

THE DEZINCIFICATION OF BRASS AND ITS INHIBITION IN ACIDIC CHLORIDE AND SULPHATE SOLUTIONS

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Abstract—The dezincification of 60/40 brass has been studied in acidic chloride and sulphate solutions under accelerated experimental conditions using weight loss and potential measurement techniques. A particular variation of potential with immersion time was observed to be the characteristic feature of dezincification. The results obtained support substantially the operation of both selective dissolution of zinc and simultaneous dissolution of copper and zinc followed by redeposition of copper, alternatively with time, during dezincification. The effect of surface active compounds such as thiourea, thioglycolic acid, thioglycol and halo-acetic acids on dezincification of brass has been discussed on the basis of models proposed for synergistic effects of organic molecules and anions involved in the medium.

INTRODUCTION

IN THE field of non-ferrous alloys, the subject of de-alloying is of current interest. Dezincification is one of the well-known de-alloying processes by means of which brass loses its valuable physical and mechanical properties leading to the total failure of the structure. The literature survey on the mechanism of de-alloying¹ in general and dezincification² in particular provides a good basis for understanding various aspects of dezincification and its inhibition. The work of Abrams³ in 1922, dealing with the critical analysis of the various environmental factors on dezincification, contributed a basic understanding of the problem. Due to its industrial significance, dezincification has been an active field of research and attempts have been made using chemical and electrochemical,⁴⁻⁹ radiometric¹⁰ and optical techniques¹¹ to resolve the controversy over the mechanism of the process. Despite the extensive work on this subject, still there is no universally acceptable mechanism.

The diversity of opinion and widespread interest in the problem, prompted the present investigation which attempts primarily to understand the mechanism of dezincification and the role of inhibitors in the process.

EXPERIMENTAL METHOD

All chemicals used were of AR grade and the solutions were prepared using freshly distilled triple distilled water. Brass having the composition Cu 59.8%, Zn 40.08%, Fe trace, Sn trace and free from Pb and As has been used for the study. The specimen in cylindrical form (10.0 mm dia. and 15.0 mm length) was fixed in Tygon tubing so that only the cross-sectional area would be exposed to the medium. The surface was mechanically polished successively on different grades of emery paper (2/0 to 4/0) using ethanol as a lubricant. Subsequently, it was subjected to further polishing for desired smoothness and brightness on wet chamois leather using fine carborundum powder (600 mesh). The finished surface was then washed thoroughly with running distilled water, degreased, cleaned with triple distilled water and used for dezincification studies.

The weight loss studies were carried out by immersing the sample in the medium for a desired period and colorimetrically analysing the solution for individual contents of copper and zinc. Individual as well as

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the overall dissolution rates ($\text{mg cm}^{-2} \text{h}^{-1}$) were calculated using these values. For galvanostatic polarization studies, a 90 V battery was used as a constant current source across a series of variable resistances. A saturated calomel electrode and a platinized platinum electrode were employed to serve as reference and auxiliary electrodes, respectively. The corrosion potentials and overpotentials were recorded with an accuracy of ± 2 mV using a high impedance VTVM. The detailed experimental procedure has been given elsewhere.^{12,13}

EXPERIMENTAL RESULTS

Dezincification characteristics

Dissolution rates. Dezincification was observed when brass was kept immersed in stirred aerated 0.1 M HNO_3 having various concentrations of chloride or sulphate ions at 30°C . The kinetics of dissolution and the degree of dezincification (defined by the ratio of individual dissolution rates of copper and zinc, i.e. $r = \text{Cu}/\text{Zn}$) of brass were found to depend significantly on the anion (Cl^- or SO_4^{2-}) concentration in the medium. Figure 1 illustrates the dependence of overall dissolution rates and corresponding changes in the degree of dezincification as a function of anion concentration. As the chloride concentration was varied from 10^{-6} to 10^{-4} M, the total dissolution rate decreased gradually and then more rapidly to a minimum value. Further increase in chloride content beyond 10^{-4} M resulted in negligible dissolution even after prolonged immersion. In the presence of sulphate ions, the rate continuously decreased as a result of gradual increase in sulphate content from 10^{-5} to 10^{-2} M. An increase of anion concentration exhibited a progressive increase in the tendency for dezincification (i.e. decrease in r values) as shown in Fig. 1. Thus under the conditions tested, slow dissolution favoured dezincification. The effective concentration at which anions exhibit a pronounced effect on dissolution or dezincification is characteristically different for chloride and sulphate ions.

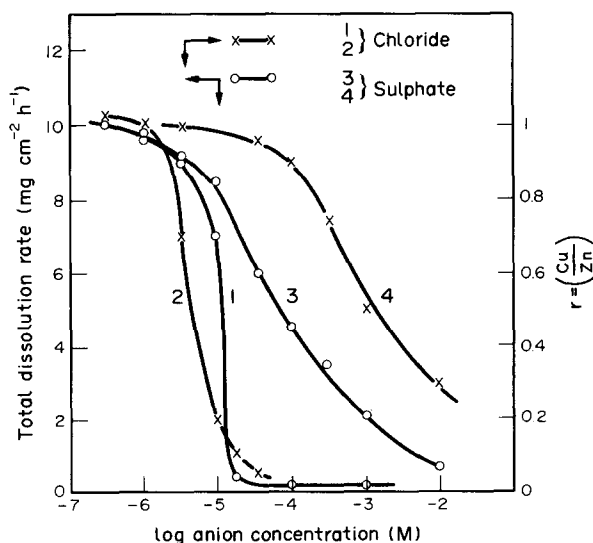


Fig. 1. The dependence of total dissolution rate and degree of dezincification (r) of brass on anion concentration in stirred 0.1 M HNO_3 .

TABLE 1. THE VARIATION OF TOTAL DISSOLUTION RATE AND DEGREE OF DEZINCIFICATION (r) IN STIRRED HNO_3 SOLUTION OF VARIOUS CONCENTRATIONS CONTAINING 10^{-5} M CHLORIDE IONS AT 30°C (IMMERSION PERIOD: 4 h)

Acid concentration (M)	Total dissolution rate ($\text{mg cm}^{-2}\text{h}^{-1}$)	Degree of dezincification ($r = \text{Cu/Zn}$)
0.08	0.5	0.08
0.02	3.2	0.10
0.05	5.5	0.15
0.10	7.4	0.20
0.20	15.0	0.42
0.50	26.0	0.75
1.00	38.0	0.94

Experiments were also conducted under identical conditions using HNO_3 solutions of various concentrations containing fixed amount of chloride (10^{-5} M) or sulphate (10^{-2} M) ions. When the nitric acid concentration was increased from 0.01 to 1.0 M, the dissolution was accelerated, an effect accompanied by a decreased tendency for dezincification. Table 1 shows the influence of HNO_3 on the corrosion and dezincification of brass in a stirred solution containing chloride. Similar trends with different dissolution rates were also observed in sulphate solutions. The data in Table 1 indicate that preferential dissolution of zinc was at a maximum (low r value) in 0.01 M HNO_3 at which the overall rate was low. This is notably consistent with the earlier observations (Fig. 1) that conditions of slow dissolution favoured dezincification while those of fast dissolution showed increased tendency for simultaneous removal of copper and zinc.

The dezincification experiments were performed after adding Zn^{2+} and Cu^{2+} ions to both chloride and sulphate solutions. It was found that the presence of these metal ions, individually or in combination (in different proportions) up to 0.05 M, brought negligible effect either on dissolution rate or on degree of dezincification observable otherwise in their absence.

The samples were kept immersed continuously for various periods during dezincification in 0.1 M HNO_3 containing chloride or sulphate ions and the observed time dependent changes in weight loss are shown in Fig. 2. These experiments reveal that brass continued to dissolve resulting in a linear variation of weight loss (Fig. 2) without causing much change in the degree of dezincification.

Corrosion potential variations. During simultaneous corrosion of brass in 0.1 M HNO_3 (free from chloride or sulphate), its potentials decreased continuously with immersion time and attained steady values (Fig. 3). However, during its dezincification in 0.1 M HNO_3 containing chloride or sulphate, the potentials exhibited a different trend in variation with time. As indicated in Fig. 3, from the moment of immersion of the specimen, corrosion potentials continuously decreased to a minimum value (negative shift), after which they continuously increased (positive shift) and finally attained steady values with time. After attaining the steady values, they remained more or less constant during further dissolution. It is emphasized that this type of potential-time relationship was a characteristic feature observed only

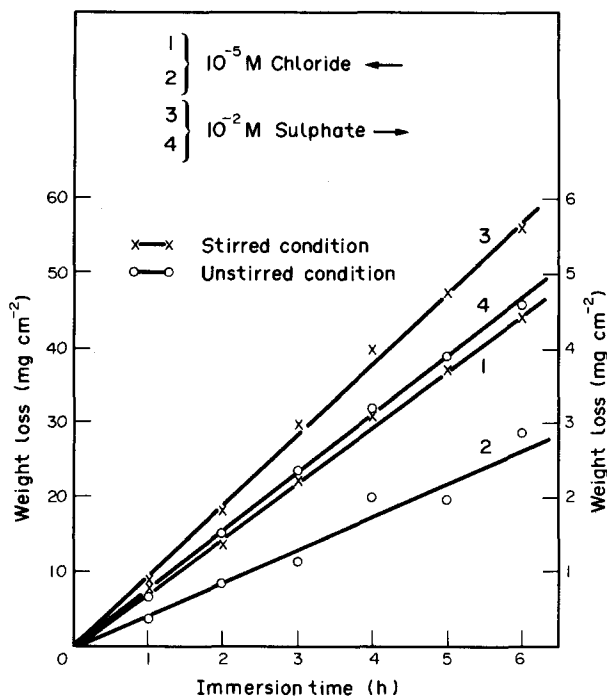


Fig. 2. The variation of weight loss as a function of immersion time during dezincification of brass in 0.1 M HNO_3 containing anions.

when brass experienced dezincification in chloride or sulphate solution. From the potential time characteristics of the process supported by weight loss measurements at different concentrations of HNO_3 with chloride or sulphate, it is also notable that the changes in potential time curves are indicative of changes in the extent of dezincification. Thus in the presence of 10^{-5} M chloride, as the HNO_3 concentration was varied from 0.02 to 1.0 M, the hump of the potential-time curves (Fig. 4) gradually decreased, accompanied by a gradual fall in the degree of dezincification (Table 1) and resulted in a hump-free curve at 1.0 M HNO_3 where the system exhibited simultaneous corrosion. The changes of this kind were also observable under comparable conditions in the presence of 10^{-2} M sulphate.

Surface features. After each dissolution test, the surface of brass was examined visually under a metallurgical microscope. The dissolution of brass in 0.1 M HNO_3 produced an etched surface exhibiting exposed alloy phases with well-defined boundaries, and retaining the true colour of brass. These features did not appear on the surface when brass was subjected to dezincification. Instead the surface exhibited a copper-like appearance, as a result of dezincification. Prolonged immersion during dezincification produced a thick non-coherent deposit of copper on the surface.

Polarization behaviour. Brass was anodically polarized under galvanostatic conditions at different current densities ($0.5\text{--}20.0$ mA cm⁻²) in stirred 0.1 M HNO_3 containing either 10^{-5} M chloride or 10^{-2} M sulphate ions. Individual trials were

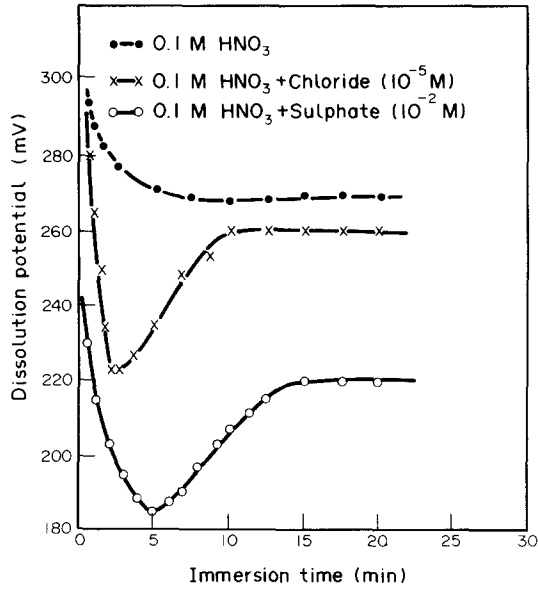


Fig. 3. The variation of dissolution potential with immersion time during dezincification in stirred acidic chloride and sulphate solutions.

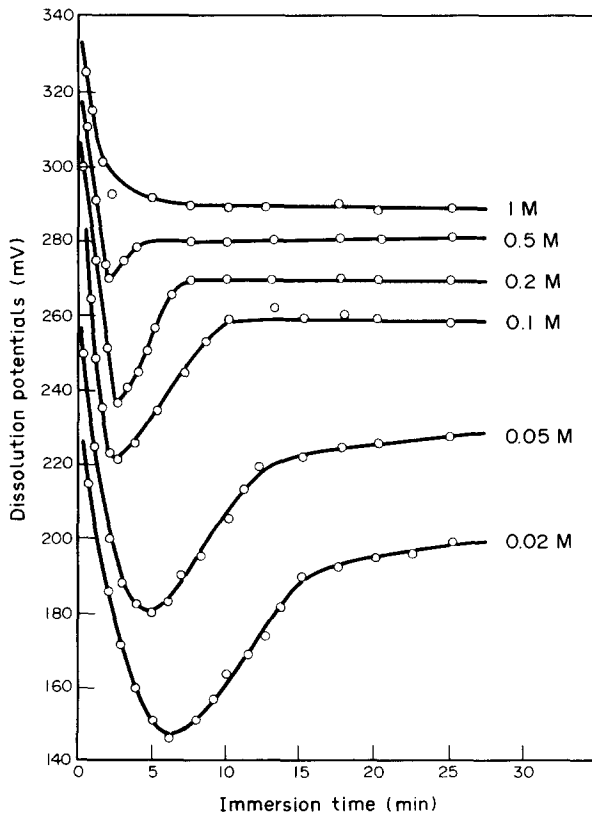


Fig. 4. Potential-time curves of brass during dezincification in stirred nitric acid of various concentrations containing 10⁻⁵ M chloride ions.

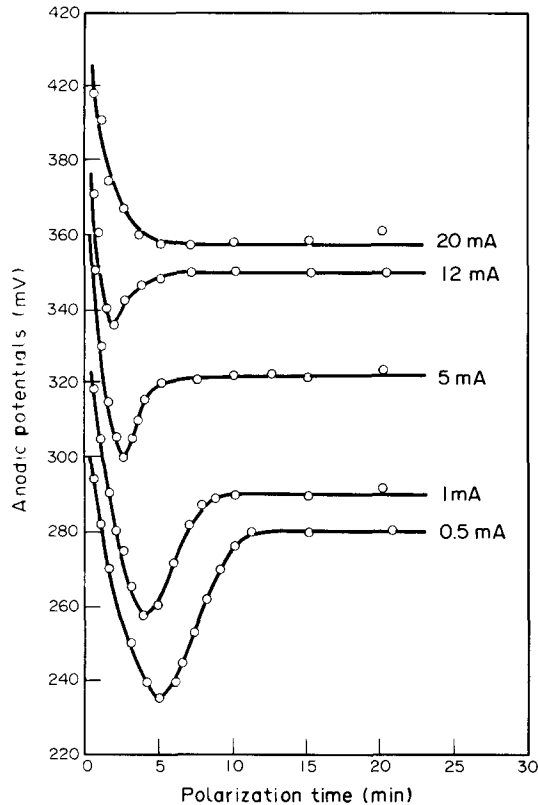


FIG. 5. The variation of anodic potential with time when brass was polarized anodically during dezincification in stirred 0.1 M HNO_3 having 10^{-5} chloride ions.

conducted at each applied current density and the variations of anodic potentials were recorded as a function of time. As observed during dezincification under free dissolution conditions (Fig. 4), anodic polarization also reflected a similar trend in variation of potential with time. While time dependent variations of anodic potential remained virtually similar under comparable conditions in both 10^{-5} M chloride and 10^{-2} M sulphate solutions, those observed in chloride media are illustrated in Fig. 5. As shown in Fig. 5, if the current density was varied from 0.5 to 20.0 mA cm^{-2} , the hump of the curve gradually disappeared producing finally a hump-free curve, thus indicating the transition of the process from dezincification to simultaneous dissolution. The occurrence of dezincification at each applied current density was also confirmed by analysis of the solution. The steady anodic potentials obtained at various current densities were used to construct anodic Tafel plots. Figure 6 represents Tafel curves derived under the typical conditions both of dezincification and of simultaneous dissolution of brass.

The influence of inhibitors on corrosion and dezincification of brass

Surface active organic compounds such as thiourea (TU), thioglycolic acid (TGA), thioglycol (TG), *n*-octyl amine (*n*-OA), chloro-acetic acid (CAA), bromo-acetic acid (BAA), iodo-acetic acid (IAA), etc. exhibited a marked effect on kinetics

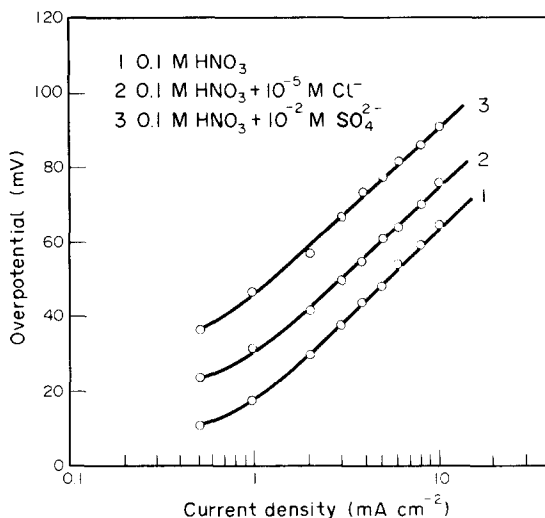


FIG. 6. Anodic Tafel plots for the dissolution of brass in stirred 0.1 M HNO₃ with and without anions which cause dezincification.

of dissolution and dezincification of brass in acidic chloride and sulphate solutions. Figures 7 and 8 illustrate the influence of these inhibitors on the process as a function of their concentration in chloride solution while similar observations were also made in sulphate solutions. Considering the trend in variation of the dissolution rate, the inhibitors could be grouped into two different sets. With the first set to which the halo-acetic acids and amines belong, the dissolution rate decreased continuously to a minimum value (Fig. 7) while with the second set to which thio compounds belong, the rate showed a gradual decrease followed by a rapid fall (Fig. 8) to a minimum, in response to an increase in inhibitor concentration from 10^{-7} to 10^{-2} M.

The efficiency of the inhibitor in inhibiting the process was evaluated as

$$\%P = \frac{W_0 - W}{W_0} \times 100$$

where W and W_0 are the values of weight loss of brass obtained with and without the inhibitor, respectively. Tables 2 and 3 summarize the data on the relative performance on these inhibitors. Under comparable conditions, the effectiveness of the inhibitor was shown to depend upon the nature of the inhibitor and its concentration.

Besides their influence on the overall kinetics of the dissolution process, the added compounds also affected the ratio of individual dissolution rates of copper and zinc, depending on their concentration in the medium (Figs 7 and 8). Regardless of the inhibitor involved, if the inhibitor concentration was low, i.e. when the inhibition of the process was less than 80%, the ratio of individual dissolution rates and hence the degree of dezincification was hardly affected. However, if the inhibitor content was sufficient to cause more than 80% inhibition, the dissolution rates of the alloy components were relatively affected, tending towards simultaneous dissolution (i.e. $r = >0.9$). Thus at 90% inhibition, at which the net dissolution rate was very low, brass experienced simultaneous corrosion. This was observable when the immersion period was extended up to 30 h, during which detectable weight loss occurred.

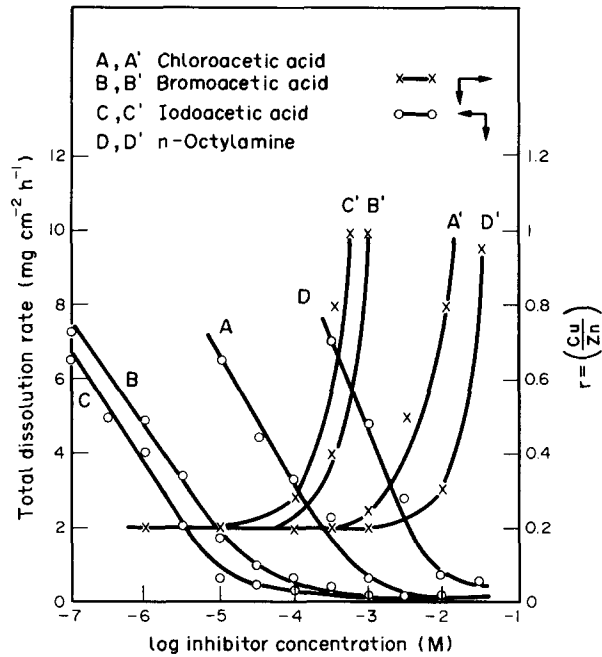


FIG. 7. The effect of inhibitor concentration on total dissolution rate (O—O) and degree of dezincification (X—X) of brass in stirred 0.1 M HNO₃ containing 10⁻⁵ M chloride ions.

DISCUSSION

The present status of knowledge on the subject advances three hypotheses on the mechanism of dezincification of brass; (1) residual copper theory—according to which zinc dissolves preferentially leaving behind copper in the crystalline lattice, (2) copper redeposition theory—in which both copper and zinc dissolve simultaneously followed by redeposition of copper, and (3) the combined theory of both

TABLE 2. INHIBITOR EFFICIENCY (%P) AT DIFFERENT CONCENTRATIONS OF *n*-OCTYL AMINE AND HALO-ACETIC ACIDS DURING DEZINCIFICATION OF BRASS IN STIRRED 0.1 M HNO₃ CONTAINING 10⁻⁵ M CHLORIDE IONS AT 30°C (IMMERSION PERIOD: 4 h)

Inhibitor concentration (M)	Inhibitor efficiency (%P)			
	<i>n</i> -OA	CAA	BAA	IAA
10 ⁻⁷				12.0
10 ⁻⁶			28	42.0
5 × 10 ⁻⁶			49	70.0
10 ⁻⁵		11.5	70	90.0
5 × 10 ⁻⁵		35.0	83	95.0
1 × 10 ⁻⁴		56.0	90	98.0
5 × 10 ⁻⁴	10.2	70.2	95	100.0
1 × 10 ⁻³	30.0	90.6	98	—
5 × 10 ⁻³	58.5	96.0	100	—
1 × 10 ⁻²	84.0	100.0	100	—

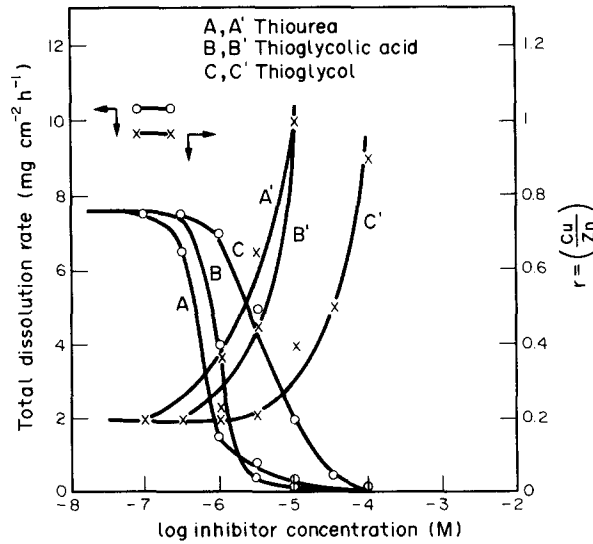


FIG. 8. The effect of inhibitor concentration on total dissolution rate (O—O) and degree of dezincification (X—X) of brass in stirred 0.1 M HNO₃ containing 10⁻⁵ M chloride ions.

(1) and (2). Based on the experimental findings, earlier workers expressed their views in support of both copper residual¹⁴⁻¹⁷ and copper redeposition^{3,18,19} theories.

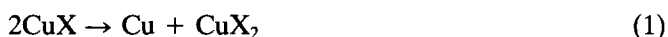
Dezincification occurs under well-defined circumstances in solutions containing specific chemical species. Previous work²⁰ revealed that anions such as thiocyanate, bromide and iodide ions did not cause dezincification while chloride or sulphate ions in certain concentrations induced dezincification. This observation emphasizes the specific action of chloride and sulphate ions on the dissolution of brass in dilute HNO₃. Anions are known to affect the kinetics of dissolution of metals or alloys due to their specific action on the surface. In general the inorganic anions referred to above are accelerators of zinc corrosion while the same species are effective inhibitors of copper corrosion in acidic media. The observed variation in the kinetics of dissolution and the degree of dezincification (Fig. 1) in both chloride and sulphate

TABLE 3. INHIBITOR EFFICIENCY (%P) AT VARIOUS CONCENTRATIONS OF THIOLYCOL (TG), THIOLYCOLIC ACID (TGA) AND THIOUREA (TU) DURING DEZINCIFICATION OF BRASS IN 0.1 M HNO₃ CONTAINING 10⁻⁵ M chloride ions at 30°C (IMMERSION PERIOD: 4 h)

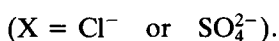
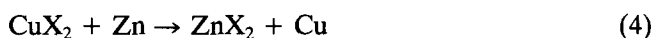
Inhibitor concentration (M)	Inhibitor efficiency (%P)		
	TG	TGA	TU
5 × 10 ⁻⁷	0.0	0.0	15
1 × 10 ⁻⁶	10.5	42.0	81
5 × 10 ⁻⁶	30.2	98.8	92
1 × 10 ⁻⁵	76.0	98.0	98
5 × 10 ⁻⁵	95.0	100.0	100
1 × 10 ⁻⁴	100.0	100.0	100

media could be essentially due to the interaction between copper and the anions involved. Thus under the circumstances in which dezincification was observed, it can be supposed that the process involves the formation of a cuprous compound (CuCl or Cu_2SO_4) *in situ* at the interface. Unlike CuSCN , CuBr or CuI (which, being sparingly soluble, are usually precipitated on the corroding surface), cuprous chloride and cuprous sulphate are metastable in aqueous solution²¹ and may decompose in the following ways resulting in redeposition of copper.³

Scheme I



Scheme II



These events occur at the interface that serves as a stage for the electrode reactions. The formation of a cuprous compound appears to be the basic requirement for the observation of dezincification in acidic solutions containing chloride or sulphate ions. Therefore, even though both copper and zinc dissolve simultaneously from brass, copper can be redeposited resulting in the preferential loss of zinc. Thus these arguments favour copper redeposition theory.

The availability of Cu^+ ions for the formation of cuprous compounds is possibly due to their rapid formation as the intermediate species in the dissolution reaction²² followed by rate controlling oxidation of Cu^+ to Cu^{2+} .



This suggests that the prior presence of either Cu^{2+} or Zn^{2+} or both (at low concentration) in the medium, as experimented, will not bring about any appreciable effect on dezincification.

The degree of dezincification is dependent on chloride or sulphate concentration (Fig. 1). Below a critical concentration of the anions (where the solubility product is not reached), the probability of the formation of a cuprous compound is less and hence there is little tendency for dezincification. An increase of anion concentration above the critical level (where the solubility product conditions are met) promotes the chances of formation of cuprous compound which in turn provides more favourable conditions for the dezincification process. In addition, depending upon the nature of anions involved, the rapid formation of cuprous compound as a result of step (5), accompanied by its controlled dissociation steps (1) and (2), permits the precipitation and accumulation of Cu_2SO_4 or CuCl which gets absorbed onto the corroding surface and retards the overall rate of the process. If the anion concentration exceeds a limit (10^{-4} for chloride, Fig. 1) the adsorbed species progressively covers and then passivates the surface. As tested in solutions having 10^{-5} M chloride or 10^{-2} M sulphate, the steady increase in weight loss with time (Fig. 2) clearly indicates the absence of such protective film on the surface during dezincification.

The characteristic variation of dissolution potential with immersion time during the course of dezincification (in chloride or sulphate solutions) under the accelerated conditions of free dissolution (Figs 3 and 4) and anodic polarization (Fig. 5), relates to the changes taking place on the surface. The identical trends in potential–time relationship reflect essentially the view that the process follows common dissolution mechanism under both the conditions. Similar potential variations have also been observed by other workers¹⁰ during dezincification of brass under anodic polarization in chloride medium. Based on their study, the negative shift of potential in the initial stages of the process is attributed to the selective removal of zinc leaving behind copper in the alloy matrix. Many investigators^{2,9,10,23,24} in the field have studied the subject by different methods and also reported that zinc dissolves preferentially in the initial stages of dezincification. The selective attack can exist for a limited period until it penetrates to several monolayers on the surface of brass. Further removal of zinc by the same process becomes less probable as it needs extra energy for zinc atoms to diffuse through the solid phase^{5,23} and hence a new mode of attack becomes necessary. As a result, after the lapse of certain time, copper also begins to go into solution along with zinc at comparatively low rate causing the shift of potentials (Figs 3–5) then indicates simultaneous dissolution of copper and zinc.¹⁰ The redeposition of copper immediately follows simultaneous dissolution leaving behind zinc in the solution. In the light of these comments and interpretations, it is proposed that the dezincification phenomenon is initiated by selective dissolution of zinc and propagated by simultaneous dissolution followed by redeposition of copper. Thus both the dissolution mechanisms are expected to operate alternately with time during dezincification.

Due to the establishment of galvanic coupling, preferential dissolution usually starts at sites abnormally rich in zinc (active component) such as grain boundaries or phases.²⁵ In 60/40 brass, an alloy of $\alpha\beta$ -phases free from arsenic, the process may initiate on the zinc-rich β -phase which is anodic to the α -phase, leading to preferential dissolution of zinc in the initial stages. Since phases in an alloy are interdependent, β -phases or grain boundaries alone will not be sites for preferential dissolution.^{26,27} In the course of time during the process, the attack also affects the other phase, spreads throughout the surface and penetrates to a certain depth. Subsequently simultaneous dissolution prevails, followed by copper redeposition process.

Simultaneous dissolution and copper redeposition processes are mutually independent of each other, but both the processes respond to changes in the experimental conditions. Thus increase of nitric acid concentration (Fig. 4, Table 1) or anodic polarization (Fig. 5) enhances the oxidizing power of the system which tends to promote dissolution and prevent redeposition. Therefore, in the present system (free from inhibitors) conditions of slow dissolution favoured dezincification while fast dissolution ensured simultaneous attack. In pure nitric acid brass undergoes simultaneous dissolution²⁸ and polarization studies produced an anodic Tafel plot (Fig. 6) having a slope of 40 ± 5 mV decade⁻¹. Similarly polarization of brass during dezincification also produced Tafel curves (of the same slope) quite parallel to that obtained in pure nitric acid (Fig. 6). This observation suggests the existence of a common mode of dissolution in both the solution conditions and substantiates the view that brass components dissolve simultaneously during the propagation stage (i.e. steady state potential conditions). Subsequent reaction, i.e. copper redeposition, takes place as the secondary process.

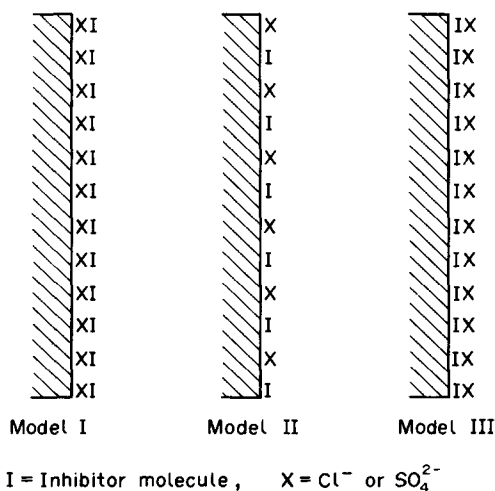


FIG. 9. Proposed models for adsorption of both inhibitor molecules and anions on the surface.

The dependence of inhibitor efficiency or total dissolution rate on the inhibitor concentration in the case of halo-acetic acids and amines (Fig. 7) resembles a typical adsorption isotherm which suggests that inhibition of the process occurs due to their simple molecular adsorption²⁷ on the surface. But the observed variation of dissolution kinetics with the concentration of thiocompounds (Fig. 8), a case typical of film forming inhibitors, shows that they exercise their action through adsorption followed by complex formation on the surface. All the inhibitors used in the study, besides dissolution kinetics, have also affected the degree of dezincification (Figs 7 and 8). The role of inhibitors in bringing changes in dezincification characteristics is discussed below based on the models proposed for the synergistic effects of organic molecules and the anions.²⁹⁻³¹

(a) The presence of the inhibitors in traces can affect the overall dissolution rate due to their adsorption at the interface which may not effect the extent of dezincification—Fig. 9, Model I.

(b) On increasing the inhibitor concentration, the inhibitor molecules tend to replace the adsorbed anions, thereby showing the possibility of co-adsorption of the inhibitor molecules and anions—Fig. 9, Model II. The presence of adsorbed inhibitor molecules may affect copper redeposition process, causing a change in the degree of dezincification.

(c) When the concentration of the inhibitor is sufficient enough to bring high inhibition (>80%), the competitive adsorption of inhibitor molecules predominates—Fig. 9, Model III. This type of preferential adsorption effectively hinders the adsorption of anions and also affects redeposition process. Under these conditions, it is quite possible that brass may dissolve at a very slow rate without any indication of dezincification.

The activity of an inhibitor at the interface (hence its influence on the electrode process) is known to depend upon its nature and its concentration. Thus strongly adsorbable/complexing type inhibitors such as thiocompounds show more effect on dezincification than non-complexing type compounds, like halo-acetic acids.

CONCLUSIONS

(1) The formation and dissociation of cuprous sulphate and cuprous chloride constitute an essential step for dezincification.

(2) Under the test conditions, the observed data are consistent with the operation of both selective dissolution (initiation stage) and simultaneous dissolution followed by copper redeposition (propagation stage), alternately with time during dezincification.

(3) The occurrence of dezincification is characterized by the potential–time relationship.

(4) Conditions of fast dissolution favour simultaneous corrosion while slow dissolution favours dezincification in acidic chloride and sulphate solutions (free from inhibitors).

(5) Strongly adsorbable but complexing type inhibitors exhibit more effect on dezincification than non-complexing type compounds.

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