Oxidation of Mixed Nickel-Cobalt Sulfide*

By Teruo Tanabe**, Tsuyoshi Mitarai***, Zenjiro Asaki** and Yoshio Kondo**

Dense plates of Ni$_3$S$_2$-10 mass% Co$_9$S$_3$ were oxidized in a mixed O$_2$-N$_2$ gas stream at 923, 973 and 1023 K. Oxygen partial pressure was maintained at $2.0 \times 10^4$ Pa. At an earlier stage of oxidation, the sample mass increased in accordance with the parabolic rate law. The rate of mass gain was higher than in the oxidation of Ni$_3$S$_2$ which was previously reported. A very small amount of SO$_2$ gas was evolved in the initial few hundred seconds of oxidation, and no SO$_2$ gas was evolved thereafter. A duplex oxide was formed on the surface: The inner oxide was mixed Ni-Co oxide, (Ni, Co)O, and the outer one was Co$_3$O$_4$ in which a small amount of nickel was contained. The thickness of (Ni, Co)O increased rapidly at an earlier stage of oxidation at 1023 K. After about 2 ks from the start of oxidation Co$_3$O$_4$ was started to form, and the growth rate of the thickness of (Ni, Co)O was lowered. The increase in the thickness of these oxides was also in accordance with the parabolic rate law. The apparent activation energy for the formation of (Ni, Co)O was estimated at 240 kJ·mol$^{-1}$. The concentration profile of CoO in the (Ni, Co)O was measured by EPMA. It was also calculated based on the diffusion of Ni and Co in the same oxide. A good agreement was obtained between the observed and calculated profiles.

(Received June 11, 1986)

Keywords: mixed nickel-cobalt sulfide, duplex oxide, Co$_3$O$_4$, (Ni, Co)O, solid state diffusion, uphill diffusion

I. Introduction

Sulfide concentrate supplied to the nonferrous metallurgical processes is usually the mixed sulfide. The smelting of complex sulfide concentrate is an urgent problem at present and in future, and it is requested to study the behavior of mixed sulfide in the smelting processes. The oxidation of mixed sulfide is one of the important bases for the elucidation of the processes.

Many works have been reported on the oxidation of fine particles of mixed Cu–Fe(1)(2), Zn–Cd(3), Zn–Cu(4) and Pb–Zn sulfides(5). In the oxidation of fine sulfide particles in the form of packed bed, the progress of oxidation becomes more complicated, and it is difficult to elucidate the oxidation mechanism. Previous works have also been made using pellets of mixed Cu–Fe(6) and Zn–Pb sulfides(7). In the oxidation of a pellet of mixed sulfide, the diffusion of gas in the outer porous shell of oxidized particles cannot be ignored and affects the overall rate of oxidation.

In order to avoid the above-mentioned difficulties inherent in the packed bed and pellet of small sulfide particles, the authors used dense plates of the sample in the kinetic study on the oxidation of mixed Cu–Fe sulfide(8). It was found from TG and microscopic observation that iron was preferentially oxidized: Copper and sulfur were concentrated in the inner sulfide core at an earlier stage of oxidation and a duplex oxide of Fe$_3$O$_4$ and Fe$_2$O$_3$ was formed. It was also reported that the oxidation rate was determined by the diffusion of iron in the mixed sulfide at the initial stage and subsequently by the diffusion through the formed oxide. This oxidation behavior is attributed to the fact that mixed Cu–Fe sulfide is stable in a wide range of composition.

As a continuation of kinetic studies of the oxidation of mixed sulfide, it is intended in the present work to study the oxidation of a dense

---

* This paper was originally published in Japanese in J. Japan Inst. Metals, 49 (1985), 633.
** Department of Metallurgy, Faculty of Engineering, Kyoto University, Kyoto 606, Japan
*** Former Undergraduate Student, Kyoto University, Kyoto. Present address: Mikka-ichi Smelter, Nikko Zinc Co., Kurobe, Toyama 938, Japan
plate of mixed Ni–Co sulfide. The oxidation of mixed Ni–Co sulfide is of basic importance in the smelting of cobalt bearing nickel sulfide. It is known that NiO and CoO are mutually soluble in a wide range of composition(9), and the oxidation of mixed Ni–Co sulfide is thought to be considerably different from that of mixed Cu–Fe sulfide in which iron is preferentially oxidized. The authors(10) also studied the oxidation of dense Ni$_3$S$_2$ plates and reported that the overall rate of oxidation was controlled by the diffusion of Ni through the oxide shell formed on the surface. It is also of interest to examine the effect of Co sulfide addition to Ni$_3$S$_2$ on the rate of oxidation.

II. Experimental

1. Sample preparation

The phase diagram for the system Ni–Co–S at 973 K(11) is shown in Fig. 1. The composition of the sample used in the present work, Ni$_3$S$_2$–10 mass% Co$_9$S$_8$, is denoted with an open circle in Fig. 1. This composition was chosen, because the solubility of Co$_9$S$_8$ in Ni$_3$S$_2$ is high and a mixed Ni–Co sulfide is stable over a wide range of composition.

The mixed Ni–Co sulfide was prepared by heating a mixture of weighed amount of Co$_9$S$_8$, NiS and Ni particles in vacuum. First, Co$_9$S$_8$ was synthesized by heating weighed mix-

Fig. 1 Phase diagram for the system Ni–Co–S at 973 K(11).
III. Results and Discussion

1. Progress of oxidation

The time variation of the sample mass per unit surface area during the oxidation is shown in Fig. 2. The mass was gained rapidly during the first 2 ks of oxidation. Then the rate of mass gain was lowered. The mass gain was larger at higher temperatures, as seen in this figure. A small amount of SO$_2$ gas was evolved in the initial few hundred seconds, and no SO$_2$ gas was detected thereafter. It is thought that any mass gain without the evolution of SO$_2$ gas is due to the diffusion of cations from the interior of sulfide to the surface where they are oxidized. The mass gain in the oxidation of dense Ni$_3$S$_2$ plate is also shown in Fig. 2. It is seen that the rate of mass gain of mixed Ni-Co sulfide is much higher than Ni$_3$S$_2$ at 973 and 1023 K, though the difference between these two sulfides is not very evident at 923 K. This is due to the difference in the formed oxide, as mentioned later: Only NiO was formed in the oxidation of Ni$_3$S$_2$.

Micrographs of the cross section of the samples oxidized for 36 ks at 923 and 973 K, and for 28.8 ks at 1023 K are demonstrated in Fig. 3. As seen in this figure, a dense duplex oxide was formed on the surface. The thickness of outer oxide is very thin at 923 K. EPMA profiles of elements along the cross sections of the same samples are shown in Fig. 4. It is seen that the Co concentration increases in the oxide from the inner sulfide/oxide interface. On the other hand, Ni concentration decreases toward outer surface. Because the thickness of oxide layer is not large and the diameter of electron beam is about 1 to 2 μm, the profiles of O and Co are seen to have a peak. Only CoO was detected by powder X-ray diffraction in the oxide formed at 923 K, and both CoO and Co$_3$O$_4$ were identified at 973 and 1023 K.

It can be said from the above EPMA profiles and X-ray diffraction that the outer oxide is
Co$_3$O$_4$ in which a small amount of Ni is contained, and the inner oxide is mixed Ni–Co oxide, or (Ni, Co)O, which is the solid solution of NiO and CoO. The crystal structure and the lattice constant of CoO scarcely change, when it contains a considerable amount of Ni, because of the closeness of the ion radii of Ni (0.069 nm) and Co (0.072 nm)\(^{12}\).

Scanning electron micrographs of the fracture of samples oxidized at 1023 K for 0.54, 7.2 and 28.8 ks are shown in Fig. 5. It is seen that only (Ni, Co)O was formed at an early stage of oxidation for 0.54 ks and both (Ni, Co)O and Co$_3$O$_4$ were formed at a later stage.
2. Rate of oxidation

The rate of mass gain shown in Fig. 2 is much lower even at the initial stage of oxidation than the rate on the presumption of gas film mass transfer control. Thus the resistance of gas film mass transfer can be neglected and the diffusion in the dense oxide may be significant.

The thickness of (Ni, Co)O and Co₃O₄ formed in the oxidation at 1023 K was measured at about 20 different positions on each SEM shown in Fig. 5. The mean value was plotted in Fig. 6 against the square root of time. The standard deviation of the measured thickness was between 0.2 and 0.8 μm. As seen in this figure, straight lines can be applied to the observed points in both (Ni, Co)O and Co₃O₄ layers, indicating that the growth rates are controlled by the diffusional process in these layers. The growth of outer Co₃O₄ was delayed for about 2 ks from the start of oxidation. The inner (Ni, Co)O grew rapidly at an early stage of oxidation. The growth rate of (Ni, Co)O was lowered after the formation of Co₃O₄, and the thickness of both (Ni, Co)O and Co₃O₄ increased in accordance with the parabolic rate law.

The growth rate of (Ni, Co)O was lowered after the formation of Co₃O₄ as mentioned above: neglecting the gradient of pO₂ in the gas boundary film on the solid surface, the outer surface of (Ni, Co)O was in contact with O₂– N₂ gas mixture of pO₂ at 2.0 × 10⁴ Pa during an early stage of oxidation. After Co₃O₄ was formed on the surface, (Ni, Co)O was in contact with outer Co₃O₄, and pO₂ at (Ni, Co)O/Co₃O₄ interface is approximately at the dissociation pressure of Co₃O₄, which is 58 Pa at 1023 K.(13) On the assumption that the growth rate of (Ni, Co)O is controlled by the cation diffusion in the oxide, the growth rate is lowered when the oxygen potential at the outer interface of (Ni, Co)O decreases.

The measured mass gain was plotted against the square root of reaction time in Fig. 7. The measurements were repeated at 973 and 1023 K. It was shown in Fig. 6 that Co₃O₄ was formed after about 2 ks from the start of oxidation at 1023 K. On the other hand, Co₃O₄ scarcely grew in the oxidation at 923 K. Then the straight lines were fitted to the mass gain at an earlier stage of oxidation where Co₃O₄ was not formed, and the parabolic rate constant, k_p, was obtained. The k_p-value thus obtained is thought to be the rate constant for the growth of (Ni, Co)O. From the Arrhenius plot shown in Fig. 8, an activation energy of 240 kJ·mol⁻¹ was obtained. The parabolic rate constant for the oxidation of dense Ni₃S₂(10) is also shown for comparison in the same figure. The activation energy for the oxidation of Ni₃S₂ is slightly lower and was 204 kJ·mol⁻¹.
3. Concentration profile of CoO in (Ni, Co)O

The concentrations of Ni and Co were measured by EPMA at different positions of (Ni, Co)O, and the mole fractions of NiO and CoO were obtained. The measured concentration profiles of CoO in (Ni, Co)O formed in the oxidation at 1023 K for 2.4, 7.2 and 14.4 ks are shown in Fig. 9. As seen in Fig. 6, Co₃O₄ was formed at the outer interface of (Ni, Co)O. The abscissa is a normalized distance in (Ni, Co)O, and the points of y=0 and 1 represent the inner and outer interfaces of (Ni, Co)O, respectively. It is seen in this figure that the difference among the normalized concentration profiles is not significant and that the "uphill diffusion" of Co takes place.

Dalvi and Coates(14) derived theoretical equations for the concentration profiles of CoO and NiO in (Ni, Co)O based on cation diffusion in a solid(15), and an outline of the derivation is as follows.

The fluxes of diffusion of Co and Ni in the (Ni, Co)O layer are written as

\[ J_{Co} = -\frac{D_{Co}}{V_m} \left( \frac{\partial \ln a_{Co}}{\partial x} \right) \]

and

\[ J_{Ni} = -\frac{D_{Ni}(1 - \xi)}{V_m} \left( \frac{\partial \ln a_{Ni}}{\partial x} \right) \]

respectively.

The sum of fluxes of Co and Ni is related to the growth rate of the thickness of (Ni, Co)O as

\[ (J_{Co} + J_{Ni}) V_m = \frac{dx_z}{dt}. \]

When the growth rate of the oxide thickness is controlled by the diffusional process, it is inversely proportional to \( x_s \) and

\[ \frac{dx_z}{dt} = k \]

On the other hand, the distance in the oxide from the sulfide/oxide interface is normalized by eq. (5).

\[ y = x / x_s \quad (0 \leq y \leq 1). \]

Assuming that the solid solution of NiO and CoO is ideal, the following equations are derived from the above equations (1) to (5)(14).

\[ \frac{d \ln a_{Co}}{dy} = \left\{ \frac{k'}{\beta^{(p-1)}a_{Co}^{p-1}} - (p-1) \frac{d \xi}{dy} \right\} / [p - (p-1)\xi] \]

and
In these equations

\[
\begin{aligned}
(p-(p-1)\xi)^2 \frac{\partial^2 \xi}{\partial y^2} &+ \left\{ \left(1-\frac{1}{\nu}(p-1)+[p-(p-1)\xi] \ln \beta \right) \times \left( \frac{d \xi}{d y} \right)^2 + \beta \xi - \beta \right\} \\
&+ \left( \frac{p(1-\frac{1}{\nu}) - \nu [p-(p-1)\xi]^2}{(1-\xi)(p-1)} \right) \frac{\partial \xi}{\partial y} \\
&\times \left( \frac{d \xi}{d y} \right)_{y=1} = 0.
\end{aligned}
\]

Equations (6) and (7) can be solved simultaneously to give a relationship between \(y\) and \(\xi\) which is independent of time, \(t\). Two boundary values \([\xi(y=0) = \xi(y=1)] = \xi^*\) and one boundary value \([a_0(y=1) = a_0^*]\) are required for the solution of eqs. (7) and (6), respectively.

Wood et al.\(^{16}\) measured the concentration profile of CoO in (Ni, Co)O formed on the surface of Ni-Co alloy oxidized at 1273 K in the oxygen gas stream. Since Co$_3$O$_4$ was not formed at 1273 K\(^9\), (Ni, Co)O was in contact with O$_2$ gas at a pressure of 1.01 x $10^5$ Pa, and thus \(a_0^* = 1\). The measured concentration profile was in good agreement with the \(\xi\)-value calculated by Dalvi and Coates\(^{14}\) using eqs. (6) and (7). In this calculation, the values of \(k' = 0.036\), \(p = 0.5\), \(\nu = 2.5\) and \(D_{Co}^c = 3.3 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}\) were used.

It is also intended in this work to calculate the concentration profile of CoO in (Ni, Co)O using eqs. (6) and (7). As the boundary conditions, the \(\xi\)-value was estimated from the experimental results shown in Fig. 9 to be 0.580 and 0.935 at \(y=0\) and 1, respectively. The \(a_0^*\)-value was taken as $2.4 \times 10^{-2}$, approximating the oxygen partial pressure at \(y=1\) to the dissociation pressure of Co$_3$O$_4$. Furthermore, the parabolic rate constant, \(k\), defined by eq. (4) was obtained as $1.62 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ from Fig. 6, and \(D_{Co}^c\)-value was estimated at $4.50 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ by extrapolating the data of Chen et al.\(^{17}\). Then \(k' = k/D_{Co}^c = 0.36\).

The values of the parameters \(\beta\), \(p\) and \(\nu\) were determined by trial and error so that the calculated \(\xi\)-value might coincide with the measurement. The calculated value is shown in Fig. 9 with a solid line. It is in good agreement with the measurement. In this calculation, the parameters were determined as \(\beta = 50\), \(p = 0.4\) and \(\nu = 3.0\) which were slightly different from those of Dalvi and Coates. Among the above parameters, \(\nu\)-value is discussed below. When cation diffusion takes place via vacancies, the diffusivity can be assumed to be in proportion to the concentration of cation vacancies. The variation of the vacancy concentration due to oxygen partial pressure is generally expressed in terms of \(p_{O_2}^{1/2}\), and the \(n\)-value is in the range from 4 to 6 for CoO and NiO\(^{14}\). Fisher and Tannhauser\(^{18}\) investigated the variation of vacancy concentration in CoO with \(p_{O_2}\) and reported that \(n=4\) at higher \(p_{O_2}\) and it increases to 6 at lower \(p_{O_2}\). Since (Ni, Co)O formed at 1023 K in the present work was in contact with Co$_3$O$_4$, \(p_{O_2}\) at the (Ni, Co)O/Co$_3$O$_4$ interface is relatively lower. It is thought reasonable that the \(n\)-value of 6 \((\nu = 3)\) obtained in this work is higher than \(n=5\) \((\nu = 2.5)\) obtained by Dalvi and Coates at \(p_{O_2}\) of $1.01 \times 10^5$ Pa.

IV. Summary

Dense plates of Ni$_3$S$_2$-10 mass\% Co$_9$S$_8$ were oxidized in a mixed O$_2$-N$_2$ gas stream at 923, 973 and 1023 K. The oxygen partial pressure was maintained at $2.0 \times 10^4$ Pa. The results are summarized as follows.

1. The sample mass was gained in accordance with the parabolic rate law during the oxidation, and the rate of mass gain is elevated at higher temperature. The observed rates of mass gain at 973 and 1023 K are much higher than the rate in the oxidation of Ni$_3$S$_2$. A very small amount of SO$_2$ gas was evolved at the in-
initial stage of oxidation, and no SO\textsubscript{2} gas was detected thereafter.

(2) A duplex oxide was formed on the surface: The inner oxide was (Ni, Co)O and the outer oxide was Co\textsubscript{3}O\textsubscript{4} containing a small amount of Ni.

(3) The thickness of (Ni, Co)O increased rapidly at an early stage of oxidation at 1023 K. After a period of about 2 ks from the start of oxidation, Co\textsubscript{3}O\textsubscript{4} started to grow on the surface of (Ni, Co)O, and the growth rate of (Ni, Co)O was lowered. The thickness of both (Ni, Co)O and Co\textsubscript{3}O\textsubscript{4} increased in accordance with the parabolic rate law, indicating that the growth rates of (Ni, Co)O and Co\textsubscript{3}O\textsubscript{4} layers were controlled by the diffusional processes in these oxide layers.

(4) The parabolic rate constant for the formation of (Ni, Co)O was obtained from the measured rate of mass gain at the initial stage of oxidation, and the activation energy was obtained as 240 kJ·mol\textsuperscript{-1}.

(5) From the measurements of the concentration profile of CoO in (Ni, Co)O, it was found that the “uphill diffusion” of Co took place. The concentration profile of CoO was calculated based on cation diffusion, and the results were in a good agreement with the measurement.

**Nomenclature**

\( a \): activity [-]
\( a'' \): activity at \( y = 1 \) [-]
\( D_{Co}, D_{Ni} \): diffusivity of Co and Ni in (Ni, Co)O, respectively [m\textsuperscript{2}·s\textsuperscript{-1}]
\( D_{Co}^{\infty} \): diffusivity of Co in CoO [m\textsuperscript{2}·s\textsuperscript{-1}]
\( J_{Co}, J_{Ni} \): flux of diffusion of Co and Ni in (Ni, Co)O, respectively [mol·m\textsuperscript{-2}·s\textsuperscript{-1}]
\( k \): parabolic rate constant [m\textsuperscript{3}·s\textsuperscript{-1}]
\( k_p \): parabolic rate constant [kg\textsuperscript{2}·m\textsuperscript{-4}·s\textsuperscript{-1}]
\( \beta \): ratio of \( k \) to \( D_{Co}^{\infty} \) [-]
\( N_{CoO}^{\infty}, N_{NiO}^{\infty} \): mole fraction of cation vacancies in CoO and NiO, respectively [-]
\( n \): =2\( v \) [-]
\( p \): ratio of \( D_{Ni} \) to \( D_{Co} \) [-]
\( p_{O_2} \): partial pressure of oxygen [Pa]

\( t \): time [s]
\( V_{m} \): average molar volume of (Ni, Co)O [m\textsuperscript{3}·mol\textsuperscript{-1}]
\( x \): distance in (Ni, Co)O [m]
\( x_{o} \): thickness of (Ni, Co)O layer [m]
\( y \): normalized distance [-]
\( z \): valence [-]
\( \xi \): mole fraction of CoO in (Ni, Co)O [-]
\( \xi'' \): mole fraction of CoO at \( y = 1 \) [-]
\( v \): parameter which represents the variation of \( D_{Co} \) due to the oxygen activity.

**REFERENCES**

(1) E. V. Margulis: Zhur. Priklad. Khim., 34 (1964), 2164.
(2) E. T. Bumazhnov and A. S. Lenchev: Metalurgiya (Sofia), 27 (8-9), (1972), 33.
(3) I. R. Polyvyannyi: Izvěst. Akad. Nauk Kazakh. S. S. R., Ser. Met., Obogashchen i Ogneporov (1958), 52.
(4) G. S. Frents and E. I. Navikova: Issled. Metal. v Zhidkom i Tverd. Sootoyaniyakh, Akad. Nauk SSSR, (1964), 55.
(5) A. A. Bundel, Z. I. Guretskaya, I. I. Ivanovskaya and T. V. Kukleva: Deposited Doc., VINITI 1627-75 (1975), 67.
(6) M. M. Rao and K. P. Abraham: Indian J. Tech., 3(9), (1965), 291.
(7) D. L. Canham and J. A. Charles: Trans. Inst. Min. Metall. (Sec. C), 90 (1981), C35.
(8) H. Tsukada, Z. Asaki, T. Tanabe and Y. Kondo: Metall. Trans. B, 12B (1981), 603.
(9) E. M. Levin, C. R. Robbins and H. F. McMuride: Phase Diagram for Ceramicists, Am. Cer. Soc., (1964), p. 52.
(10) Z. Asaki, K. Hajika, T. Tanabe and Y. Kondo: Metall. Trans. B, 15B (1984), 127.
(11) Von G. Lamprecht: N. Jb. Miner. Mh., (1978), 176.
(12) R. C. Weast and M. J. Astle: Handbook of Chemistry and Physics, CRC Press Inc., Florida, (1982), F-179.
(13) O. Kubaschewski, E. Ll. Evans and C. B. Alcock: Metallurgical Thermochemistry, 4th ed., Pergamon Press, Oxford, (1974), p. 396.
(14) A. D. Dalvi and D. F. Coates: Oxid. Metals, 3 (1971), 203.
(15) C. Wagner: Corros. Sci., 9 (1969), 91.
(16) G. C. Wood and J. M. Ferguson: Nature, 208 (1965), 369.
(17) W. K. Chen, N. L. Peterson and W. T. Reeves: Phys. Rev. 186 (1969), 887.
(18) B. Fisher and S. D. Tannhauser: J. Electrochem. Soc., 111 (1964), 1194.