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Solubility and Diffusion Coefficient of Sulfur in Silver

Kazuo Fueki, Kenichiro Ota,* and Kohji Kishio

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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Synopsis. The solubility N_s and the diffusion coefficient D of sulfur in silver were determined at 604—752 °C by means of a previously proposed method.[1] The results can be represented by the following equations:

$$\log N_s(\text{atom fraction}) = -0.818 - \frac{2.28\times 10^3}{T},$$

$$D = 2.34 \times 10^{-3} \exp\left(-\frac{26300}{RT}\right) \text{ cm}^2 \text{ s}^{-1}.$$

In the high temperature oxidation of alloys, the rate is significantly affected by the formation of an internal oxidation layer. Since this internal oxidation is caused by the diffusion of oxygen atoms into the alloy from the metal-oxide interface and the formation of dispersed particles of the less noble constituent, the knowledge of the solubility and the diffusion coefficient of oxygen in the alloy are necessary in order to analyze the oxidation rate of alloys.

Similarly, the solubility and the diffusion coefficient of sulfur in metals must be known to study the sulfidation of alloys. The solubility of sulfur can be determined by the combustion method and the vacuum fusion method. The solubility and diffusion coefficient can be measured by means of the tracer method, X-ray diffraction method, and the electrochemical method using solid electrolytes. However, these methods are rather complicated.

Fueki and Ouchi have studied the solubility and the diffusion coefficient of sulfur in copper by a new method wherein a thin cuprous sulfide film was formed on copper specimens and the decrement of the film after diffusion annealing was determined by the coulometric method.[1] In the present study the solubility and the diffusion coefficient of sulfur in silver were determined by the method proposed by Fueki and Ouchi and compared with data obtained by other methods.

Experimental

The experimental method employed was similar to that of the study on the solubility and diffusion of sulfur in copper.[1] Rectangular silver specimens, 15 mm × 6 mm in area and 0.015—0.02 mm in thickness, were used. The result of the chemical analysis of silver is given in Table 1. The specimens were polished with alumina polishing powder, rinsed in alcohol, and dried in a desiccator. The surface of the specimen was anodized in a 2 g/l-Na_2S solution at a current density of 10^{-1} mA/cm^2 to form a thin sulfide film. The surface film thickness was determined by means of the coulometric method.

Table 1. Results of chemical analysis

Impurity	Content (wt %)
Cu	0.060
Si	0.0039
Fe	0.00062

The silver specimen covered with silver sulfide was placed in a Vycor tube, which was then evacuated to 10^{-4} Torr and sealed. The sealed tube was placed in an electric furnace kept at the desired annealing temperature (within ±2 °C). After a length of time the tube was taken out from the furnace and the thickness of the remaining sulfide film was determined coulometrically. The specimen was immersed in a 0.1M-KCl solution and the surface sulfide was reduced cathodically at a constant current density of 10^{-1} mA/cm^2. From the reflection point of the potential-time curve, the electric charge necessary for the reduction of sulfide was calculated.

During annealing, the silver sulfide on the surface decomposes into sulfur and silver and the sulfur diffuses into silver; thus

$$Ag_2S(\text{film}) = 2Ag + S(\text{in Ag}). \tag{1}$$

The amount of sulfur $\bar{N}_t$ (atom fraction) in silver after annealing was calculated from the difference between the initial and final amounts of sulfide film. The solubility of sulfur N_s was obtained from the saturation value of the $\bar{N}_t$-t plot.

When a silver specimen is covered with a thin sulfide film and sulfur is allowed to diffuse from both surfaces of the specimen, the diffusion is expressed by the following equation:[1]

$$\log\frac{N_s-\bar{N}_t}{N_s} = \log\left(\frac{8}{\pi^2}\right) - \frac{\pi^2 D}{2.303}\left(\frac{t}{l^2}\right), \tag{2}$$

where l is the thickness of the specimen and D is the diffusion coefficient of sulfur in silver. Therefore, the diffusion coefficient can be determined from the slope of the plot of log $\{(N_s-\bar{N}_t)/N_s\}$ against t/l^2.

Results and Discussion

Figure 1 shows the amount of sulfur in silver $\bar{N}_t$ plotted against t/l^2 and Fig. 2 gives the Arrhenius plots for N_s. The data obtained by the previous investigators are also plotted in the same figure. Barbouth *et al.* used the radio isotope ^{35}S to measure the solubility.[2] Raub

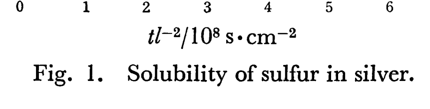

Fig. 1. Solubility of sulfur in silver.

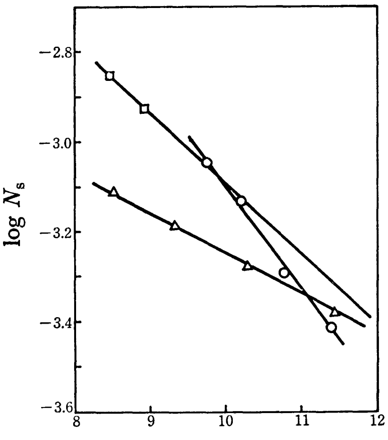

Fig. 2. Arrhenius plot of solubility of sulfur in silver. ○ This work, △ Barbouth,[2] □ Raub.[3]

measured the sulfide formation temperature during the cooling of a silver–sulfur solution and determined the solubility.[3] The data of the present work agree well with the other two. The solubility of the present work is represented by the following equation:

$$\log N_\mathrm{s} = -0.818 - 2.28 \times 10^3\left(\frac{1}{T}\right). \tag{3}$$

From Eq. 3 the enthalpy and entropy change for the dissolution of sulfur in silver were calculated. They are as follows:

$$\Delta H^\circ = 10.4\,\mathrm{kcal/mol}$$
$$\Delta S^\circ = -3.74\,\mathrm{cal/mol{\cdot}deg}.$$

Figure 3 shows the relation between $\log\{(N_\mathrm{s}-N_t)/N\}$ and t/l^2. The diffusion coefficient D of sulfur was determined from the slope of the plot. Figure 4 shows the Arrhenius plot of D. For comparison, Barbouth's results obtained by the tracer method[4] and Wang's results obtained by means of the relaxation method[5] are shown in the same figure. These results agree with each other. The Arrhenius equation for the present work is

$$D = 2.34 \times 10^{-3}\exp\left(-\frac{26300}{RT}\right)\,\mathrm{cm^2\,s^{-1}}, \tag{4}$$

where R is the gas constant (cal/mol·deg).

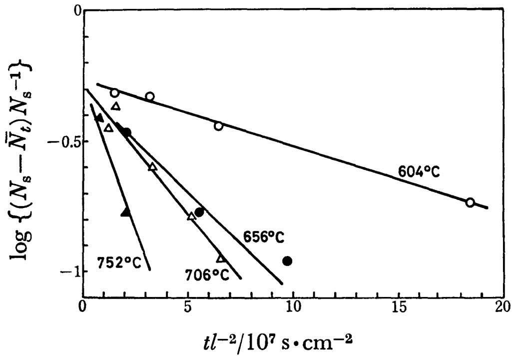

Fig. 3. Relation between $(N_\mathrm{s}-\bar{N}_t)/N_\mathrm{s}$ and t/l^2.

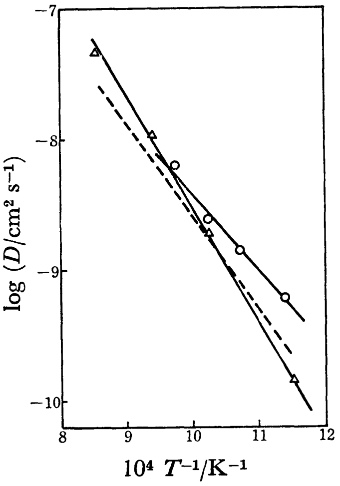

Fig. 4. Arrhenius plot of diffusion coefficient. ○ This work, △ Barbouth,[4] ---- Wang.[5]

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