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CRACKING OF α - BRASS

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ABSTRACT

A study has been made of the stress-corrosion cracking, rate of weight loss, and surface condition of an alloy containing 70% copper and 30% zinc in $\sim$ 15N aqueous ammonia. The behavior is shown to be strongly dependent on the concentration of the cupric complex ion $Cu(NH_3)_5^{2+}$ present in the environment. Stress-corrosion life decreased significantly with increasing complex ion concentration, the relationship exhibiting a well-defined inflection at a critical concentration. Specimens immersed in solutions of concentrations exceeding the critical value were tarnished, while those exposed to less concentrated solutions appeared tarnish-free. These and other observations indicate that two mechanisms of stress-corrosion cracking are operative, one in the presence of tarnish and the other in the absence of this layer. Possible mechanisms are discussed.
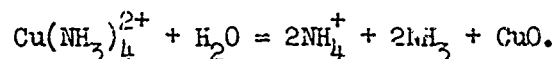
A model has been developed to explain the dependence of the tarnishing reaction on the chemical composition of the environment.

§I. INTRODUCTION

The tarnish-rupture theory, proposed by Forty and Humble (1963) and developed by McEvily and Bond (1965), represents a significant advance in our understanding of the stress-corrosion cracking of α-brass in aqueous ammoniacal solutions. According to this theory, cracking is mechanical and is confined to the characteristic black oxide layer, commonly termed the tarnish, proceeding by the repeated formation and rupture of this layer. Electron-diffraction studies (Forty and Humble 1963) suggest that the tarnish consists largely of Cu_2O set in a brass matrix depleted with respect to zinc.

While there is good supporting evidence for the tarnish-rupture model (Forty and Humble 1963, McEvily and Bond 1965), it has yet to be correlated with several other significant observations. In particular, it has not been reconciled with the fact that cupric complex ions, $Cu(NH_3)_n^{2+}$, play an important role in the stress-corrosion process (Althof 1944, Graf and Richter 1961, Mattsson 1961, Pugh and Westwood 1964, 1965). The role of the complex ions has not been explained. Graf and Richter (1961) have suggested that the complex ion $Cu(NH_3)_4^{2+}$ is important because of the reaction

$$Cu(NH_3)_4^{2+} + H_2O = 2NH_4^+ + 2NH_3 + CuO.$$

According to these workers, large concentrations of the complex ion favour the forward reaction and result in the deposition of the oxide. This view is attractive since it would account for the dependence of tarnishing[†] on the complex-ion concentration. However, certain aspects of this model for oxide formation can be questioned, for example;

[†] The equation may readily be rewritten, replacing CuO by Cu_2O, so that it becomes consistent with the electron-diffraction studies of Forty and Humble (see above).

(i) The above reaction does not involve zinc, and therefore indicates that the tarnish should be formed on pure copper surfaces. However, there is no evidence for such a layer, or for associated stress-corrosion cracking.

(ii) The view that the tarnish is deposited from solution is not consistent with the observations of Forty and Humble (1963) and McEvily and Bond (1965), which suggest that growth of the tarnish layer involves diffusion of ions through the tarnish itself.

It is apparent, then, that there are aspects of the stress-corrosion failure of α-brass which require further clarification, particularly those concerned with the chemistry of the process. The present work was undertaken with this in mind.

§2. EXPERIMENTAL

The bulk of the studies was carried out on an α-brass containing 70% copper and 30% zinc (by weight). Tensile specimens, approximately 45mm $\times$ 12mm in size and having gauge dimensions of 10mm $\times$ 3mm, were stamped from cold rolled sheet, approximately 0.5mm thick, using a punch and die. These specimens were annealed at 650°C in argon, producing a grain diameter of $\sim$ 0.25mm, and then etched for several minutes with a $\sim$ 4% aqueous ferric chloride solution. A limited number of te ts were also carried out on pure copper (99.99%). Specimens were stamped from annealed sheet, plastically strained 4%, and then annealed at 900°C in argon. This treatment produced an irregular grain size, but each specimen contained regions within the gauge length which contained coarse grains, some $\sim$ 0.7mm in diameter.

In the majority of stress-corrosion tests, specimens were subjected to a static tensile load while immersed in concentrated aqueous ammonia ($\sim$ 15N) containing various concentrations of cupric complex ions. These solutions, subsequently referred to as "preconcentrated", were prepared by dissolving pure copper powder in concentrated aqueous ammonia under an oxygen pressure of 10 psi.

The cupric complex ions formed when copper is dissolved in oxygenated aqueous ammonia can be represented by $Cu(NH_3)_n^{2+}$. The number of ammonia molecules, n, can vary from 1 to 5, depending on the ammonia concentration of the environment (Cotton and Wilkinson 1962). Spectrophotometric studies of preconcentrated solutions indicated that maximum absorption occurred at $\sim$ 6500$\mathring{A}$ in each case, demonstrating that the copper was present as the complex ion $Cu(NH_3)_5^{2+}$ (Cotton and Wilkinson 1962, Jorgensen 1962). The peak optical density, which was directly proportional to the concentration of the $Cu(NH_3)_5^{2+}$ ions, was found to vary linearly with the copper content of the solutions. Thus the complex-ion concentration of the preconcentrated solutions was directly proportional to their copper contents.

§3. RESULTS AND DISCUSSION

3.1. Stress-Corrosion Studies.

Earlier work has indicated that the time to failure, t_F, surface condition, and fracture mode depend critically on the concentration of the complex ion $Cu(NH_3)_5^{2+}$ (Pugh et al. 1965). To investigate these effects more fully, specimens were tested at an engineering stress (i.e. the stress based on the initial cross-sectional area) of 17 Kg/mm^2 in a range of preconcentrated solutions; the earlier work indicated that this was a suitable stress level (Pugh et al. 1965). Tests were carried out in large (500 ml) well-agitated volumes

so that the complex-ion concentration was not significantly increased during the test by dissolution of the specimen. The results are presented in fig. 1(a). The points represent the average of at least 4 tests, each conducted in freshly prepared solution, and the bars indicate the highest and lowest values of t_F. It can be seen that t_F decreases with increasing copper content, as expected from the earlier studies, but that a well-defined inflection occurs at a copper content of ~ 2.7 g/l.

The surface condition and fracture mode also depended on the copper content of the solution, as follows:

Range I (below ~ 0.5 g/l copper content). Fracture was ductile. Specimens were free from visible films and the surfaces exhibited etch facets.

Range II (0.5 - 1.5 g/l copper). Specimens tested in this range were coated with a brown film. The film was loosely adherent, and could be partially removed by washing with an ultrasonic cleaning device. Fracture was partly trans- and partly intercrystalline, and many secondary cracks of both types were evident. In some cases, the transcrystalline cracks were numerically predominant but they appeared shallow and blunt compared to the intercrystalline cracks. Moreover, they occurred in regions where massive deformation had taken place, such as near the main fracture or near deep secondary intercrystalline cracks. Transcrystalline cracks were never observed in regions free from intercrystalline cracking; on the other hand, isolated intercrystalline cracks were common.

Range III (1.5 - 3.25 g/l copper). Specimens were free from visible surface films and the surfaces showed well-defined facets. Several secondary intercrystalline cracks were present, and in some instances these were accompanied by transcrystalline cracks.
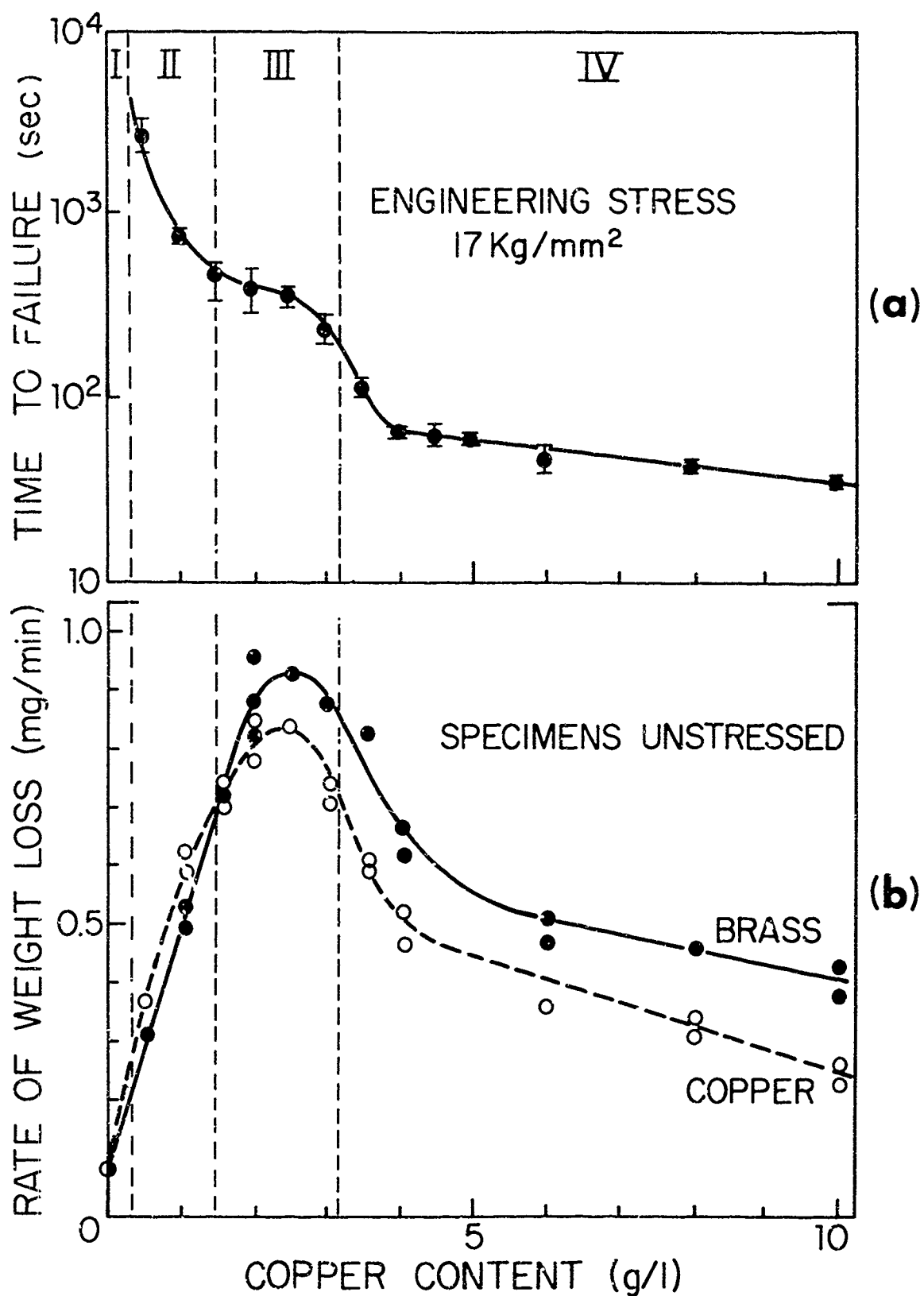
Fig. 1.- Effect of copper content of preconcentrated solutions on (a) time to failure of brass, and (b) rate of weight loss of unstressed brass and copper specimens.

Range IV (above ~ 3.25 g/l copper). Specimens were coated with the characteristic tarnish layer. Fracture was intercrystalline and many secondary intercrystalline cracks occurred throughout the gauge length. Limited transcrystalline cracking was observed near the main fracture in some instances.

Tests were also performed on pure copper. Specimens were stressed at ~ 14 Kg/mm^2 in preconcentrated solutions from Ranges II, III, and IV, respectively. In no case was stress-corrosion cracking observed.

3.2. Metallographic Studies.

A significant feature of the stress-corrosion results is the inflection in the t_F curve which coincides approximately with the appearance of the tarnish, fig. 1(a). To study the onset of tarnishing in more detail, optical microscopic studies were made of specimens immersed for various times in solutions containing 2.5 g/l (Range III) and 3.5 g/l (Range IV), respectively.

The surface condition produced by the standard etching treatment with ferric chloride is illustrated in fig. 2(a). When such surfaces were exposed to preconcentrated solutions containing 2.5 g/l copper, small but well-defined facets were produced. Examination of the facets using objectives of the highest possible (optical) resolution indicated that they were featureless. There was no evidence, (e.g. interference effects) to suggest that surface films were present.

When specimens having the standard surface condition were immersed in preconcentrated solutions containing 3.5 g/l copper, discrete particles were formed on the surfaces, fig. 2(b). Continued immersion caused the growth of the particles, fig. 2(c), until a continuous tarnish was formed, fig. 2(d).
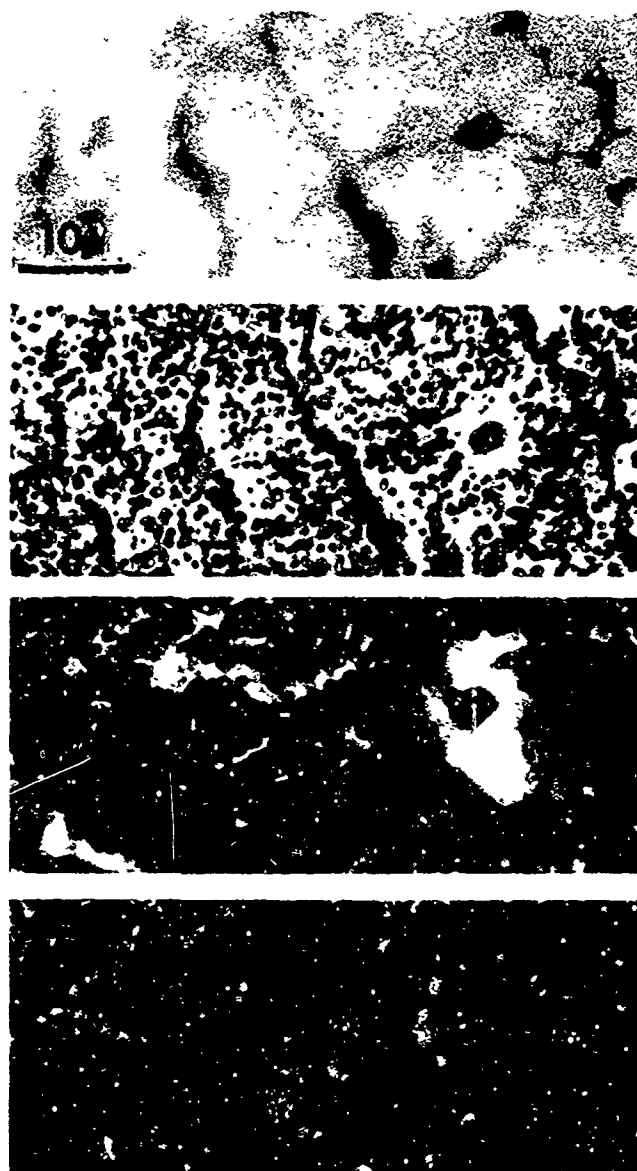
Fig. 2.- Illustrating the surface of a brass specimen (a) after the standard treatment with ferric chloride solution, and approximately the same field as in (a) after immersion in a preconcentrated solution containing 3.5 g/l copper (Range IV) for (b) 5 sec, (c) 15 sec, and (d) 3 min, respectively.

3.3.   Weight-Loss Studies.

Earlier reports (Althof 1944, Mattsson 1961, Pugh et al. 1965) have indicated that the presence of cupric complex ions in the ammoniacal environments results in higher rates of dissolution. To correlate these changes in rates of dissolution with changes in stress-corrosion behavior, unstressed specimens were immersed in preconcentrated solutions of various copper contents, under the same conditions as those used in the stress-corrosion tests, fig. 1(a) -- that is, using 500 ml. of solution and the same rate of stirring. The relationship between weight loss[†] and immersion time was essentially linear for all solutions investigated, e.g. fig. 3. However, in the case of solutions which caused tarnishing, the rates of dissolution were initially high, gradually decreasing to the constant value after 10-15 min (e.g. relationship for solution containing 6 g/l copper, fig. 3).

In fig. 1(b), the rate of weight loss, taken from the linear portion of the weight loss/time relationships, is plotted against the copper content of the solutions. The rate can be seen to increase markedly with increasing concentration, attaining a maximum value at ~ 2.7 g/l, and then to decrease gradually. Comparison with the stress-corrosion data, fig. 1(a), indicates that the maximum rate of weight-loss occurs at approximately the same copper content at which the inflection in t_F is observed. Moreover, this critical concentration is in good agreement with that at which tarnishing is detected (between 2.5 and 3.5 g/l).

The weight-loss experiments were extended to annealed copper specimens. In this case, the relationship between weight-loss and immersion time was linear for all the solutions investigated. However, the variation in rate of weight

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[†]Since the surface area of the specimens was constant (~ 8 cm^2), the weight loss is expressed simply in mg rather than in mg/cm^2.
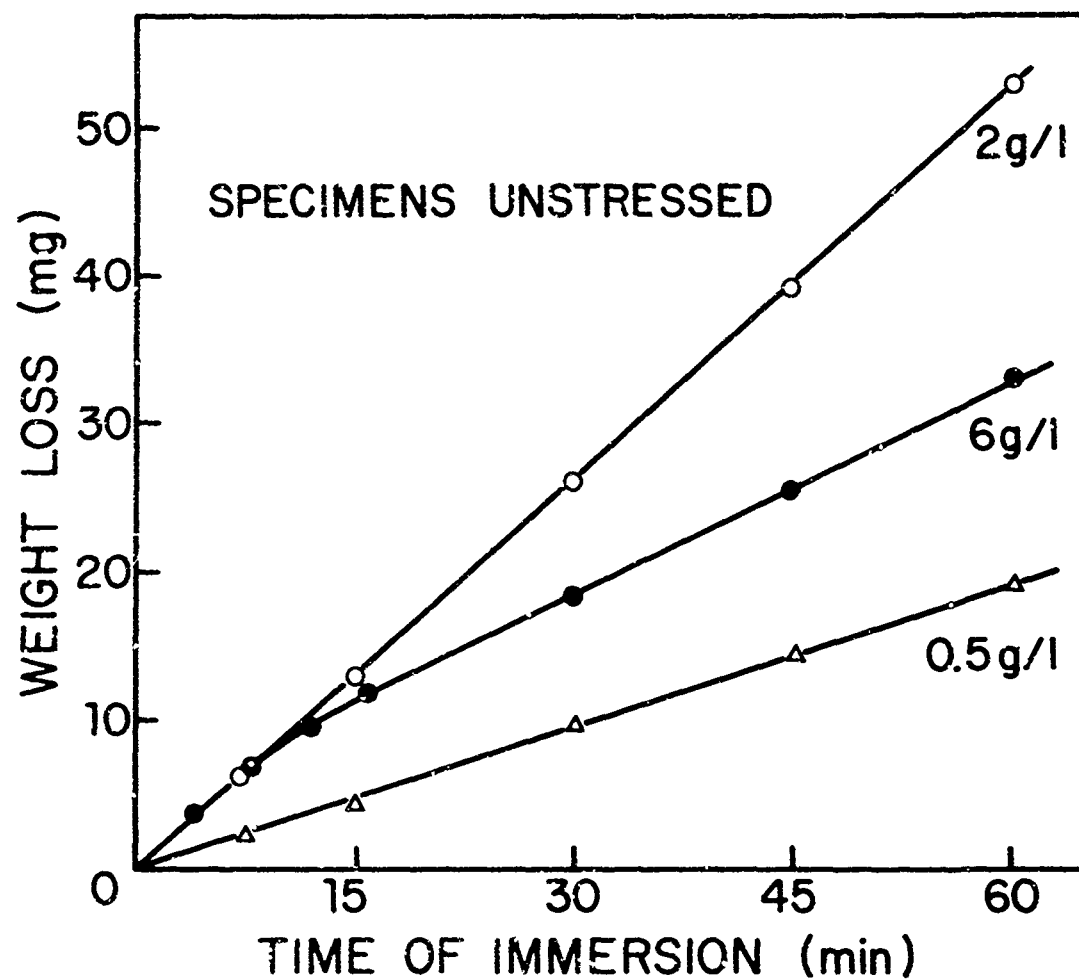
Fig. 3.- Relationship between weight loss and time of immersion for unstressed brass specimens tested in preconcentrated solutions of various copper contents. The solution containing 6 g/l copper caused tarnishing, while those containing 0.5 and 2 g/l, respectively, did not.

The tarnish produced by this solution was not uniform, isolated areas remaining free from a continuous coating even after several hours immersion. On the other hand, specimens immersed in solutions of copper content exceeding ~ 5 g/l were observed to become uniformly tarnished after relatively short periods (~ 15 min).
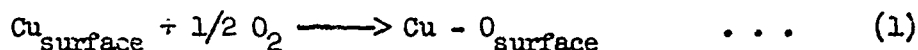
These observations indicate that (i) the tarnish is produced by the formation and growth of many discrete particles, and (ii) the particles cannot be resolved by the optical microscope on the surfaces of specimens immersed in Range III solutions. The electron-microscope studies of Pickering and Swann (1963) are relevant to these observations. Using the transmission technique, these workers studied thin foils of α-brass exposed either to ammonium hydroxide solutions or to ammonia vapour. Although it is difficult to relate their results directly to the present studies, because of the unspecified composition of the environments used, it is interesting to note that discrete particles were detected on the surfaces; selected-area diffraction indicated that the particles consisted mainly of cuprous oxide. It is probable that these particles correspond to an early stage of the growth of those observed in the present work, fig. 2(b) and 2(c). Further, it is possible that the particles are present on specimens immersed in Range III solutions, but that they cannot be detected by optical microscopy. However, it appears unlikely in view of these considerations that a continuous tarnish layer is produced by these solutions. The presence of etch facets would itself suggest the absence of a continuous film, for it has been argued (Vermilyea 1960) that the existence of such films prevents the formation of facets.

loss with copper content was closely similar to that of brass, fig. 1(b), and, in particular, the curve exhibited a maximum at approximately the same copper content as for the brass.

While a pronounced black tarnish was not observed in the case of copper, nevertheless the surface condition showed definite variation. In Ranges I and III, the surfaces appeared bright when viewed directly, and well-defined facets were observed under the optical microscope. Surface films were present in Range II and IV, and no facets could be identified. Significant differences were noted between these surface films. Those formed in Range II were matte, while those of Range IV were optically reflective. Moreover, the former could be partially removed by washing with an ultrasonic cleaning device, while the latter were adherent and dense. It is considered that the film present in Range II is similar to the brown coating observed for brass in this range, and that the film in Range IV is a continuous oxide layer, similar to the tarnish in brass but of considerably reduced thickness.

Before discussing   loss data it is necessary to consider the dissolution of pure copper in "resh" aqueous ammonia. According to Halpern (1953), two reactions are involved:
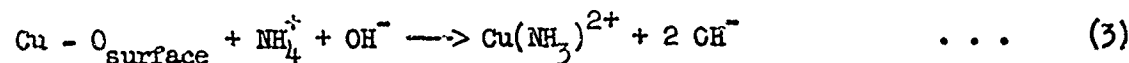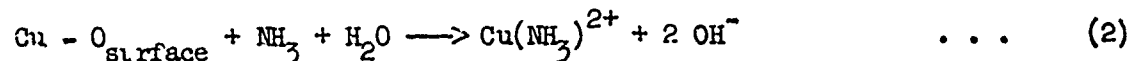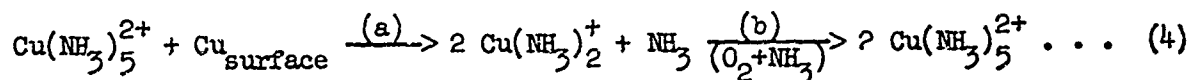
(i) Adsorption of oxygen at the surface to form an oxide:

$$Cu_{surface} + 1/2\ O_2 \longrightarrow Cu - O_{surface} \quad \cdots \quad (1)$$

The oxide is represented by Cu - O. The electron-diffraction studies (Forty and Humble 1963, Pickering and Swann 1963) suggest that it is probably Cu_2O.

(ii) Reaction of ammonia with the oxide to form the highly soluble cupric complex ion. Since ammonia dissociates in aqueous solution then two dissolution

reactions must be considered:

$$Cu - O_{surface} + NH_3 + H_2O \longrightarrow Cu(NH_3)^{2+} + 2\ OH^- \qquad \cdots \quad (2)$$

$$Cu - O_{surface} + NH_4^+ + OH^- \longrightarrow Cu(NH_3)^{2+} + 2\ OH^- \qquad \cdots \quad (3)$$

The $Cu(NH_3)^{2+}$ ions formed by reactions (2) and (3) gain additional ammonia molecules in solution. The high ammonia concentrations used in the present studies result in the formation of $Cu(NH_3)_5^{2+}$. It has been shown (Pugh et al. 1965) that this ion, in the presence of oxygen, takes part in an auto-catalytic reaction at copper or brass surfaces, represented by

$$Cu(NH_3)_5^{2+} + Cu_{surface} \xrightarrow{(a)} 2\ Cu(NH_3)_2^+ + NH_3 \xrightarrow[(O_2+NH_3)]{(b)} ?\ Cu(NH_3)_5^{2+} \quad \cdots \quad (4)$$

For brass, zinc will also enter solution, where it exists as a stable complex ion, probably $Zn(NH_3)_4^{2+}$ (Cotton and Wilkinson 1962). The mechanism of zinc removal is discussed below.

Consider now the weight-loss data. Several features require explanation:

3.3.1. The initial increase in rate of weight loss with increasing copper content.

This can be explained in terms of reaction (4), according to which the rate of removal of copper atoms will increase with increasing $Cu(NH_3)_5^{2+}$ content.

3.3.2. The maximum in the rate of weight loss curves.

It is possible to account for this by assuming that reaction (4a) occurs only at tarnish-free surfaces. Many of the preceding observations are consistent with this assumption. For example, the formation of a detectable tarnish occurred in solutions containing between 2.5 and 3.5 g/l copper (3.2), in good agreement with the maximum in the rate of weight loss curve, fig. 1(b). Further, the rate of weight loss in solutions which caused tarnishing was initially more rapid than

the final constant value (e.g. data for solution containing 6 g/l copper,
fig. 3). This can be attributed to the operation of reaction (4) during the
time necessary for the formation of a continuous tarnish, that is, during the
stage of particle growth. Specimens immersed in solutions of copper contents
between 3.5 and ~ 5 g/l were not completely tarnished, areas remaining free
from a continuous coating, and thus in these cases reaction (4) would occur
at the tarnish-free surfaces. In solutions containing more than ~ 5 g/l copper,
where specimens became completely tarnished, dissolution is then considered to
proceed by reactions (2) and (3) (zinc also enters solution in the case of
brass). Note that the rate of weight loss decreased linearly with increasing
copper content at concentrations exceeding ~ 5 g/l, fig. 1(b). The cause of
the decreasing rate is discussed in the following section.

3.3.3. The formation of the tarnish at a critical copper content.

It is thought that the oxide is formed by reaction of adsorbed oxygen
at the surface according to reaction (1). Growth of the oxide then depends
on the supply of oxygen to the oxide-liquid interface, and on the rates of
diffusion of the anions and cations in the oxide phase. The metallographic
observations (3.2) indicated that nucleation occurs at many sites, and that the
individual particles grow to form a continuous layer, Note that this view of
oxide formation differs fundamentally from that of Graf and Richter (1961),
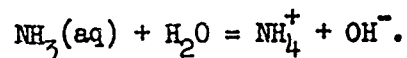discussed above (§1).

The occurrence of a continuous oxide layer is considered to depend on
two competing processes, (i) growth of the oxide and (ii) dissolution of the
oxide by reactions (2) and (3). Formation of a continuous oxide layer is there-
fore favoured by an increase in rate (i) and/or a decrease in rate (ii). If

it is assumed that the rate of oxide growth does not vary significantly with copper content of the solution, then the appearance of the tarnish layer at a critical copper content can be explained by proposing that the rates of reactions (2) and/or (3) are decreased by increasing copper concentration. Thus at low copper contents, rate (ii) > rate (i) so that a detectable oxide layer is not formed. However, as the copper concentration increases rate (ii) decreases, until a stage is reached when rate (i) > rate (ii). This stage corresponds to the critical copper concentration, ~ 3.25 g/l in the present experiments.

It would be attractive to attribute a reduction in the rates of reactions (2) and/or (3) to the increasing $Cu(NH_3)_5^{2+}$ concentration, which can decrease reaction rates by decreasing the free ammonia content, since each $Cu(NH_3)_5^{2+}$ ion anchors five ammonia molecules. However, the amounts of copper in solution are small relative to the ammonia concentration. For example, the most concentrated solutions investigated contained only $\sim 0.08N$ copper, so that the free ammonia content can only be reduced by $\sim 0.4N$. Such a reduction would not appear to be significant in view of the high initial ammonia content ($\sim 15N$).

An alternative possibility is that the OH^- concentration of the solution plays an important role. The preconcentrated solutions were prepared by dissolving pure copper in oxygenated aqueous ammonia, a dissolution process involving reactions (2) and (3). Thus the OH^- ion concentration of the preconcentrated solutions would be expected to increase with increasing copper content. It is not possible to confirm the increase in OH^- ion concentration in the case of $\sim 15N$ aqueous ammonia because the pH is initially > 13. However, measurements on $\sim 1N$ aqueous ammonia indicated that the addition of 2 g/l copper caused the pH to increase from 11.5 to 11.8 (± 0.05).

Increasing OH^- ion concentration can be expected to cause a reduction in NH_4^+ ion concentration in order to maintain equilibrium for the dissociation
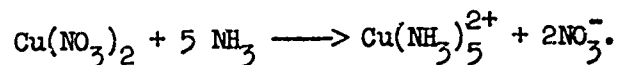
$$NH_3(aq) + H_2O = NH_4^+ + OH^-.$$

The effect of lowering the NH_4^+ ion concentration would be to reduce the rate of reaction (3). Moreover, Halpern (1953) reported that the rate of reaction (3) is considerably greater than that of reaction (2), the specific reaction rate constants being ~ 1550 and ~ 84 mg $Cu/cm^2/hr/mole$, respectively. It is suggested, therefore, that the reduced rates of oxide dissolution in preconcentrated solutions of high copper contents result from the increase in OH^- ion concentration and the concomitant decrease in concentration of NH_4^+ ions.

To test this hypothesis, the following additional experiments were performed:

(i) Additions of ammonium chloride crystals were made to a preconcentrated solution containing 10 g/l copper. Solutions containing $\geq$ ~ 10 g/l ammonium chloride did not cause tarnishing. This is attributed to the increase in NH_4^+ ion concentration.

(ii) Preconcentrated solutions were prepared by dissolving cupric nitrate in concentrated aqueous ammonia under 10 p.s.i. oxygen, according to

$$Cu(NO_3)_2 + 5\ NH_3 \longrightarrow Cu(NH_3)_5^{2+} + 2NO_3^-.$$

These solutions thus had approximately the same $Cu(NH_3)_5^{2+}$ ion concentrations as the standard preconcentrated solutions, but did not contain high OH^- concentrations. On the basis of the preceding argument, the use of these solutions would be expected to move the maximum in the rate of weight loss curves to

higher copper contents. The results, fig. 4, are in full agreement with this prediction. In fact, a maximum was not observed in the range investigated (0-10 g/l copper), the rate of weight loss increasing continuously with increasing copper content. Moreover, the specimens were not tarnished but were coated with a brown film which appeared identical with that in Range II for standard preconcentrated solutions. The density of this coating increased progressively with increasing copper content.

Weight-loss experiments were also conducted on copper. The rate of weight loss was found to be significantly lower than for brass, fig. 4, and, further, the surfaces remained apparently film free and faceted throughout the range.

(iii) Preconcentrated solutions containing 1, 2, and 3 g/l copper were prepared by dissolving copper in oxygenated concentrated aqueous ammonia, but in addition 10 g/l sodium hydroxide were added to each solution. In this case, it was predicted that the addition of OH^- ions would move the maximum in the rate of weight loss curve, which is associated with the appearance of the tarnish, to lower copper contents. This was again confirmed by the results, fig. 5. The maximum occurred at a copper content of ~ 1 g/l and specimens immersed in solutions containg > 1 g/l copper were tarnished. It was not possible to produce a continuous tarnish layer in solutions containing < 1 g/l copper. For example, additions of 15, 20 and 25 g/l sodium hydroxide to concentrated aqueous ammonia (unpreconcentrated) caused the formation of detectable oxide particles, similar to those illustrated in fig. 2(b), but these particles did not grow into a continuous layer.
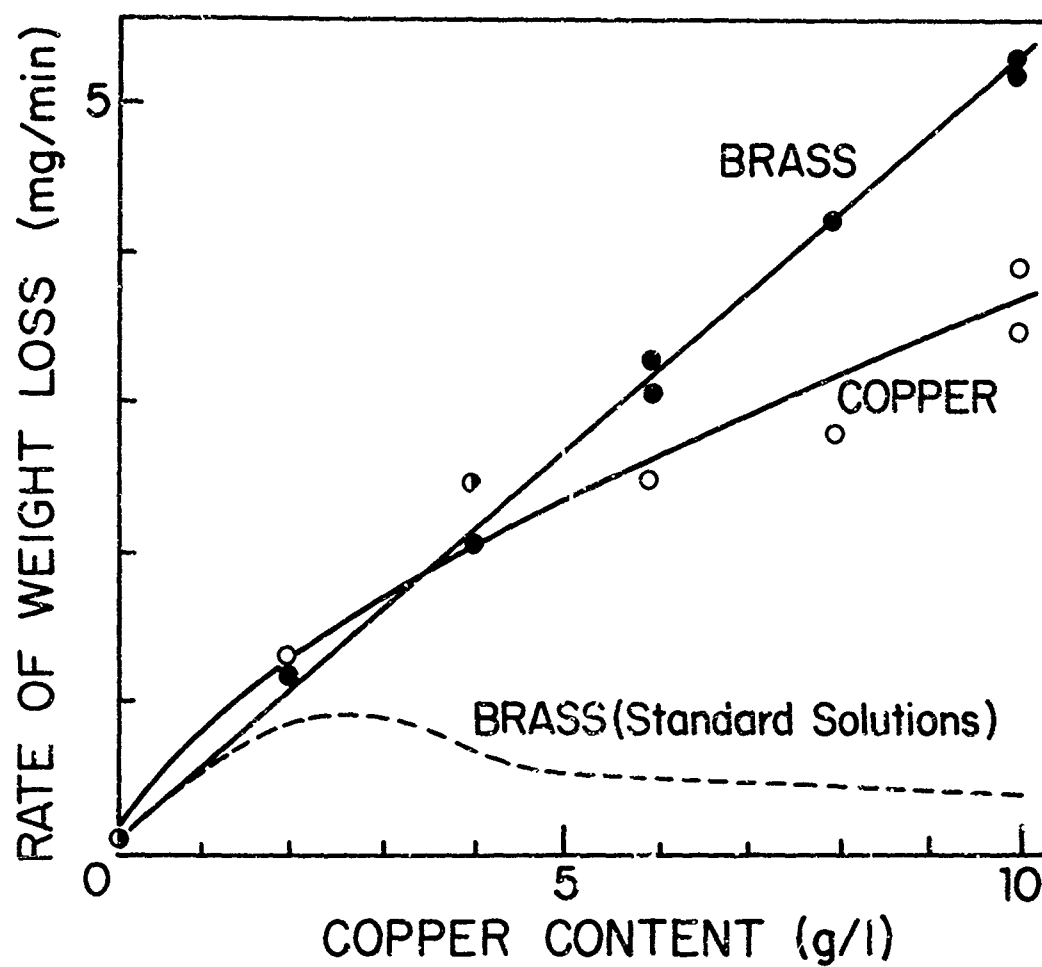
Fig. 4.- Effect of copper content of preconcentrated solutions, prepared by dissolving cupric nitrate in concentrated aqueous ammonia under 10 lb/in^2 oxygen, on the rate of weight loss of unstressed brass and copper specimens.
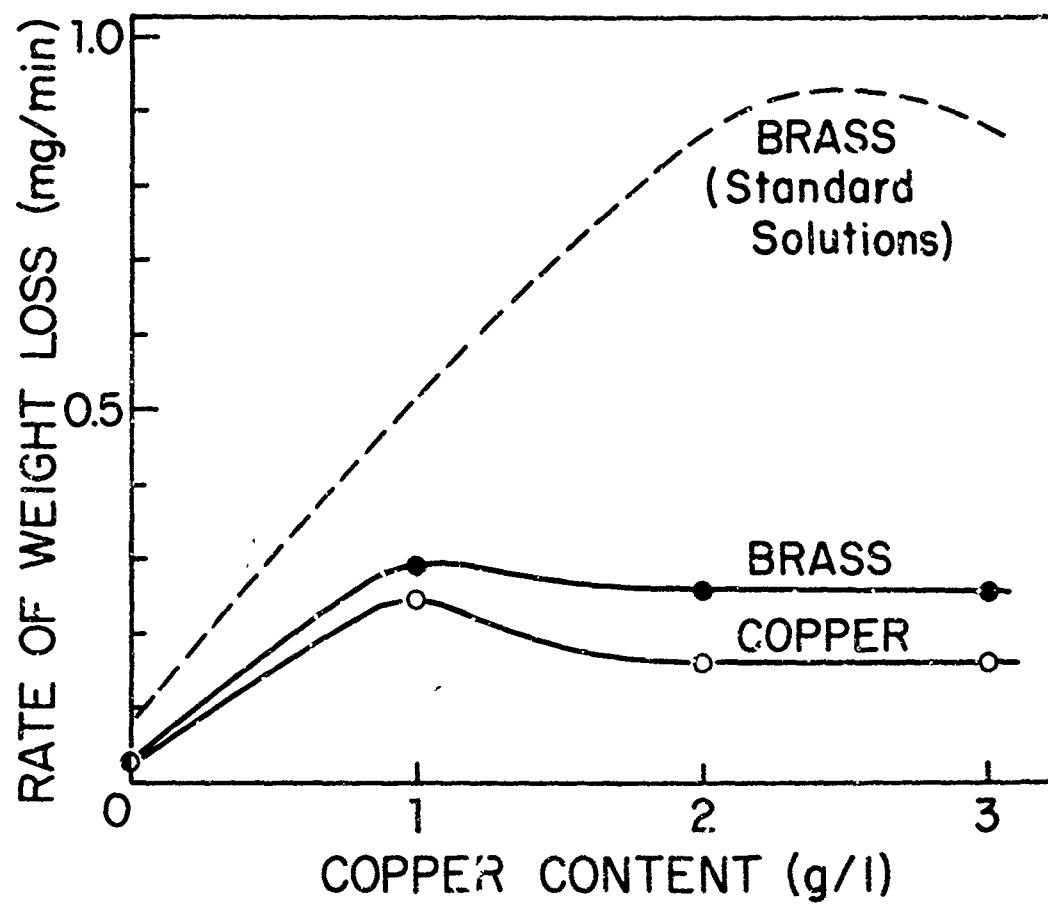
Fig. 5.- Effect of the addition of 10 g/l sodium hydroxide to standard pre-concentrated solutions (containing 0, 1, 2, and 3 g/l copper, respectively) on rates of weight loss of brass and copper specimens.
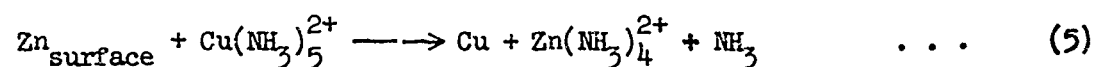
It is considered that these experiments confirm the hypothesis that the formation of the tarnish depends on two competing processes, namely (i) growth of oxide, and (ii) the dissolution of oxide.

3.3.4. The growth of the tarnish to considerable thickness in brass, but not in copper.

It was proposed above that the growth of the oxide depended on both the sup᷁ ·of oxygen to the oxide surface, and on the rates of diffusion of ions in the oxide phase. Since the oxygen contents of the solutions are essentially the same in all cases, then the differences in the rate of oxide growth in copper and brass may be attributed to the fact that the rates of diffusion are greater in the latter. It is then necessary to consider how the presence of zinc leads to increased diffusion rates in the oxide layer. A possible answer follows readily from the suggestion of Forty (1959), that the preferential removal of zinc from essentially film-free brass surfaces leads to the injection of vacancies into the surface layers. Applying this approach to the oxide layer, it is suggested that preferential removal of zinc leads to the injection of vacancies, which in turn leads to increased rates of diffusion in the oxide phase.

It might be argued that it is not necessary to postulate preferential dezincification, and that high diffusion rates would result in some way from the presence of zinc in the oxide layer. However, if this were so, then the tarnish would be expected in many oxygenated aqueous solutions, in oxygenated water for example. The fact that tarnishing occurs only in specific solutions supports the view that selective removal of zinc from the oxide is essential.

The fact that it was not possible to produce a tarnish layer in brass in solutions containing less than 1 g/l copper (i.e. in solutions of low $Cu(NH_3)_5^{2+}$ ion concentration) strongly suggests that the complex ion $Cu(NH_3)_5^{2+}$ is involved in the dezincification process. A possible reaction is:

$$Zn_{surface} + Cu(NH_3)_5^{2+} \longrightarrow Cu + Zn(NH_3)_4^{2+} + NH_3 \qquad \ldots \qquad (5)$$

Note, however, that if the complex ion is in fact responsible for the preferential removal of zinc from the oxide surface, then this invalidates the assumption made above (3.3.3) that the rate of oxide growth is not significantly affected by the copper content of the solution. In this case, increasing copper content would lead to increased rates of oxide growth, thus further favouring the formation of the tarnish.

3.3.5. The nature and origin of the brown film.

The fact that the density of the brown film on specimens immersed in preconcentrated solutions prepared from cupric nitrate increased with increasing copper content again suggests that $Cu(NH_3)_5^{2+}$ ions play an important role in the formation of this film. Moreover, the absence of a brown film in pure copper in these solutions indicates that the presence of zinc in solid solution is also important. These facts can be rationalized if it is assumed (i) that the film consists of copper and (ii) that the copper is deposited by reaction (5). Note that the exchange reaction, if it occurs, would in this case take place at tarnish-free surfaces. It is also interesting to note that similar brown films were formed on pure zinc specimens when they were immersed in standard preconcentrated solutions. It is possible, then, that the complex ion undergoes the exchange reaction with zinc at several apparently widely differing surfaces.

Several factors concerning the brown film formed in standard precon-
centrated solutions remain to be explained, for example;

(i) The nature and mode of formation of the surface coating observed
on pure copper in Range II, fig. 1.

(ii) The absence of films in Range III.

3.4. Additional Stress-Corrosion Tests.

3.4.1. Specimens of brass were tested at an engineering stress of
17 Kg/mm^2 in the preconcentrated solutions used in the weight-loss studies
described in section 3.3.3. The results are presented in fig. 6 and compared
with those for standard preconcentrated solutions.

Consider first the data for the solutions prepared from cupric nitrate.
It can be seen that t_F decreases continuously with increasing copper content,
that is, with increasing $Cu(NH_3)_5^{2+}$ ion concentration. Comparison with fig. 4
indicates that increasing susceptibility to stress-corrosion cracking is accom-
panied by increasing rates of weight loss. The failures were identical with
those in Range II for standard preconcentrated solutions.

The data for tests in standard solutions containing 10 g/1 sodium hydr-
oxide fell on a curve which was essentially an extension of the Range IV data
for standard solutions, fig. 6. Fracture was identical with that of Range IV.

Tests were also carried out on copper specimens. In no cases were
stress-corrosion cracks observed.

3.4.2. It has been shown that cracking can be produced in α-brass by repeatedly
immersing specimens in tarnishing ammoniacal solutions, and stressing them in
the absence of the environment (Forty and Humble 1963, Pugh 1965). This obser-
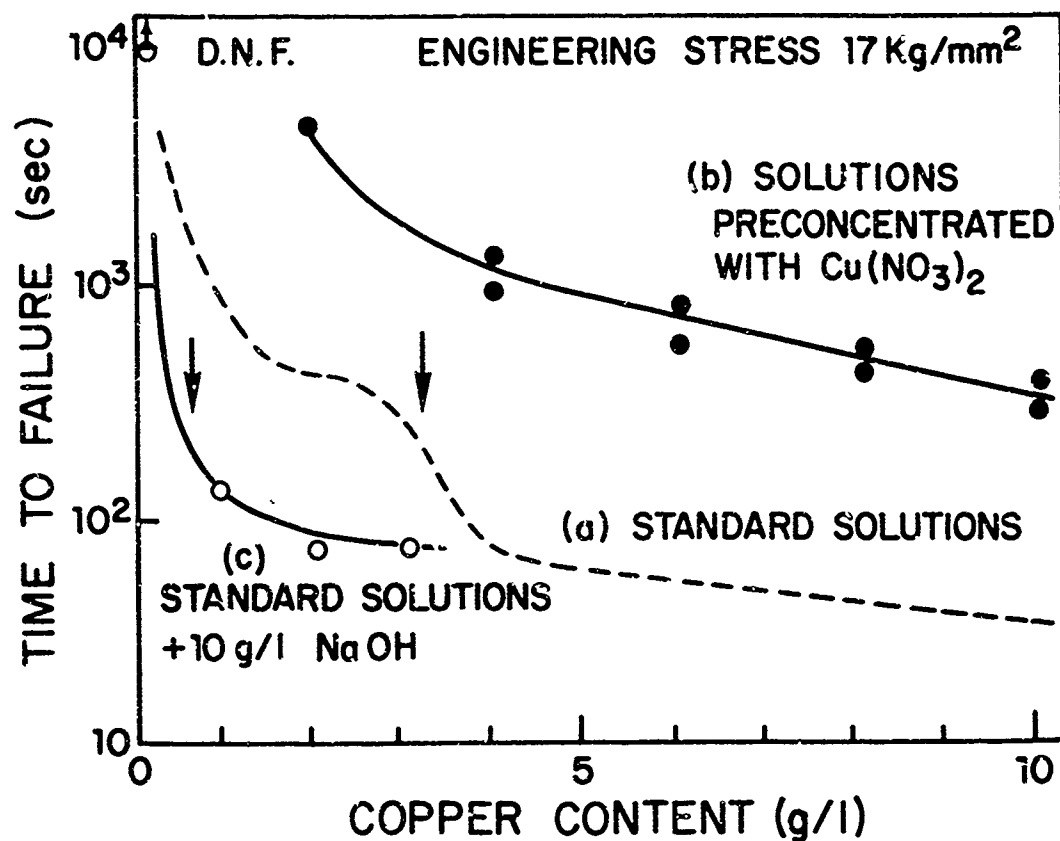vation is considered to support the tarnish-rupture mechanism, described above

Fig. 6.- Relationship between time to failure and copper content of pre-concentrated solutions for brass specimens tested in (a) standard solutions (b) solutions prepared using cupric nitrate, and (c) standard solutions + 10 g/1 sodium hydroxide. The copper contents at which visible tarnishing occurs are indicated with arrows (solutions (b) did not cause tarnishing).

(§1). It is difficult to reconcile such observations with other theories, e.g. the dissolution model proposed by Graf and Richter (1961). Similar experiments were conducted in the present studies, using the standard poly-crystalline specimens, with the aim of distinguishing between the mechanisms of cracking in solutions from Ranges II, III, and IV, respectively.

Specimens were immersed, unstressed, in the solutions for 10 min, removed, washed and dried. They were then stressed in air by means of a manually-operated tensile jig, the gauge length being studied during stress-ing using a low-power microscope. The following observations were made:

Range II. Severe straining caused rupture of the brown film. How-ever, removal of the film by cleaning ultrasonically indicated that the effect, even after several cycles, was confined to the film itself. Cracking did not extend into the brass. This is in contrast to the transcrystalline cracks produced in standard tests in these solutions (i.e. stressing during immersion), which extended into the substrate.

Range III. In no case were cracks produced.

Range IV. Stressing tarnished specimens into the plastic range pro-duced cracks at several grain boundaries throughout the gauge length. Repeated cycles of immersion followed by stressing in air caused continued crack growth until complete intercrystalline failure occurred. These observations are dis-cussed in greater detail elsewhere (Pugh 1965).

The observation of cracking in tarnished specimens in the absence of the environment strongly supports the tarnish-rupture mechanism. Conversely, the failure to produce cracking after exposure to solutions from Ranges II and III supports the view that a different mechanism of stress-corrosion crack-ing is operative in these solutions.

§4. MECHANISMS OF STRESS-CORROSION CRACKING IN α-BRASS

The observations and discussions in the preceding sections are considered to indicate that cracking in tarnishing solutions occurs by the tarnish-rupture model, and that a different mechanism is operative in solutions which do not cause tarnishing. It now remains to consider the mechanism of failure in the latter case.

It has been suggested that an adsorption-dependent mechanism, similar to that thought to occur in the embrittlement of metals by liquid metals (Westwood and Kamdar 1963), may be operative in stress-corrosion cracking (Nichols and Rostoker 1963). Moreover, the embrittlement of polycrystalline AgCl in certain aqueous environments, which exhibits many of the phenomenological characteristics of stress-corrosion cracking in metals, has been found to result from the adsorption of specific silver complex ions (Westwood et al. 1964, 1964a, 1965). Therefore it would be attractive to propose that failure in tarnish-free specimens results from adsorption of $Cu(NH_3)_5^{2+}$ ions. However, the high rates of dissolution accompanying cracking make such a mechanism unlikely. Indeed, the fact that decreasing stress-corrosion life of tarnish-free specimens is attended by increasing rates of weight loss, cf. figs. 1(a) and 1(b), figs. 6 and 4, suggests that the autocatalytic process, reaction (4), may be responsible for cracking. This possibility, however, discussed previously by Pugh and Westwood (1964), would appear to be ruled out by the absence of cracking in copper.

An alternative possibility is that cracking results from dezincification. It was argued above (3.3.4) that dezincification may occur by reaction of $Cu(NH_3)_5^{2+}$ ions with zinc at tarnish-free brass surfaces, according to reaction (5). Thus in tests in preconcentrated solutions prepared from cupric

nitrate, in which tarnishing was prevented, t_F decreased continuously with increasing complex-ion concentration, fig. 6. Furthermore, the density of the brown film, considered to be copper, was observed to increase with increasing complex-ion concentration. This is consistent with reaction (5) which indicates that dezincification is accompanied by deposition of copper.

A possible model for failure, based on reaction (5), follows from the mechanism proposed by Tromans and Nutting (1963). According to these workers, a prerequisite for stress-corrosion cracking is the segregation of solute atoms to dislocations, "thus changing the chemical reactivity of these regions". On the basis of the preceding argument, zinc may be considered to be removed from these sites by reaction (5). Tromans and Nutting proposed that the path of cracking is determined by the dislocation distribution, which is in turn controlled by stacking-fault energy. Electron-microscope studies of 70:30 brass (low stacking-fault energy), indicated that relatively low strains produced pile-ups at grain boundaries and were thus considered to lead to intercrystalline cracking; at higher strains, pile-ups were also observed within the grains, favouring transcrystalline cracking. This proposal is consistent with the present observations on specimens tested in solutions which produce the brown film. Cracking in these cases was both trans- and intercrystalline, but the former was confined to regions of gross plastic deformation near deep intercrystalline cracks.

Studies are in progress to investigate these aspects further.

§5. SUMMARY

The observations indicate that two mechanisms of stress-corrosion cracking are operative in the α-brass-aqueous ammonia system. Failure in tarnished specimens occurs by the tarnish-rupture mechanism (Forty and Humble 1963).

For tarnish-free specimens, the mechanism is not fully understood, but it is suggested that the failure involves preferential removal of zinc by reaction of $Cu(NH_3)_5^{2+}$ ions at the metal surface, according to reaction (5).

The presence or absence of a detectable tarnish is considered to depend on two competing processes, (i) the growth of the oxide layer and (ii) oxide dissolution. The rate of oxide growth is controlled largely by diffusion rates of the anions and cations in the oxide layer. The fact that it was not possible to produce tarnishing in the absence of $Cu(NH_3)_5^{2+}$ ions indicates the importance of these ions in the tarnishing reaction. It is considered that their role is to preferentially remove zinc from the oxide surface, again by reaction (5). The preferential removal of zinc leads to the injection of vacancies, which cause increased rates of diffusion. The rate of oxide dissolution is dependent on the NH_4^+ ion concentration, which is in turn dependent on the concentration of OH^- ions. It is shown that the onset of tarnishing can be controlled by varying the concentration of these ions.

It appears, then, that the importance of the complex ion $Cu(NH_3)_5^{2+}$ in the stress-corrosion cracking of brass stems from the ability of this ion to react with zinc at both the metal and the tarnish surface.

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