Control of Oxide Particle Size by Oxygen Pressure for Internally Oxidized Silver Base Alloys*

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Silver base alloys containing 11.3Cd, 11.4Cd-0.24Ni, 7.62Zn-0.45Te, 6.13Zn-0.97Sn-0.48Te, and 6.05Zn-1.03Sn-0.99In-0.47Te (at%) have internally been oxidized at 1023, 1073 and 1123 K under continuously changing pressure of oxygen and in air. The size of oxide particles has been controlled by oxygen pressure.

(1) In order to disperse the same size of oxide particles in all internal oxidation layers, the oxygen pressure P should be controlled with time t as $P = K^4 P_a^2 t^2 / 4 X_a^4$, where K is the velocity constant of internal oxidation at a constant oxygen pressure P_a , and X_a is the distance from the surface. The value of K depends on the composition of specimens and the temperature of internal oxidation. (2) The activation energies for internal oxidation of the alloys are smaller than 92 kJ/mol estimated from the diffusion of oxygen in silver. (3) The diffusivity of oxygen in internal oxidation layers and its activation energy are evaluated to be smaller than those in silver.

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I. Introduction

The internal oxidation process has been applied widely to the production of dispersion hardening materials or electrical contact materials. The dispersed structure of oxide particles precipitated in a silver matrix depends on the composition of specimens and the conditions of internal oxidation: The size of the oxide particles decreases with decreasing solute concentration and internal oxidation temperature, and decreases with increasing oxygen pressure. Moreover, it is well known that the size increases as the internal oxidation proceeds to inner direction⁽¹⁾⁻⁽¹¹⁾. Some characteristics of internally oxidized alloys depend on the composition of specimens and the dispersed structure of oxide particles⁽⁵⁾⁽¹²⁾⁻⁽¹⁴⁾. Especially, for electrical contact materials with dispersed structures different from position to position in internal oxidation layers, the resistance to welding adhesion changes as the erosion progresses by switching operations⁽¹⁵⁾. If a uniform dispersed structure is obtained in all the internal oxidation layers, the characteristics of electrical contacts are stable and

the reliability is improved. In order to disperse the same size of oxide particles in all the layers, it must be considered to control the oxygen pressure or the temperature in the internal oxidation process⁽²⁾⁻⁽⁴⁾⁽⁶⁾⁽⁷⁾⁽¹⁰⁾.

In the present work, therefore, we investigated the internal oxidation behavior for Ag-Cd and Ag-Zn base alloys used as electrical contact materials, and tried to control the size of oxide particles by continuously changing pressure of oxygen in the internal oxidation process.

II. Experimental

Table 1 shows the chemical compositions of specimens used. The specimens were prepared in a size of 10×10×10 mm after melting 0.6 kg of components from Ag of 99.9%, Cd of 99.9%, Ni of 99.9%, Zn of 99.8%, Sn of 99.9%, In of 99.999% and Te of 99.99%, and were internally oxidized in continuously changing

Table 1 Chemical compositions of specimens (at%).

Specimen	Cd	Ni	Zn	Sn	In	Te	Ag
CdO	11.3	—	—	—	—	—	Bal
CdON	11.4	0.24	—	—	—	—	Bal
800T	—	—	7.62	—	—	0.45	Bal
610T	—	—	6.13	0.97	—	0.48	Bal
611T	—	—	6.05	1.03	0.99	0.47	Bal

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pressure of oxygen and in air at 1023, 1073 and 1123 K.

The dispersed structures of oxide particles were observed using an optical microscope.

III. Results

Photograph 1 shows the microstructures of the specimens internally oxidized in air at 1073 and 1123 K. The size of oxide particles is found to increase as the internal oxidation proceeds to inner direction and as the temperature increases. The dispersed structures depend on the composition of specimens, and further, on the stability of oxides and the diffusivity of solute elements⁽⁶⁾⁽¹²⁾⁽¹⁶⁾.

Figure 1 shows the relation between the thickness X of the layer internally oxidized in

air and the time t , where (a) is oxidized at 1023 K, (b) at 1073 K, and (c) at 1123 K. The thickness X is proportional to $t^{1/2}$.

Now, we will consider how the size of oxide particles is controlled by the oxygen pressure in the internal oxidation process. The thickness X has been given by Wagner⁽¹⁾ as

$$X = \left(\frac{2N_0 D_0 t}{v N_m} \right)^{1/2}, \quad (1)$$

where N_0 is the equilibrium solubility of oxygen in the solvent metal for the given oxidizing atmosphere, N_m is the mole fraction of the solute element in the alloy before internal oxidation, D_0 is the diffusivity of oxygen in the internal oxidation layer, v is the ratio in number of oxygen atoms to solute atoms of the precipitated oxide, and t is the oxidation time.

Photo. 1 Microstructures of specimens internally oxidized in air. (a) CdO, (b) CdON, (c) 800T, (d) 610T, (e) 611T. (A) Internally oxidized at 1073 K. (B) Internally oxidized at 1123 K.

Fig. 1 Relation between layer thickness X internally oxidized in air and time t . (a) Internally oxidized at 1023 K. (b) Internally oxidized at 1073 K. (c) Internally oxidized at 1123 K.

When the composition of specimen and the temperature of internal oxidation are fixed,

$$\left(\frac{2D_0}{vN_m}\right)^{1/2} = K_1, \quad (2)$$

where K_1 is a constant. Equation (1) can be rewritten as

$$X = K_1(N_0 t)^{1/2}. \quad (3)$$

When the gradient of oxygen concentration in the oxidation layer decreases, the diffusion range of solute element increases, because the supply of oxygen to the internal oxidation front decreases. The size of oxide particles increases, therefore, as the internal oxidation proceeds to inner direction. Namely, the size may have a strong dependence on the ratio of the number of the solute atoms to that of oxygen atoms supplied to the internal oxidation front⁽⁶⁾⁽⁷⁾. When the ratio is constant, the internal oxidation velocity X' is constant. In this case the uniform size of oxide particles will be controlled in all the layers. From Eq. (3) when

$$N_0 \propto t, \quad (4)$$

X' is constant. Silver has sufficiently high oxygen solubility, in this case, the relation between the oxygen pressure P and N_0 is given by

$$N_0 = K_2 P^{1/2}. \quad (5)$$

The thickness X is given by⁽⁶⁾

$$X = K P^{1/4} t^{1/2}. \quad (6)$$

In order to obtain the same size of oxide particles as that at $X = X_a$ when the internal oxidation proceeds in the constant pressure P_a of oxygen and at a constant temperature, the value of X' is given from the differentiation of Eq. (6) by t as

$$X' = \frac{K P_a^{1/4}}{2 t_a^{1/2}}, \quad (7)$$

and the thickness X must be in proportion to the time t as

$$X = X' t. \quad (8)$$

The constant K is obtained from substituting the layer thickness X_b , formed by internal oxidation during the time t_b , into Eq. (6) as

$$K = \frac{X_b}{P_a^{1/4} t_b^{1/2}}. \quad (9)$$

Table 2 shows the values of K obtained from substituting the results of Fig. 1 into Eq. (9),

Table 2 Velocity constant K of internal oxidation in air.

Specimen	K		
	1023 K	1073 K	1123 K
CdO	1.21×10^{-7}	1.50×10^{-7}	1.84×10^{-7}
CdON	1.20×10^{-7}	1.49×10^{-7}	1.82×10^{-7}
800T	1.46×10^{-7}	1.79×10^{-7}	2.80×10^{-7}
610T	1.36×10^{-7}	1.65×10^{-7}	2.35×10^{-7}
611T	1.26×10^{-7}	1.57×10^{-7}	2.03×10^{-7}

where the units of X_b , P and t_b are m, Pa and s, respectively. The time t_a during which the internal oxidation proceeds from the surface to X_a is given from Eq. (6) as

$$t_a = \frac{X_a^2}{K^2 P_a^{1/2}}. \quad (10)$$

When the oxygen pressure P changes with the time t as

$$P = K_a t^2, \quad (11)$$

Equation (6) is represented by Eq. (8). The constant K_a can be obtained as follows: In Eq. (8) the time t_c corresponding to $X = X_a$ is given by

$$t_c = \frac{X_a}{X'}. \quad (12)$$

Since P reaches P_a at $t = t_c$, the constant K_a is given by

$$K_a = \frac{P_a}{t_c^2}. \quad (13)$$

The oxygen pressure P is obtained from Eqs. (7), (9), (10), (11), (12) and (13) as

$$P = \frac{K^4 P_a^2}{4 X_a^4} t^2 = \frac{P_a X_b^4}{4 X_a^4 t_b^2} t^2. \quad (14)$$

When P changes with t following Eq. (14), the dispersed structure with the same size of oxide particles as that at X_a may be controlled in the whole layer.

Moreover, when K_a is arbitrary in Eq. (11), X' and X_a are obtained from Eqs. (7), (10), (12) and (13) as

$$X' = \frac{KK_a^{1/4}}{2^{1/2}}, \quad (15)$$

and

$$X_a = \frac{KP_a^{1/2}}{2^{1/2} K_a^{1/4}}. \quad (16)$$

Figure 2 shows the condition under which the dispersed structure with the same size of oxide particles as that of each position shown with arrows in Photo. 1 is controlled in the whole layers. Figure 2(a) shows the relation

Fig. 2 Relations between oxygen pressure P , layer thickness X and time t of internal oxidation. (a) Internal oxidation temperature 1073 K. (b) Internal oxidation temperature 1123 K.

between the oxygen pressure P and the time t obtained from Eq. (14), and the relation between the layer thickness X and the time t obtained from Eqs. (8) and (15), in the case of internal oxidation at 1073 K under an oxygen pressure of 2×10^4 Pa (in air). The positions of X_a are 0.200 mm for the specimen CdO, 0.199 mm for CdON, 0.238 mm for 800 T, 0.220 mm for 610 T and 0.208 mm for 611 T, as shown with arrows in Photo. 1(A). Figure 2(b) shows the case of internal oxidation at 1123 K. The positions X_a are 0.200 mm for CdO, 0.198 mm for CdON, 0.305 mm for 800 T, 0.256 mm for 610 T and 0.221 mm for 611 T, as shown with arrows in Photo. 1(B).

Photograph 2 shows the microstructures of

the internally oxidized specimens when the oxygen pressure is changed continuously, as shown in Fig. 2. The same size of oxide particles as that shown with arrows in Photo. 1 is found to be controlled, except for a thin layer about $10 \mu\text{m}$ distant from the surface. In the thin layer the oxide particles are fine. It is known that near the surface, i.e. at the place about $10 \mu\text{m}$ distant from it, the diffusion process is complicated and different from the diffusion in a solid⁽¹⁶⁾. Moreover, Cd and Zn in the alloys are evaporated selectively from the surface before oxygen is supplied, after the temperature of specimens has reached the equilibrium, because the vapor pressure of the elements is high. Therefore, near the surface the solute concentration will decrease.

Photo. 2 Microstructures of specimens internally oxidized at controlled oxygen pressure as shown in Fig. 2. (a) CdO, (b) CdON, (c) 800T, (d) 610T, (e) 611T. (A) Internally oxidized at 1073 K. (B) Internally oxidized at 1123 K.

IV. Discussion

We will examine the activation energy for internal oxidation, and the diffusivity of oxygen and its activation energy in the internal oxidation layer in which the oxide particles are dispersed in the silver matrix. When the internal oxidation proceeds under the constant pressure of oxygen, $(K P_a^{1/4})^2 = K_0$, Eq. (6) can be rewritten as

$$X^2 = K_0 t. \quad (17)$$

Figure 3 shows the relation between the constant K_0 obtained from K in Table 2 and the reciprocal of temperature T^{-1} . Table 3 shows the activation energy obtained from the gradient of each line using the Arrhenius equation. Here, the values of K_0 for specimens 800 T, 610 T and 611 T at 1123 K were excepted

Fig. 3 Relation between velocity constant K_0 of internal oxidation in air and reciprocal of temperature T^{-1} .

Table 3 Activation energy Q obtained from K_0 .

Specimen	$Q/10^3 \text{ J} \cdot \text{mol}^{-1}$
CdO	78
CdON	81
800T	75
610T	71
611T	80
Ag	92*

* after Eichenauer and Müller⁽²⁾.

because the temperature approaches the liquidus and K_0 increases abruptly. The values of K_0 are also obtained from Eqs. (1) and (17) as

$$K_0 = \frac{2N_0 D_0}{v N_m}, \quad (18)$$

where the values of v and N_m are determined from the composition of specimens. Therefore, the activation energy obtained from the experimental value of K_0 may agree with that obtained from $N_0 D_0$. The activation energies for all the specimens are smaller than 92 kJ/mol which was obtained from $N_0 D_0$ of oxygen in silver by Eichenauer *et al.*⁽²⁾⁽⁴⁾. Moreover, we will compare the value of D_0 of oxygen in the internal oxidation layers in which the oxide particles are dispersed in the silver matrix. The D_0 in silver has been given by Eichenauer *et al.*⁽²⁾⁽⁴⁾ as

$$D_0 = 3.66 \times 10^{-7} \exp\left(\frac{-46030}{RT}\right) \text{ m}^2 \text{ s}^{-1}. \quad (19)$$

On the other hand, in order to obtain D_0 from $N_0 D_0$ of oxygen in the internal oxidation layers obtained experimentally, the value of N_0 must be known at each temperature. The value of N_0 in the layers is approximated by that in silver⁽²⁾⁽⁴⁾⁽⁹⁾, namely,

$$N_0 = 6.69 \times 10^{-2} \exp\left(\frac{-49620}{RT}\right), \quad (20)$$

at $P = 10^5 \text{ Pa}$.

Table 4 shows the values of D_0 obtained from Eqs. (5), (18), (20) and the values of K_0 obtained from K in Table 2. The value of D_0 for each specimen is smaller than that for silver obtained from Eq. (19). It has been reported⁽⁵⁾⁽⁷⁾

Table 4 Diffusivity D_0 of oxygen in internal oxidation layers.

Specimen	$D_0/10^{-9} \text{ m}^2 \text{ s}^{-1}$		
	1023 K	1073 K	1123 K
CdO	1.33	1.57	1.83
CdON	1.36	1.60	1.85
800T	1.47	1.68	—
610T	1.35	1.51	—
611T	1.35	1.59	—
Ag	1.63*	2.10*	2.65*

* after Eichenauer and Müller⁽²⁾.

Table 5 Activation energy Q obtained from D_0 .

Specimen	$Q/10^3 \text{ J} \cdot \text{mol}^{-1}$
CdO	31
CdON	31
800T	26
610T	22
611T	31
Ag	46*

* After Eichenauer and Müller⁽²⁾.

that D_0 in the internal oxidation layers changes when the diffusion occurs in the interface between oxide particles and matrix, and when the cross-sectional area to the diffusion of oxygen decreases with dispersion of oxide particles. Therefore, the value of D_0 depends on the size and the density of oxide particles. In such dispersed structures as shown in Photo. 1, the decrease in D_0 due to the decrease in the cross-sectional area may overcome the increase in D_0 due to the diffusion in the interface, because the particle size is large. Table 5 shows the activation energy obtained from D_0 in Table 4. The activation energies of D_0 for specimens are smaller than 46 kJ/mol in Eq. (19) for silver. The activation energy of the diffusion in the interface is smaller than that of the diffusion in solid. However, since from the value of D_0 examined above the dependence of the diffusion in the interface is considered to be small, the small activation energy of D_0 in the internal oxidation layers can not be explained only by the existence of oxide particles. The size of oxide particles decreases and its density increases with decreasing internal oxidation temperature, as found in Photos. 1 and 2. Therefore, the ratio of D_0 in the internal oxidation layers to D_0 in silver may become high because the effect of the diffusion in the interface increases with decreasing internal oxidation temperature. Oxygen diffuses from the surface in the direction of the internal oxidation front, and on the other hand, the solute element diffuses from the unoxidized region to the front. Therefore, when the whole area of specimen is internally oxidized, a zone deficient in oxide particles appears in the center of specimen. It has been reported⁽⁶⁾ that the width of the

depleted zone is inversely proportional to the square root of the diffusion velocity ratio of solute element to oxygen and this ratio changes with the internal oxidation temperature, and the width increases with increasing temperature. Namely, when a sufficiently thick specimen is internally oxidized, the value of N_m in Eq. (1) may increase up to that of the original alloy with increasing temperature. Since the value of D_0 was obtained from the value of N_m for the original alloy, the ratio of D_0 in the internal oxidation layers to D_0 in silver decreases with increasing temperature. Moreover, in Eq. (1) the value of v was used for the stoichiometric oxide, but the precipitated oxide is in an oxygen poor type. Since the degree of oxygen poorness is affected by the temperature, the value of D_0 and its gradient change. Since these factors are multiplied together, the activation energy of the diffusion of oxygen in the internal oxidation layers may be smaller than the real value.

When the internal oxidation proceeds in continuously changing pressure of oxygen at a constant temperature, the value of N_0 in Eq. (1) changes. Therefore, the condition controlling the dispersed structure is determined easily. On the other hand, in order to control the dispersed structure by the temperature, the temperature must decrease as the internal oxidation proceeds inwardly from the surface. This means a decrease in the value of K_0 in Eq. (17) with increasing time t (layer thickness X). The oxidation velocity extremely decreases as the internal oxidation proceeds inwards. Moreover, when silver base alloys are internally oxidized under a constant pressure of oxygen, the size of oxide particles in a layer 100 μm distant from the surface is much smaller than that in the inside, as found in Photo. 1. In order to control the size of oxide particles near the surface, the temperature must extremely increase. For silver base alloys the maximum temperature is about 1120 K, limited from the melting temperature. Namely, it is very difficult to control the dispersed structure near the surface by the temperature.

V. Summary

The internal oxidation behavior in Ag-Cd

and Ag-Zn base alloys was investigated, and it was tried to control the size of oxide particles under continuously changing pressure of oxygen.

(1) In order to disperse the same size of oxide particles in all the internal oxidation layers, the oxygen pressure P should be controlled with the time t as $P = K^4 P_a^2 t^2 / 4 X_a^4$, where K is the velocity constant of internal oxidation under a constant oxygen pressure P_a , and X_a is the distance from the surface. The value of K depends on the composition of specimens and the temperature of internal oxidation. (2) The activation energy for the internal oxidation obtained is smaller than 92 kJ/mol estimated from the diffusion of oxygen in silver by Eichenauer and Müller. (3) The diffusivity of oxygen in internal oxidation layers and its activation energy are evaluated to be smaller than those in silver.

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