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Determination of the Self-diffusion Coefficient of Nickel Atoms in Nickel Sulfide

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The self-diffusion coefficient of ions or atoms in such crystals as halides, oxides and sulfides can be determined from the rate of the diffusion-controlled solid-state reaction as well as by the tracer method. In the present study, the self-diffusion coefficient of nickel atoms in nickel sulfide was determined from the rates of the sulfidation and desulfidation of nickel sulfide in H_2S-H_2 gas mixtures. The results agreed well with the data obtained by the previous investigators employing the tracer technique.

Although the self-diffusion coefficients of atoms in halides, oxides, sulfides and other crystals have been measured by tracer methods, it is also possible to determine them from the kinetic data of diffusion-controlled solid-state reactions, such as the parabolic oxidation of metals and sintering reactions. This paper will deal with the determination of the self-diffusion coefficient of nickel atoms in nickel sulfide from the kinetic data of the sulfidation and desulfidation of nickel sulfide.

The Ni–S binary system has several phases: Ni_3S_2, $Ni_3S_{2+\delta}$, Ni_6S_5, $Ni_{1-\delta}S$, NiS_2 and so on. The stability region for these sulfides has been established by Rosenquvist,[1] Leine and Laffitte,[2] and by other investigators. According to the result of the previous investigators, nickel monosulfide is a metal-deficient compound and is expressed by the formula $Ni_{1-\delta}S$, where δ is the metal deficit, varying from 0 to 0.05. In the present study, the sulfidation and desulfidation of this sulfide in H_2S-H_2 mixtures were followed by the gravimetric method, and the self-diffusion coefficient of nickel atoms was determined.

In order to confirm the predominant migrating species in nickel sulfide, a marker study was also carried out. Nickel atoms were found to be the predominant migrating species.

Experimental

Marker Study. A high-purity nickel specimen, 10×30×0.1 mm, on both surfaces of which a slurry of fine Cr_2O_3 particles had been placed, was dried and then sulfidized in H_2S at 550°C until the nickel had been completely converted to nickel sulfide. The nickel is electrolytic Ni, 99.98% pure (impurities: 0.013% Co, 0.001% Cu, 0.002% C, 0.0003% S). After the sulfidation, the specimen was mounted in resin and sectioned in order to observe the location of Cr_2O_3

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[1] T. Rosenquvist, *J. Iron Steel Inst.*, **176**, 37 (1954).

[2] G. Leine and M. Laffitte, *Compt. Rend.*, **256**, 3306 (1963); M. Laffitte, *Bull. Soc. Chim. France*, **1959**, 1223.

markers. The positions of the markers were determined by means of a metallographic microscope and X-ray microanalyzer.

Kinetic Study of the Sulfidation and Desulfidation of Nickel Sulfide. Purification of Gases. Hydrogen sulfide gas, 99.9% pure, was supplied by the Suzuki Shokan Co. The gas was passed through a $Mg(ClO_4)_2$ column, and then a tube filled with porcelain pieces was heated at 500°C to convert the oxygen impurity into water vapor by the following reaction:

$$2H_2S + O_2 \longrightarrow 2H_2O + S_2$$

The gas was then dried again by passing it through a $Mg(ClO_4)_2$ column and stored in a bulb.

Hydrogen was passed through a $Mg(ClO_4)_2$ column on a Pd-asbestos catalyst in order to remove oxygen in the form of water vapor. The gas was then stored.

Apparatus. The apparatus used for the rate measurement of the sulfidation and desulfidation is shown in Fig. 1. A is a magnetic device used to raise and lower the specimen, suspended with the quartz fiber, and also to transfer them to and from the beam of the Gulbransen microbalance, C. H is the circulation pump for the gas, and G is a mercury manometer.

Specimens. The nickel sulfide specimens employed for the measurements of the sulfidation and desulfidation rates and for the determination of the metal deficit were prepared in the following manner. Nickel coupons, $10 \times 30 \times 0.1$ mm, were taken from a rolled sheet of highly-pure nickel, polished chemically with a mixture of nitric acid and sulfuric acid, and annealed in hydrogen (10 mmHg) for 4 hr at 550°C. A finished and weighed nickel specimen was then hung from a quartz spring balance and sulfidized in hydrogen sulfide (400 mmHg) for about 5 hr at 550°C. When the weight indicated the complete sulfidation of the nickel into nickel sulfide, the sulfidized specimen was quenched, annealed for a sufficient length of time in a H_2S-H_2 gas mixture of a desired composition in order to obtain a specific metal deficit of nickel sulfide, and weighed.

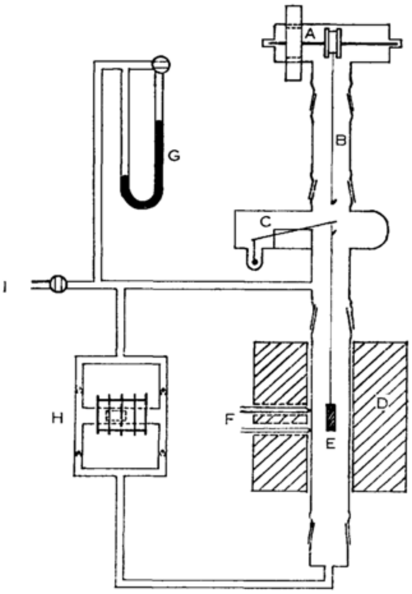

Fig. 1. Schematic diagram of apparatus.

From the weights before and after the sulfidation, the metal deficit of the nickel sulfide specimen was calculated. The thickness of the specimen was determined by means of a micrometer.

Experimental Procedure. A nickel sulfide specimen of a known composition was suspended from a chain by means of a fine quartz fiber, and the entire system was evacuated. Then a H_2S-H_2 gas mixture of a desired composition was introduced into the system and circulated by a circulation pump in order to keep its composition uniform. After the temperature of the furnace had attained the reaction temperature, the specimen was lowered to the heated zone, transferred, together with the quartz fiber, to the beam of the balance, and the weight change was followed by observing a marked point on the beam by means of a cathetometer. During the run the gas mixture was circulated except for those intervals when cathetometer readings were made. After the weight had reached the equilibrium value, the specimen and the quartz fiber were transferred to the chain and raised to the initial position, and the weight of the specimen was determined.

Results and Discussion

Marker Study. A section of a specimen completely converted to nickel sulfide is shown in Fig. 2. The markers are located at the center of the compact sulfide layer. It may be concluded from these results that the formation of nickel sulfide proceeded by means of the outward migration of nickel atoms. Since nickel sulfide is a metal-deficient compound, it is considered that nickel atoms migrate *via* nickel vacancies.

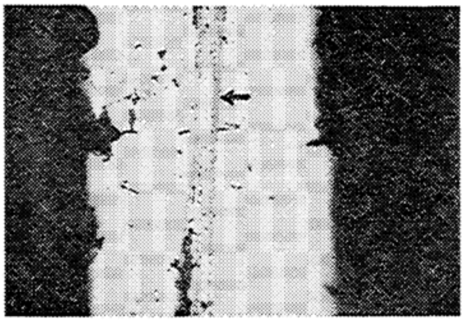

Fig. 2. Section of NiS. ← shows the Marker

Kinetic Study. Figure 3 shows some typcial weight change - time curves of sulfidation. In the figure, M_t is the weight change at the time t and M_∞ is the weight change after sufficient time has lapsed. When the total pressure of the gas mixture was changed while the other conditions, such as the thickness and the metal deficit of sulfide and the pressure ratio of H_2S to H_2, were kept constnat, the values of M_t/M_∞ obtained at a certain temperature lie on the same curve, which is only dependent on the temperature. This means that the reaction is controlled by the diffusion, because

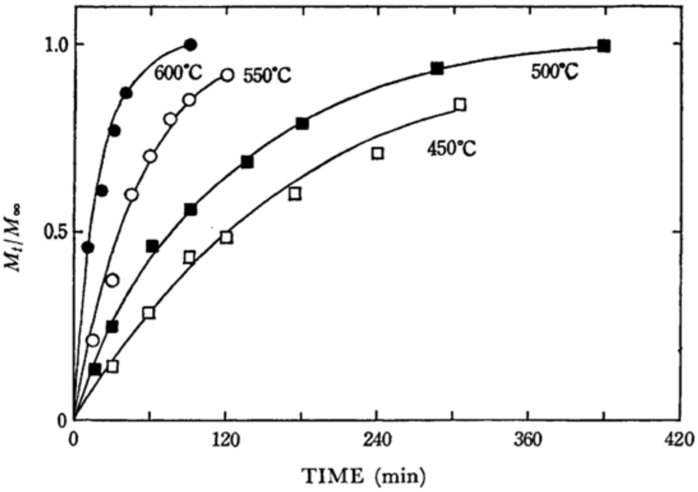

Fig. 3. Typical weight change time curves.
600°C=0.007 → 0.013 500°C=0.008 → 0.018

the rate of the diffusion-controlled reaction depends not on the total pressure but on the pressure ratio.

If a nickel sulfide slab is exposed to a H_2S-H_2 gas mixture which has sulfur with a higher activity than the sulfide, the specimen is sulfidized and the weight is increased. In this case sulfide atoms and nickel vacancies are introduced into sulfide at the gas-sulfide interface. Since nickel atoms migrate in nickel sulfide predominantly *via* nickel vacancies, as has been found in the marker experiment, nickel vacancies introduced at the gas-sulfide interface diffuse inwards. The rate equation for this process is:

$$\frac{\partial C_\square}{\partial t} = D_\square \frac{\partial^2 C_\square}{\partial x^2} \tag{1}$$

where $C_\square$ and $D_\square$ are the concentration and the self-diffusion coefficient of nickel vacancies respectively.

Solving the equation under the boundary conditions:

$$\left.\begin{aligned} C_\square &= C^\circ_\square \text{ for } -l < x < l \text{ and } t = 0 \\ C_\square &= C'_\square \text{ for } x = \pm l \text{ and } t > 0 \end{aligned}\right\} \tag{2}$$

one can obtain this equation:

$$\frac{C_\square - C^\circ_\square}{C'_\square - C^\circ_\square} = 1 - \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{(2n+1)} \times \exp\left\{\frac{-D_\square(2n+1)^2\pi^2 t}{4l^2}\right\} \times \cos\frac{(2n+1)\pi x}{2l} \tag{3}$$

where $C^\circ_\square$ is the vacancy concentration before the reaction, $C'_\square$ is the vacancy concentration at the gas-sulfide interface during the reaction, and $2\,l$ is the thickness of the sulfide slab. The replacement of the concentrations by M_t and M_∞ and integration with regard to x yields:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty}\frac{8}{(2n+1)^2\pi^2} \times \exp\left\{\frac{-D_\square(2n+1)^2\pi^2 t}{4l^2}\right\} \tag{4}$$

Omitting the higher terms of the series, one obtains:

$$-\ln\left(1 - \frac{M_t}{M_\infty}\right) = \frac{\pi D_\square t}{4l^2} \tag{5}$$

Figure 4 shows the plot of $-\log(1-M_t/M_\infty)$

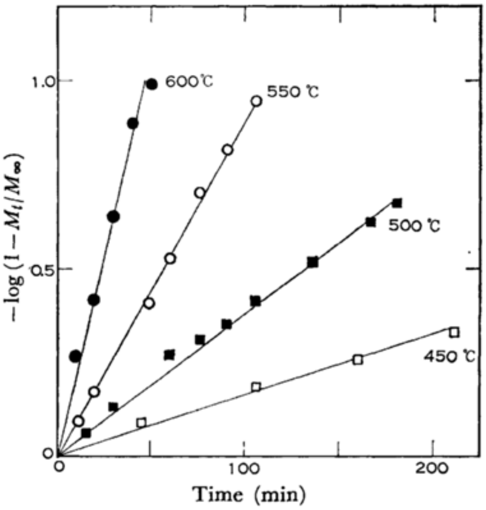

Fig. 4. Plot of $-\log\left(1-\dfrac{M_t}{M_\infty}\right)$ *vs.* time.

600°C=0.007 → 0.013
550°C=0.007 → 0.018
500°C=0.008 → 0.018
450°C=0.009 → 0.016

vs. *t*. A linear relationship is obvious. From the slope of the plot, $D_\square$, the self-diffusion coefficient of nickel vacancies is determined. When nickel atoms diffuse by the vacancy mechanism, the following relationship exists:

$$D_\square C_\square = DC \tag{6}$$

where D and C are the self-diffusion coefficient and the concentration of nickel atoms respectively, accordingly, D can be determined from $C_\square/C$ and $D_\square$.

Since $C_\square$ and C are related to the metal deficit, δ, by the following equation:

$$\delta = \frac{C_\square}{C_\square + C}$$

and since $C_\square$ is small enough to be neglected, we obtain:

$$\delta \doteqdot \frac{C_\square}{C}$$

The metal deficit determined gravimetrically is given in Fig. 5 as a plot of δ *vs*. $\log(P_{H_2S}/P_{H_2})$.

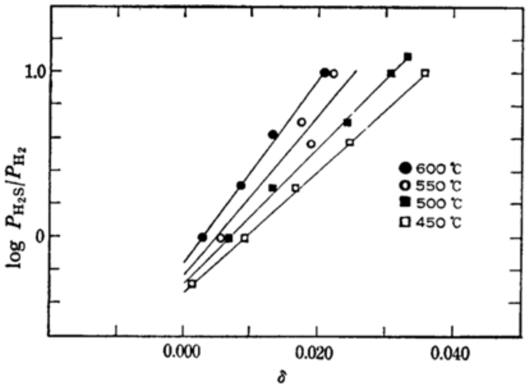

Fig. 5. Metal deficit of nickel sulfide as a function of temperature and P_{H_2S}/P_{2H}.

This result agrees well with the equilibrium data of Rosenquvist.[1] It can easily be seen that $C_\square/C$ ranges from 0 to 0.05. Assuming that $C_\square/C$ is the avarage of the initial and final values, we can obtain the D values by Eq. (6). These values are summarized in Table 1. Figure 6 shows the Arrhenius plot for the self-diffusion coefficient of nickel in nickel sulfide. The open circles indicate the data of this work. The present data are expressed by the equation:

TABLE 1

Temp °C	Change in δ	$C_\square/C$	$D_\square \times 10^7$ (cm^2/sec)	$D \times 10^9$ (cm^2/sec)
600	0.007→0.013	0.010	1.45	1.45
	0.013→0.008	0.011	1.61	1.69
550	0.018→0.005	0.012	0.470	0.541
	0.007→0.018	0.013	0.511	0.638
500	0.008→0.018	0.013	0.236	0.307
	0.018→0.008	0.013	0.241	0.313
450	0.009→0.016	0.013	0.0977	0.127

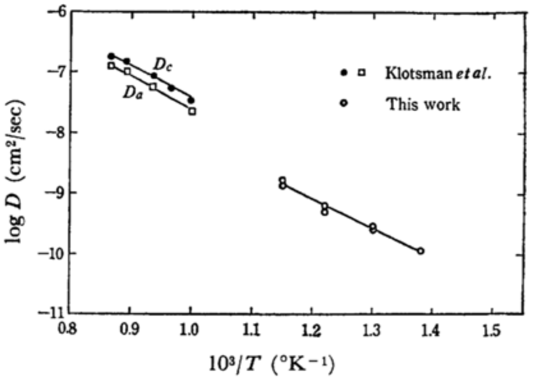

Fig. 6. Arrhenius plot of diffusion coefficient.

$$D = 3.2 \times 10^{-4} \exp\left(\frac{-21300}{RT}\right) cm^2/sec \tag{7}$$

For comparison, the data obtained by Klotsman and his collaborators,[3] who employed the tracer method, are indicated by closed circles and squares in the same figure. The diffusion coefficients obtained by Klotsman and his collaborators are about three times higher than those extrapolated from the present data. They used nickel sulfide with a metal deficit of 0.03, while in the present work a deficit of 0.010—0.013 was employed. Since the diffusion coefficient is proportional to the vacancy concentration, the difference in diffusion data must be due to the difference in vacancy concentration of the sulfide employed in the experiments.

Summary

(1) The diffusivity of nickel was found, by means of a marker experiment on the sulfidation of nickel, to be much higher than that of sulfur.

(2) The rates of the sulfidation and desulfidation of nickel sulfide in H_2S-H_2 atmospheres were determined gravimetrically, and the diffusion coefficients of nickel vacancies were calculated.

(3) The metal deficit of nickel sulfide was determined as a function of the partial pressure ratio of H_2S to H_2 and of the temperature.

(4) From the concentrations and diffusion coefficients of nickel vacancies, the self-diffusion coefficients of nickel atoms were obtained.

The values agreed well with those determined by previous investigations employing the tracer technique.

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3) S. M. Klotsman, A. M. Timofeyev and I. Sh. Trakhtenberg, *Physics of Metals and Metallography*, **16**, 92 (1963).