
is lowered after periods of 0.1, 0.2 and 0.4 ks
have elapsed from the start of oxidation at
1023, 973 and 923 K, respectively. Rapid mass
increase at the initial stage of oxidation was
also observed in the oxidation of mixed Cu-Fe
sulfide(1). It was reported that iron dif-
fused from the interior of sulfide toward the
surface and was oxidized to form Fe oxide and
that the oxidation rate was controlled by the Fe
diffusion in the sulfide when the thickness of
oxide layer was less than about 10 µm. The
mass gain in the initial 0.1 ks of oxidation is
due mainly to the formation of Fe₃O₄, as will
be mentioned later. The thickness of Fe₃O₄
layer formed by the oxidation at 1023 K for
0.1 ks was estimated at about 1.2 µm from Fig.
9. It is thought reasonable, therefore, that the
oxidation rate in the first 0.1 ks is controlled by
the Fe diffusion in the sulfide(4).

The diffusion of Fe in the sulfide is expressed
as
\[
\frac{\partial c}{\partial t} = D_{Fe} \frac{\partial^2 c}{\partial y^2}
\]  
(1)
where \(c\) and \(D_{Fe}\) denote the Fe concentration
and diffusivity in the sulfide, respectively. The
initial and boundary conditions are as follows.

\[
\begin{align*}
c &= c_0, & t = 0, \\
c &= c_1, & y = 0 \text{ (sulfide/Fe₃O₄ interface)} \\
n & = 0, & y = a \text{ (center of the sulfide)},
\end{align*}
\]  
(2)
where \(c_0\) is the initial Fe concentration and \(c_1\) is
the Fe concentration at the sulfide/Fe₃O₄ inter-
face. The rate of the sample mass gain is ex-
pressed as follows using the solution of eq. (1).

\[
\frac{d\Delta W}{dt} = \frac{2}{3} A M_{O_2} D_{Fe} \frac{dc}{dy} \bigg|_{y=0},
\]  
(3)
where $A$ is the surface area of the sample. It was reported that the mass gain obtained from eqs. (1) to (3) was represented approximately by the following parabolic rate equation:

$$\left(\frac{\Delta W}{A}\right)^2 = k_p t.$$

The proportional constant $k_p$ in eq. (4) includes the diffusivity of Fe in the sulfide, the thickness of the sample plate and the concentration difference ($c_o-c_i$). The $k_p$-value was obtained from the initial slope of the straight lines shown in Fig. 9, and plotted in Fig. 10 against the reciprocal temperature. From this figure, the activation energy of 190 kJ·mol$^{-1}$ was obtained. This activation energy is related to the process of Fe diffusion in the sulfide core. This value is far higher than the value of 130 kJ·mol$^{-1}$ in the oxidation of mixed Cu–Fe sulfide.

4. Growth rate of Fe oxide at the subsequent stage of oxidation

As shown in Fig. 9, the rate of mass gain due to oxidation was lowered after a rapid mass gain at the initial stage, and the sample mass continued to increase in accordance with the parabolic rate law. SEM photographs of the cross section of samples oxidized at 973 K for 0.54, 1.8 and 18 ks are shown in Fig. 11. It is seen that both layers of mixed Ni–Fe oxide and Fe oxide grow with time. The growth rate of Fe oxide layer is first discussed in this section.

Figure 12 is a micrograph of the sample oxidized at 973 K for 36 ks. The formation of two layers of Fe$_3$O$_4$ and Fe$_2$O$_3$ is clearly observed. Fe$_2$O$_3$ is extremely thin, and the total thickness of Fe$_3$O$_4$ and Fe$_2$O$_3$ layers was measured from the SEM photographs shown in Fig. 11. The measured thickness of Fe oxide layer was plotted in Fig. 13 against the square root of time. It is seen that Fe oxide grows in accordance with the parabolic rate law in the oxidation for 4.5 to 40 ks depending on the temperature, and the growth rate is markedly lowered at the later stage of oxidation. The growth rate of Fe oxide obeying the parabolic rate law is thought to be controlled by the Fe diffusion through Fe$_3$O$_4$\textsuperscript{11}–\textsuperscript{16}. The straight lines connecting the observed points do not pass the origin. It is due to the rapid oxidation...
The parabolic rate constant, \( k_p \), for the growth of Fe oxide layer was obtained from the slope of the straight lines shown in Fig. 13, and it was plotted in Fig. 14 against the reciprocal temperature. The activation energy of 127 kJ\( \cdot \)mol\(^{-1}\) was obtained. This energy is regarded as being the activation energy of Fe diffusion in the Fe\(_3\)O\(_4\), since the Fe\(_2\)O\(_3\) layer is very thin.

Channing et al.\(^{11,12}\), Surman\(^{13}\) and Hussey et al.\(^{14}\) obtained values of 130 to 135 kJ\( \cdot \)mol\(^{-1}\) in the oxidation of Fe for the activation energy to form Fe\(_3\)O\(_4\) at temperatures below 900 K where wustite is unstable. These values are close to the value obtained in the present work. On the other hand, Davies et al.\(^{15}\) and Himmel et al.\(^{16}\) obtained the values of 190 to 200 kJ\( \cdot \)mol\(^{-1}\) in the oxidation of FeO to Fe\(_3\)O\(_4\) at temperatures above 1123 K. It is noted that the activation energy for the diffusion process in Fe\(_3\)O\(_4\) is markedly affected by the starting materials.

In order to know the reason of markedly lowered growth rate of Fe oxide at the later stage, the variation of Fe concentration in the inner sulfide core with oxidation was calculated. In the oxidation of mixed Ni–Fe sulfide without the evolution of SO\(_2\) gas, Fe concentration in the sulfide is lowered due to the preferential Fe oxidation. The amount of oxidized Fe was estimated from the thickness of the formed Fe oxide layer. It reaches 85 to 100\% of the original amount of Fe in the sample, when the growth rate was lowered. It can be said that the majority of Fe in the sulfide was consumed when the growth rate of Fe oxide was lowered.

5. Increase of Ni concentration in mixed Ni–Fe oxide at the later stage of oxidation

The thickness of Ni\(_x\)Fe\(_{3-x}\)O\(_4\) layer was

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Fig. 12 Micrograph of a cross section of the sample oxidized at 973 K for 36 ks.

Fig. 13 Parabolic plot of thickness of iron oxide layer.

Fig. 14 Arrhenius plot of parabolic rate constant for growth of Fe\(_3\)O\(_4\) layer.
measured from the SEM photographs, and the
time variation was shown in Fig. 15. It is seen
in this figure that the thickness of Ni$_x$Fe$_{3-x}$O$_4$
layer increases in accordance with the parabolic rate law at the earlier stage of oxidation
and that the growth rate scarcely depends
on temperature. It is seen in Figs. 13 and 15
that the times at which the growth of Ni$_x$Fe$_{3-x}$O$_4$ layer stops and the growth rate of Fe$_3$O$_4$ layer is lowered are fairly well coincided
with each other except for 923 K. Both of them
are due to the lack of iron in the inner sulfide.
It is also seen in Fig. 15 that the thickness of
the layer increased again after 36 ks had elaps-
ed from the start of oxidation at 1023 K. This
is due to the formation of NiO layer between
Ni$_x$Fe$_{3-x}$O$_4$ and sulfide, which was shown in
Fig. 8. The NiO layer could be scarcely
discriminated from Ni$_x$Fe$_{3-x}$O$_4$ in the SEM
photographs.

The measured Ni concentration in
Ni$_x$Fe$_{3-x}$O$_4$ with EPMA is shown in Fig. 16.
The x-value shown in this figure represents the
average concentration over the Ni$_x$Fe$_{3-x}$O$_4$
layer. It increases linearly with the square root
of time, and the rate of increase is elevated at
the later stage of oxidation. It is seen from
Figs. 15 and 16 that the rate of increase in the
Ni concentration becomes higher when the
thickness of the layer becomes unvaried. It is
also seen that the x-value increases approx-
imately to unity at the later stage of oxidation
at 1023 K. After it has attained unity, NiO
starts to be formed, as seen in Fig. 15. Since
the solid solution of NiFe$_2$O$_4$ and Fe$_3$O$_4$ is
stable in the whole range of the composition(17),
it is thought that NiFe$_2$O$_4$ of higher Ni concen-
tration is formed near the Ni$_x$Fe$_{3-x}$O$_4$/sulfide
interface, and Ni diffuses outward, resulting in
the growth of Ni$_x$Fe$_{3-x}$O$_4$ layer.

As seen in Figs. 15 and 16, Ni concentration
in Ni$_x$Fe$_{3-x}$O$_4$ continues to increase after the
thickness of the layer becomes unvaried. The
following diffusional process is presumed at
this stage of oxidation: Ni diffuses from the in-
ner sulfide to the Ni$_x$Fe$_{3-x}$O$_4$ layer of a constant
thickness. Though the diffusivity of Ni, $D_{Ni}$, in
Ni$_x$Fe$_{3-x}$O$_4$ varies with the composition, it is in-
tended to estimate the average diffusivity from
the increasing rate of Ni concentration in the
Ni$_x$Fe$_{3-x}$O$_4$ layer of a constant thickness. The
diffusion of Ni is expressed as

$$\frac{\partial c_{Ni}}{\partial t} = D_{Ni} \frac{\partial^2 c_{Ni}}{\partial y^2}. \quad (5)$$

When the time, $t$, at which the thickness of
Ni$_x$Fe$_{3-x}$O$_4$ layer attains a constant value is
taken as zero, the initial concentration profile
of Ni for eq. (5) is determined by the diffu-
sional process at the earlier stage of oxidation
where the Ni$_x$Fe$_{3-x}$O$_4$ layer is in growth. It
makes the solution of eq. (5) more difficult.
Then, the following hypothetical initial and
boundary conditions are assumed to obtain an
approximate value of diffusivity.
where $c_i$ is the Ni concentration in NiFe$_2$O$_4$. Under the condition of $\sqrt{D_{Ni} t/l^2} \leq 0.5$, the following expression is obtained from eqs. (5) and (6)\(^{(10)}\):

\[
\frac{n}{n_\infty} = 2 \sqrt{\frac{D_{Ni} t}{\pi l^2}},
\]

where $n$ and $n_\infty$ are the total numbers of moles of Ni which diffuse into the oxide layer during time $t$ and infinite time, respectively. Since the maximal Ni concentration in Ni$_x$Fe$_{3-x}$O$_4$ is equal to the concentration in NiFe$_2$O$_4$, the left-hand side of eq. (7) is equal to the $x$-value in Fig. 16. Consequently, the $D_{Ni}$-value can be obtained from the slope of straight lines at the later stage of oxidation in Fig. 16. The thickness of the oxide layer, $l$, was taken from Fig. 15 as 2.5, 3.8 and 4.4 $\mu$m at 1023, 973 and 923 K, respectively. The $D_{Ni}$-value was estimated as $3.1 \times 10^{-16}$, $1.4 \times 10^{-16}$ and $6.7 \times 10^{-17}$ m$^2$·s$^{-1}$ at 1023, 973 and 923 K, respectively, and the activation energy of 121 kJ·mol$^{-1}$ was obtained from the Arrhenius plot of $D_{Ni}$ shown in Fig. 17.

In the above calculation, $D_{Ni}$ was estimated by extrapolating the straight lines at the later stage of oxidation to the zero-time. The concentration profile of Ni in the Ni$_x$Fe$_{3-x}$O$_4$ layer was determined from eqs. (5) and (6) assuming that the thickness of the layer already attained $l$. This concentration profile might be slightly different from that in the layer during the growth, and the obtained $D_{Ni}$ has approximate values. Furthermore, the condition, $\sqrt{D_{Ni} t/l^2} \leq 0.5$, under which eq. (7) was valid was examined by using the obtained $D_{Ni}$-value. The maximal $\sqrt{t}$-value was obtained from $D_{Ni}$- and $l$-values as 70, 160 and 270 s$^{1/2}$ at 1023, 973 and 923 K, respectively. It can be said, therefore, that the range of time in which eq. (7) can be applied is rather limited at higher temperature.

IV. Summary

Dense plates of mixed Ni–Fe sulfide having a composition of Ni$_3$S$_2$–3 mass% FeS was oxidized at 923, 973 and 1023 K in a mixed O$_2$-N$_2$ gas stream of which O$_2$ partial pressure was maintained at 2.02 $\times$ 10$^4$ Pa. The mass change of the sample and SO$_2$ concentration in the exit gas were measured continuously during the oxidation. Identification on the oxidation products was carried out, and the composition of the formed mixed Ni–Fe oxide was determined. The results are summarized as follows.

(1) The sample mass increased with the progress of oxidation, and the rate of mass gain was much higher than in the oxidation of Ni$_3$S$_2$. Though a very small amount of SO$_2$ gas was evolved in the initial few hundred seconds, no SO$_2$ gas was evolved thereafter during the oxidation for 72 ks.

(2) The sample mass increased rapidly in the initial 0.1 ks of oxidation, and the Fe$_3$O$_4$ layer of about 1.2 $\mu$m in thickness was formed on the sample surface. The oxidation rate at this stage was controlled by the diffusion of Fe in the mixed Ni–Fe sulfide, and the activation energy of 190 kJ·mol$^{-1}$ was obtained.

(3) A duplex oxide was formed on the sam-
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ple surface at the subsequent stage of oxidation: The outer and the inner layer are Fe oxide and \( \text{Ni}_x\text{Fe}_{3-x}\text{O}_4 \), respectively. Both layers grew in accordance with the parabolic rate law, until the Fe concentration in the inner sulfide core was considerably lowered.

4) The Fe oxide was mainly composed of \( \text{Fe}_3\text{O}_4 \) and a thin layer of \( \text{Fe}_2\text{O}_3 \) was also formed on the surface of \( \text{Fe}_3\text{O}_4 \). The activation energy for the growth of Fe oxide was calculated as being 127 kJ·mol\(^{-1}\).

5) The Ni concentration in \( \text{Ni}_x\text{Fe}_{3-x}\text{O}_4 \) increased with the progress of oxidation until the \( x \)-value attained unity. Subsequently, NiO was formed between \( \text{NiFe}_2\text{O}_4 \) and the inner sulfide at 1023 K.

6) The diffusivity of Ni in \( \text{Ni}_x\text{Fe}_{3-x}\text{O}_4 \) was estimated at 10\(^{-16}\) to 10\(^{-17}\) m\(^2\)·s\(^{-1}\) under the experimental conditions employed in this work. The activation energy of 121 kJ·mol\(^{-1}\) was obtained for the diffusion of Ni in \( \text{Ni}_x\text{Fe}_{3-x}\text{O}_4 \).

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