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Protection of 60/40 Brass from Dezincification by Corrosion Inhibitors

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Abstract

Five different types of copper or zinc complexing agents as dezincification inhibitors for 60/40 brass were tested using a potentiostatic acceleration technique in 0.5 M NaCl solution containing an acetic acid-sodium acetate buffer solution of pH 4.43. The potential of 60/40 brass electrode was maintained for 3 hours at a potential -200 mV vs. S. C. E. which was $100\sim 150$ mV higher than the corrosion potential in the solution at 60°C . Benzotriazole (BTA) and tolyltriazole (TTA) were found to be effective inhibitors not only in preventing anodic dissolution of both copper and zinc but also in controlling the growth rate of dezincification layer in the 60/40 brass. 2,5-dimercaptothiadiazole (DMTDA) and 2-mercaptobenzothiazole (MBT) are effective inhibitors for the anodic dissolution but they are not as effective as BTA and TTA in the process of dezincification layer formation. Phytic acid (PA) shows an acceleration of 60/40 brass corrosion. The inhibition mechanism of these four inhibitors is probably due to the formation of copper and/or zinc complex films on the metal surface. It is concluded that an addition of the most promising inhibitors such as BTA and TTA to corrosive environments is an alternative method to prevent dezincification attack of 60/40 brass.

1. Introduction

Commercial brasses can be resistant to a variety of corrosive environments including marine conditions. Variation in corrosion resistance can be dependent on the differences in chemical composition and metallographic structure. Localized attacks such as pitting corrosion, dezincification and grain boundary attack are prevalent types of corrosion failures among commercial brasses. Increasing the zinc content causes a tendency to increase dezincification attack; $\alpha + \beta$ phase brasses are more prone to dezincification attack than α phase brasses. Protection of brasses from the dezincification attack has been made by an addition of a small amount of alloying elements such as Sn, Sb, As, Ni and/or heat treatment of manufactured components.

Nielsen and Rislund⁽¹⁾ made a comparative investigation of tests for determining the propensity to dezincification of eleven different brasses. They concluded that the potentiostatic acceleration method gives reproducible results which are in good agreement with the dezincification observed under the most corrosive conditions in domestic water. In this method the brass electrode potential was maintained at -200 mV vs. S. C. E. for 3 hours at 60°C in aerated 0.5 M NaCl buffered by adding 0.05 M acetate buffer solution to obtain a constant pH. This is a modified method of galvanostatically accelerated test in 0.5 M NaCl solution previously used by Marshakov and Bogdanov.⁽²⁾

Although numerous papers have been published on the development of dezincification resistive brasses by addition of alloying elements or heat treatment, very little information is available on the protection of brasses from dezincification attack with corrosion inhibitors. In the present paper an alternative technique to reduce dezincification attack of 60/40 brass ($\alpha + \beta$ phase brass) by adding some organic complexing agents to corrosive environments as inhibitors is presented together with data indicating how manner in which the addition of the inhibitors to corrosive environments retard dezincification corrosion. The potentiostatic acceleration method was employed to evaluate the performance of five different additives for dezincification of 60/40 brass in the 0.5 M NaCl solution. The inhibitors tested are benzotriazole (BTA), tolyltriazole (TTA), 2,5-dimercaptothiadiazole (DMTDA), 2-mercaptobenzothiazole (MBT) and phytic acid (PA). BTA and TTA are most effective and widely used corrosion inhibitors for copper and copper alloys followed by MBT in various environments.^{(3) (4)} DMTDA is one of the most effective inhibitors for brass⁽⁵⁾, a wet stain inhibitor for zinc⁽⁶⁾ and a chelating polymer for steels.⁽⁷⁾ PA is a hexaphosphoric acid ester of myo-inositol and an effective inhibitor for preventing wet storage stain of zinc.⁽⁸⁾

2. Experimental

Chemical structures of the organic additives used are shown in Figure 1. BTA and

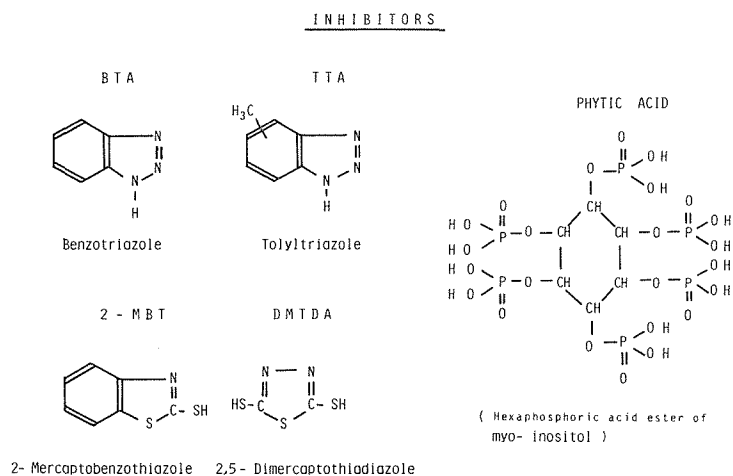


Figure 1. Chemical structure of inhibitors used.

TTA are commercially available corrosion inhibitors of Cobratec-99 and Cobratec-100, respectively. These chemicals were supplied by Sherwin Williams Company. DMTDA and MBT are analytical grade reagents of Wako Pure Chemicals Industries Co, Ltd. Phytic acid was supplied by Mitsui Toatsu Chemicals, Inc. Dezincification test electrodes were cut from cold-rolled 60/40 brass sheet to the size of $10 \times 10 \times 1$ mm. Chemical composition of the 60/40 brass is as follows, Cu 60.22, Zn 39.76, Sn, Pb, Fe ≤ 0.005 . The surface preparation of the electrode included mechanical polishing with No. 500 SiC paper, degreased in acetone, and then washed in double distilled water prior to the test. Dezincification measurements were carried out in air-saturated, non-stirred electrolyte containing 0.5 M NaCl, acetic acid-sodium acetate buffer solution of pH 4.43 at 60°C. Solutions were prepared using reagent grade chemicals and double distilled water. The solution temperature was controlled within $\pm 0.5^\circ\text{C}$. The experiments were performed in a water-jacketed glass vessel containing 500 ml of the test solution. A platinum sheet was used as a counter electrode and potentials of the electrode were measured against a saturated calomel electrode. The 60/40 brass electrode was polarized to -200 mV vs. S. C. E. in the test solution and anodic current was recorded using NICHIA model HP V100 potentiostat and HITACHI recorder 056. Chemical analysis of copper and zinc ions in the solution was made using HITACHI 170-50A atomic absorption spectrophotometer. Distribution of copper and zinc in the cross section of dezincified 60/40 brass specimen was determined by JEOR JXA 50A electron probe microanalyzer.

3. Results and discussion

Figure 2 shows the amount of copper and zinc dissolved in the test solution increased linearly with an increase of polarization time within 4 hours, and zinc and copper dissolved at a constant ratio for the initial period of anodic polarization. Then the dissolution ratio of zinc/copper increased with time, i. e., the dezincification was more accelerated. A relatively homogeneous thick dezincified layer was formed in the 60/40 brass by three hour polarization at -200 mV vs. S. C. E. Chemical composition of the electrochemically dezincified layer was almost copper, as shown in Figure 3. From X-ray microprobe analysis the zinc content

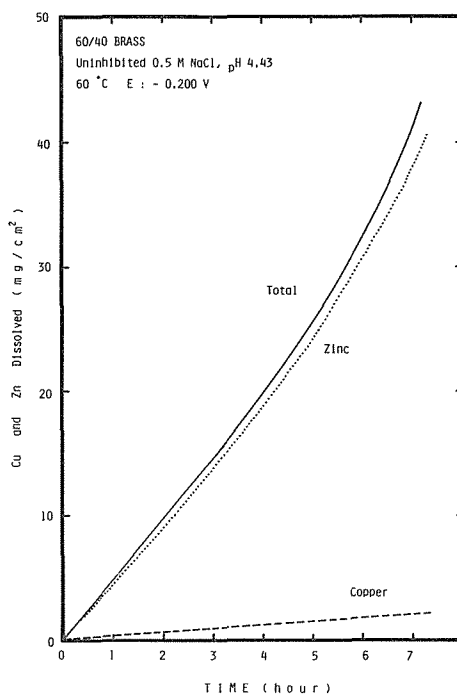


Figure 2. Amount of anodic dissolution of copper and zinc from 60/40 brass as a function of polarization time in uninhibited 0.5 M NaCl solution at 60°C.

in the dezincified layer was in the range of 2 to 5 % of the alloy matrix composition.

Figure 3 to 7 show examples of anodic current density variation with polarization time at -200 mV vs. S. C. E. for the 60/40 brass as a parameter of inhibitor concentration at 60°C . An anodic peak current followed by a steady current was observed in uninhibited solutions. This behavior is due to simultaneous dissolution of zinc and copper from the brass followed by redeposition of copper. In inhibited solutions anodic current decreased with the increase of inhibitor concentration at the concentrations of more than 10^{-4} M for BTA, TTA, MBT and DMTDA, as shown in Figures 3 to 6. Below concentrations of 10^{-4} M little change was seen in anodic current behavior. At concentrations more than 10^{-2} M for BTA and TTA, 2×10^{-3} M for DMTDA and 5×10^{-3} M for MBT anodic current density was less than $1 \mu\text{A}/\text{cm}^2$ after 1 hr polarization. At these concentrations neither dezincified layers nor corrosion products were observed in or on the brass surface. DMTDA and MBT are found to be effective in complexing and stabilizing the zinc component of the brass. These compounds, however, are disadvantageous for practical use because of their being sparingly soluble in water. The inhibitive action of BTA, TTA, DMTDA and MBT are attributed to the formation of multi-layers, i. e., brass/mainly Cu_2O /complex films, on the surface of 60/40 brass, as described in the earlier paper.⁽⁹⁾ PA showed little inhibition effect on the anodic dissolution current. White products, presumably soluble chelate formed of

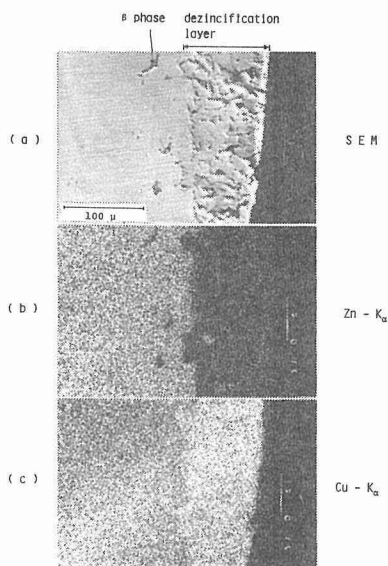


Figure 3. Typical appearance of electrochemically dezincified 60/40 brass in 0.5 M NaCl solution for 3 hours at 60°C . (a) Scanning electron micrograph of dezincified area, (b) Zinc X-ray distribution map, (c) Copper X-ray distribution map.

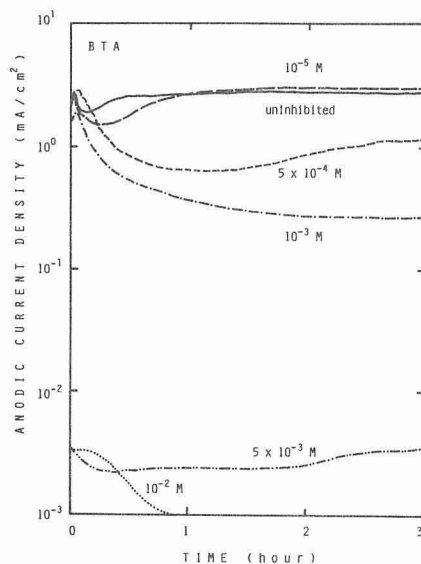


Figure 4. Change in anodic current density with time at different concentrations of BTA.

PA with zinc and copper, were observed on the surface of the brass electrode and during the polarization in the test solution containing PA. The products has no protective nature.

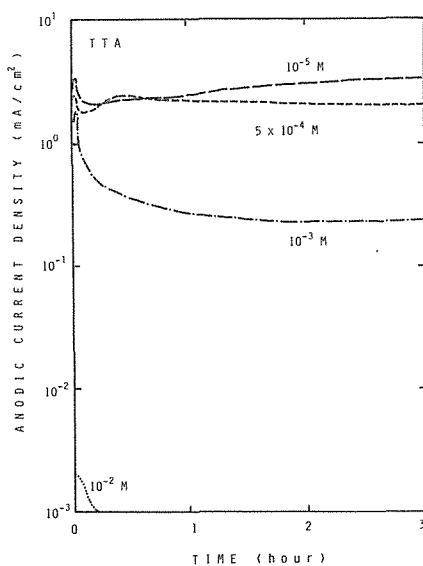


Figure 5. Change in anodic current density with time at different concentrations of TTA.

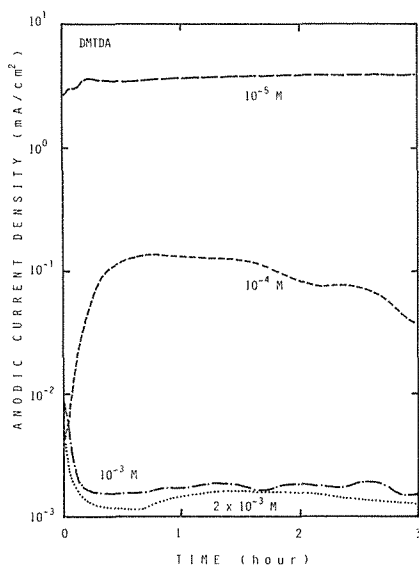


Figure 6. Change in anodic current density with time at different concentrations of DMTDA.

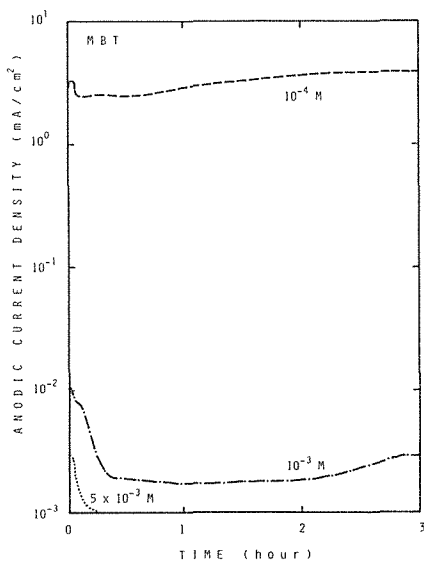


Figure 7. Change in anodic current density with time at different concentration of MBT.

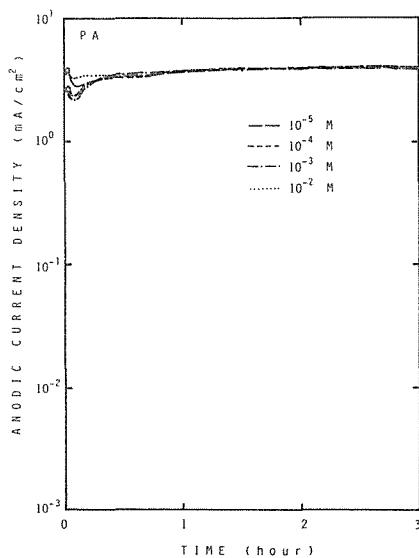


Figure 8. Change in anodic current density with time at different concentration of PA.

Inhibition efficiency data for the five compounds at concentrations of 10^{-4} , 10^{-3} and 10^{-2} M are presented in Table 1. The inhibition efficiency E is defined as follows; $E = \{(w_0 - w_i)/w_0\} \times 100$, where w_0 is amount of copper, zinc or both in the uninhibited solution, w_i is amount of copper, zinc or both in the inhibited solution. The inhibition efficiency increases with the inhibitor concentration. A particularly significant increase in the inhibitive efficiency was observed in the concentration range from 10^{-4} to 10^{-3} M for the four inhibitors. PA showed acceleration of corrosion. Although BTA is not nearly as effective in complexing zinc into a stable, insoluble, film forming product as it does in copper, apparently BTA inhibits zinc dissolution more intensely than copper dissolution.

Preferential attack in 60/40 brass dezincification was often observed, as shown in Figure 9-(b), in the solution with insufficient inhibitor concentration. Complete protection was not afforded to the brass at the 10^{-4} M BTA. There are cavities (in black) delineated along the grain boundary. Inside the grain boundary a characteristic dezincified area in copperish-red color was predominated. As shown in the photograph of Figure 9-(a) homogenous dezincification layer was formed in the uninhibited solution.

An experiment was made to test retardation action of the dezincification layer growth for the five additives. After 1 hr polarization of 60/40 brass at -200 mV vs. S. C. E. in an uninhibited solution to form a dezincification layer an inhibitor was added to the solution. An addition of the inhibitor the solution was stirred for 2 minutes to ensure an homogeneous inhibitor concentration in the bulk solution. Figure 10 shows a

Table 1 Effect of inhibitor concentration on inhibition efficiency toward 60/40 brass dissolution in 0.5 M NaCl solution.

INHIBITOR	CONCENTRATION (mol/l)	Cu	Zn	Cu+Zn
		(% inhibition)		
BTA	10^{-4}	25.50	86.05	82.61
	10^{-3}	77.51	89.21	88.55
	10^{-2}	94.76	96.99	96.58
TTA	10^{-4}	5.45	45.66	43.38
	10^{-3}	92.25	87.52	87.79
	10^{-2}	96.25	95.97	95.99
DMTDA*	10^{-4}	32.26	4.37	5.95
	10^{-3}	98.51	98.20	98.22
	10^{-2}	99.39	99.96	99.93
MBT*	10^{-4}	35.66	26.90	27.39
	10^{-3}	98.51	99.91	99.89
	10^{-2}	99.38	99.96	99.92
PA	10^{-4}	41.90	- 12.28	- 9.20
	10^{-3}	- 4.04	- 9.43	- 9.12
	10^{-2}	- 23.45	- 7.43	- 8.34

* dissolved in methanol

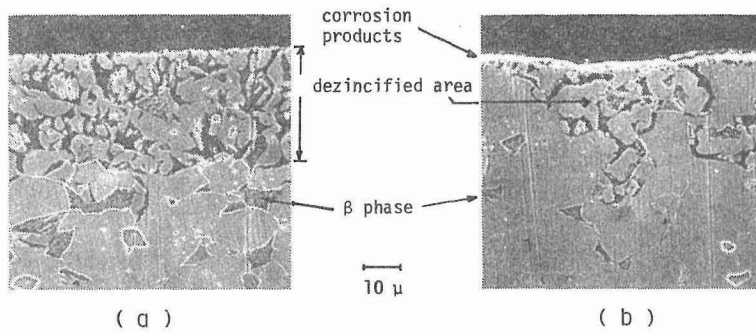


Figure 9. Cross section of 60/40 brass specimen which had been electrochemically dezincified at 60°C for 3 hours in (a) uninhibited solution and (b) the solution with 10^{-4} M BTA.
 $Q: 40.6 \text{ C/cm}^2$ $Q: 11.0 \text{ C/cm}^2$
 (Lightly etched by acidified FeCl_3 solution)

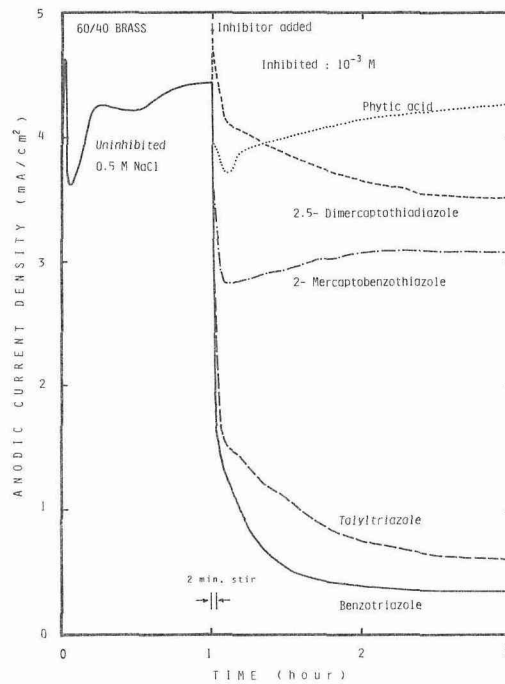


Figure 10. Anodic current density variation with time before and after inhibitor addition.

typical example of change in anodic current density with time before and after addition of the inhibitor. The anodic current density sharply decreased by the addition of BTA or TTA and reached a steady current density. In this process protective films of copper-inhibitor complex were produced on top of the dezincified layer. This complex films retards further dezincification of the brass. The growth rate of the dezincified

layer will be controlled by their protective nature, which is adherent, non-porous and dense. The inhibitor performance can be evaluated by the amount of charge passed after addition of inhibitor; the lesser the amount of charge is more protective. The amount of charge was in the increasing order of BTA (3.97), TTA (5.01), MBT (21.29), DMTDA (25.74) and PA (29.77 coulomb/cm²). It is concluded that BTA and TTA are more effective than MBT and DMTDA in interfering dezincification layer growth.

4. Conclusions

From the present investigation the following conclusion can be drawn:

- (1) BTA and TTA are effective inhibitors for preventing in both the initiation and growth of dezincification layer in 60/40 brass.
- (2) DMTDA and MBT are effective inhibitors only for the initiation of dezincification layer in 60/40 brass.
- (3) PA has no inhibitive action for 60/40 brass under the conditions studied.
- (4) The inhibitive action of the four compounds are believed to be due to the formation of protective multi-layer complex with copper and/or zinc on the brass surface.
- (5) For practical purposes BTA and TTA are appropriate additives to dezincification prone environments.

Acknowledgment

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