JOURNAL OF APPLIED ELECTROCHEMISTRY 25 (1995) 137–141

Inhibiting effects of benzotriazole on the corrosion of α-Al-bronze in saline water

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Received 7 February 1994; revised 10 June 1994

The inhibiting effect of benzotriazole (BTA) on the corrosion of α-Al-bronze (Cu–7% Al) in 3.4% NaCl was studied. BTA showed good inhibition effects from short up to extended periods of time (about six weeks). The morphologies of the alloy surface were monitored after various periods of corrosion in the absence and presence of BTA, using SEM. The corrosion products were identified by X-ray diffraction. Corrosive attack occurs very early in the absence of BTA, leading to general and pitting corrosion. BTA was found to have a stronger inhibiting effect on the anodic dissolution of copper than on the cathodic reduction of oxygen. The current–potential relation is divided into two regions: region I within which BTA has a strong effect on the charge transfer kinetics, and a limiting current region where BTA has no significant inhibiting effect. It is also shown that the interaction of BTA with a Cu_2O-covered alloy surface is faster than on reduced alloy surfaces, although the protection efficiency on the latter is slightly better than on the former.

1. Introduction

Aluminium bronzes are used extensively in sea water applications [1], for the manufacture of gears for pumps, and valves. They have good strength [1–5] and superior resistance to cavitation–erosion and impingement attack [6]. Alloying elements are added to improve their corrosion resistance and mechanical properties [1–5]. The single phase α-Al-bronze undergoes extensive corrosion in 3.4% NaCl [7], although it is less susceptible to selective de-aluminification [5, 8] than the duplex Al-bronzes, i.e. those containing more than 9% aluminium. In an effort to minimize the corrosion of α-Al-bronze in 3.4% NaCl, benzotriazole (BTA) was used as an inhibitor. BTA is known to be a good inhibitor for copper, although the mechanism of its inhibitive action is the subject of continuous debate [9–18].

The purpose of this paper is to evaluate the efficiency of BTA as a corrosion inhibitor for α-Al-bronze in 3.4% NaCl, which is a particularly corrosive medium, and to explore the mechanism of its inhibiting action. This electrolyte is frequently used to simulate sea water.

2. Experimental details

The aluminium bronze alloy was supplied by The Non-Ferrous Metallic Industries Company, Helwan (Egypt) and had the composition: 7% Al, 0.04% Fe, 0.01% Ni, 0.04% Si, 0.006% Mg, the rest being Cu. Rectangular coupons ($2\,\text{cm} \times 5\,\text{cm} \times 0.1\,\text{cm}$) were polished successively with 320, 500 and 800 grade silicon carbide papers, degreased with acetone, rinsed with distilled water, dried and weighed. The coupons were allowed to corrode in 3.4% NaCl for varying lengths of time (1–45 days) at $24 \pm 2^\circ$C. At the end of a run, the adherent corrosion products (on some samples) were stripped by dissolving in 1 M H_2SO_4 for 10 min. These samples were rinsed, dried and weighed. The weight loss of the samples was determined. Some other corroded samples, retaining the corrosion products, were examined using a scanning electron microscope (SEM), JSM-T20, Jeol (Japan) and an X-ray diffractometer, XRD 610, Shimadzu (Japan) with a copper tube ($K_{\alpha 1}$, $\lambda = 154.051$ pm) operating at 30 kV and 20 mA.

A conventional three-electrode cell was used with a saturated calomel reference electrode. The alloy electrodes were successively polished and cleaned as described above. The electrochemical measurements were performed using a Wenking potentiostat (model LT 73).

3. Results and discussion

3.1. *Weight loss*

The effect of BTA on the integral weight loss ΔW_i of the alloy is shown in Table 1 at various immersion times. The integral weight loss ΔW_i at a certain time of immersion is the total amount of weight loss during the entire length of the test. Table 1 shows that BTA suppresses the corrosion of the alloy

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Table 1. Variation of the integral weight loss of α-Al-bronzes in 3.4% NaCl solution in absence and in presence of 1×10^{-2}, 2×10^{-2} *M BTA*

Electrolyte	*Integral weight loss*/mg cm^{-2} *Time*/days *2*	*4*	*7*	*10*	*15*	*32*	*45*
3.4% NaCl	0.27	0.45	0.69	0.91	1.29	1.42	1.50
3.4% NaCl + 10^{-2} M BTA	0.04	0.04	0.04	0.04	0.04	0.04	0.04
3.4% NaCl + 2×10^{-2} M BTA	–	–	0.02	–	0.00	0.00	0.02

efficiently from very early times. While the samples corroded in 3.4% NaCl tarnished heavily and lost considerable amounts of corrosion product to the container as soluble or solid corrosion products, those immersed in the inhibited solutions remained bright after the six weeks of tests. No corrosion products were detected, either in the container or on the alloy surfaces, as shown below.

The morphology of the corroded surfaces was followed using both optical and SEM microscopy throughout the six week tests. While the uninhibited 3.4% NaCl attacked the alloy very early (i.e. as early as only one hour after immersion) leading to extensive general corrosion, nucleation, growth and eventual coalescence of pits [7], the presence of 10^{-2} M BTA retarded the corrosion process efficiently. We obtained several SEM micrographs of the alloy surfaces corroded for various periods of times in the absence and presence of 10^{-2} M BTA (which are not shown here). Although the alloy underwent severe corrosion in the 3.4% NaCl solution [7], the presence of 10^{-2} M BTA inhibited its corrosion for extended periods of time, to the extent that the SEM of the alloy immersed in the protected solution appeared identical to that of the blank alloy. Furthermore, while pitting was observed in 3.4% NaCl [7], the presence of BTA (10^{-2} M) inhibited the pitting corrosion. It is noteworthy that Arvia *et al.* [14] have recently reported extensive pitting of copper in solutions of sodium perchlorate in the presence of benzotriazole.

3.2. *X-ray diffraction*

The above findings were confirmed by X-ray diffraction measurements. Figure 1 illustrates the diffraction patterns obtained on the fresh alloy, the alloy tested for 32 days in 3.4% NaCl and the alloy tested for 32 days in 3.4% NaCl + 2×10^{-2} M BTA. The third sample gives a virtually identical diffraction pattern to that of the fresh surface, while the alloy corroded in 3.4% NaCl shows a sharp peak at a *d*-spacing of 246.7 pm ($2\theta = 36.4°$). This peak is characteristic of Cu_2O and was shown previously [7] to be very sensitive to the onset of corrosion, being detected as early as only 1 h of corrosion. This indicates that BTA inhibits the corrosion of Al-bronze quite efficiently, starting from very early times. The X-ray technique did not detect any corrosion products on the surface of the alloys tested in the presence of BTA.

3.3. *Electrochemical measurements*

Current–potential relations were obtained on Al-bronze surfaces in 3.4% NaCl in the absence and presence of BTA (10^{-2}, 2×10^{-2} M) (Fig. 2). These curves were obtained using a potential staircase program of 20 mV min^{-1}. The presence of BTA has a much stronger inhibiting effect on the anodic than on the cathodic reaction at potentials up to about 500 mV vs NHE. At 300 mV, BTA (at 2×10^{-2} M) lowers the anodic dissolution current by about three orders of magnitude. This indicates that BTA acts as

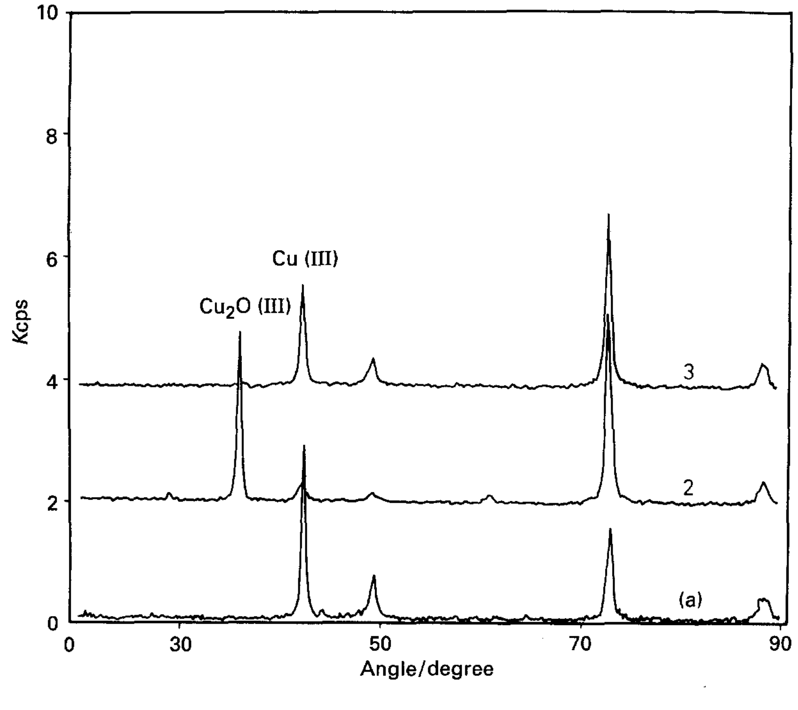

Fig. 1. X-ray diffraction patterns of the alloy surface after various treatments: (a) Blank, uncorroded, (b) corroded for 32 days in 3.4% NaCl and (c) corroded for 45 days in 3.4% NaCl + 2×10^{-2} M BTA.

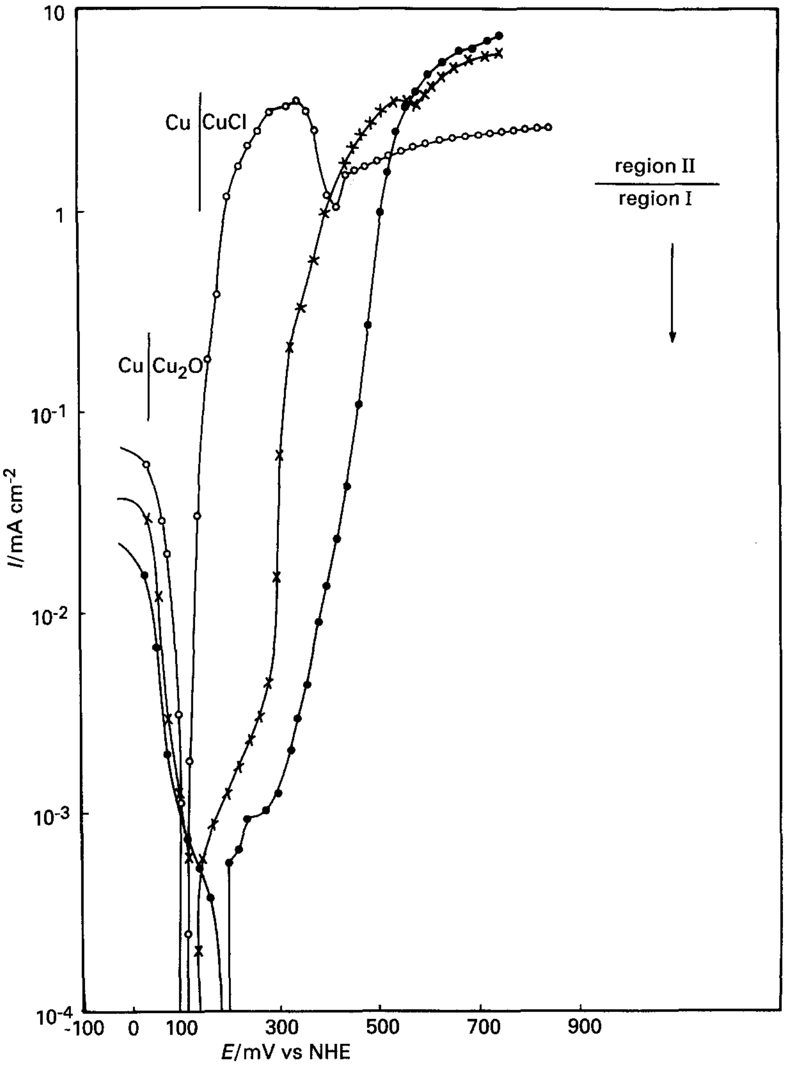

Fig. 2. Polarization curves of Al-bronzes in 3.4% NaCl in absence and in presence of BTA. Key: (○) 3.4% NaCl, (×) 3.4% NaCl + 10^{-2} M BTA and (●) 3.4% NaCl + 2 × 10^{-2} M BTA.

a predominantly anodic inhibitor, in agreement with previous results [9, 13, 19]. The anodic polarization curves in Fig. 3 are divided into two regions: region I under which the anodic reaction is under charge transfer control at low to moderate anodic potentials, and region II in which there is a poorly defined limiting current at higher anodic potentials, above 500 mV, in which the reaction is under mass transport control. Although the anodic polarization curves are sensitive to the potential and level of BTA in region I, they are less so in region II.

In the electrolytes tested in this work copper, which is the major component of the alloy, is involved in several competing equilibria [9], that is

$$2Cu + H_2O = Cu_2O + 2H^+ + 2e^- \quad (1)$$

$$Cu + Cl^- = CuCl + e^- \quad (2)$$

$$nCu + nBTA^- = [Cu(I)BTA]_n + ne^- \quad (3)$$

where $[Cu(I)BTA]_n$ is a polymeric form of the Cu(I)BTA [9] complex which inhibits the corrosion of copper [9–18]. Although the equilibrium potential of Reaction 3 in the present medium is not known, the equilibrium potentials of Reactions 1 and 2 are given by [9]

$$E_{Cu_2O/Cu} = 0.461 - 0.059\,pH \quad (4)$$

$$E_{CuCl/Cu} = 0.117 - 0.059 \log a_{Cl^-} \quad (5)$$

where a_{Cl^-} is the activity of the chloride ion, which is taken as 0.4 for the 3.4% (0.58 M) NaCl. For a solution of 3.4% NaCl of pH 6.6, Equations 4 and 5 give equilibrium potentials of 0.07 and 0.14 V vs NHE, respectively.

In view of these equilibrium potentials, it follows that the anodic current in the absence of BTA is supported by Reaction 1. This continues through most of the anodic curve, until the equilibrium potential of Equation 2 is reached. Above this potential, Equation 2 contributes to the anodic reaction.

In the presence of BTA, the situation is quite different, i.e. the current is 2–3 orders of magnitude lower than that supported by either Reactions 1 or 2. Consequently, the current in this case is attributed to Reaction 3, which has much slower charge transfer kinetics than either Reactions 1 or 2.

It has long been believed that BTA forms a very thin surface layer of a polymeric complex of Cu(I) BTA [20, 21] on the metal surface. The protection imparted to copper by the BTA was attributed to the retarding effect of the Cu(I) BTA film on the outward diffusion of copper ions which result from the dissolution of copper [9, 10, 22]. There are opposing views as to whether the corresponding Cu(II) BTA

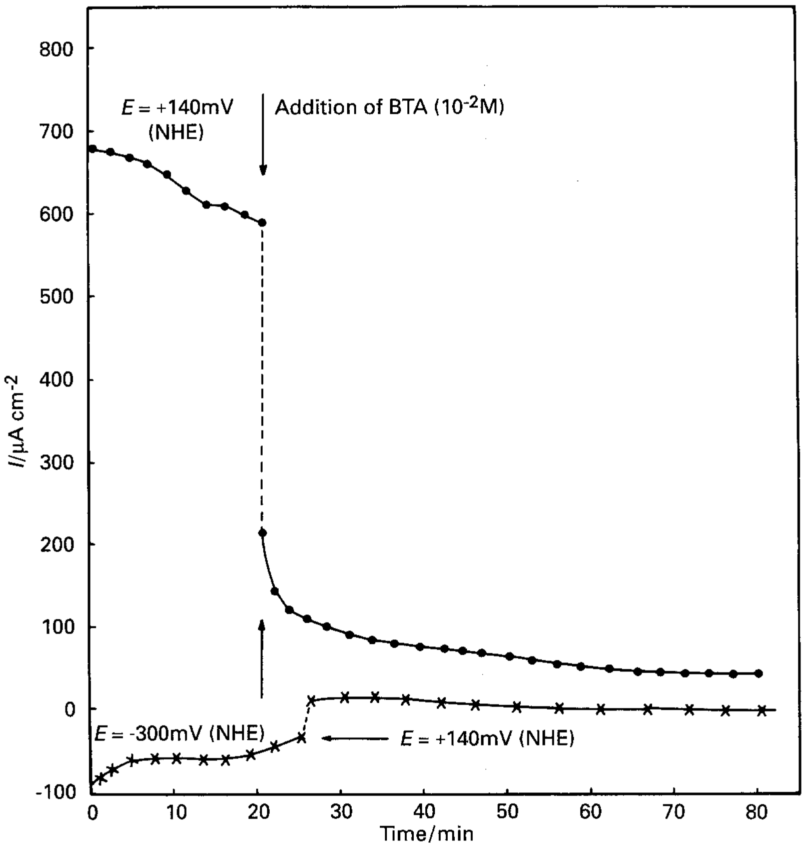

Fig. 3. Potentiostatic current–time transients of the alloy in 3.4% NaCl before and after BTA injection for various pretreatments.

species is protective or not [18, 23, 24]. The results of Fig. 2 indicate that in region I BTA has a strong effect on the charge transfer kinetics of the anodic dissolution reaction, and virtually a negligible, or even an accelerating effect, on the rate of diffusion in the diffusion-limited region, i.e. region II.

The kinetics of the interaction of BTA with the alloy surface were followed under different conditions. Figure 3 shows the effects of BTA additions on the potentiostatic current–time transients of alloy electrodes subjected to various pre-treatments. The requisite amount of a concentrated BTA solution in 3.4% NaCl was added and stirred quickly while the current transient was recorded. The alloy electrodes were potentiostated at +140 mV vs NHE which is about the middle of region I, where the anodic dissolution reaction is under charge transfer control. Under this condition, the alloy surface is covered with Cu_2O and Al_2O_3 [7]. Upon addition of BTA, there is a fast (about fivefold) decrease in the current which takes place almost immediately. This is followed by about a 2–3 fold decrease in current which occurs much slower, over a time interval of about 30 min, before the current reaches a steady value of about 50 μA cm^{-2}.

Some alloy electrodes were subjected to a reducing pre-treatment at −300 mV vs NHE for 20 min before the addition of BTA. After 5 min the electrode was put under anodic polarization at +140 mV vs NHE. The current transients during these treatments are shown in Fig. 3. Upon switching to the anodic potential (+140 mV vs NHE) the current adopted a fairly constant value of about one order of magnitude smaller than the steady current obtained after the anodic pre-treatment in the same electrolyte. This indicates that BTA interacts faster with the Cu_2O-covered alloy surface than with that which was subjected to a reducing pretreatment. However, the results of Fig. 3 also indicate that the Cu–BTA complex, which forms on the reduced alloy surface, has a slightly better inhibiting efficiency than that formed on the Cu_2O-covered alloy surface. The literature has references to opposing views regarding this matter.

4. Conclusions

(i) BTA inhibits the corrosion of α-Al-bronze in 3.4% NaCl from short up to extended periods of time (about six weeks).

(ii) BTA was found to have a much stronger inhibiting effect on the anodic dissolution of copper than on the cathodic reduction of oxygen. Furthermore, it was found to affect the charge transfer kinetics of the anodic reaction and to have virtually no effect on the limiting diffusion current.

(iii) The X-ray diffraction pattern of the alloy in the BTA-inhibited solution is identical to that of the uncorroded alloy.

(iv) BTA interacts faster with the Cu_2O-covered alloy surface than with the surfaces subjected to reducing pretreatments. However, the Cu–BTA film which results in the latter case has a slightly better inhibiting efficiency than that in the former.

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