Effect of Ti and Zr Additions on the Internal Oxidation of Cu-Si Alloy

By Teruo Takahashi*, Yasuhiko Hashimoto** and Koichiro Koyama**

The dilute Cu-Si, Cu-Si-Ti and Cu-Si-Zr alloys were internally oxidized in the temperature range of 973–1323 K. The crystal structures of dispersed oxides in the internally oxidized alloys were identified by X-ray diffractometry. The measurements of mean particle sizes, analysis of dispersed particles and the observation of precipitate morphology were carried out with an analytical transmission electron microscope. The hardness measurements were performed using a micro-Vickers hardness tester.

The oxide particles in the internally oxidized Cu-Si binary alloys were initially dendritic and subsequently transformed to spherical in process of time. By addition of Ti and Zr into the Cu-Si alloy, the dispersed oxide particles became remarkably finer. The oxide phase in the internally oxidized Cu-Si alloys in the temperature range of 973–1073 K was amorphous SiO_2 , but at 1173–1323 K α -cristobalite was precipitated in addition to amorphous SiO_2 . The amount ratio of α -cristobalite to amorphous SiO_2 was increased with increasing oxidation temperature. The dispersed oxide phases in the internally oxidized Cu-Si-Ti alloy were amorphous SiO_2 and rutile-type TiO_2 , and in the Cu-Si-Zr alloy amorphous SiO_2 , monoclinic ZrO_2 , tetragonal ZrO_2 and ZrSiO_4 were precipitated. Pairs of SiO_2 and TiO_2 , or SiO_2 and ZrO_2 were formed in the ternary alloys. The oxide particles precipitated in the ternary alloys were finer than those in the binary alloys. The effect of Zr on refining dispersed oxide particles was greater than that of Ti. The hardness values of internally oxidized ternary alloys were higher than those of binary alloys.

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I. Introduction

Oxide-dispersion-strengthened Cu alloys⁽¹⁾⁻⁽³⁾ prepared from dilute Cu base alloy powders by internal oxidation followed by hot-extrusion are more excellent in the creep property at elevated temperatures than conventional age-hardened alloys. For example, the Cu- Al_2O_3 alloy⁽³⁾ is served as a spot welding electrode especially under a severe operating condition instead of conventional pure Cu or Cu-Cr alloys. The present authors have investigated the internally oxidized Cu- Al_2O_3 - TiO_2 ⁽⁴⁾ and Cu- ZrO_2 ⁽⁵⁾ alloys in order to improve the strength at elevated temperatures. In the Cu- Al_2O_3 - TiO_2 alloy, the effects of Ti addition as a third alloying element on the internal oxida-

tion phenomenon of Cu-Al binary alloy were investigated. In the Cu- ZrO_2 alloy, the phase and morphology of ZrO_2 precipitated by internal oxidation were studied, and the relationship between monoclinic and tetragonal ZrO_2 precipitates was clarified.

With regard to the internal oxidation of Cu-Si binary alloys, many reports⁽⁶⁾⁻⁽¹⁵⁾ have already been published. Saito and Hikage⁽¹⁶⁾ have discussed in detail on the internal oxidation of Cu-Si alloys up to 2.30 mass% Si. However, on the internal oxidation of the ternary Cu-Si-X alloy systems, only Cu-Al-Si alloys by Daneliya *et al.*⁽¹⁷⁾ and Grishchina and Fedorov⁽¹⁸⁾, and Cu-Si-Co alloys by Toth *et al.*⁽¹⁹⁾ have been studied about dispersed oxide phases and/or mechanical properties.

In the present study, the effect of Ti and Zr additions on the internal oxidation of Cu-Si alloy, especially the morphology of dispersed oxide particles and the mechanism of refining of the precipitates will be discussed.

* Industrial Research Institute of Hyogo Prefecture, Kobe 654, Japan.

** Department of Materials Science, Himeji Institute of Technology, Himeji 671-22, Japan.

II. Experimental Procedure

Table 1 shows the nominal chemical compositions of the alloys used in the present study. The calculated oxide volume ratio $V_{\text{SiO}_2}:V_{\text{TiO}_2}$ or $V_{\text{SiO}_2}:V_{\text{ZrO}_2}$ and calculated dispersive oxide volume percentage after internal oxidation are also shown. In this table it is assumed that amorphous SiO_2 , rutile-type TiO_2 and monoclinic ZrO_2 are precipitated by internal oxidation. The starting materials used were electrolytic copper powder deoxidized in a purified hydrogen atmosphere at 733 K for 21.6 ks before use, and high purity Si, Ti and Zr powders. These powders were mixed in prescribed chemical compositions, compacted and arc-melted in an argon atmosphere. The ingots obtained were annealed for homogenization at 1223 K for 18.0 ks, quenched into cold water and cold-rolled to the plates about 0.5 mm in thickness.

These plates were embedded in the mixed powder with a mass ratio of $\text{Cu}:\text{CuO}_2:\text{Al}_2\text{O}_3 = 1:2:3$, vacuum-sealed in a quartz tube and internally oxidized in the temperature range

Table 1 Chemical composition, calculated oxide volume ratio and calculated oxide volume percentage of copper alloys for internal oxidation.

Alloy No.	Nominal concentration (mass%) Si Ti Zr		Calculated oxide volume ratio, $V_{\text{SiO}_2}/V_{\text{XO}_2}$	Calculated oxide volume percentage
1	0.33		—	2.50
2	0.56		—	4.13
3	0.29	0.12	5:1	2.50
4	0.22	0.24	2:1	2.50
5	0.17	0.37	1:1	2.50
6	0.28	0.61	1:1	4.13
7	0.11	0.49	1:2	2.50
8	0.06	0.61	1:5	2.50
9	0.30		10:1	2.50
10	0.29	0.21	5:1	2.50
11	0.22	0.41	2:1	2.50
12	0.17	0.62	1:1	2.50
13	0.28	1.03	1:1	4.13
14	0.11	0.82	1:2	2.50
15	0.06	1.03	1:5	2.50

* X=Ti, Zr

of 973–1323 K. After internal oxidation, the phases of (1+1) nitric-acid-insoluble residues (oxide dispersoids) were analyzed by a X-ray diffraction method using a $\text{CuK}\alpha$ radiation monochromatized with a graphite monocrystal. The morphologies of dispersed oxide particles were investigated by an analytical transmission electron microscope (AEM) using an extraction replica method. A solution of $\text{FeCl}_3\text{--HCl}$ was used as an etchant in order to prepare the extraction replicas. Micro-Vickers hardness was measured (load:0.245N (25gf)) on the cross-section of each specimens.

III. Results and Discussion

1. Identification and analyses of nitric-acid-insoluble residues

Table 2 shows the results of X-ray diffraction analysis of (1+1) nitric-acid-insoluble residues obtained from Cu–Si binary alloys internally oxidized in the temperature range of 973–1323 K. The dispersed oxide phase precipitated in internally oxidized Cu–Si binary alloys at temperatures below 1173 K was only amorphous SiO_2 at any Si contents investigated. At temperatures above 1173 K, α -cristobalite was precipitated in addition to amorphous SiO_2 . The numeral results in the temperature range of 1173–1323 K in Table 2 indicate the ratio of the diffracted peak height

Table 2 X-ray identification of oxide phases in internally oxidized Cu–Si alloys.

Alloy No.	Oxidation temp.(K)	Time (ks)	Oxide volume (%)*	α -Cristobalite/ A- SiO_2 **
1	973	320.4		(only A- SiO_2)
	1073	46.8		(only A- SiO_2)
	1173	21.6	2.50	7.9
	1273	21.6		9.3
	1323	21.6		16.0
2	973	320.4		(only A- SiO_2)
	1073	46.8		(only A- SiO_2)
	1173	21.6	4.13	9.0
	1273	21.6		13.5
	1323	21.6		36.2

* calculated value

** A: amorphous

of α -cristobalite 101 diffraction line at $2\theta=21.9^\circ$ to the maximum peak strength of amorphous SiO_2 at $2\theta=21.5^\circ$. From these results, it is obvious that the ratio of α -cristobalite to total oxide increases with increasing internal oxidation temperature at a constant concentration of Si, and with increasing concentration of Si at a constant internal oxidation temperature.

Table 3 shows the results of X-ray diffraction analysis of (1+1) nitric-acid-insoluble residues obtained from ternary alloys corresponding to an oxide volume ratio $V_{\text{SiO}_2}:V_{\text{XO}_2}=1:1$ and a total oxide of 2.50 vol% (Alloy No. 5 and 12). The dispersed oxide phases in the internally oxidized Cu-Si-Ti alloys were amorphous SiO_2 and rutile-type TiO_2 . However, anatase-type TiO_2 detected in the internally oxidized Cu-Ti alloys⁽⁴⁾⁽²⁰⁾ and α -cristobalite detected in the Cu-Si binary alloys were not identified in the present alloys.

In the internally oxidized Cu-Si-Zr alloys, the amorphous SiO_2 , monoclinic ZrO_2 , tetragonal ZrO_2 and zircon (ZrSiO_4) were identified. Although amorphous SiO_2 was detected in the alloys oxidized at temperature up to 1173 K, it was rapidly increased above 1273 K and the amount of ZrSiO_4 increased rapidly. The diffraction lines of monoclinic ZrO_2 was very strong up to 1273 K, but at 1273 K the intensity from it was slightly decreased. Although the diffraction lines from tetragonal ZrO_2 were weak at 1073 K, it become strong above 1073 K in contrast. In the internally oxidized Cu-Si-Zr alloys as well as in the internally oxidized Cu-Si-Ti alloys α -cristobalite was not identified.

In the Cu-Si-Zr system, in order to clarify the precipitation of ZrSiO_4 particles, the Cu-Si-Zr alloys corresponding to 4.13 vol% of oxide (Alloy No. 13) were internally oxidized at 1323 K for various time. Figure 1 shows the change in the ratio of the integrated intensity of ZrSiO_4 (200) and T- ZrO_2 (111) to M- ZrO_2 (11 $\bar{1}$) obtained from insoluble-residues of these alloys. The ratio of ZrSiO_4 (200) to M- ZrO_2 (11 $\bar{1}$) by internal oxidation for 1.8 ks is very small. However, it becomes larger rapidly with increasing heating time. The intensity ratio of T- ZrO_2 (111) to M- ZrO_2 (11 $\bar{1}$) gradually decreases with increasing heating time. This phenomenon should be attributed to the faster change of the fine T- ZrO_2 particles⁽⁵⁾ inside Cu grains to ZrSiO_4 than that of the large M- ZrO_2 particles⁽⁵⁾ at Cu grain boundaries and inside Cu grains. From these results, it should be con-

Fig. 1 Change in the ratio of integrated intensity of $\text{ZrSiO}_4(200)$ and T- $\text{ZrO}_2(111)$ to M- $\text{ZrO}_2(11\bar{1})$ obtained from the insoluble-residues of the Alloy No. 13 internally oxidized at 1323 K for various time, t .

Table 3 Oxide phases in internally oxidized Cu-Si-Ti (Alloy No. 5) and Cu-Si-Zr (No. 12) alloys.

Alloy(No.)	Temperature (K)	Time (ks)	R- TiO_2	A- SiO_2	M- ZrO_2	T- ZrO_2	ZrSiO_4
Cu-Si-Ti (No. 5)	1073	32.4	s	vs			
	1173	21.6	vs	vs			
	1273	21.6	vs	s			
Cu-Si-Zr (No. 12)	1073	32.4		vs	vvs	w	nd
	1173	21.6		vs	vvs	s	nd
	1273	21.6		s	vvs	s	w
	1323	21.6		vw	vs	s	vs

R: rutile A: amorphous M: monoclinic T: tetragonal nd: not detected

cluded that ZrSiO_4 particles do not precipitate by internal oxidation, but are formed by the reaction of ZrO_2 and SiO_2 after internal oxidation.

2. Measurement of dispersed oxide particle size

Figure 2 shows the relationships between the mean particle size and the distance from the surface of the Cu-Si alloy internally oxidized at 1073–1273 K corresponding to 2.50 vol% of dispersed oxide (Alloy No. 1). Similar to the internally oxidized Cu-Al-Ti system⁽⁴⁾, the mean particle sizes of dispersed oxide increase with increasing internal oxidation temperature, and with the distance from the surface. Figure 3 shows the relationships between the mean particle size and the distance from the surface in the Cu-Si-Ti (Alloy No. 5) and Cu-Si-Zr (Alloy No. 12) alloys internally oxidized at 1073–1273 K. In the Cu-Si and Cu-Al-Ti alloys, the mean particle sizes of oxide dispersoids increase with the distance from the surface. Figures 2 and 3 indicate that the addition of Ti

Fig. 2 Change in the oxide particle size d with the distance from the surface x for Cu-Si (Alloy No. 1) alloys internally oxidized at 1073–1273 K.

Fig. 3 Change in the oxide particle size d with the distance from the surface x for (a) Cu-Si-Ti (Alloy No. 5) and (b) Cu-Si-Zr (Alloy No. 12) alloys internally oxidized at 1073–1323 K.

and Zr to the Cu-Si alloy is very effective for refining the dispersive oxide particles, and that the effect of Zr is greater than that of Ti.

3. Observations of dispersed oxide morphology

Figure 4 shows the typical oxide morphologies precipitated in the Cu-Si (Alloy No. 2), Cu-Si-Ti (No. 6) and Cu-Si-Zr (No. 13) alloys corresponding to 4.13 vol% of oxide formed by the internal oxidation at 1273 K. In the internally oxidized Cu-Si alloy, many spherical particles similar to those shown in Fig. 4(a) were observed over the whole area. The selected area electron diffraction (SAD) pattern in Fig. 4(a') shows halos indicating that these spherical particles are amorphous. Figure 4(b) and (c) show the oxide morphologies in the internally oxidized Cu-Si-Ti and Cu-Si-Zr alloys. The SAD pattern in Fig. 4(b')

TiO_2 as a crystalline phase. Anatase-type TiO_2 which had been detected in the internally oxidized Cu-Al-Ti alloy⁽⁴⁾ was not identified. The SAD pattern in Fig. 4(c') suggests the existence of many tetragonal ZrO_2 particles and a few monoclinic ZrO_2 .

Figure 5(a) and (b) show the TEM images of the oxide particles in the Cu-Si-Zr alloy corresponding to a nominal oxide volume ratios $V_{\text{SiO}_2}:V_{\text{ZrO}_2}=10:1$ and $1:5$ (Alloy No. 9 and 15) internally oxidized at 1273 K, respectively. These oxide particles show characteristic morphologies. Figure 5(c) and (d) show the TEM-EDX spectra obtained from area 1 and 2 in Fig. 5(a), respectively. Since only Zr from area 1 and only Si from 2 are detected, it is clarified that these oxide particles consist of SiO_2 and ZrO_2 . Similarly to the case of internally oxidized Cu-Si-Zr alloy, the oxide particles in the internally oxidized Cu-Si-Ti alloys form pairs of SiO_2 and TiO_2 as shown in Fig. 4(b).

Fig. 4 Typical morphologies and selected area diffraction patterns of the dispersed oxide particles in the Cu-Si (a, a'), Cu-Si-Ti (b, b') and Cu-Si-Zr (c, c') alloys internally oxidized at 1273 K for 21.6 ks.

Fig. 5 Change in the oxide morphology with the oxide volume ratio in the Cu-Si-Zr alloys internally oxidized at 1273 K.

Nominal oxide volume ratio $V_{\text{SiO}_2}:V_{\text{ZrO}_2}$ of (a) and (b) are 10:1 (Alloy No. 9) and 1:5 (Alloy No. 15), respectively. EDX spectra in (c) and (d) which obtained from the areas 1 and 2 showing in (a) indicate that this oxide particle is not complex oxide but a pair of ZrO_2 and SiO_2 .

Fig. 6 Change in the morphology of precipitates near the oxide precipitation front in Cu-0.56% Si (Alloy No. 2) internally oxidized at 1173 K.

Figure 6 shows the oxide morphology at the oxide precipitation front in the Cu-0.56 mass% Si alloy (Alloy No. 2) internally oxidized at 1173 K. The dispersed oxides are initially dendritic in shape, and subsequently they change to spherical in process of time. They become perfectly spherical at a distance by about 10 μm from the precipitation front. The existence of dendritic SiO_2 at the precipitation

front in the internally oxidized Cu-Si alloy was already reported by Bolsaitis and Kahlweit⁽¹³⁾, Stobbs⁽¹⁴⁾ and Saito and Hikage⁽¹⁶⁾. The present results agree with them. The SAD pattern from these dendritic precipitates indicates a halo. It should be interesting to note that the material precipitating in the dendritic morphology is amorphous. Although Bolsaitis and Kahlweit⁽¹³⁾ did not describe the crystal struc-

ture of the dendritic SiO_2 near the precipitation front, Saito and Hikage⁽¹⁶⁾ already reported the existence of amorphous SiO_2 . More detailed examination of this phenomenon should be necessary.

Figure 7(a) shows the morphology of precipitates near the precipitation front in the Cu-Si-Ti alloy corresponding to 4.13 vol% of oxide and $V_{\text{SiO}_2}:V_{\text{TiO}_2}=1:1$ (Alloy No. 6) internally oxidized at 1273 K. Figure 7(b) and (c) show the EDX spectra obtained from the oxide particles indicated with circles 1 and 2 in Fig. 7(a), respectively. It is revealed from both the TEM image and EDX spectra taken at the precipitation front that only TiO_2 particles are formed in the zone A of about 300 nm width and both SiO_2 and that TiO_2 are formed in the zone B. From these results, it is clear that the preferential oxidation of Ti takes place at the precipitation front, and that the TiO_2 particles work as a nucleation site of SiO_2 particles.

In the Cu-Si-Zr alloy, as is shown in Fig. 1, the dispersed oxide particles precipitated as ZrO_2 and SiO_2 . It is assumed that the situation of internally oxidized Cu-Si-Zr alloys was similar to that in the Cu-Si-Ti alloys. However, the dispersed particles at the

precipitation front could not be observed by the extraction replica method. The reason is as follows: Since the solubility⁽²¹⁾ of Zr in Cu is small, the excess Zr beyond solubility exists as the intermetallic compound of CuSiZr (ϵ -phase)⁽²²⁾. Internal oxidation does not occur by direct oxidation of the dispersed CuSiZr , but by local dissolution⁽¹⁾ of the CuSiZr phase ahead of the advancing precipitation front. Therefore the precipitation front in the Cu-Si-Zr alloy becomes obscure than that of the Cu-Si-Ti alloy.

As reported by Saito and Hikage⁽¹⁶⁾, the dendritic precipitation of SiO_2 occurs in the Cu-Si binary alloy containing nearly the same amount of Si with the present ternary alloy. Consequently it should be concluded that the addition of Ti and Zr prevents the precipitation of the large dendritic oxide and refine the dispersed oxide particles remarkably.

4. Oxide band in the internally oxidized Cu-Si-Ti alloy

Figure 8 shows a microstructure of Cu-Si-Ti alloy corresponding to 4.13 vol% of oxide and $V_{\text{SiO}_2}:V_{\text{TiO}_2}=1:1$ (Alloy No. 6) internally oxidized at 1273 K. In this figure, the areas A and B

Fig. 7 Change in the morphology of precipitates near the precipitation front in Cu-Si-Ti alloy (Alloy No. 6) internally oxidized at 1273 K. EDX spectra (b) and (c) were obtained from the oxide particles in the circles 1 and 2 showing in Fig. (a), respectively.

are already internally oxidized, and the area **C** is not. In the area **B**, many oxide bands with a Liesegang structure are observed. Figure 9 shows the SEM image, and Si and Ti profiles of an EPMA analysis along the line **X-Y** in this area. It can be seen that Si and Ti are condensed at black stripes, and the concentrations of Si and Ti become higher in the inner oxide bands, whereas the concentrations of Si and Ti in the area between the oxide bands decrease with the distance from the surface. At the area **M** between the oxide bands, however, the concentrations of Si and Ti increased with the distance from the surface due to the counter-diffusion⁽¹⁾, and this enrichment⁽¹⁾ was observed in many alloys.

Although the mechanism of the formation of oxide bands in the area **B** is not clear because the diffusivity of Ti in the ternary Cu alloy is not available, it should be explained qualitatively as follows: In general the rate of internal oxidation obeys the parabolic law⁽²⁰⁾⁽²³⁾ and is decelerated with increasing amount of the alloying element⁽⁴⁾. At the outer area **A**, since the rate of internal oxidation is faster than the rates of counterdiffusion of Ti and Si, the oxide band is not formed. At the inner area **B**, since the rate of internal oxidation is gradually decelerated, the rates of counterdiffusion of Ti and Si exceed that of internal oxidation. Therefore, the enrichment of Ti and Si takes place and the first oxide band has been built up. When the first oxide band has been

Fig. 9 SEM image (a), SiK α (b) and TiK α (c) X-ray profiles obtained from Cu-Si-Ti alloy (Alloy No. 6) internally oxidized at 1273 K.

Fig. 8 Microstructure of Cu-Si-Ti alloy (Alloy No. 6) internally oxidized at 1273 K for 9 ks.

built up, the concentrations of alloying elements near the precipitation front decrease, and the rate of internal oxidation increases after the formation of the first oxide band. As the precipitation front advances the rate of internal oxidation decreases again and the enrichment of Ti and Si takes place. Consequently the second oxide band has been built up. By repeating this process, the oxide band with the Liesegang structure should be formed as shown in Fig. 8.

Figure 10 shows the microstructure of the area **B** in Fig. 8 using an extraction replica method with TEM. The area 1 in which oxides are densely precipitated and the area 2 sparsely

Fig. 10 Oxide bands formed in the Cu-Si-Ti alloy (Alloy No. 6) internally oxidized at 1273 K.

are periodically formed. The mean oxide particle size in the area 1 is larger than that in the area 2 in which the concentrations of alloying elements decrease, in accordance with the tendency of ordinary internal oxidation⁽⁴⁾⁽²⁰⁾.

5. Hardness

Figure 11 shows the hardness values at the position of 40 μm from the surface of Cu-Si (Alloy No. 1) and Cu-Si-Zr (No. 10 and 11) alloys corresponding to 2.50 vol% of oxide

Fig. 11 Effect of Zr on the hardness at 40 μm from the surface of internally oxidized Cu-Si (Alloy No. 1) and Cu-Si-Zr (Alloys No. 10 and 11) alloys as a function of oxidized temperature, T .

formed by internal oxidation at 1273 K. The hardness increases with the amount ratio of alloying element Zr, and with decreasing internal oxidation temperature. These results are explained by the variation of mean particle size shown in Figs. 2 and 3.

IV. Conclusion

The effect of Ti and Zr on the internal oxidation of Cu-Si alloy was discussed. The results obtained were as follows:

(1) The dispersed oxides in the internally oxidized binary Cu-Si alloys precipitate initially in a dendritic morphology. They become spherical in process of time. All of these precipitates are amorphous up to the oxidation temperature of 1073 K. Above 1173 K, however, the amount ratio of α -cristobalite increases with increasing internal oxidation temperature.

(2) In internally oxidized Cu-Si-Ti alloys, amorphous SiO_2 and rutile-type TiO_2 precipitate, and the anatase-type TiO_2 is not detected. In internally oxidized Cu-Si-Zr alloys, the dispersed oxide phases are amorphous SiO_2 , monoclinic ZrO_2 , tetragonal ZrO_2 and zircon ZrSiO_4 . The ZrSiO_4 is formed by reaction of ZrO_2 and SiO_2 after internal oxidation.

(3) In the internally oxidized Cu-Si-Ti alloys, the preferential precipitation of TiO_2 particles occurs and these particles serve as nucleation sites of SiO_2 particles. In the Cu-Si-Zr alloys, it was assumed that the preferen-

tial precipitation of ZrO_2 particles occurs. Consequently the dispersed particles in ternary alloys form the pairs of SiO_2 and TiO_2 or SiO_2 and ZrO_2 regardless of the oxide volume percentage and the volume ratio $V_{\text{SiO}_2}:V_{\text{TiO}_2}$ or $V_{\text{SiO}_2}:V_{\text{ZrO}_2}$.

(4) The dispersed oxide particles in the internally oxidized ternary alloys are remarkably refined by the addition of Ti and Zr into Cu-Si binary alloys. The dendritic SiO_2 at the precipitation front observed in the internally oxidized Cu-Si alloys is not formed in the internally oxidized ternary alloys.

(5) The hardnesses of internally oxidized Cu-Si-Ti and Cu-Si-Zr ternary alloys are higher than the hardness of internally oxidized Cu-Si binary alloy.

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