

# DEALLOYING AND STRESS-CORROSION CRACKING OF COPPER ALLOYS IN $Cu(I)$ SOLUTIONS

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**Abstract** Natural cases of dealloying or stress-corrosion cracking in copper alloys normally occur in oxygenated solutions, where the cathodic reactant is  $O_2$  or  $Cu^{2+}$ . Within cavities or under deposits, the local environment is enriched in cuprous ions (e.g.  $CuCl_2^-$ ,  $Cu(NH_3)_2^+$ ) and the potential is close to the  $Cu/Cu^+$  equilibrium. Such conditions can be simulated macroscopically by stirring powdered  $Cu_2O$  and  $Cu$  in  $NaCl$  or  $NH_3$  solutions, and the rate of dealloying can be monitored electrochemically at the  $Cu/Cu^+$  equilibrium potential. For  $\alpha$ -Brass, the gross form of dealloying seen in chloride solutions does not normally cause stress-corrosion cracking, which is correlated with the superficial form of dealloying seen in ammonia solutions or in chloride solutions containing ammonium ions. The latter is especially significant, as the effect occurs at pH 5 where there is only a minute complexing action of ammonia. The results indicate that  $NH_4^+$  ions have a special action in relation to dealloying, which is quite separate from the complexing action of  $NH_3$  in neutral or alkaline solutions. The action of alloyed arsenic in inhibiting dealloying seems to be similar to the action of  $NH_4^+$  ions. Thin dealloyed layers formed in cuprous ammonia solutions have been shown to nucleate unstable cleavage fracture in thin foils of  $\alpha$ -Brass.

**چکیده** خوردگی زدایش روی و خوردگی تنش در آلیاژهای مس معمولاً در محلولهای حاوی اکسیژن رخ می دهند که در آنها عامل واکنش کاتدی  $O_2$  یا  $Cu^{2+}$  هستند. محیط در زیر لایه های رسوب یافته و یا در داخل حفره های موجود بر سطح این آلیاژها، بطور موضعی از یونهای یک ظرفیتی مس اشباع است (مثل یونهای  $CaCl_2^-$  و  $Cu(NH_3)_2^+$ ) و پتانسیل سیستم خیلی نزدیک به پتانسیل تعادل  $Cu/Cu^+$  می باشد. چنین محیطی را می توان بطور ماکروسکوپی با بهم زدن پودر  $Cu_2O$  و  $Cu$  در محلولهای آمونیاکی یا کلرور سدیم بوجود آورد و سرعت خوردگی زدایش روی در این محلولها را می توان بطور الکتروشیمیایی در پتانسیل تعادلی  $Cu/Cu^+$  اندازه گیری کرد. برای آلیاژ برنج  $\alpha$ ، خوردگی زدایش روی که در محلولهای کلریدی اتفاق می افتد معمولاً تولید خوردگی تنش نمی کند و در واقع عامل اصلی خوردگی تنش در این آلیاژها وجود لایه های بسیار نازک حاصل از خوردگی زدایش روی می باشد که معمولاً در محلولهای آمونیاکی و یا محلولهای کلریدی حاوی یونهای آمونیوم بوجود می آید. مشاهده خوردگی تنش مخصوصاً در محیط های کلریدی حاوی یونهای آمونیوم بسیار حائز اهمیت است زیرا در pH حدود 5 اتفاق می افتد و در این pH تمایل تشکیل ترکیبات کمپلکس برای  $NH_3$  بسیار کم می باشد. نتایج نشان می دهند که یونهای  $NH_4^+$  دارای عملکرد ویژه ای در ارتباط با خوردگی زدایش روی بوده که کاملاً از عملکرد کمپلکس تشکیل دهندگی  $NH_3$  در محیط های خنثی و قلیایی مجزا است. همچنین نتایج نشان می دهند که مکانیزم مسامتت کنندگی «آرسنیک در مقابل خوردگی زدایش روی کاملاً شبیه مکانیزم مسامتت کنندگی» یونهای  $NH_4^+$  می باشد. لایه های بسیار نازک حاصل از خوردگی زدایش روی که در محلولهای آمونیاکی حاوی یونهای یک ظرفیتی مس تشکیل می شوند باعث ایجاد شکست ترد ناپایدار در فولهای برنج  $\alpha$  می گردند.

## INTRODUCTION

The use of cuprous ion solutions to study dealloying and stress-corrosion cracking of copper alloys, especially  $\alpha$ -brass, has been described in earlier publications [1, 2]. The rationale is that natural dealloying or SCC occurs within cavities or under deposits in oxygenated solutions, where the local environment tends towards the  $Cu/Cu^+$  equilibrium [3, 4]. The advantage of using

cuprous solutions in the laboratory is that the rate of dealloying can be monitored electrochemically by controlling the potential at or near zero volts versus a copper reference electrode.

Figure 1 shows the correlations between dealloying and SCC for Cu-Zn and Cu-Al alloys in cuprous ammonia solutions [1]. In these solutions the dealloying is very superficial, as indicated by the lack of color

change of the brass over periods of several days, but the first few hundred of attack occurs quite rapidly—typically at  $\sim 1$  mA/cm<sup>2</sup>. This contrasts with cuprous chloride solutions (Figure 2), where sustained dealloying can be obtained to depths of mm [2]. This macroscopic dealloying has an inverse correlation with SCC in this system. The presence of 0.03% As was shown to inhibit dealloying almost completely.

The purpose of this paper is to show how simple electrochemical methods can be used to explore further the relationship between dealloying and SCC. The behavior of artificial crevices in NaCl solutions free from cuprous ions has been correlated with the behavior in the synthetic crevice solution shown in Figure 2. The dealloying in cuprous ammonia solutions has been followed for long periods, and the ability of the resulting layers to nucleate cleavage of thin foils has been studied. The effect of NH<sub>4</sub>Cl additions to NaCl-based dealloying media (as used in Figure 2) has been

examined.

## EXPERIMENTAL PROCEDURE

The experiment in chloride solution used 3.5% (0.6M) NaCl solution at 60°C, stirred with excess powdered Cu, Cu<sub>2</sub>O and CuCl in a sealed conical flask with copper counter and reference electrodes, as described previously [2]. Oxygen in the solution and small air space was consumed by reaction with the copper powder (via the Cu<sup>2+</sup> state). The brass specimens (annealed commercial Cu<sup>30</sup>Zn and Cu - 30Zn - 0.03 As) were mounted in epoxy resin, wet-abraded to 4000-grit, washed with methanol, air-dried, and masked with lacquer to leave an exposed surface area of  $\sim 2$  mm<sup>2</sup>. Ammonium chloride was added in some tests. The potential of the copper reference electrode was measured against an SCE in each solution.

The experiments in ammonia solution were done at 20°C and used a similar arrangement. The solution was 15M

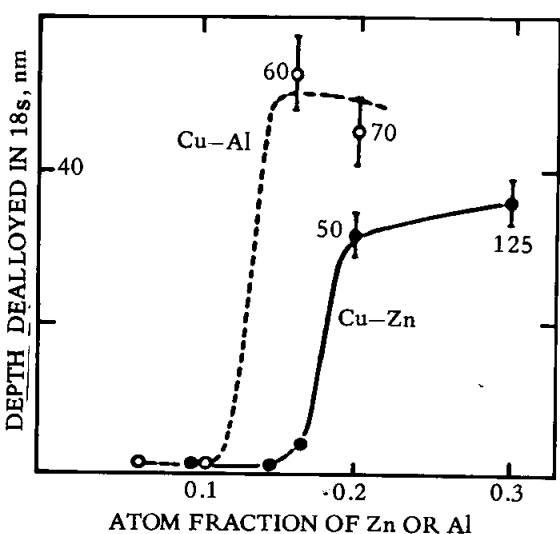


Figure 1. Dealloying of Cu-Zn and Cu-Al alloys, as measured in scratch tests at  $0 V_{Cu}$  in 15M NH<sub>3</sub> + 0.05M Cu solution [1]. The numbers next to the data points denote the SCC velocities, in nm/s, measured in slow strain rate tests of monocrystals in the same solution; no number indicates no SCC.

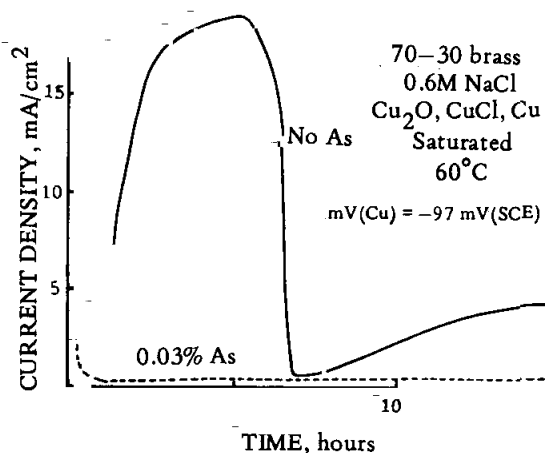


Figure 2. Dealloying kinetics of 70-30 brass, with and without arsenic, in 0.6M NaCl stirred with excess Cu, CuCl and Cu<sub>2</sub>O at  $0 V_{Cu}$  and 60°C [2].

ammonia, stirred with copper and enough  $\text{Cu}_2\text{O}$  to give 0.04M cuprous ions (this time the solution was not saturated with  $\text{Cu}^+$ ). In addition to the 30Zn and 30Zn-0.03As alloys, a nominally 37Zn (actually 35Zn) alloy was purchased from Goodfellow Metals as 500  $\mu\text{m}$  and 12.5  $\mu\text{m}$  sheets. Both were at least 98% and probably 100% alpha phase. The 500  $\mu\text{m}$  sheet was annealed at 550°C for one hour (giving 100% $\alpha$ -phase) and mounted for current-time measurements, as described above, while the 12.5  $\mu\text{m}$  sheet was cut into 4 mm-wide strips which were gently dry-abraded with 4000-grit paper and simply immersed in the solution for 100 minutes. Some of these were manually strained to fracture in the solution (strain rate > 100%/s), while others were removed, washed in distilled water and methanol, air-dried, and strained to fracture in air. A complete account of this part of the work is given elsewhere [5].

Crevice experiments were carried out on 3 mm-dia. disc electrodes of the 30Zn and 30Zn-0.03As alloys, mounted in cylindrical 32 mm-dia. epoxy mounts as used for metallography. Short lengths of 100  $\mu\text{m}$ -dia. copper wire were used as spacers between the specimen mounts and PTFE discs of the same radius, held on with elastic bands, i.e. the outer perimeter of each brass electrode was 14.5 mm from the mouth of its crevice. These specimens were anodically polarized in 3.5% NaCl solution at 60°C, using the same potential that was measured (with respect to SCE) for a copper electrode in the same solution stirred with excess Cu,  $\text{Cu}_2\text{O}$  and CuCl - i.e. if the center of the crevice achieves saturation in cuprous ions, and if there is no IR drop down the crevice (unfortunately there always is), then the electrodes should behave similarly in the

crevice tests and the macroscopic crevice simulation solution.

## RESULTS AND DISCUSSION

### Simulated Crevice Solutions

Figure 2 shows the typical behavior of the brasses in the 3.5% NaCl solution equilibrated with Cu,  $\text{Cu}_2\text{O}$  and CuCl at 60°C. The potential in this test was -97 mV (SCE). The result for the Cu-30Zn alloy was not perfectly reproducible in the early stages, as the initiation of dealloying in the air-formed oxide film was localized, giving an initially hemispherical layer growth [2] as shown in Figure 3. The two layers in each hemispherical region correspond to the material formed before and after the abrupt drop in the current after ~ 6 hours in Figure 2; this drop was reproducible and may be due to a blocking of porosity in the layer by copper plating from negatively charged cuprous ions ( $\text{CuCl}_2^-$ ) migrating into the layer under the influence of the ohmic potential gradient [2]. The inner layer has been found to retain a few percent of zinc, while the outer layer is essentially pure copper.

Clearly this type of test has considerable potential for alloy testing development, since it neatly displays the inhibiting effect of alloyed arsenic as shown in Figure 2.

Addition of  $\text{NH}_4\text{Cl}$  to the 3.5% NaCl solution dramatically inhibited the dealloying, and at 0.01M  $\text{NH}_4\text{Cl}$  there was scarcely any difference between the 30Zn and 30Zn - 0.03As alloys (Figure 4). No dealloying was detectable on polished cross-sections of these surfaces. The effect of  $\text{NH}_4\text{Cl}$  on the potential of the copper reference electrode was less than 1 mV - not surprisingly, as the pH of the solution is 5.1



Figure 3. Typical cross-sectional appearance of dealloyed layers grown on non-arsenical brass in chloride solution, as in Figure 2. Shows localized initiation and hemispherical layer growth. The macro-porosity is a polishing artifact, but the layered appearance is real - see text.

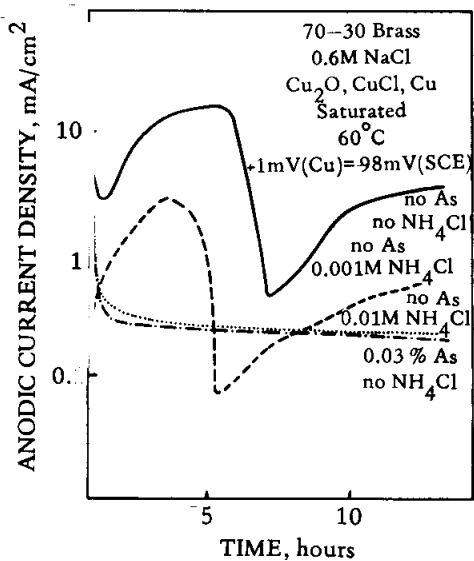


Figure 4. Current-time curves for 70-30 brass, with and without arsenic, showing the inhibiting effect of adding  $\text{NH}_4\text{Cl}$  to the solution used in Figure 2.

and there is only a minute complexing action of ammonia at this pH [6]; thus the effect is clearly a surface one associated with adsorption of  $\text{NH}_4^+$ . There appears to be a close analogy between the effects of alloyed As and dissolved  $\text{NH}_4^+$  (or dissolved As [7]).

It is tempting to note that N and As are both in Group Vb of the periodic table, and seem to have similar effects on dealloying; also to note that any alloying element from Group Vb will enhance chloride SCC of austenitic stainless steels [8] which is also probably due to dealloying [9]. Apparently N or As can hinder the surface diffusion of copper atoms which opens up the channels for penetration of electrolyte to the dealloying front; the extremely fine (nanoporous) structure obtained with N or As is required for SCC, since it is only by subdividing at a nm level that an fcc metal can be rendered brittle [10].

In future work, we hope to confirm that SCC of non-arsenical  $\alpha$ -brass occurs in the cuprous solution containing 3.5% NaCl and 0.01M  $\text{NH}_4\text{Cl}$ , but not in the solution containing NaCl only [11]. This would be the first demonstration that SCC of  $\alpha$ -brass can be induced by ammonium salts under

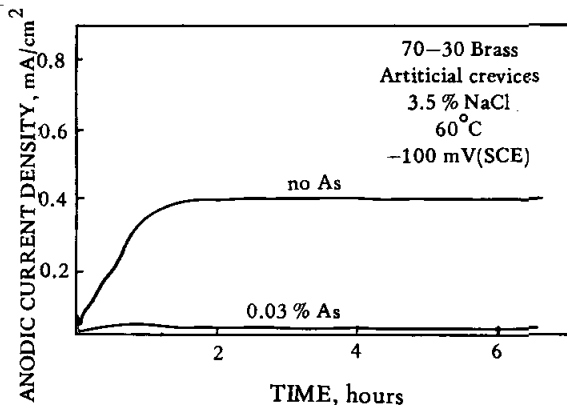


Figure 5. Current-time curves for artificial crevice specimens of 70-30 brass, with and without arsenic, in 3.5% NaCl solution without cuprous ions at  $60^\circ\text{C}$  and  $-100\text{ mV (SCE)}$ .

conditions where virtually no complexation by  $\text{NH}_3$  is possible, provided that another complexant of  $\text{Cu(I)}$  is also present.

### Artificial Crevices in NaCl Solution

The crevices tests in NaCl solution at  $60^\circ\text{C}$  and  $-100\text{ mV (SCE)}$  gave a good indication of the beneficial effect of arsenic, as shown in Figure 5. Because of the crevice geometry, there was a significant IR potential drop, and the anodic current density on the non-arsenical alloy was much less than in Figure 2. There seems to be no pressing reason to use artificial crevices in any standard electrochemical test procedure, (where the current is the criterion of dealloying) but they could be useful for a potentiostatic immersion test in which the dealloying is evaluated metallographically.

### Cuprous Ammonia Solutions

Dezincification in cuprous ammonia solutions was much slower than in any of the chloride solutions, reaching only a few tens of nm in several hours; apparently the scratch tests used previously [1] greatly accelerated the early stages of dealloying.

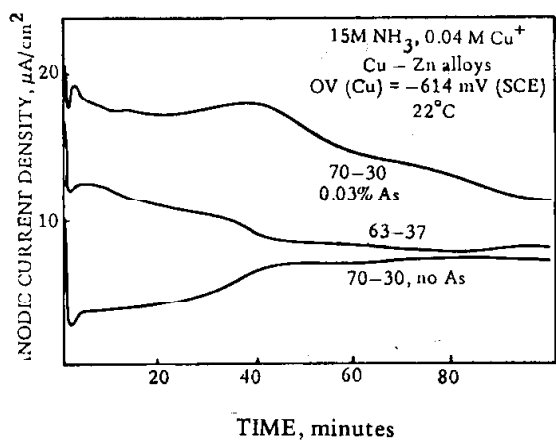


Figure 6. Dealloying kinetics of 30Zn, 30Zn-0.03As and 35Zn ("37Zn") brasses in cuprous ammonia solution.

The small extent of dealloying was confirmed by the lack of a color change on specimens immersed for many hours at  $0\text{ V}_{\text{Cu}}$ . Figure 6 displays typical current - time curves for three alloys, indicating that alloyed arsenic has little or no effect on this superficial form of dealloying - in fact it reproducibly gave higher current densities. This is consistent with the well - known susceptibility of arsenical brasses to ammonia-induced SCC [12]. The "37%" (actually 35%) alloy dealloyed significantly more rapidly than the 30% non-arsenical alloy, as might be expected.



(a)



(b)

Figure 7. Fracture surfaces of Cu-35Zn foils after 100 min. immersion in cuprous ammonia solution: (a) removed, washed and dried before rapid-straining ( $> 100\%/s$ ); (b) rapid-strained while still in the solution.

12 $\mu$ m-thick foil specimens of the 35% Zn brass were embrittled by this superficial dealloying, so long as they were strained in the solution or after quick-freezing in liquid nitrogen without rinsing; if the dealloyed surfaces were washed and/or dried at room temperature, the foils regained their strength and fractured in a ductile manner [5]. Apparently the dealloyed layer retains its nanoporous condition at room temperature, enabling it to nucleate cleavage [10, 13], so long as ammonia is in contact with the surface, but if the ammonia is removed there is a rapid aging process (e. g. coarsening of the porosity by surface diffusion) which renders the layer ductile. Fracture surfaces of two foil specimens are shown in Figure 7.

## CONCLUSIONS

1. Electrochemical measurements in Cu (I) solutions reproduce the effects of alloy and environment composition on the dealloying and SCC of  $\alpha$ -brass.
2. The role of crevices in dezincification has been demonstrated.
3. Ammonia or ammonium ions actively inhibit coarsening of the porosity within dealloyed layers on  $\alpha$ - brass. There are close parallels between this action and that of alloyed arsenic. The superficial, very fine porosity is required for cleavage nucleation during SCC, whereas gross dealloying in chloride solutions does not

normally lead to SCC.

4. The effect of ammonia in causing SCC of brass is a dual one: it complexes copper ions and provides a favorable (Cu(I) - containing) local environment, but more importantly it adsorbs on the surface and produces the right kind of dealloyed layer. The latter action does not require any complexation by  $\text{NH}_3$  so long as another complexant of Cu(I), such as chloride, is present.

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