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AN ELECTRON MICROPROBE STUDY OF THE COMPOSITION
OF TARNISH FILMS ON COPPER-ZINC, COPPER-ALUMINUM AND
COPPER-NICKEL ALLOYS

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MASTER

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
EXPERIMENTAL PROCEDURE	4
RESULTS	7
Microprobe Analysis of Sectioned Specimens .	7
Microprobe Analysis of Extracted Particles .	9
DISCUSSION AND CONCLUSIONS	11
REFERENCES	23

INTRODUCTION

The stress-corrosion cracking of alpha-phase copper alloys in the presence of aqueous ammonia is a common industrial failure and is generally termed season-cracking. The corrosion reaction in these systems produces a dark blue surface film, commonly referred to as the tarnish; this film is thought to play an important role in the stress-corrosion process. Specifically, it has been proposed that the cracking takes place by the repeated formation and rupture of the brittle tarnish film at the tip of the advancing crack, and that the rate of cracking is controlled by the rate of growth of the tarnish to the critical thickness ($1000\text{\AA}$) at which cracking occurs (1,2). Thus an understanding of the mechanism of tarnish formation is essential for further progress towards a solution to the season-cracking problem.

The structure and morphology of the tarnish has been studied in Cu-30Zn. The tarnish has been found to attain thicknesses of $\sim 5\mu$ on unstressed specimens exposed to certain ammonical solutions (3). Limited electron-optical studies suggest that the tarnish is made up of a porous aggregate of platelets, approximately $500\text{\AA}$ in diameter and $100\text{\AA}$ in depth (4), but no attempt has been made to confirm this result or to correlate structure with substrate composition and solution chemistry. Electron (4-6) and x-ray (7) diffraction carried out on the

tarnish indicates that it consists of cuprous oxide, and that it is epitaxed to the substrate. Electron-microprobe studies showed that the tarnish is depleted with respect to zinc (3,8).

The mechanism of tarnish growth is poorly understood. Based on early work, it was suggested that the tarnish formation involves the solid-state diffusion of cuprous ions across a fully dense tarnish film followed by reaction with oxygen at the tarnish surface (9). However, it is difficult to reconcile this model with the report that the tarnish is zinc depleted (3,8). Moreover, studies of the rates of film growth on copper and a range of alpha-brasses indicate that the kinetics of solid-state diffusion through the tarnish film are not sufficiently rapid to account for the observed growth rates of $\sim 10^{-8}$ cm/sec for copper to $\sim 10^{-5}$ cm/sec for Cu-30Zn (5). In fact, if the diffusivity of cuprous ions in cuprous oxide is taken as 10^{-26} cm²/sec the growth rate would be $\sim 10^{-24}$ cm/sec. Note that the kinetic data indicate that the tarnish is non-protective and thus supports the electron-microprobe observation that the tarnish is porous (4).

Recent work suggests that tarnish formation occurs by a "dissolution-reprecipitation model" (10). In this model, it is assumed that the platelets of tarnish are permeated with solution and that the anodic dissolution of metal takes place at the metal tarnish interface while the cathodic reaction, the reduction of cupric complex ions, takes place at the tar-

nish surface and is supplied with electrons, generated by the oxidation of the metal, by conduction through the tarnish film. A concentration gradient of cuprous ions is thought to exist across the tarnish, such that the solubility of cuprous oxide is exceeded only at or near the metal-tarnish interface. Thus formation of tarnish by the reaction

is restricted to the interface region.

According to the model, one would expect that the tarnish would be depleted with respect to zinc, since the concentration of zinc in the solid and hence in the solution near the surface is relatively low and since zinc forms a highly soluble ammonium complex ion (11). Accordingly, the model received strong support from the electron-microprobe studies on Cu-30Zn which indicated that the tarnish is essentially solute depleted (3,8). The purpose of the present studies was to confirm this observation, and to extend the microprobe analysis to alpha-brasses of different zinc contents and to other alpha-phase copper alloys, namely Cu-Al and Cu-Ni. Again the solubilities of these alloying elements in aqueous ammonia are high so that they would not be expected to precipitate from solution within the tarnish.

EXPERIMENTAL PROCEDURE

The experimental work was carried out on a range of binary alpha-phase copper-zinc, copper-nickel, and copper-aluminum alloys. The compositions of these alloys and the methods used for chemical analysis are listed in Tables 1 and 2. The alloys were rolled to sheets 0.005 in. thick, cut into specimens of dimensions $3/8$ in. x $1/2$ in., annealed in evacuated quartz tubes for 60 min. at 500°C , and then air cooled. After heat treatment, the specimens were etched for 5 min. in a 5% ferric-chloride solution and then were cleaned ultrasonically in water, in deionized water and, finally, in acetone. They were allowed to dry in air.

Each specimen was suspended by a nylon thread in an individual stoppered test tube containing 70 ml of standard tarnishing solution which has been used in previous studies (3,5,9). This solution is prepared by dissolving 8 g of copper dust per l of 15 N aqueous ammonia. An immersion time of 2 days was employed for all specimens, after which the specimens were thoroughly rinsed in deionized water and then in acetone. After being allowed to dry in air, they were mounted in a room-temperature setting epoxy resin and sectioned perpendicular to the plane of the sheet. The sectioned surfaces were abraded using wet silicon-carbide papers to the 600 grit stage, then polished using diamond abrasives of 6 and 1μ diameter, respectively. Retention of the brittle tar-

nish was found to be optimized if the specimens were polished perpendicular to the length of the cross section in one direction only. Finally, the specimens were polished for 20 min. with a vibratory polisher, using 0.05μ cerium-oxide particles. Typical polished sections are presented in Figs. 1-6 and it can be seen that considerable chipping and cracking occurs but that regions exist where the tarnish and the metal-tarnish interface are undamaged. These latter areas commonly occurred at the ends of the sections where the tarnish tends to be thicker, and were generally used in the microprobe studies. It is necessary that surfaces be electrically-conducting for electron-microprobe analysis. The epoxy resin is a poor conductor and thus the sectioned surfaces were finally coated with a layer of carbon in a vacuum evaporator.

Electron-microprobe analysis was carried out using an Applied Research Laboratories (ARL) instrument. An accelerating voltage of 25 KV was used in the analysis of Cu-Zn and Cu-Ni samples, while 15 KV was used for the Cu-Al samples. This instrument produces an electron beam of $1-2\mu$ in diameter. Analyses were made at 1μ intervals along a straight line traversing the metal, tarnish and mounting material, as indicated in Figs. 1-6, using a counting time of 10 sec at each point. To a first approximation, the weight percent of the element under investigation is given by the k-ratio, i.e., the ratio of the elemental characteristic x-ray intensity from the

specimen to that from a standard of the pure element (12). This value was corrected for such factors as variations in electron-beam current, atomic number effects, backscatter loss, absorption effects, electron stopping power effects and fluorescence effects using a standard computer program (13). Computer-generated plots of the weight percent of the constituent elements versus distance (see Figs. 1-6) were printed out using a Calcomp drum plotter.

In some alloys, it was not possible to carry out microprobe analysis on sectioned specimens, either because the tarnish film was too thin (due to the $2\text{-}4\mu$ limit of resolution of the microprobe) or because the sections could not be polished satisfactorily. To analyze these specimens, particles of tarnish were stripped from the tarnish surfaces by means of a Bioten film backed with a standard 100 mesh grid. The Bioten was softened in acetone for 1 sec before it was placed in contact with the tarnish. The acetone was allowed to evaporate for 10 min. and then the "sandwich" was scraped from the tarnish surface with a razor blade. The grid was placed in a vacuum evaporator and the extracted particles were coated with a layer of carbon. The specimens were then rinsed in acetone to completely dissolve the Bioten layer, leaving the tarnish particles embedded in the layer of carbon, e.g., Fig. 7. Microprobe analyses were carried out on the larger of these particles. An accelerating voltage of 15 KV was used for all of these analyses. The data obtained were analyzed in the same way as those from the sectioned samples.

RESULTS

Microprobe Analysis of Sectioned Specimens

Typical results are presented graphically in Figs. 1-5; the arrows in the accompanying micrographs indicate the approximate path traversed by the electron beam. The most significant feature of the data is that in each case the concentration of the alloying elements decreases dramatically as the beam crosses the metal-tarnish interface. The copper content can be seen to show a corresponding discontinuity. In the graphs, the concentrations appear to vary continuously across the interface over a distance of 2-4 μ , but this is due to the fact that, because of its finite width, the beam simultaneously samples both metal and the tarnish at sampling points in the proximity of the interface. It is considered that the variation in concentration across the interface is in fact discontinuous.

Portions of the data of Figs. 1-5 are presented in tabular form in Table 3. It can be seen that the magnitude of the concentration of alloying elements in the tarnish is small, but not zero. Moreover, with the exception of Cu-1.5Al, it is evident that concentration gradients exist in the tarnish; the concentration of the alloying elements being larger near the metal-tarnish interface. Note that the copper content does not show a corresponding gradient, ruling out the possi-

bility that the effect is due to the beam overlapping the interface.

The concentrations of alloying elements in the metal, as determined by the microprobe, were generally in good agreement with the results of chemical analysis (Table 1). However, in the case of a Cu-Al alloy the microprobe data (Fig. 3) indicate that the aluminum content is 2.5% while chemical analysis showed it to be 1.3%. This discrepancy is not fully understood, but may be due to an error in chemical analysis. It can be seen in Table 3 that the copper contents of the alloys were consistently below those determined by chemical analysis. These results were shown to be reproducible by recalibrating the instrument and repeating the analyses. It should be noted that an error of this magnitude, 2-4%, would not be significant in the analysis of the alloying elements.

The data, Fig. 1-5 and Table 3, indicate that the copper content of the tarnish ranges from approximately 73% for Cu-10Zn to approximately 81% for Cu-1.5Al. These values did not vary in any systematic fashion, i.e., there was no apparent relationship to the copper content of the metal or to the type of alloying element.

The interpretation of data in Fig. 1-5 is relatively straightforward. However, in some analyses, e.g., Fig. 6, more complex curves were obtained. It is thought that the

fluctuations of the type evident in Fig. 6 arise because of irregularities in the metal-tarnish interface and because of damage in the tarnish. For example, it is speculated that the increase in nickel content of the tarnish at A and the associated decrease of copper content is due to the fact that the electron beam is sampling metal at the base of the crack in the tarnish and that the x-ray intensity is reduced by subsequent absorption in the tarnish.

Microprobe Analysis of Extracted Particles

The data presented in Table 4 are in qualitative agreement with the data of the previous section in that the tarnish particles were found to contain only small concentrations of alloying elements. The data in this table are presented to only one decimal place because the results showed considerable scatter. The variation in results from particle to particle in the same sample is probably attributable to its small size and irregular shape, which caused difficulties in focusing and hence in maintaining a constant beam diameter at the particle surface. The copper content of the particles fell over a larger range, approximately 71% for Cu-5Zn to approximately 86% for Cu-3Al, then for the sectioned data, and this is considered to be due to the increased scatter.

In general, this technique was limited to the analysis

of specimens that could not be analyzed using the sectioning method. However, to obtain a direct comparison between the two techniques, an analysis was carried out on a particle extracted from Cu-10Zn. The values can be seen to be in reasonable agreement, cf. Tables 3 and 4.

DISCUSSION AND CONCLUSIONS

The most significant feature of the results is the small concentration of Al, Ni and Zn in the respective tarnish films. This observation is consistent with the dissolution-reprecipitation mechanism for tarnish growth. It was seen above that, according to the model, ions of both copper and the alloying element enter solution at the metal-tarnish interface, and that some of the copper reprecipitates at or near that interface, reportedly as cuprous oxide, the remainder diffusing in solution through the porous tarnish to the bulk solution. The low solute concentrations observed in the tarnish confirm the speculation stated in the introduction that the solubility of these alloying elements is large enough to deter their precipitation in the tarnish.

The fact that the concentration of the alloying element in the tarnish is not zero is thought to result from entrapment of solution, and hence ions of the elements in the porous tarnish following removal of the sample from the test solution. It is unlikely that the subsequent cleaning process would remove all of these ions and thus, on drying, small amounts of these elements would be expected to remain in the tarnish. The form (i.e., compound) in which these elements exist in the tarnish is not known. The results for the sectioned specimens, Figs. 1-5 and Table 3, indicated that

with the exception of Cu-1.5Al, a concentration gradient existed in the tarnish, the solute concentration being higher in the vicinity of the metal-tarnish interface. It is considered that this results because of the concentration gradient which existed during the dissolution process.

According to the model, the cuprous-oxide tarnish is formed by precipitation from solution by the reaction (1). Thus it would be expected that the composition of the film would be the same for each different alloy, and would approximate the stoichiometric composition of cuprous oxide, viz: 88.82 wt. % Cu. However, the results for sectioned specimens indicate that the tarnish contained considerably less than this value, e.g., from approximately 73-81 wt. % Cu, depending on the composition of the substrate. Clearly such values are not consistent with the tarnish being cuprous oxide, since it is unlikely that such deviations from stoichiometry can exist or that the microprobe analysis is in error by these amounts. It should be noted, in connection with the latter point, that the porous nature of the tarnish would not be expected to introduce significant error (12).

The view that the tarnish is predominantly cuprous oxide is based on diffraction studies by several workers on Cu-Zn alloys (4-7). However, it should be noted that x-ray diffraction by Sparkes and Scully (14) on the tarnish formed on Cu-1.8Be in ammonical solution indicated that the film

was cupric oxide. The stoichiometric composition of CuO is 79.88 wt. % Cu, and is in far better agreement with the present data. The majority of the diffraction studies on Cu-Zn alloys were carried out on tarnish films produced in different types of solution than that used in the present program, and thus it might be argued that the films produced are basically different. However, the electron-diffraction studies of Green et al. (4) on Cu and several Cu-Zn alloys employed a solution which was nominally identical to that used in our experiments. These workers reported that the film was cuprous oxide in each case, although no experimental data were presented.

It is evident from the preceding discussion that further diffraction studies are necessary to establish the structure of the tarnish. However, it can be concluded from the present results that the tarnish is essentially depleted with respect to the alloying elements, thus providing strong support for the dissolution-reprecipitation model for tarnish growth.

Table 1. Chemical Analysis of Samples

<u>Nominal Composition</u>	<u>Weight % Copper*</u>	<u>Weight % Solute</u>
Cu-5Zn	94.77 $\pm$.10	5.12 $\pm$.05**
Cu-10Zn	90.02 $\pm$.09	9.98 $\pm$.05**
Cu-20Zn	79.6 $\pm$.2	--
Cu-30Zn	70.05 $\pm$.07	--
Cu-.5Al	99.65 $\pm$.10	.47 $\pm$.02**
Cu-1.5Al	98.48 $\pm$.1	1.32 $\pm$.05**
Cu-3Al	96.86 $\pm$.1	3.07 $\pm$.15**
Cu-6Al	94.14 $\pm$.1	5.76 $\pm$.23**
Cu-2Ni	97.95 $\pm$.10	2.06 $\pm$.04***
Cu-5Ni	94.89 $\pm$.17	5.13 $\pm$.05***
Cu-15Ni	84.98 $\pm$.1	15.03 $\pm$.1 ***
Cu-25Ni	74.80 $\pm$.08	--

*Electrodeposition

**Flame Emission

***Titrimetric

Table 2. Trace Chemical Analysis (Mass Spectrographic Analysis)

Elements*	Nominal Composition of Alloy							
	Cu-5Zn	Cu-10Zn	Cu-20Zn	Cu-30Zn	Cu-.5Al	Cu-1.5Al	Cu-3Al	Cu-6Al
Pb	30	20	3	60	6	2	1	1.5
Sn	30	30	-	40	1	1	.6	.8
Ag	60	25	2	30	9	5	.6	3
Ga	-	-	-	-	2	5	4	.25
Zn	-	-	-	-	1	2	7	.8
Ni	25	12	.5	65	3	6	3	3
Fe	100	90	60	130	15	35	30	60
Mn	.5	2	.5	3	5	2	3	3
Cr	-	-	-	-	.3	.3	.3	1
V	-	-	-	-	2	3	3	.8
Ti	-	-	-	-	1	3	2	10
Ca	8	3	.3	2	.2	.5	1	3
K	8	2	-	3	-	-	-	4
Cl	-	-	-	-	.1	7	.1	4
P	.1	.8	-	.1	.2	.03	.1	.2

*All values given in ppm, atomic. This is a semiquantitative analysis with an accuracy of $\pm$ a factor of 3. Thus if 10ppm is reported, the true value lies between 30 and 3ppm.

Table 2. (Continued)

<u>Elements*</u>	<u>Cu-5Zn</u>	<u>Cu-10Zn</u>	<u>Cu-20Zn</u>	<u>Cu-30Zn</u>	<u>Cu-.5Al</u>	<u>Cu-1.5Al</u>	<u>Cu-3Al</u>	<u>Cu-6Al</u>
Si	60	9	5	5	6	15	20	45
Mg	-	-	-	-	10	15	4	12
Na	-	-	-	-	-	-	3	3
Nb	-	-	-	-	-	-	-	-
Al	6	1	.2	.8	-	-	-	-

*All values given in ppm, atomic. This is a semiquantitative analysis with an accuracy of $\pm$ a factor of 3. Thus if 10ppm is reported, the true value lies between 30 and 3 ppm.

Table 2. (Continued)

<u>Elements*</u>	<u>Cu-2Ni</u>	<u>Cu-5Ni</u>	<u>Cu-15Ni</u>	<u>Cu-25Ni</u>
Pb	2	3	3	5
Sb	-	-	-	-
Sn	-	-	-	-
Ag	6	k5	6	8
Ga	-	-	-	-
Zn	14	35	80	60
Ni	-	-	-	-
Fe	9	20	25	15
Mn	8	3	8	8
Cr	1	2	1	.7
V	.2	.2	.3	.2
Ti	-	-	-	-
Ca	20	20	3	.3
K	20	-	-	15
Cl	-	-	-	-
P	-	-	-	-
Si	80	80	270	120
Mg	750	750	430	600
Na	-	-	3	10
Nb	.03	.06	.1	.03
Al	5	15	15	15

*All values given in ppm, atomic. This is a semiquantitative analysis with an accuracy of $\div/x$ a factor of 3. Thus if 10ppm is reported, the true value lies between 30 and 3ppm.

Table 3. Point-by-Point Listing of Portions of the
Data Shown Graphically in Figs. 1-5

<u>Nominal Composition</u>	<u>Weight % Copper</u>	<u>Weight % Solute</u>	
Cu-10Zn	85.2	9.3	METAL
	85.7	9.4	
	85.8	9.2	
	86.2	9.3	
	85.8	9.3	
	84.4	8.6	INTERFACE REGION
	79.8	4.6	
	75.0	2.5	
	72.1	1.6	TARNISH
	72.0	1.3	
	72.4	1.2	
	72.4	1.1	
	72.8	1.0	
	73.6	1.0	
	73.7	.9	
	74.0	1.0	
	73.9	.98	
	73.1	.84	
	73.9	.93	
	74.0	.88	
	74.1	.85	
	73.6	.89	
	74.1	.84	
	73.7	.85	
	73.3	.81	
	73.6	.83	
	73.1	.76	
	72.7	.81	
	72.4	.84	
	72.2	.78	
	71.9	.72	
	72.5	.78	
	72.0	.78	
	71.7	.70	
	71.3	.69	
	71.2	.65	
	71.2	.70	
	71.8	.71	
	71.9	.61	
	71.5	.62	
	72.1	.71	
	72.6	.71	
	73.4	.76	
	73.4	.70	

Table 3. (Continued)

<u>Nominal Composition</u>	<u>Weight % Copper</u>	<u>Weight % Solute</u>	
Cu-30Zn	68.2	30.2	METAL
	68.2	29.7	
	68.4	29.7	
	68.2	29.6	
	68.6	29.2	
	70.2	23.9	INTERFACE
	75.6	10.8	REGION
	78.9	3.5	TARNISH
	79.6	2.4	
	78.8	2.0	
	79.5	1.7	
	79.0	1.5	
	75.5	1.5	
Cu-1.5Al	97.4	2.8	METAL
	97.0	2.5	
	96.7	2.5	
	95.8	2.4	
	96.9	2.4	
	96.0	2.3	
	94.3	2.1	INTERFACE
	92.1	1.6	REGION
	87.5	1.2	
	83.8	.58	
	82.9	.21	TARNISH
	82.2	.19	
	82.4	.19	
	82.8	.21	
	81.9	.32	
	83.1	.26	
	82.6	.23	
	81.5	.26	
	81.1	.19	
	81.2	.19	
	80.8	.30	
	81.3	.26	
	81.1	.21	
	80.7	.17	
	80.0	.23	
	80.6	.19	
	80.5	.22	
	79.7	.20	
	78.8	.16	
	79.3	.25	
	80.4	.18	

Table 3. (Continued)

<u>Nominal Composition</u>	<u>Weight % Copper</u>	<u>Weight % Solute</u>	
Cu-1.5Al (Continued)	79.7	.17	
	80.7	.28	
	80.9	.20	
	81.6	.24	
	80.9	.23	
	81.3	.15	
	81.6	.22	
	81.3	.27	
	80.9	.30	
	81.7	.29	
	80.7	.20	
	80.6	.28	
	80.7	.22	
Cu-2Ni	94.2	2.2	METAL
	93.0	2.1	
	94.0	2.2	
	94.2	2.1	
	91.8	2.0	INTERFACE
	85.8	1.3	REGION
	80.3	.77	TARNISH
	79.7	.59	
	79.1	.43	
	79.7	.32	
	78.9	.28	
	79.7	.33	
	79.2	.26	
	78.6	.30	
	76.9	.30	
	78.2	.27	
	76.9	.21	
	76.2	.18	
	76.3	.19	

Table 3. (Continued)

<u>Nominal Composition</u>	<u>Weight % Copper</u>	<u>Weight % Solute</u>	
Cu-5Ni	90.6	5.4	METAL
	90.6	5.5	
	90.9	5.4	
	90.4	5.3	
	86.8	4.8	INTERFACE REGION
	81.7	2.4	
	79.6	1.0	
	79.4	.83	
	78.5	.70	TARNISH
	78.5	.65	
	78.4	.64	
	78.3	.53	
	77.4	.54	
	77.4	.55	
	77.1	.52	
	75.8	.45	
	76.7	.47	
	76.3	.43	
	76.5	.40	
	76.2	.41	
	75.7	.36	
	74.2	.37	
	75.5	.35	
	74.6	.37	
	74.4	.33	
	74.9	.33	
	74.8	.33	
	74.5	.32	
	73.5	.35	
	74.6	.37	
	75.9	.36	

Table 4. Results of Microprobe Analysis on Extracted Tarnish Particles

<u>Nominal Composition</u>	<u>Weight % Copper</u>	<u>Weight % Solute</u>
Cu-5Zn	70.9	1.2
Cu-10Zn	73.	1.3
Cu-20Zn	81.5	0
Cu-.5Al	85.5	.3
Cu-3Al	85.9	.1
Cu-6Al	82.7	.7

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Fig. 1. Cu-10Zn (Arrow on micrograph indicates approximate path traversed by the electron beam.)

Fig. 2. Cu-30Zn (Arrow on micrograph indicates approximate path traversed by the electron beam.)

Fig. 3. Cu-1.5Al (Arrow on micrograph indicates approximate path traversed by the electron beam.)

Fig. 4. Cu-2Ni (Arrow on micrograph indicates approximate path traversed by the electron beam.)

Fig. 5. Cu-5Ni (Arrow on micrograph indicates approximate path traversed by the electron beam.)

Fig. 6. Cu-15Ni (Arrow on micrograph indicates approximate path traversed by the electron beam.)

Fig. 7. Particles of tarnish extracted from Cu-5Zn.