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Kinetic Study on the Sulfidation of Copper by Hydrogen Sulfide

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The sulfidation of copper by hydrogen sulfide was studied kinetically in a temperature range of 400 to 500°C.

It was found that the sulfidation obeyed the so-called linear law and that the linear rate constant was proportional to the partial pressure of hydrogen sulfide. It was also found that the sulfidation rate was independent of the partial pressure of hydrogen. The activation energy was 21.3 kcal/mol.

Microscopic observation on the cross section and the surface of sulfide film revealed that the sulfide film is singly layered and compact.

X-ray diffraction study showed the sulfide to be cuprous sulfide.

From these results, it is concluded that the sulfidation is controlled by the reaction at the sulfide-gas interface.

On the basis of the theory and experiment by Kobayashi and Wagner, the independence of sulfidation rate on partial pressure of hydrogen is also discussed.

1. Introduction

The tarnishing of metals consists of three elementary processes; the diffusion of reactants across the product layer, and the boundary reactions at the metal-product and gas-product interfaces. If the diffusion is rate controlling, the so-called parabolic law is observed, while the linear law is obeyed if either one of two boundary reactions is rate controlling.

Although many studies have been made on the diffusion-controlled tarnishing and its kinetics has been well established, the linear kinetics has not been well elucidated, because only a few studies have been made so far. In order to contribute to the elucidation of the linear kinetics, the authors have carried out a series of studies on the sulfidation of metals by H_2S - H_2 gas mixtures. This paper reports the linear kinetics of copper sulfidation in H_2S - H_2 atmospheres.

As to the studies made so far on the sulfidation of copper in H_2S - H_2 atmospheres, an investigation has been made below 224°C by Dravenieks and Neymark¹⁾, who found the reaction obeyed the following rate equation

$$\frac{dw}{dt} = A \cdot t^B \quad (1)$$

where w is the weight gain per unit area, t is time, and A and B are constants. Eq.(1) means that the reaction at such low temperatures is governed by the nucleation and nuclear growth of sulfide on the copper surface. Other studies have been carried out by Gurgey²⁾, and Backland and Backland³⁾. Their studies were made to obtain the practical corrosion data rather than to aim at the elucidation of reaction mechanism.

In the present work, investigation was carried out in a temperature range where the linear law was observed.

2. Experimental

a) Specimens and Surface Treatment

Copper coupons, 2cm long and 1cm wide, were taken from a sheet of copper, 0.1mm thick and 99.99% pure, polished with No. 1000 emery papers washed with soap, water and alcohol, and dried in a dessiccator.

Fig. 1 Apparatus for the rate measurement.

b) Apparatus

The apparatus used for the rate measurement was shown in Fig. 1. The reaction rate was measured, using a quartz spring balance A, the sensitivity of which was 77.0mg/div. The temperature of electric furnace E was kept constant within $\pm 1^\circ\text{C}$ by means of a Chromel-Alumel thermocouple and a controller. The measurement of the temperature was made by a pyrometer of potentiometer type.

Hydrogen sulfide was purified by passing it through a tube filled with small porcelain pieces heated at 450°C and a tube filled with magnesium perchlorate. Impurity oxygen in hydrogen was converted into water vapor by Pd-asbestos catalysis kept at 200°C, and the water vapor thus formed was removed with silica-gel and magnesium perchlorate. Purified gases were stored in storage bulbs.

c) Experimental Procedure

A finished and weighed specimen was suspended from the spring balance with a fine quartz fibre and the entire system was evacuated. Then, hydrogen gas of 15mm Hg was introduced.

The temperature of the furnace was raised to 500°C and kept at the temperature for one hour to remove any surface oxide and strain. After the temperature was kept at a desired value and the entire system was evacuated again, the reactant gas was introduced, and weight changes were followed by means of micrometer microscope. After the run was over, the sulfidized specimen was taken out and weighed.

Fig. 2 Weight gain-time curves at various temperature, $P_{H_2S} = 40\text{mmHg}$

Fig. 3 Dependence of k_L on P_{H_2S} .

Table 1. Pressure dependence of the sulfidation rate on H_2 pressure, at 450°C, $P_{H_2S} = 40\text{ mm Hg}$

P_{H_2} (mm Hg)	$k_L \times 10^5$ (g/cm ² ·min)
20	2.06
40	2.02
80	1.99
120	1.84

3. Results

Typical weight gain-time curves are given in Fig. 2. It is evident from this figure that the sulfidation obeys the linear law. From the slope of the curves, the linear rate constants k_L were determined. Fig. 3 shows the plot of k_L vs. P_{H_2S} , the partial pressure of hydrogen sulfide. A good linear relationship is seen between k_L and P_{H_2S} . To examine the dependence of reaction rate on the partial pressure of

hydrogen, rate measurements were carried out at different H_2 pressures at a fixed H_2S pressure of 40mmHg. Results are given in Table 1, which indicates that the pressure of H_2 has little effect on the sulfidation rate.

From the results mentioned above, it is concluded that the sulfidation of copper obeys the linear law and that the rate is expressed by the equation

$$k_L = k_L^\circ \cdot P_{H_2S} \quad (2)$$

Fig. 4 Temperature dependence of k_L .

The temperature dependence of k_L is shown in Fig. 4. The activation energy was determined to be 21.3 kcal/mol.

The sulfide formed on copper was examined in situ by the microscopic and X-ray diffraction methods. Microscopic observation on the surface and cross-section of sulfide film revealed that the sulfide was singly layered and compact, as shown in Fig. 5. X-ray diffraction study on the sulfide quenched to the

room temperature as rapidly as possible, showed that the sulfide was $Cu_{2,000}S$ which was said to be cuprous sulfide in equilibrium with copper.

Fig. 5 Cross-section of sulfidized copper specimen

4. Discussion

The sulfidation of copper by hydrogen sulfide is considered to proceed by the following steps.

i) Adsorption of hydrogen sulfide on the Cu_2S surface

ii) Dissociation of adsorbed hydrogen sulfide

where $\oplus$ represents positive hole in cuprous sulfide. Formation of S^{2-} ion at the gas-sulfide interface results in the depletion of cuprous ions.

iii) Inward diffusion of positive holes and outward diffusion of cuprous ions.

iv) Formation of cuprous ions and annihilation of positive holes at the metal-

sulfide interface.

Since Eq.(2) holds for the present case, Step (i) or (ii) is considered to be rate controlling. Since the dissociation is more difficult to occur than the adsorption, Step (ii) would be rate determining. From the proportional relationship between k_L and $P_{\text{H}_2\text{S}}$, it is considered that the adsorption of hydrogen sulfide on cuprous sulfide is weak.

As to the independence of reaction rate on the partial pressure of hydrogen, the following explanation would be given. According to the theory and experiment by Kobayashi and Wagner⁴⁾, the reduction rate, k_r , of cuprous sulfide by hydrogen is expressed by the equation

$$k_r = k' P_{\text{H}_2} - k P_{\text{H}_2\text{S}} a_{\text{S}}^{-1} \quad (3)$$

where a_{S} is the activity of sulfur at the sulfide-gas interface. Accordingly, the sulfidation rate, k_s , should be

$$k_s = k P_{\text{H}_2\text{S}} a_{\text{S}}^{-1} - k' P_{\text{H}_2} \quad (4)$$

Fig. 6 Schematic representation of the activity of sulfur in a case where the reaction at the sulfide-gas interface is rate determining.

When the sulfidation of copper is controlled by the reaction at the sulfide-gas interface, the activity of sulfur is considered to drop appreciably at the interface, as shown in Fig. 6. That is,

the composition of growing sulfide is considered to be that in coexistence with copper. This was confirmed by the X-ray diffraction study on the quenched specimen. The activity of sulfur, $(a_{\text{S}})_{\text{eq}}$, where cuprous sulfide coexists with copper, is obtained by equating k_s to zero.

$$(a_{\text{S}})_{\text{eq}} = \frac{k}{k'} \left(\frac{P_{\text{H}_2\text{S}}}{P_{\text{H}_2}} \right)_{\text{eq}} \quad (5)$$

where $(P_{\text{H}_2\text{S}}/P_{\text{H}_2})_{\text{eq}}$ represents the pressure ratio in a case where cuprous sulfide coexists with copper. Insertion of Eq.(5) into Eq.(4) yields

$$k_s = \frac{k'}{\left(\frac{P_{\text{H}_2\text{S}}}{P_{\text{H}_2}} \right)_{\text{eq}}} \cdot P_{\text{H}_2\text{S}} - k' P_{\text{H}_2} \quad (6)$$

since, the value of $(P_{\text{H}_2\text{S}}/P_{\text{H}_2})_{\text{eq}}$ is about 10^{-4} , the first term is about 10^4 larger than the second term. Therefore, the sulfidation rate of copper is nearly independent of P_{H_2} over a pressure range of the present work.

Summary

- (1) The sulfidation of copper by hydrogen sulfide was studied kinetically in a range of 400 to 550°C.
- (2) It was found that the sulfidation obeyed the linear law and that the rate constant was proportional to the partial pressure of hydrogen sulfide.
- (3) Independence of sulfidation rate on partial pressure of hydrogen was observed.
- (4) The activation energy was 21.3 kcal/mol.
- (5) The sulfide film formed on copper was found to consist of cuprous sulfide of composition $\text{Cu}_{2.000}\text{S}$.
- (6) The mechanism of sulfidation was discussed.

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Potentiodynamic Oxidation of Iron in Neutral Solution.*

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The dynamic characteristics of the anodic oxidation processes of iron, including film growth and oxygen evolution, were investigated by application of a potential sweep at various constant rates to passivated iron in a boric acid-borate neutral solution. The film growth begins as a fast process followed by a slow steady growth, with the initial fast process taking place in two successive steps. It is found that the oxygen evolution always succeeds the oxide film growth.

A three dimensional diagram (E -log i - ΔQ) is presented according to the rate equation $i = k \exp(\beta E - \Delta Q/B)$ to show the transitions from the initial stages of the film growth to the steady thickening of the film and from the film growth to the oxygen evolution. Dependence upon kinetic constants B and β of the potential sweep rate is represented as a spectrum in reaction rate for the anodic oxidation of iron, demonstrating that, if the rate of potential sweep is chosen properly, one can measure the initial stages, the steady film growth and the oxygen evolution separately.

1. Introduction

Anodic oxidation reactions of passivated iron in neutral solution are complex and consist of oxide film formation and

oxygen evolution. In a previous paper¹⁾ Sato and Cohen have studied the oxide film growth on iron in neutral solution using the potentiostatic and galvanostatic oxidation techniques and presented the following rate equations for the initial stages of the film thickening

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