ON THE DISSOLUTION OF 63/37 BRASS IN AQUEOUS AMMONIA CONTAINING COPPER AND NITRATE IONS

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The influence of copper and cupric nitrate additions on the dissolution as well as tarnishing of 63/37 Brass in 15.7N NH_4OH was studied using weight loss and electrochemical methods. Copper when added as electrolytic metal powder, accelerates the dissolution of the brass in ammonia. The dissolution rate increases with the copper concentration upto 4 g/l, beyond which the rate decreases because of the formation of a black tarnish film. When copper was added as cupric nitrate, it was found that the nitrate accelerated the dissolution process much more and prevented tarnish film formation on the brass surface. The presence of copper in ammonia made the dissolution of brass, a cathodically controlled process. The presence of NO_3^- ions caused high anodic and cathodic currents. Open Circuit Potential values of the brass in these solutions and their variations with time supported these results. The observations are explained on the basis of the Chemistry of the system.

Dissolution of brass in aqueous ammonia has been a subject of much interest [1] because ammonia is the principal environment which causes stress corrosion cracking of brasses. It has been observed that in aqueous ammonia pre-concentrated with copper beyond a certain concentration and at specific ranges of pH, the brass surface become covered with a thick, black, lustrous film commonly referred to as tarnish [2]. This porous polycrystalline film consists predominantly of Cu_2O [3,4]. According to the revised potential-pH diagram of brass-ammonia-water system [5], there exists two pH-regions where tarnishing is possible. One is at pH 3 to 7.3 and the other at pH > 11. The susceptibility of brass towards corrosion and stress corrosion cracking in the latter range of pH was studied extensively by Pugh and co-workers[6,7,8] using 15.7 N NH_4OH pre-concentrated with specific amounts of copper. According to their observations [6], 15.7 N NH_4OH solution containing 8 g/l Cu added as copper powder was a tarnishing solution, but when the same amount of copper was added as $Cu(NO_3)_2\ 3H_2O$ the solution became non-tarnishing. No reason for this change in characteristics was given. Since the tarnishing reaction is of great importance in stress corrosion cracking of brasses, it was of interest to study the effect of NO_3^- on the dissolution and tarnishing of brass in ammonia. This paper evaluates the effect of copper and NO_3^- on the corrosion and tarnishing of 63/37 Brass in 15.7 N NH_4OH. Weight loss measurements and electrochemical methods were used in this study.

EXPERIMENTAL

A commercial grade 63/37 brass sheet of 1 mm thickness was used for the study. It contained 63.27 wt.% Cu and 36.69 wt.% Zn. For weight loss experiments, rectangular specimens of 20 x 15 mm size were cut from the brass sheet. They were polished with emery papers, pickled in 20% H_2SO_4 for 5 seconds, washed with distilled water, degreased with acetone and dried. For electrochemical studies, 20 x 10 mm sized specimens, prepared as above were used. The working electrode was prepared by fitting the sample on a Teflon holder using a brass screw. The electrical contact to the specimen was made through the screw and an insulated copper wire connected to it. The exposed surface area was restricted to 2.4 cm^2 in all experiments.

Laboratory grade ammonia solution of sp.gr. 0.89, normality 15.7, pH 13.4 and containing 30 to 32% by weight of ammonia was used for preparing the experimental solutions. Experiments were conducted in solutions containing various amounts of copper ranging

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from 2 g/l to 10 g/l added as AR grade cupric nitrate or electrolytic copper powder. Tests were done in 15.7 N NH_4OH also. The pH of all the solutions were measured and it was found that, Cu added as copper powder does not alter the pH while copper added as cupric nitrate lowered the pH to 13.0 at the maximum concentration of 10 g/l Cu.

In weight loss studies the pre-weighed brass specimens were totally immersed in 100 ml of the test solution by suspending them using polythene fibres and were taken out at specific intervals ranging from 1 to 24 hrs, washed with distilled water, degreased with acetone, dried and weighed.

A Wenking, Model POS 73, Potentioscan was used for the electrochemical studies. The variation of open circuit potential of the brass with time was studied as a function of the copper content of ammonia. The potentiostatic polarization curves were determined for the brass specimens in solutions containing 8 g/l Cu added as cupric nitrate or copper powder as well as in pure 15.7 N NH_4OH. The specimen exposed to the solution was first polarized cathodically upto -800 mV, brought back to open circuit potential and polarized anodically upto -200 mV. Separate specimens were used for the cathodic and anodic polarization studies in the media containing 8 g/l Cu as copper powder, in order to study the rapid tarnishing process on the fresh brass surface during anodic polarization. The currents were noted at intervals of 10 to 25 mV with respect to a saturated calomel electrode. The specimen was stabilised for 1 minute after applying each potential.

RESULTS

Weight Loss Measurements

Fig. 1 & 2 show the weight loss data obtained from the total immersion tests in 15.7 N NH_4OH solution with copper added as copper powder and cupric nitrate, respectively. Weight loss increased with increasing exposure time in all cases. When copper was added as copper powder, the weight loss increased at any given exposure time with copper concentration upto a copper content of 4 g/l. Tarnish formation took place at 6 g/l and the weight loss of the brass decreased drastically. Further increase in copper concentration leads to a slight reduction in the weight loss. In support of Pugh's observations [6], cupric nitrate solutions were found to be non-tarnishing eventhough the conditions[5] such as pH and

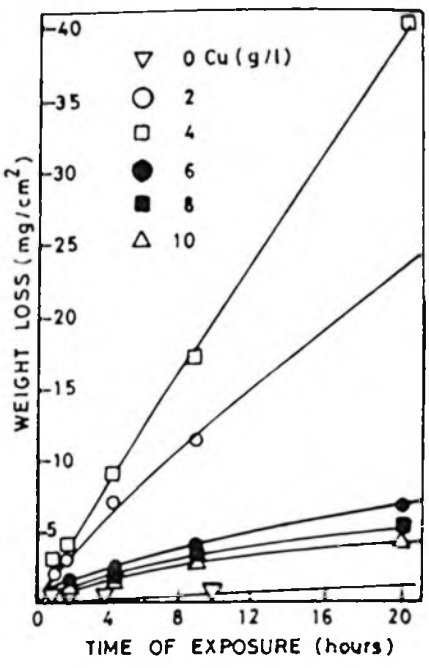


Fig. 1 Weight loss data for 63/37 brass in 15.7 N NH_4OH at different copper concentrations with copper added as copper powder.

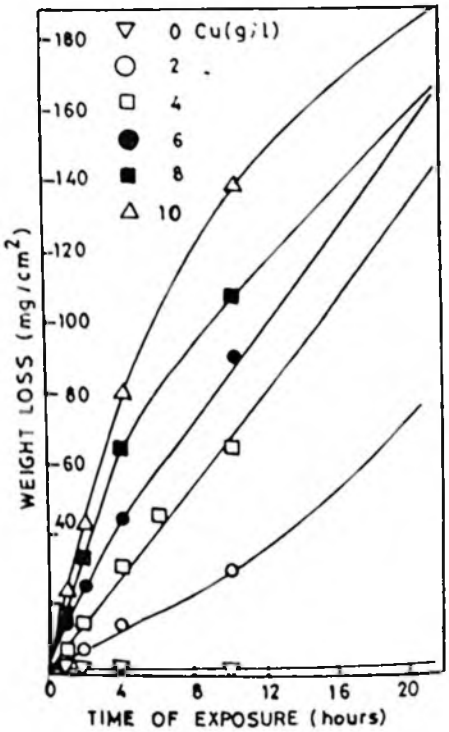


Fig. 2 Weight loss data for 63/37 brass in 15.7 N NH_4OH at different copper concentrations with copper added as cupric nitrate

copper concentration in the solution were satisfied for the formation of the tarnish film. The weight losses observed in cupric nitrate solutions were 2 to 3 times higher than those in ammonia with copper powder and were increasing continuously with the increase in copper concentration (Fig.2).

Table 1 shows the corrosion rates calculated from the weight loss data. The brass dissolves at much higher rates in cupric nitrate solutions as compared to those in copper solutions. Addition of copper to ammonia enhances the corrosion rates by several orders of magnitude. Even after a tarnish film is formed at copper concentrations above 4 g/l, the corrosion rates were 10 times faster than those in pure ammonia. In ammonia containing copper and nitrate ions, the brass dissolves 4 to 5 times faster than that in media containing copper only. As there is no tarnish formation, the corrosion rates were high at all concentrations of copper. The effect of NO_3^- on the dissolution of brass in 15.7 N NH_4OH solution is shown in Fig.3. This data was obtained by subtracting the weight loss data given in Fig.1 from that of Fig.2, so that the effect of copper is eliminated. The weight loss increased continuously with the increase in concentration of NO_3^- at all specific exposure periods shown. These results show the poisoning effect of NO_3^- on the dissolution of brass in ammonia solutions containing copper.

Electrochemical Studies

Variation in the open circuit potential

TABLE 1

CORROSION RATES OF 63/37 BRASS IN 15.7 N NH_4OH AT DIFFERENT CONCENTRATIONS OF COPPER

Copper concentration in ammonia (g/l)	Average corrosion rate after 24 hr. (m.p.y.)	
	Copper added as	
	Copper (electrolytic) powder	$Cu(NO_3)_2 3 H_2O$
0	9	9
2	496	1681
4	590	2888
6	133	3277
8	91	3227
10	91	3530

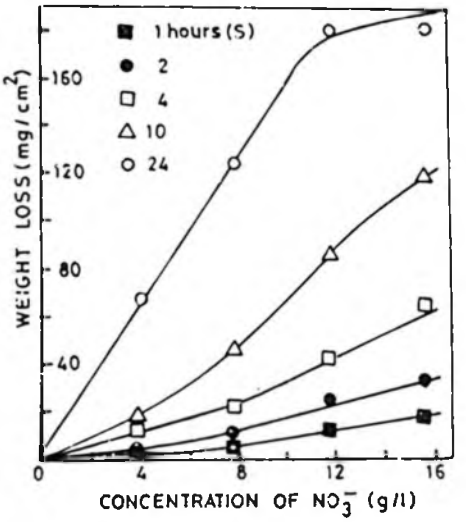


Fig. 3 Effect of NO_3^- on the dissolution of 63/37 brass in 15.7 N NH_4OH at various exposures times

(o.c.p.) of the brass was measured in 15.7 N NH_4OH with no added copper and with copper concentrations ranging from 2 g/l to 10 g/l added as copper powder and cupric nitrate. Fig.4 & 5 show the data obtained. In all cases the o.c.p. shifted to noble potentials. At low copper concentrations the o.c.p. shifts continuously in the noble direction because of dezincification which leaves behind a nobler copper matrix at the brass surface. At Cu, concentrations above 6 g/l the o.c.p. curves show an initial sudden shift towards the noble direction after which a gradual change in potential was observed. In the case of solutions containing copper added as copper powder, the formation of the tarnish film explains this drastic shift, and once a stable film is formed, the change in potential is gradual.

Fig.5 for cupric nitrate solutions also shows features similar to those in Fig.4. Continuous dezincification shift the electrode potential to nobler values. The sudden shift in potential seen in 8 g/l and 10 g/l copper solutions may be attributed to the formation of a loose corrosion product film on the brass surface. A loose greyish deposit was observed on the brass surface in these exposure studies and this may act as a diffusion barrier for further dissolution of the alloy.

The potentiostatic polarization data (Fig.6) showed that the presence of 8 g/l copper in 15.7 N NH_4OH raises the o.c.p. of the brass to

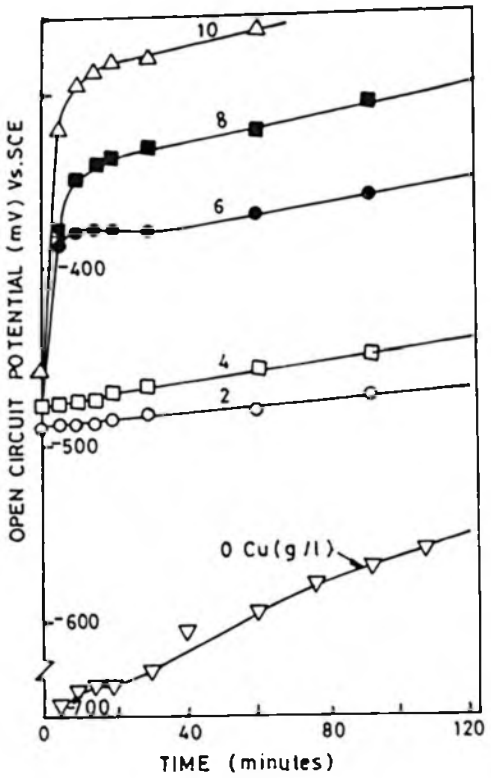


Fig.4 Variation in the open circuit potential of 63/37 brass in 15.7 N NH_4 OH at different copper concentrations with added copper powder

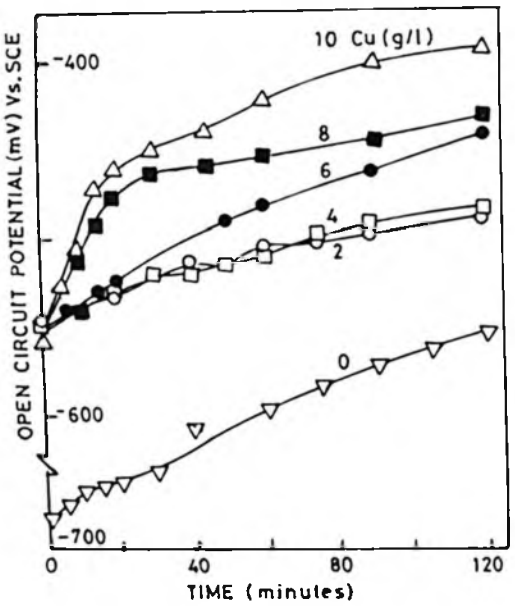


Fig. 5 Variation in the open circuit potential of 63/37 brass in 15.7 N NH_4OH at different copper concentrations with copper added as cupric nitrate

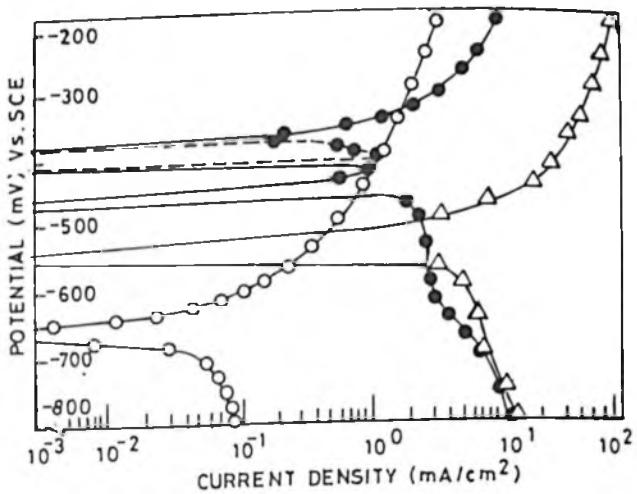


Fig. 6 Potentiostatic polarization curves for 63/37 Brass in 15.7 N NH_4OH with no added copper and with 8 g/l copper added as copper powder or cupric nitrate

much nobler values and shifts the cathodic polarization curve towards higher current densities. During anodic polarization as the applied potentials exceeded the o.c.p. (-470 mV) the specimen surface became covered with a black tarnish film, which was followed by a cathodic loop in the polarization curve in the potential region -410 mV to -380 mV. This behaviour means that two stable mixed potentials are present for the same redox system [9]. In the present case, the reduction of cuprous ions in the solution, in presence of oxygen causing the precipitation of Cu_2O [10] on the alloy surface (tarnish film) explains the observed cathodic loop. The increasing anodic polarization caused the gradual dissolution of the tarnish film and the current densities assuming high positive values. Above -380 mV the anodic dissolution currents were not significantly different from those in pure 15.7 N NH_4OH without any added copper. When copper was added as cupric nitrate, the anodic curve was shifted to higher current densities, but no discontinuity was observed. The cathodic curve was almost identical to that in solutions containing 8 g/l copper added as copper powder. Nitrate ions shifted the o.c.p. of the brass to more active values, but nobler than that of the alloy in 15.7 N NH_4OH.

DISCUSSION

The observed role of NO_3^- on corrosion and tarnishing of brass in 15.7 N NH_4OH can be

explained by considering the chemistry of the system. When brass is exposed to ammonia solution, the major anodic reactions taking place are [11].

$$Cu^{\circ} + 2NH_3 \longrightarrow [Cu(NH_3)_2]^+ + e^- \quad ...(1)$$

$$Zn^{\circ} + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{++} + 2e^- \quad ...(2)$$

where Cu° and Zn° are the copper and zinc from the alloy.

In aerated solutions, the cuprous ions react with oxygen forming cupric complex ions

$$2[Cu(NH_3)_2]^+ + \tfrac{1}{2}O_2 + H_2O + 4NH_3 \longrightarrow 2[Cu(NH_3)_4]^{++} + 2OH^- \quad ...(3)$$

The reduction of dissolved oxygen is the cathodic reaction in copper-free solutions [10].

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^- \quad ...(4)$$

But in solutions pre-concentrated with cupric ions, the reduction of cupric complex ions become the predominant cathodic reaction [11]

$$[Cu(NH_3)_4]^{++} + Cu^{\circ} \longrightarrow 2[Cu(NH_3)_2]^+ \quad ..(5)$$

The tarnish formation is due to the reaction [10]

$$2[Cu(NH_3)_2]^+ + 2OH^- \longrightarrow \underbrace{Cu_2O}_{\text{Tarnish}} + 4NH_3 + H_2O \quad ..(6)$$

Equation 6 shows that tarnish formation is favoured by the availability of $[Cu(NH_3)_2]^+$ in the solution.

In aqueous solutions copper exhibits an equilibrium,

$$Cu^{++} + Cu^{\circ} \rightleftharpoons 2Cu^+; \quad K = \frac{[Cu^+]^2}{[Cu^{++}]} = 10^{-6}$$

Due partly to the greater lattice and solvation energies of the cupric ion, the cuprous ion can exist only in exceedingly low concentrations in aqueous solutions [12,13].

The critical stability constants and other thermodynamic data for Cu^+ and Cu^{++} states in aqueous ammonia, [14]

$$Cu^+ + 2NH_3 \rightleftharpoons [Cu(NH_3)_2]^+ \quad \log K = 10.58$$

$$\Delta H = -16 \text{ K cal/mole}$$

$$\Delta S = -5 \text{ cal/mole/deg}$$

$$Cu^{++} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{++} \quad \log K = 13.00 \pm 0.05$$

$$\Delta H = -22.0 \pm 0.1 \text{ Kcal/mol}$$

$$\Delta S = -14 \text{ cal/mol/deg}$$

also supports the greater stability of Cu^{++} state.

The relative stabilities of Cu^+ and Cu^{++} depend very strongly on the nature of anions and other ligands present in the solution [12]. In the presence of NO_3^- the $[Cu(NH_3)_4]^{++}$ will form a dark blue neutral complex, $[Cu(NH_3)_4](NO_3)_2$ (tetramminecopper(II)nitrate) [15,16].

$$[Cu(NH_3)_4]^{++} + 2NO_3 \longrightarrow [Cu(NH_3)_4](NO_3)_2 \quad ..(7)$$

Thus the stability of Cu^{++} state is further favoured by the formation of these ions in aqueous ammoniacal solutions. The availability of Cu^+ ions for the tarnish formation (Eqn 6) becomes very less and thus the tarnishing is prevented in the presence of NO_3^- ions.

The tendency of NO_3^- ions to stabilise Cu^{++} state in ammoniacal solutions by the formation of the complex, $[Cu(NH_3)_4](NO_3)_2$ (Eqn 7) increases the rate of the reactions (3) and (1) which eventually results in an enhanced dissolution of the alloy.

The potentiostatic polarization data show that the presence of copper in 15.7 N NH_4OH makes the dissolution process, a cathodically controlled one. The anodic reaction during the dissolution of brass in aerated ammonia solution, preconcentrated with copper is part of the autocatalytic process,

$$[Cu(NH_3)_4]^{++} + Cu^{\circ} \xrightarrow{\text{Cathodic}} 2[Cu(NH_3)_2]^+$$

$$2[Cu(NH_3)_4]^{++} + 4NH_3 + O_2 \xleftarrow{\text{Anodic}} \quad ..(8)$$

which along with a replacement reaction [6]

$$[Cu(NH_3)_4]^{++} + Zn^{\circ} \longrightarrow [Zn(NH_3)_4]^{++} + Cu \quad ..(9)$$

causes the dissolution of the alloy. Thus the dissolution process become cathodically controlled.

From the present studies, it is concluded that the process of dissolution of brass in ammonia is a cathodically controlled one when copper is present in the solution. The presence of NO_3^- in the solution not only prevents the tarnish formation on the alloy surface but also enhanced the dissolution rate of the alloy.

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