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copper dissolution. The conditions for tarnish formation and the nature of this cuprous-oxide layer were also studied.

Potentiostatic studies of the potential dependence of SCC of annealed Cu-30Zn established that the critical potential for cracking corresponds to the reversible potential for copper dissolution. Moreover, SCC was shown to be predominantly intergranular in potential ranges where tarnishing occurs and transgranular in non-tarnishing ranges. These and other observations lend support to our view that inter- and transgranular SCC involve different mechanisms. The former is considered to occur by the film-rupture model. The mechanism of transgranular cracking has not been established, but fractographic and acoustic-emission studies of both Cu-30Zn and Admiralty Metal indicated that this form of cracking occurs by discontinuous cleavage on {110} planes.

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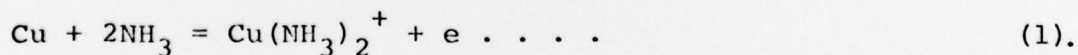
INTRODUCTION

This report summarizes the results of an investigation carried out at the University of Illinois at Urbana-Champaign during the period March 1, 1974 - February 28, 1977. The work was a continuation of an earlier program at the University of Illinois (Grant No. ARO-DG-70) and at the Martin-Marietta Corporation (Contract No. DA-31-124-ARO-D-258). The program has dealt with the corrosion and stress-corrosion cracking (SCC) of alpha-phase Cu-Zn alloys, specifically Cu-30Zn and Admiralty Metal, in aqueous ammonia. While the studies have been restricted to this specific system, the mechanistic conclusions are considered to have broad application to other systems.

SUMMARY OF MAIN FINDINGS

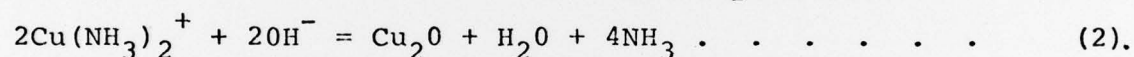
1. Corrosion Behavior of Unstressed Material

Understanding of the stress-corrosion phenomena requires a detailed knowledge of the chemistry and electrochemistry of the system, and thus attention was also directed to the behavior of unstressed copper and α -brasses in the ammoniacal solutions. Our previous work, reviewed at NATO Conferences (1, 2), indicated that exposure of the materials to these solutions can lead to rapid anodic dissolution in the absence of detectable surface films, or to the formation of a thick "tarnish" layer, depending on the composition of the solution. Weight-loss and corrosion-potential measurements (3) suggested that the corrosion process in non-tarnishing solutions is under concentration polarization, being controlled by the transport of the primary cathodic species, $\text{Cu}(\text{NH}_3)_4^{2+}$, to the surface. Extensive polarization studies during the period under report confirmed this view (4,5). In addition, the polarization data led to the determination of the reversible potential, the exchange current density and the Tafel slope for the copper dissolution reaction



The reversible potential, in particular, will be seen to be important in the interpretation of stress-corrosion behavior. It is also interesting to note that increasing the zinc content of the brass was found to cause a progressive increase in the exchange current density for reaction (1), with no significant change in the reversible potential or Tafel slope.

Interpretation of our data has been greatly assisted by the model of Bertocci (6,7), based on a description of the transport processes in solution; part of this model (7) was developed during the Principal Investigator's sabbatical leave at the National Bureau of Standards (August - December 1976). According to the model, concentration gradients are set up at the metal surface during dissolution in the tarnish-free range as shown in Fig. 1. The near-surface concentration of cuprous complex ions is considered to increase with increasing concentration of cupric complexes in the bulk until, at a critical value, the solubility of the tarnish, Cu_2O , is exceeded,



The model permits the calculation of the near-surface concentration of cuprous ions in terms of the bulk concentration of dissolved copper and thus the value of the latter at which tarnishing first occurs can be estimated using the equilibrium constant for reaction (2). This value has been found to be in excellent agreement with our experimental data (4,8).

Microscopical (optical and SEM), potentiostatic and ellipsometric studies have been made of the growth of the tarnish film (4,8). Tarnishing was found to commence with the formation of a thin ($250 \text{ \AA}$ max) passive film of Cu_2O , which subsequently breaks down locally to form a thick (up to $\sim 10 \text{ }\mu\text{m}$) precipitated Cu_2O layer. The kinetics of passive film growth were not significantly influenced by the zinc content of the substrate, but film breakdown was more rapid as the zinc content increased. No systematic

investigation was made of the structure and composition of the protective film, or of the breakdown process. Auger analysis by other workers (9) suggests that it contains significant amounts of zinc. Electron microprobe studies of the thick precipitated layers formed on Cu-Zn (and Cu-Al and Cu-Ni alloys) established that, in contrast, the Cu_2O is essentially depleted with respect to zinc (and the other alloying elements), consistent with the view that these layers are formed by a dissolution-reprecipitation mechanism (10,11).

2. Stress-Corrosion Behavior

Stress-corrosion failures occur in both non-tarnishing and tarnishing solutions, but significant differences in characteristics exist (2). For example, annealed Cu-30Zn undergoes intergranular stress-corrosion cracking (I-SCC) in tarnishing solutions and predominantly transgranular cracking (T-SCC) in the non-tarnishing case. On the basis of our work, it seems probable that two different mechanisms are operative in the two cases.

During the period covered by this report, a systematic study has been made of the effects of applied potential on the SCC of annealed Cu-30Zn in various solutions preconcentrated with copper (12). The results, e.g., Fig. 2, confirmed the general relationship between stress-corrosion failure time, t_f and potential reported by Uhlig, Gupta and Liang (13), but provided considerable further information. In particular, it was found that the

path of cracking is I in potential ranges where the tarnish film is formed (except at potentials near the upper limiting potential where rapid anodic dissolution occurred), whereas cracking is T in non-tarnishing ranges, Fig. 2. Moreover, the lower limiting potential, termed the critical potential by Uhlig et al. (13) and considered by these workers to be the potential below which adsorption of the damaging ionic species does not occur, was found to approach (within 20-30 mV) the reversible potential for copper dissolution discussed above. In the preconcentrated solutions used in our experiments and by Uhlig et al. (13), copper deposition occurs at potentials below the reversible value, and this in itself would be expected to inhibit SCC. In oxygenated ammoniacal solutions containing no added copper (before the test), no cracking occurs at E_{cor} , despite the fact that it is above the reversible potential for copper dissolution, and further anodic overvoltage must be applied potentiostatically to induce T-SCC (3). Thus it appears that the reversible potential per se has no fundamental significance in the stress-corrosion process, but that a critical potential for SCC does exist, which is either equal to or greater than the reversible potential. The interpretation of the critical potential for SCC will be discussed further below.

Our results, both during the present period and in previous periods, are consistent with I-SCC of annealed Cu-30Zn occurring by the classical Logan-Champion film-rupture mechanism, that is, by preferential anodic dissolution of film-free metal at the crack

tip where the passive Cu_2O film is continually ruptured by localized plastic deformation. Thus, in our studies, I-SCC of annealed Cu-30Zn is confined to conditions where the protective film is produced. The view that propagation occurs entirely by dissolution is in accord with acoustic emission (AE) studies which indicate no evidence of large-amplitude signals characteristic of mechanical fracture (12). Further, the velocity of cracking, $\sim 10^{-4}$ cm/s, requires a current density of $\sim 1 \text{ A/cm}^2$, which is not excessively large. The path of cracking is due probably to the slower repassivation of the grain-boundary regions compared to that of the grain centers. The penetration of the boundaries in unstressed specimens by the thick tarnish (14) presumably also results from this slower passivation. Thus, rather than being the basic cause of I-SCC as suggested in our earlier work (1), intergranular penetration is now considered to be a secondary effect, related to the underlying cause--the slower repassivation kinetics at grain boundaries. These comments relate mainly to propagation, and it is possible that intergranular attack plays an important role in crack initiation.

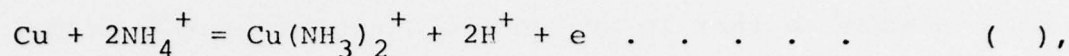
T-SCC in this and other systems is more poorly understood, and the characteristics of this type of failure have been studied extensively during the present grant (12,15). This work was carried out on both Cu-30Zn and Admiralty-Metal, the latter being used since the presence of tin apparently favors T-SCC, even in tarnishing media. The characteristics of T-SCC appear to be the same in both alloys. The fracture surfaces are cleavage-like in

appearance, being characterized by flat facets separated by serrated steps. It was established that the latter are approximately perpendicular to the crack front, and that pronounced undercutting occurs at the steps. Detailed orientation studies of Admiralty-Metal monocrystals demonstrated that the fracture facets are $\{110\}$ and the faces of the steps $\{111\}$ (15). Fractographic studies of both alloys showed the presence of crack-arrest markings, spaced at $\sim 5 \mu\text{m}$, and these indicate that propagation is discontinuous. This view was supported by the occurrence of discrete AE events during cracking, in contrast to the case of I-SCC, discussed above.

The preceding description leaves little doubt that T-SCC involves discontinuous cleavage on $\{110\}$ planes. The mechanism of embrittlement has not been established. The absence of protective surface films in non-tarnishing solutions and the discontinuous nature of cracking rule out the film-rupture model. The adsorption, or stress-sorption model (13), postulates brittle fracture and thus must be considered a candidate. However, it is difficult to rationalize discontinuous cracking in terms of this model, which would seem to predict continuous propagation at a rate controlled by the transport of the "critical" ionic species to the crack tip. Moreover, the distance of crack advance per event, $\sim 5 \mu\text{m}$, does not seem reconcilable with the adsorption concept, since the effects of adsorbed species would be felt for only a few atom layers below the surface. Another question associated with the adsorption model concerns the

identity of the critical species in this system. Uhlig et al. (13) have suggested that it is the cupric complex, $\text{Cu}(\text{NH}_3)_4^{2+}$, but it has been shown in our work (3) that the physical presence of this ion is not necessary for cracking, which can be produced in potentiostatic experiments in de-oxygenated solutions in which the cupric ions are not produced. It is possible, however, that the cuprous ions, $\text{Cu}(\text{NH}_3)_2^+$, could represent the critical species. Finally, our results support the view that a critical potential exists for T-SCC which is equal to or greater than the reversible potential for copper dissolution. The possibility that this corresponds to the potential at which adsorption of the damaging species occurs cannot be ruled out, but it is possible, alternatively, that a critical anodic current density exists for cracking. Further experiments are necessary to distinguish between these views.

An alternative possibility is that T-SCC is a form of hydrogen embrittlement (HE). The characteristics of T-SCC in Cu-Zn are closely similar to those in other systems, e.g., austenitic stainless steels, Al-Zn-Mg alloys, and Mg-Al alloys (16), and there is evidence in these cases to support HE. However, there is no such evidence in the present case--indeed, attempts in the present work to implicate hydrogen have been totally unsuccessful (15). The correlation between the critical potential and the reversible potential is particularly difficult to rationalize in terms of a hydrogen model. We have speculated that hydrogen is generated by the anodic dissolution of copper (2),



but there is no evidence for the occurrence of such a reaction. Further, the observation that T-SCC occurs in other environments, e.g., aq $\text{SO}_4^{=}$ (17,18) and aq NO_3^- (19), rules out a specific role of NH_3 as a source of hydrogen.

A further alternative mechanism for T-SCC is that it is caused by selective dissolution of zinc (20). There is some evidence for dezincification at the transgranular fracture surfaces (21), but there are a number of problems facing the model. For example, cracking does not occur in aq NaCl and other solutions which are known to cause dezincification. Moreover, pure copper has been reported to undergo cracking in non-tarnishing solutions (22), although this result is controversial (1,2).

It is concluded, then, that T-SCC in the brass-aq NH_3 system occurs by discontinuous brittle fracture (cleavage), but that the mechanism has not been established. I-SCC in this system is considered to occur by a basically different process, namely by the film-rupture mechanism. Cracking of annealed Cu-30Zn is entirely transgranular in non-tarnishing media, but the two mechanisms are competitive in tarnishing solutions. Our experiments have shown that T-SCC in such solutions favored by cold work (12) and by the addition of tin to the alloy (15). It should be noted finally that these findings are not specific to this system, but have broad generality. Thus the mechanism of T-SCC is considered to be common in the brasses and a number of other alloys including austenitic stainless steel, aluminum alloys, and magnesium alloys; I-SCC in brass is believed to involve the

same process as that in austenitic stainless steel, mild steel and other materials. The competition between I- and T-SCC is also observed in several of those other alloy systems.

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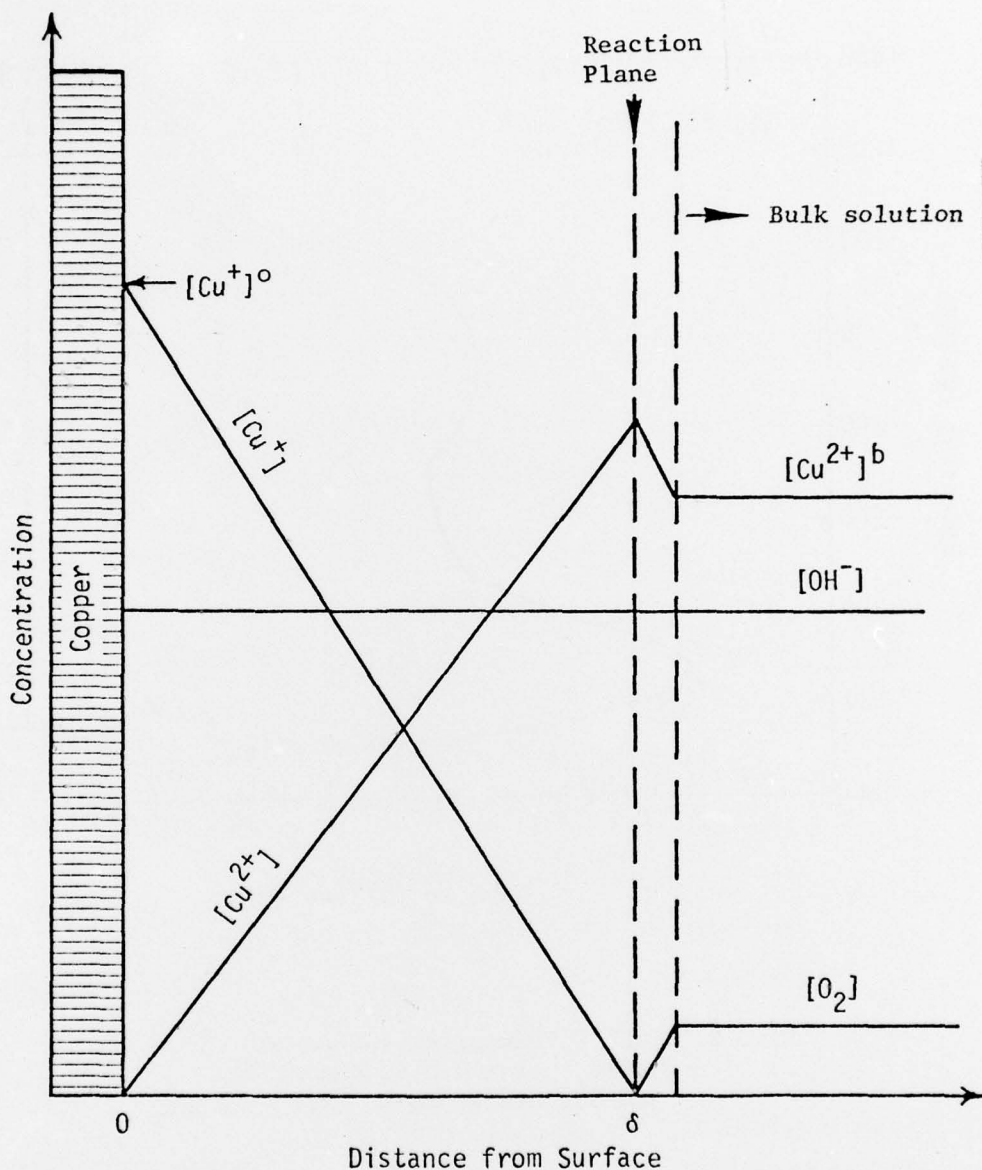


Fig. 1. Schematic illustrating the concentration gradients of cuprous complex ions, denoted by $[Cu^+]$, cupric complex ions, $[Cu^{2+}]$, and oxygen at the surface of copper in a non-tarnishing ammoniacal solution (6).

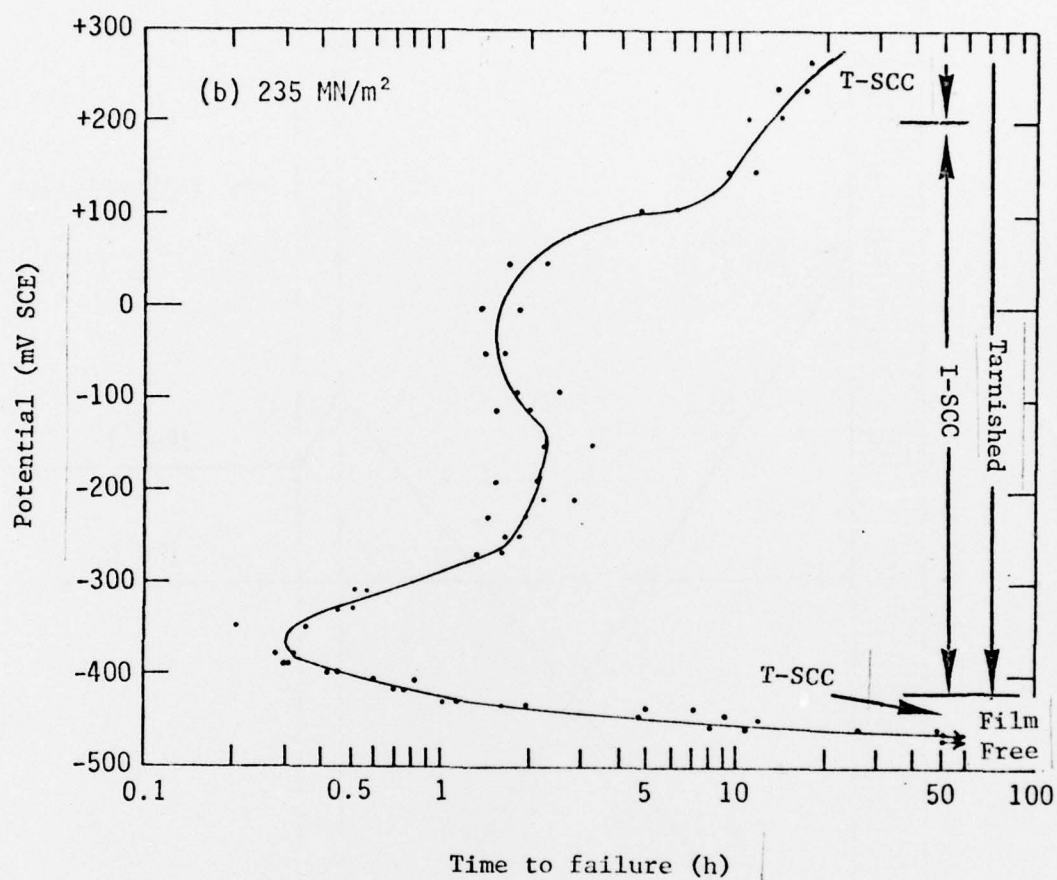


Fig. 2. The potential dependence of the time to failure of annealed Cu-30Zn in 1N aq NH₃(12).