Research Paper

Sulfurization of Mn by H_2S and $\text{H}_2\text{S-H}_2$ Gas Mixture

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The sulfurization of Mn metal has been studied in H_2S and $\text{H}_2\text{S-H}_2$ gas mixtures at 550°C to 711°C . It was found that the sulfurization obeys the parabolic law and that the parabolic rate constant is proportional to $(P_{\text{H}_2\text{S}}/P_{\text{H}_2})^{1/2}$. It was also found that the activation energy at constant pressure ratios of H_2S to H_2 is from 24.3 to 26.4 kcal/mol.

From the results of the present study and of a previous work, the rate determining step is concluded to be the diffusion of Mn ions via cation vacancies.

1 Introduction

The high temperature oxidation of metals consists of three elementary processes; the reaction at the metal oxide interface, the diffusion of chemical species across the oxide layer and the reaction at the gas-oxide interface. When the diffusion is rate controlling, the parabolic rate law is obeyed. When either one of two interface reactions is rate controlling, the oxidation obeys the linear rate law. In most cases, the rate determining step is the diffusion and the parabolic rate law is observed.

Although many studies on the oxidation have been carried out and the reaction kinetics has been well established, only a few studies have been made on the sulfurization of metals. Recently, the sulfurizations of metallic materials have become a serious problem in the fields, such as the petroleum refining industry. The purpose of the present study is to obtain the kinetic data of sulfurization of Mn metal and to elucidate the mechanism of sulfurization of the metal.

2 Experimental

2.1 Sample

Electrolytic Mn flake of 99.9% purity was used as sample, since Mn is difficult to be fabricated into sheet or plate. The flake was ground with No. 400 and No. 1,000 emery papers and polished with $0.3\ \mu$ alumina polishing powder. After that the sample was washed with soap, rinsed in alcohol and dried. The surface area was about 1.5 cm^2 , the thickness about 0.7 mm, and the weight about 300 mg.

2.2 Purification of gases

H_2S gas of 99.9% purity was passed through a $\text{Mg}(\text{ClO}_4)_2$ column to remove moisture and then

through a column which was filled with porcelain pieces and heated at $500\sim 600^\circ\text{C}$ to convert O_2 in the gas into H_2O by the reaction, $2\text{H}_2\text{S} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{S}$. Then, the water vapor formed was removed with $\text{Mg}(\text{ClO}_4)_2$ drying agent. H_2 was passed through a palladium asbestos column heated at 500°C to convert O_2 into H_2O , which was removed by $\text{Mg}(\text{ClO}_4)_2$ drying agent.

2.3 Apparatus and experimental procedure

C, D : $\text{Mg}(\text{ClO}_4)_2$ column, F : Electric furnace
Q : Palladium asbestos column
R : Porcelain pieces column, K : Gas reservoir
L : Gas reservoir for mixing, M : Mercury manometer
P : Electromagnetic piston pump
A : Magnetic clutch device
G : Gulbransen microbalance, S : Silica fibre
B : Silica basket, V : Reaction vessel

Fig. 1 Apparatus for the study of the kinetics of sulfurization

Fig. 1 shows the schematic drawing of apparatus. Desired amounts of H_2S and H_2 were taken into two bulbs separately and then both gases were mixed by means of a magnetic piston pump for 30 minutes.

A finished Mn flake was placed in a small silica basket and suspended from a hook with a fine silica fibre. Then, the reaction system was evacuated to the pressure of 10^{-2} mmHg by a rotary pump, and the H_2S - H_2 gas mixture was introduced. After the furnace was heated to the reaction temperature, the basket and the silica fibre were lowered and transferred to the beam of Gulbransen microbalance by means of a magnetic clutch device, and weight changes due to the sulfurization were followed by means of a cathetometer. The temperature of the furnace was controlled within $\pm 1^\circ\text{C}$ by means of a Ohkura EC-51 electronic controller during the run.

3 Results and Discussion

3.1 Sulfurization of Mn by H_2S

The sulfide formed on Mn was identified a α -MnS by the X-ray diffraction method. Fig. 2 is the sulfurization curves of Mn in pure H_2S at temperatures of 500, 549, 597, 647 and 709°C , and Fig. 3 is the parabolic plot. Clearly, the sulfurization of Mn by pure H_2S gas obeys the parabolic law in a temperature range 500 to 709°C except for the initial period of sulfurization. From these results, it is concluded that the rate determining step of the sulfurization of Mn by pure H_2S is the diffusion process in the sulfide.

Fig. 2 Sulfurization curves of Mn by pure H_2S gas

Fig. 3 Parabolic plot for the sulfurization of Mn by pure H_2S gas

3.2 Sulfurization by H_2S - H_2 gas mixtures

Fig. 4 shows the parabolic plot of sulfurization by H_2S - H_2 gas mixtures at 711°C . The pressure ratio $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ was changed from 0.1 to 10, while the total

Fig. 4 Parabolic plot of the sulfurization by H_2S - H_2 gas mixtures

pressure was kept at 76 ± 3 mmHg. As in the case of the sulfurization by pure H_2S , the reaction obeyed the parabolic law except for the initial period. The difference in reaction rate in the initial period is probably due to the surface condition of sample. The parabolic rate constants were determined from the data in the later period.

Let us define the pressure ratio of $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$ as the sulfur activity and denote a_s . As shown in Fig. 5, the parabolic rate constant k_p is proportional to $(a_s)^{1/n}$, where n is 3.4 at 711°C , 3.1 at 647°C and 3.0 at 597 and 549°C , respectively. This fact shows that α -MnS formed on Mn metal in the H_2S - H_2 atmosphere is a metal deficit p -type semiconductor.

○ : 711°C , △ : 647°C , □ : 597°C , ▲ : 549°C
Fig. 5 Relation between k_p and $P_{\text{H}_2\text{S}}/P_{\text{H}_2}$

According to a previous work¹⁾, the defects in α -MnS are considered to be formed as follows,

where $\text{Mn}\square^{\bullet}$ is Mn vacancies and Mn^{3+} denotes 3d holes localized on cation sites. The mass action law for reaction (1) is

$$K_1 = \frac{P_{\text{H}_2}[\text{Mn}\square^{\bullet}][\text{Mn}^{3+}]^2}{P_{\text{H}_2\text{S}}} \quad (2)$$

If $\text{Mn}\square^{\bullet}$ and Mn^{3+} are formed predominantly by reaction (1), the charge neutrality condition is

$$[\text{Mn}\square^{\bullet}] = 2[\text{Mn}^{3+}] \quad (3)$$

Insertion of Eq. (3) to Eq. (2) yields the following equation

$$[\text{Mn}\square^{\bullet}] = \left(\frac{K_1}{4} \right)^{1/3} \left(\frac{P_{\text{H}_2\text{S}}}{P_{\text{H}_2}} \right)^{1/3} = K_2 a_s^{1/3} \quad (4)$$

According to Wagner²⁾, the rational rate constant k_r , which is proportional to k_p , is expressed in terms of the self-diffusion coefficients of cations and anions and the activity of nonmetallic component. Namely,

$$k_r = Ceq \int_{a_s'}^{a_s''} \left(\frac{Z_1}{Z_2} D_1 + D_2 \right) d \ln a_x \quad (5)$$

where D_1 and D_2 are the self-diffusion coefficients of cations and anions, respectively, Z_1 and Z_2 are units of charge on cations and anions, respectively, a_x is the activity of nonmetallic element X, and Ceq is the equivalent concentration of ions. a_x'' is the activity of nonmetallic element X at the gas-scale interface and a_x' is the activity at the scale-metal interface. Since α -MnS is a metal-deficit p -type semiconductor, the diffusion of Mn ions is considered to be more rapid than S ions. Accordingly, the diffusion coefficient D_2 in Eq. (5) can be omitted. Putting $Z_{\text{Mn}} = |Z_{\text{S}}| = 2$, we obtain

$$k_r = Ceq \int_{a_s'}^{a_s''} D_{\text{Mn}} d \ln a_s \quad (6)$$

D_{Mn} is proportional to Mn vacancy concentration, therefore,

$$D_{\text{Mn}} = k_1 [\text{Mn}\square^{\bullet}] = k_2 a_s^{1/3} \quad (7)$$

From Eqs. (6) and (7) the following equation is derived.

$$k_r = k_3 (a_s'^{1/3} - a_s''^{1/3}) \quad (8)$$

Since a_s' is much smaller than a_s'' , the former can be neglected. Accordingly, the rational rate constant is expressed as follows.

$$k_r = k_3 a_s'^{1/3} \quad (9)$$

Thus, the observed dependence of k_p on the sulfur activity is well explained on the basis of the formation of defects by Eq. (1). The Arrhenius plot for parabolic rate constants in various atmospheres are given in Fig. 6. The activation energies determined from the slopes are summarized in Table 1.

■ : Pure H_2S
○ : $P_{\text{H}_2\text{S}}/P_{\text{H}_2} = 10$, △ : 2, □ : 1, ▲ : 0.5, ● : 0.1
Fig. 6 Arrhenius plot for k_p

Table 1 Activation energies

P_{H_2S}/P_{H_2}	E_A [kcal/mol]
Pure H_2S	25.3 ± 1.0
10	24.3 ± 1.0
2	24.9 ± 1.1
1	25.8 ± 0.8
0.5	26.4 ± 0.8
0.1	26.0 ± 3.0
mean	25.5 ± 0.7

3.3 Calculation of the self-diffusion coefficient of Mn ions

The self-diffusion coefficient can be calculated from k_r by a method devised by Fueki and Wagner³⁾. According to the method,

$$\frac{d k_r}{d \ln a_s} = Ceq \frac{Z_{Mn}}{|Z_S|} D_{Mn} \quad (10)$$

k_r is related to k_p as follows

$$k_r = \left(\frac{M_{MnS}}{M_S^2 d} \right) k_p \quad (11)$$

where M_{MnS} and M_S are molecular weights of α -MnS and S, respectively and d is the density of α -MnS. The concentration Ceq is expressed as follows

$$Ceq = \frac{2d}{M_{MnS}} \quad (12)$$

As mentioned above, k_p is expressed as a function of a_s as follows

$$k_p = k_0 (a_s'')^{1/3} \quad (13)$$

Insertion of Eqs. (11), (12) and (13) into (10) gives

$$D_{Mn} = \frac{k_0}{6} \left(\frac{M_{MnS}}{M_S \cdot d} \right)^2 (a_s'')^{1/3} \quad (14)$$

Using the following values,

$M_{MnS} = 87.01$, $M_S = 32.07$, $d = 4.06$ g/cm³
we obtain the value of D_{Mn} shown in Table 2.

Table 2 Diffusion coefficients of Mn
in α -MnS
 $D_{Mn} \times 10^{12}$ (cm²/sec)

P_{H_2S}/P_{H_2}	0.1	0.5	1	2	10
Temp.					
711°C	11	19	24	30	51
647	4.5	7.7	9.7	12	21
597	1.9	3.3	4.2	5.2	9.0
549	0.9	1.6	2.0	2.5	4.3

3.4 The diffusion coefficient of Mn vacancies

in α -MnS

Fueki and others¹⁾ have obtained the ratio of concentrations of Mn vacancies to Mn ions, $C_{\square}/C_{Mn}$, by the measurement of thermoelectric power. The values of $C_{\square}/C_{Mn}$ were 3.6×10^{-4} at 711°C, and 2.7×10^{-4} at 647°C respectively. When Mn ions diffuse by the vacancy mechanism, the following equation exists

$$D_{\square} C_{\square} = D_{Mn} C_{Mn} \quad (15)$$

where $D_{\square}$ is the diffusion coefficient of Mn vacancies. Accordingly

$$\frac{C_{\square}}{C_{Mn}} = \frac{D_{Mn}}{D_{\square}} \quad (16)$$

From the data of D_{Mn} and $C_{\square}/C_{Mn}$, $D_{\square}$ in α -MnS is calculated as 7×10^{-8} cm²/sec at 711°C and 4×10^{-8} cm²/sec at 647°C, respectively.

4 Summary

(1) The sulfide scale formed on the surface of Mn metal was found to be α -MnS by the X-ray diffraction method.

(2) The sulfurization of Mn by H_2S and H_2S - H_2 gas mixtures at 500~711°C was found to obey the parabolic law.

(3) The parabolic rate constant was proportional to the third root of the sulfur activity.

(4) The activation energies were found to range from 24.3 to 26.4 kcal/mol.

(5) The rate determining step of the sulfurization is concluded to be the diffusion of Mn ions via vacancies.

(6) The self-diffusion coefficient of Mn ions in α -MnS was calculated from the parabolic rate constant.

(7) The diffusion coefficient of Mn vacancies was found to be 7×10^{-8} cm²/sec and 4×10^{-8} cm²/sec at 711°C and 647°C respectively.

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References:

- 1) K. Fueki, Y. Oguri, T. Mukaibo, *This Journal* **38**, 758 (1970).
- 2) C. Wagner "Diffusion and High Temperature Oxidation of Metals" in Atom Morement, *Amer. Soc. Metals*, p. 153 (1951) Cleveland.
- 3) K. Fueki, J.B. Wagner, *J. Electrochem. Soc.* **112**, 384 (1965).