NOTES

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Determination of the Solubility of Oxygen in Copper by the Coulometric Method

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Synopsis. The solubility of oxygen in copper was determined at 800—1000 °C by means of the coulometric method. The data obtained is represented by the following equation: $\log N(\text{atom fraction}) = -2.164 - 1820/T$

At high temperatures, the oxidation rate of alloys is significantly affected by the formation of an internal oxidation layer. Since this internal oxidation is a phenomenon of oxygen diffusion into the alloy from the oxide-alloy interface, resulting in the formation of an oxide with the less noble constituent, the data of solubilities and diffusion coefficients of oxygen in the alloy are required in order to analyze the rate of alloy oxidation. The solubility of oxygen can be determined directly by the vacuum fusion method, the inert gas fusion method, the method of reduction of a metal saturated with oxygen, and the neutron or proton activation analysis. The solubility can also be determined indirectly by electric resistance measurements, lattice parameter measurements, and E. M. F. measurements by means of solid electrolytes. On the whole the direct methods are rather complicated. Since the coulometric method allows the precise determination of the thickness of thin oxide films, such as passive films, it can be applied to the estimation of the solubility of oxygen in metals and alloys. The purpose of this note is to report the determination of the oxygen solubility in copper by means of coulometric analysis.

Experimental

Rectangular slices, 20 mm × 7 mm in area and 0.2—0.8 mm in thickness, were cut from an ingot of electrolytic copper, 99.999% pure; they were polished with alumina powders, washed with soap and water, and dried in a desiccator. The polished specimens were treated in a pure hydrogen gas flow at 500 °C for 3 h to remove strains and surface oxides. Spectroscopic analysis revealed that the copper specimen contained Pb, As, Sb, Fe, and Ni, 1 ppm each, and 6 ppm of S as impurities.

Two specimens were oxidized simultaneously at 200—240 °C in air for a definite time to obtain copper(I) oxide films, 1500—2500 Å thick. One of these two specimens was used to determine the oxide film thickness by the coulometric method. It was placed in a cell as a cathode and two platinum anodes were placed to face either side of the cathodic plate. An aqueous solution of 0.1 M KCl was used as an electrolytic solution and a saturated calomel electrode as a reference electrode. Nitrogen gas was bubbled through the solution for 20 min to remove the dissolved oxygen; then the electrolysis was carried out with a current density of 67 μA/cm^2. The time variation of the potential difference between the cathode and the reference electrode was recorded. The oxide film thickness was calculated from the total amount of charge passed.[1,2]

The second specimen was sealed in a 10 mmϕ Vycor tube *in vacuo*, annealed in an electric furnace kept at each desired temperature within ±1 °C, and quenched as soon as possible after the annealing. The thickness of the remaining oxide film was then determined by the coulometric method. During the annealing, surface copper(I) oxide decomposes into copper and oxygen at the metal-oxide interface, and the oxygen diffuses inward. Therefore, the amount of dissolved oxygen was calculated from the decrease in the oxide film thickness. The amount of dissolved oxygen was plotted against t/l,[2] where t is the annealing time and 2 l is the thickness of the copper specimen. The solubility of oxygen was determind from the saturated value.

Results and Discussion

Preliminary experiments showed that a faint red-colored deposit of copper(I) oxide appeared on the inner wall of the Vycor tube in the case of prolonged annealing. Therefore, sufficiently thin copper specimens were used so that the saturation could be completed in a short annealing period.

Table 1 gives the oxygen solubility, N, expressed in terms of atomic fraction. The standard deviation of N was less than 34%. Figure 1 gives the temperature dependence of the averaged N as a plot of log N *vs.*

TABLE 1. SOLUBILITY OF OXYGEN IN COPPER

Temp T(°C)	Thickness of Cu specimen $2l \times 10^2$(cm)	Annealing time t(min)	$t/l^2 \times 10^{-6}$ (s/cm^2)	Solubility of oxygen (ppm)
1000	2.49	10.0	3.84	273
1000	2.52	15.0	5.67	245
950	5.01	30.0	2.86	229
950	3.18	20.0	4.75	198
900	3.20	30.0	7.06	203
900	3.32	30.0	6.51	187
850	4.47	30.0	3.57	160
850	2.94	35.0	9.72	142
800	4.45	30.0	3.62	115
800	5.15	30.0	2.70	164
800	7.13	35.0	1.65	166

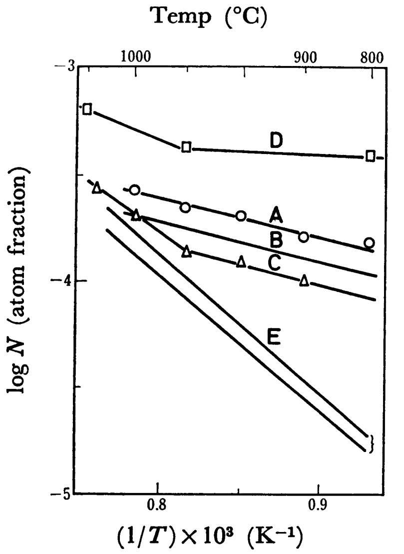

Fig. 1. Solubility of oxygen in copper.
(A) Present work, (B) Bouillon, (C) Phillips, (D) Rhines, (E) Pastrek.

$1/T$. The relationship is represented by the equation:

$$\log N = -2.164 - 1820/T \qquad (1)$$

The data obtained by the previous investigators are also plotted in the same figure. Rhines and Mathewson[3)] and Phillips and Skinner[4)] determined the solubility from the weight decrease of copper saturated with oxygen by reduction. Bouillon and Orszagh[5)] used the mass spectroscopic analysis coupled with the vacuum fusion technique. Pastrek and Rapp[6)] studied the solubility using a solid electrolyte cell. The data of the present work agree well with those from Phillips and Bouillon.

From Eq. 1, the enthalpy change, the entropy change and the free energy change for the dissolution of oxygen in copper can be derived . They are

$$\Delta H = 8330 \text{ cal/mol},$$

$$\Delta S = -9.90 \text{ cal/mol deg},$$

$$\Delta F = 8330 + 9.90\, T \text{ cal/mol}$$

respectively.

References

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