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Solubility and Diffusion Coefficient of Sulfur in Copper

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The solubility and diffusion coefficient of sulfur in copper were determined by a new method, wherein a thin copper(I) sulfide film was formed on the surface of a copper specimen and the decrement of its thickness after diffusion annealing was determined coulometrically. It was found that the solubility C_s could be represented by

$$\log C_s\ (\text{ppm}) = -0.616 - 0.410\ (10^4/T),$$

and the diffusion coefficient is given by

$$D = 0.834 \times \exp\ (-40900/RT)\ \text{cm}^2\ \text{s}^{-1}.$$

When a binary alloy is oxidized in an oxygen atmosphere, oxygen diffuses into the alloy and forms dispersed oxide particles with the less noble component. This phenomenon, called internal oxidation, has a significant effect on the oxidation rate of the alloy. Therefore, the solubility and diffusion coefficient of oxygen in the metal are most important for the elucidation of internal oxidation. Similarly, the solubility and diffusion coefficient of sulfur in metals are necessary in order to elucidate the mechanism and rate of alloy sulfidation.

The concentration of non-metallic elements in metals is usually determined by the vacuum fusion method, and in some cases by the combustion method or the tracer method. If physical properties such as resistivity and hardness are known as a function of the concentration of non-metallic elements, the solubility can be determined from the break point in the slope of the plot of physical quantity against concentration.

The diffusion coefficient of non-metallic elements is usually determined by the tracer method. In some cases, it is determined by the chemical relaxation method, which utilizes the change of physical property with time after the step-like change of ambient conditions.

The purpose of the present work is to determine the solubility and diffusion coefficient of sulfur in copper by a new method, wherein a thin copper(I) sulfide film is formed on the surface of high purity copper specimen and the decrement of the surface film after the diffusion annealing is determined by the coulometric method.

Theoretical

When a copper specimen covered with a thin copper(I) sulfide film on its surface is annealed *in vacuo* at a high temperature the copper(I) sulfide decomposes into sulfur and copper by the reaction

$$Cu_2S = 2Cu + S(\text{in Cu}), \tag{1}$$

and the sulfur diffuses inwards. If the concentration of sulfur is represented by $C(x,t)$, its differential with respect to time can be given by

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}, \tag{2}$$

where D is the diffusion coefficient. Solving the differential equation with the boundary conditions

$$C(0,t) = C_s, \tag{3}$$

$$C(l,t) = C_s, \tag{4}$$

and

$$C(x,0) = 0 \quad \text{for } 0 < x < l, \tag{5}$$

one obtains[1)]

$$C = C_s - \frac{4C_s}{\pi}\sum_{j=0}^{\infty}\frac{1}{2j+1}\sin\frac{(2j+1)\pi}{l} \times \exp\left[-\left(\frac{(2j+1)\pi}{l}\right)^2 Dt\right], \tag{6}$$

where C_s is the solubility and j is an integer. The mean concentration $\bar{C}(t)$ is

$$\bar{C}(t) = \frac{1}{l}\int_0^l C(x,t)\mathrm{d}x = C_s - \frac{8C_s}{\pi^2}\sum_{j=0}^{\infty}\frac{1}{(2j+1)^2}\exp\left[-\left(\frac{(2j+1)\pi}{l}\right)^2 Dt\right]. \tag{7}$$

In the present study, $\bar{C}(t)$ is determined by the difference in sulfide film thickness between time zero and time t. For $\bar{C} \geq 0.2C_s$ the first term of the series is an excellent approximation. Therefore, Eq. 7 can be simplified to

$$\bar{C} = C_s - \frac{8C_s}{\pi^2}\exp\left(\frac{-\pi^2 Dt}{l^2}\right). \tag{8}$$

Accordingly, from the saturation value of the $\bar{C}$-t/l^2 curve, the solubility C_s is determined. Equation 8 is rewritten into

$$\frac{C_s - \bar{C}}{C_s} = \frac{8}{\pi^2}\exp\left(-\frac{\pi^2 Dt}{l^2}\right). \tag{9}$$

Taking the logarithm of both sides of this equation, one gets

$$\log\frac{C_s - \bar{C}}{C_s} = \log\frac{8}{\pi^2} - \frac{\pi^2 D}{2.303}\cdot\frac{t}{l^2}. \tag{10}$$

Equation 10 indicates that the diffusion coefficient D is determined from the slope of the plot of $\log\ (C_s - \bar{C})/C_s$ against (t/l^2).

Experimental

Copper Specimens. Electrolytic copper, 99.999% pure and 5 mm thick, was used for samples. The result of chemical

Table 1. Result of chemical analysis

Impurity	Content
Pb	1 ppm
As	1
Sb	1
Fe	1
Ni	1
S	6

analysis of the copper is given in Table 1. The electrolytic copper was cut into rectangular specimens with a small knob at one corner. The size of each specimen was 15 mm × 7 mm × (0.2—1)mm. The copper specimens were polished with emery paper and then with alumina polishing powder of 10, 5, 0.5, and 0.3μ successively. The size of polished specimens was measured by means of a vernier caliper and the thickness was calculated from the weight and the surface area. In order to remove the strain and non- metallic elements dissolved in copper, the specimens were placed in a Vycor basket, suspended in a tube kept at 600 °C, and heat-treated in a 5% H_2–95% N_2 gas mixture for 5 h.

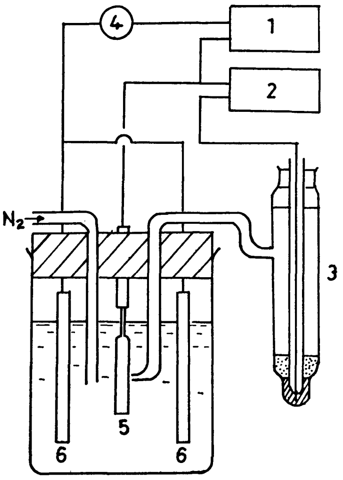

Fig. 1. Schematic drawing of electrolytic cell and electrical circuit.
1: Galvanostat, 2: recorder, 3: S.C.E., 4: ammeter, 5: test electrode, 6: counter electrode.

Formation and Determination of Surface Sulfide. The essential point of the present work is the determination of $\bar{C}(t)$, in other words, the determination of sulfide film thickness at time zero and time t. The sulfide film was as thin as about 1000 Å, so the electrochemical method was employed for the formation of sulfide film and the determination of its thickness. Figure 1 shows the drawing of the electrochemical cell and the electrical circuit for these purposes. In the first cell a 0.1 M KCl-solution was used as electrolyte. The solution was deaerated by passing nitrogen gas bubbles for 10 min and a heat-treated copper specimen was immersed in the solution. The current was made to flow between the specimen and two counter electrodes to reduce the surface oxide on the copper. The cathodic current density was 1 mA/cm^2. Then the specimen was taken out of the cell, washed with water, and transferred to the second cell which contained a 6.3×10^{-3} M Na_2S solution as electrolyte. The specimen was anodized at a current density of 0.1 mA/cm^2 for 10 to 20 min to form thin sulfide films of the desired thickness on both surfaces of copper. Usually, the thickness was chosen to be about twice or three times greater than the thickness after the diffusion annealing. Then, the specimen was taken out and washed with pure water.

The sulfide film thickness was determined by means of the coulometric method. The specimen was immersed in a 0.1 M KCl solution and the surface sulfide was reduced cathodically at a constant current density of 0.1 mA/cm^2. The potential with reference to S. C. E. was recorded. The potential was constant while the residual sulfide existed on the metal surfaces, shifted to a less noble value in an instant where the sulfide was completely removed, and remained at another constant value which corresponded to the potential of hydrogen evolution on the bare metal surface. From the reflection of the potential-time curve, the electric charge necessary for the reduction of sulfide was calculated. The charge determined from the reduction of sulfide was found to be always about 10% larger than that determined from the formation of sulfide. It was considered that the difference might be due to the reaction of copper with polysulfide ions contained in the Na_2S solution as an impurity. So the Na_2S solution of the same concentration was used for the formation of sulfide, and the film thickness formed by the reaction of copper with polysulfide ions was taken into account for the determination of the initial film thickness.

Diffusion Annealing. The copper specimen covered with copper(I) sulfide film was placed in a Vycor tube in which nitrogen gas was made to flow for 10 min to replace the air in it. Then the tube was evacuated to 10^{-4} Torr and sealed by means of a hydrogen-oxygen torch. Care was taken so that the sample would not be heated. The sealed tube was placed in an electric furnace kept at a desired annealing temperature within ±2 °C, and after a pre-determined length of time the tube was taken out from the furnace. The thickness of the remaining sulfide film was determined coulometrically and the mean concentration $\bar{C}$ in copper was calculated.

Results and Discussion

Soubility of Sulfur in Copper. The plot of $\bar{C}$ *vs.* t/l^2 is given in Figs. 2 and 3. As is seen in these figures, $\bar{C}$ approaches to a saturation value C_s with the increase of t/l^2. Figure 4 shows the plot of log C_s *vs.* $1/T$. Clearly, a linear relationship exists between log C_s and $1/T$. The equation is

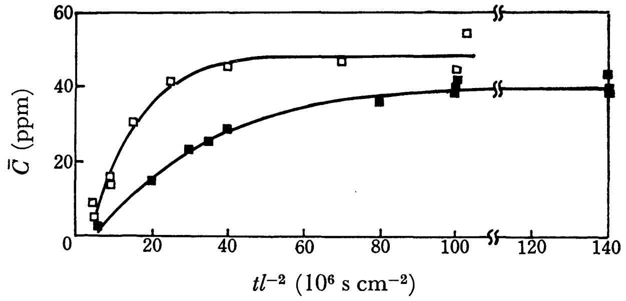

Fig. 2. Change of $\bar{C}$ with time.
■: 800 °C, □: 850 °C.

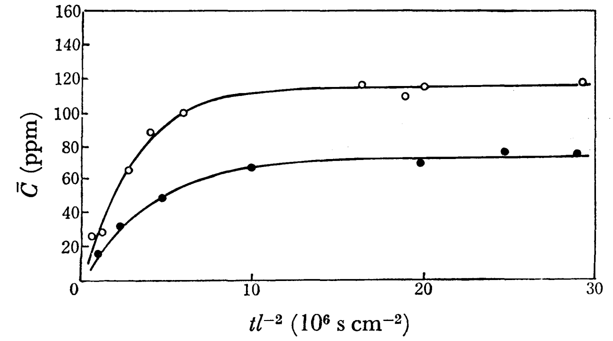

Fig. 3. Change of $\bar{C}$ with time.
●: 900 °C, ○: 950 °C.

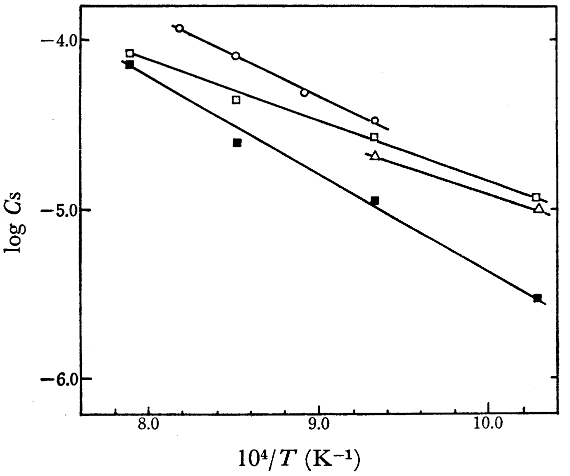

Fig. 4. Plot of log C_s *vs.* $1/T$.
○: This work, □: (Oudar): HPCu, ■: (Oudar): OFHC, △: Smart *et al.*

$$\log C_s(\mathrm{ppm}) = -0.616 - 0.410\left(\frac{10^4}{T}\right). \qquad (11)$$

If the solubility is represented in terms of mole fraction N,

$$\log N(\mathrm{ppm}) = -0.319 - 0.410\left(\frac{10^4}{T}\right). \qquad (12)$$

For comparison, Oudar's result[2] obtained by the tracer method and Smart's result[3] obtained from the relationship between sulfur content and resistivity of copper are also given in this figure These results are in good agreement with each other. The enthalpy and entropy of sulfur dissolution in copper in accordance with Eq. 1 are calculated to be 18.7 and −1.46 cal/mol·deg, respectively. The small entropy is probably due to the transfer of sulfur from solid to solid, as given by Eq. 1.

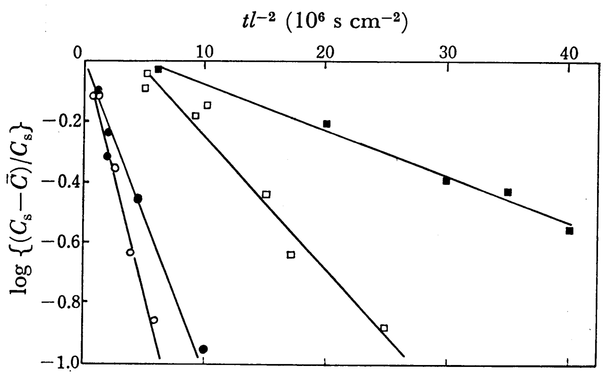

Fig. 5. Plot of log $\{(C_s-\bar{C})/C_s\}$ *vs.* t/l^2.
■: 800 °C, □: 850 °C, ●: 900 °C, ○: 950 °C.

Diffusion Coefficient. Figure 5 gives the relationship between log $(C_s-\bar{C})/C_s$ and t/l^2. A good linear relationship indicates that Eq. 9 holds for the present case and the diffusion coefficient D can be determined from the slope of the plot. The Arrhenius plot for D is given in Fig. 6. For comparison, Moya's result[4,5] obtained by the tracer method and the result obtained by Wang and Grabke[6] by means of the relaxation method are shown in the same figure. These results agree with each other. The Arrhenius equation for the present work is

$$D = 0.834 \times \exp\left(-\frac{40900}{RT}\right)\mathrm{cm^2\,s^{-1}}. \qquad (13)$$

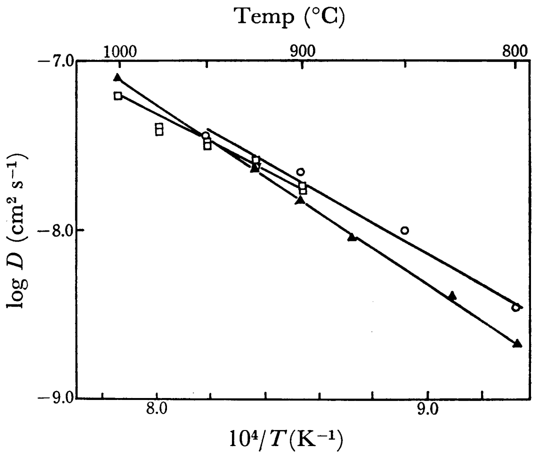

Fig. 6. Arrhenius plot for D.
○: This work, □: Wang and Grabke, ▲: Hoya.

Summary

(1) For the determination of solubility and diffusion coefficient of non-metallic elements in metals a new method was proposed. A thin compound film was formed on the metal surface and the film thicknesses before and after diffusion annealing were determined by the coulometric method.

(2) The solubility of sulfur in copper determined by the new method was given in terms of mole fraction by the equation

$$\log N_s(\mathrm{ppm}) = -0.319 - 0.410\left(\frac{10^4}{T}\right).$$

This result was in good agreement with those obtained by other methods.

(3) The diffusion coefficient of sulfur in copper in the present investigation was represented by

$$D = 0.834 \times \exp\left(-\frac{40900}{RT}\right)\mathrm{cm^2\,s^{-1}}.$$

This result agreed with the previous results obtained by other methods.

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