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Effect of benzotriazole on the corrosion of alpha brass in sulfide polluted salt water

H.S. HEGAZY[1], E.A. ASHOUR[1] and B.G. ATEYA[2,*]
[1]*National Research Centre, Physical Chemistry Department, Dokki, Cairo, Egypt*
[2]*Chemistry Department, Faculty of Science, Kuwait University, Kuwait*
*(*permanent address: Chemistry Department, Faculty of Science, Cairo University, Egypt)*

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Abstract

Benzotriazole (BTAH) is shown to decrease the extent of localized corrosion of alpha brass in salt water contaminated by sulfide ions. The results are interpreted in terms of competitive adsorption of BTAH and sulfide ions on the brass surface and in view of the catalytic effects of dissolved sulfide as well as sulfide scale on the rates of the partial reactions. As the concentration of BTAH increases, the degree of coverage of the surface with sulfide decreases and, hence, also the rates of the partial reactions and the overall corrosion reaction.

1. Introduction

Benzotriazole (BTAH) has long been known to inhibit the corrosion of copper and its alloys in aqueous media. The subject is attracting a great deal of attention in efforts to explore the nature of the protective film, its growth kinetics and its effects on the rates of the anodic and cathodic partial reactions [1–10]. It is widely accepted that BTAH adsorbs onto the metal surface and eventually forms a polymeric film of a copper-BTA complex [11–20], that is,

$$\mathrm{BTAH_{(aq)} + Cu = BTAH{:}Cu} \tag{1}$$

$$n\,\mathrm{BTAH{:}Cu} + n\,\mathrm{Cu^+} = n[\mathrm{Cu(I)BTA}] + n\,\mathrm{H^+} \tag{2}$$

where BTAH:Cu refers to BTAH adsorbed on the copper surface. Most of the above studies were concerned with clean electrolytes, that is, in absence of any species which could interfere with Reactions 1 and 2.

It is now becoming more widely realized that copper and its alloys face service environments polluted by sulfide ions, which are in the form of HS^- ion in nearly neutral media. These ions are known to promote the corrosion of copper and its alloys [21–29] through an initial adsorption process, that is,

$$\mathrm{HS^-_{(aq)} + Cu = HS^-{:}Cu} \tag{3}$$

where HS^-:Cu refers to an adsorbed sulfide ion on the copper surface. The degree of coverage of the surface with adsorbed HS^-(θ_{HS^-}) is related to its concentration in the electrolyte by an adsorption isotherm. The determination of the appropriate isotherm which describes the adsorption of sulfide and/or BTAH is beyond the scope of this paper. However, for the sake of discussion, we are using the Langmuir isotherm to illustrate the importance of the adsorption process with regard to the objective of this paper. Thus,

$$\theta_{HS^-}/(1-\theta_{HS^-}) = K_{HS^-}[\mathrm{HS^-}] \tag{4}$$

where K_{HS^-} is the adsorbability of HS^- (i.e., equilibrium constant of Reaction 3). This adsorbed HS^- catalyses the anodic dissolution reaction, that is,

$$\mathrm{HS^-{:}Cu \longrightarrow CuS + H^+ + 2\,e^-} \tag{5}$$

The resulting sulfide scale [21], as well as dissolved sulfides [22], are known to catalyse both the anodic and cathodic partial reactions, the latter of which involves the reduction of oxygen, that is,

$$\frac{1}{2}\mathrm{O_2 + 2\,e^- + H_2O = 2\,OH^-} \tag{6}$$

The overall corrosion reaction is the sum of the two partial reactions (Equations 5 and 6) which can be represented by

$$\mathrm{HS^-{:}Cu} + \frac{1}{2}\mathrm{O_2 \longrightarrow CuS + OH^-} \tag{7}$$

Consequently the rates of Reactions 5–7 are affected by θ_{HS^-}.

The presence of both species in a certain environment poses a question as to whether BTAH and sulfide ions adsorb on separate sites or on the same active sites on the metal surface and hence interfere with the adsorption of each other. This point has implications on the behaviour of copper and its alloys in electrolytes containing both BTAH and sulfide ions. The objective of this paper is to study the effect of BTAH on the corrosion of alpha brass in salt water contaminated by sulfide ions.

2. Experimental details

Commercial alpha brass (of the following composition: 71.7% Cu, 28.0% Zn, 0.006% Pb and 0.01% Fe.) was obtained from the nonferrous Metallic Industries Company, Helwan, Egypt. Rectangular coupons (2.0 cm × 5.0 cm × 0.20 cm) were polished successively down to 1000 grade silicon carbide paper, degreased with acetone, rinsed with distilled water, dried and weighed (W_1). The coupons were allowed to corrode for various lengths of time at (24 ± 2) °C in aerated 3.4% (0.58 M) NaCl with and without addition of sodium sulfide or benzotriazole. Sodium chloride was Analar grade and the water was doubly distilled. Sodium sulfide was obtained from Riedel–de Haen. At the end of a run, the adherent corrosion products were stripped by dissolving in 1 M H_2SO_4 for 30 min. The specimens were rinsed with distilled water, dried, and weighed (W_2). The integral weight loss of the sample over the duration of the test was determined from the following relation:

$$\Delta W_i = W_1 - W_2 \tag{8}$$

Some other corroded samples, retaining the corrosion products, were examined using an SEM (Jeol T-330, Japan). A conventional three electrode cell was used for polarization measurements, using a platinum counter electrode and an Ag/AgCl reference electrode (E = 0.197 V vs NHE. The alloy electrodes were polished and cleaned as described above. The electrochemical measurements were performed using an EG&G potentiostat–galvanostat PAR (model 173). The polarization curves were measured at a potential scan rate of 60 mV min^{-1} after the electrode was left under free corrosion (for about 15 min) to reach a stable potential. The potentials are reported against Ag/AgCl reference electrode.

3. Results and discussion

Figure 1 illustrates the variation of the integral weight loss, ΔW_i, of the alloy at various times of immersion in a medium containing 0.58 M NaCl and 0.625×10^{-4} M (2 ppm) sulfide ions in absence and in presence of 10^{-3} M BTAH. The results indicate that BTAH at 10^{-3} M inhibits the corrosion of brass in this medium despite the presence of sulfide ions. The percentage protection efficiency of an inhibitor (P) can be calculated from the following relation:

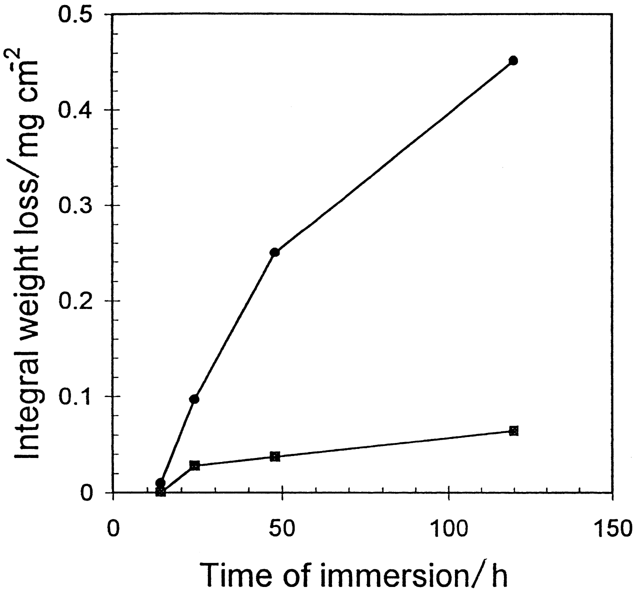

Fig. 1. Variation of integral weight loss ΔW_i, of alpha brass with time of immersion in a medium of 0.58 M NaCl + 0.625×10^{-4} M sulfide in absence (●) and in presence (■) of 10^{-3} M BTAH.

$$P = \left(1 - \frac{\Delta W_2}{\Delta W_1}\right) \times 100 \tag{9}$$

where ΔW_1 and ΔW_2 represent the integral weight losses in absence and in presence of inhibitor, respectively. The results of Figure 1 reveal that the protection efficiency of BTAH increases in presence of the sulfide ions from 71% to 85% to 86% as the time of immersion increases from 1 to 2 to 5 days. A similar phenomenon was observed with BTAH on the corrosion of copper in unpolluted acetate media of pH ≈ 5 [20].

An increase in the concentration of BTAH, at the same concentration of sulfide, leads to an increase in the protection efficiency (calculated after five days of immersion), as shown in Figure 2 for a sulfide concentration of 0.625×10^{-4} M (2 ppm). The protection efficiency increases with inhibitor concentration reaching

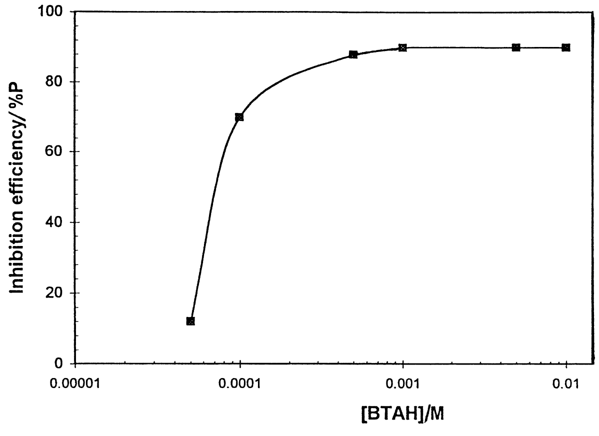

Fig. 2. Effect of the concentration of BTAH on its inhibiting efficiency, % P, against the corrosion of alpha brass in 0.58 M NaCl + 0.625×10^{-4} M sulfide.

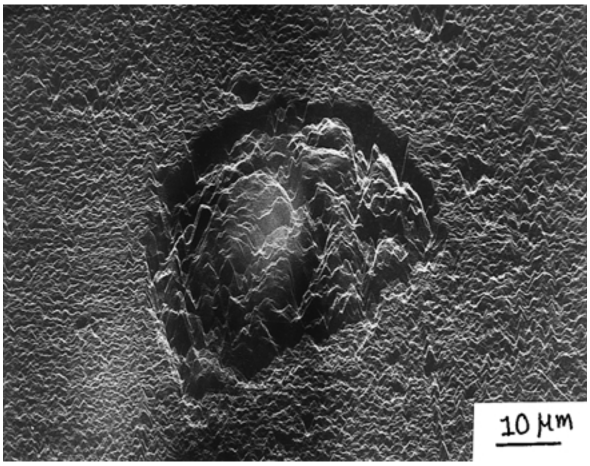

Fig. 3. SEM micrograph of alpha brass after immersion in 0.58 M NaCl + 2.5×10^{-4} M (8 ppm) sulfide for 1 h.

a plateau of about 90% starting at a concentration of BTAH of 10^{-3} M. It is interesting to note here that the protection efficiency is 90% at 10^{-2} M BTAH in the presence of 2 ppm sulfide. This value is less than the value of 98% reported earlier in absence of sulfide ions [30].

The predominant mode of corrosion in the presence of sulfide ions is localized corrosion. Figure 3 is an SEM micrograph obtained on the brass surface after immersion for 1 h in 0.58 M NaCl + 8 ppm sulfide in absence of BTAH. The extent of localized corrosion increases with the time of immersion as shown in Figure 4, which was obtained from the corroded surface under the same conditions of Figure 3 after immersion for 5 days. This explains the significant weight losses reported in Figure 1. The presence of BTAH reduces the extent of corrosion in presence of the sulfide ions. This was shown in Figure 1 in terms of weight changes. It is further supported by Figure 5 which is an SEM micrograph of the corroded surface after immersion for 5 days in 0.58 M NaCl + 8 ppm sulfide in the presence of 10^{-2} M BTAH. Upon comparing this figure to Figure 4, which was obtained under the same conditions except for the absence of BTAH, it can be concluded that BTAH reduces the extent of localized corrosion and the size of the pits considerably.

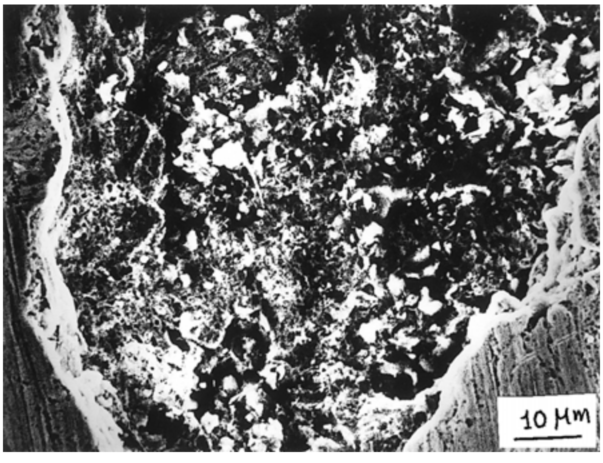

Fig. 4. SEM micrograph of alpha brass after immersion in 0.58 M NaCl + 2.5×10^{-4} M (8 ppm) sulfide for five days.

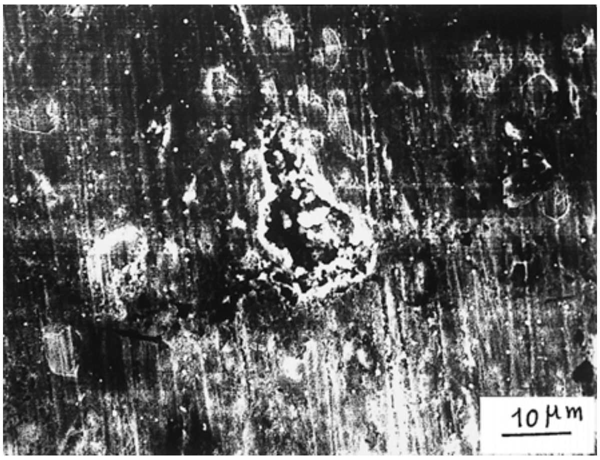

Fig. 5. SEM micrograph of alpha brass after immersion in 0.58 M NaCl + 2.5×10^{-4} M (8 ppm) sulfide + 10^{-2} M BTAH for five days.

Figure 6 illustrates the effects of the sulfide ions and of BTAH on the polarization curves obtained on alpha brass in various media. Curves (a) corresponds to 0.58 M NaCl, curve (b) corresponds to 0.58 M NaCl + 0.625×10^{-4} M (2 ppm) sulfide and curve (c) same as (b) $+10^{-3}$ M BTAH. The addition of 0.625×10^{-4} M (2 ppm) sulfide shifts the polarization curve and the free corrosion potential significantly in the active direction. For instance at an anodic current of 10^{-6} A cm^{-2}, the presence of sulfide ions lowers the potential by about 150 mV. The shift of the free corrosion potential is of a comparable value. This indicates that the sulfide ions catalyze the anodic dissolution of the alloy and, hence, lower the polarization required to support a certain dissolution rate. On the other hand, the addition of 10^{-3} M BTAH to the sulfide contaminated medium shifts the polarization curve and the free corrosion potential in the noble direction indicating that BTAH inhibits the anodic dissolution of the alloy in the presence of sulfide ions. The magnitude of this shift is much smaller than that caused by the sulfide ions. This indicates that BTAH did not entirely counteract the promoting effects of the sulfide ions on the corrosion of the alloy.

The inhibiting efficiency of BTAH on the corrosion of the alloy in the presence of sulfide ions can be calculated from the results of Figure 6 using Equation 9 with corrosion currents instead of weight losses. The calculated protection efficiency is 84% at a concentration of BTAH of 10^{-3} M and a sulfide concentration of 0.625×10^{-4} M for this test which lasted for about 15 min. This value is to be compared with a value of 90% calculated using integral weight losses over a test that lasted for five days.

The above results can be rationalized on the basis of competitive adsorption of HS^- and BTAH on the same active sites on the brass surface and the promoting

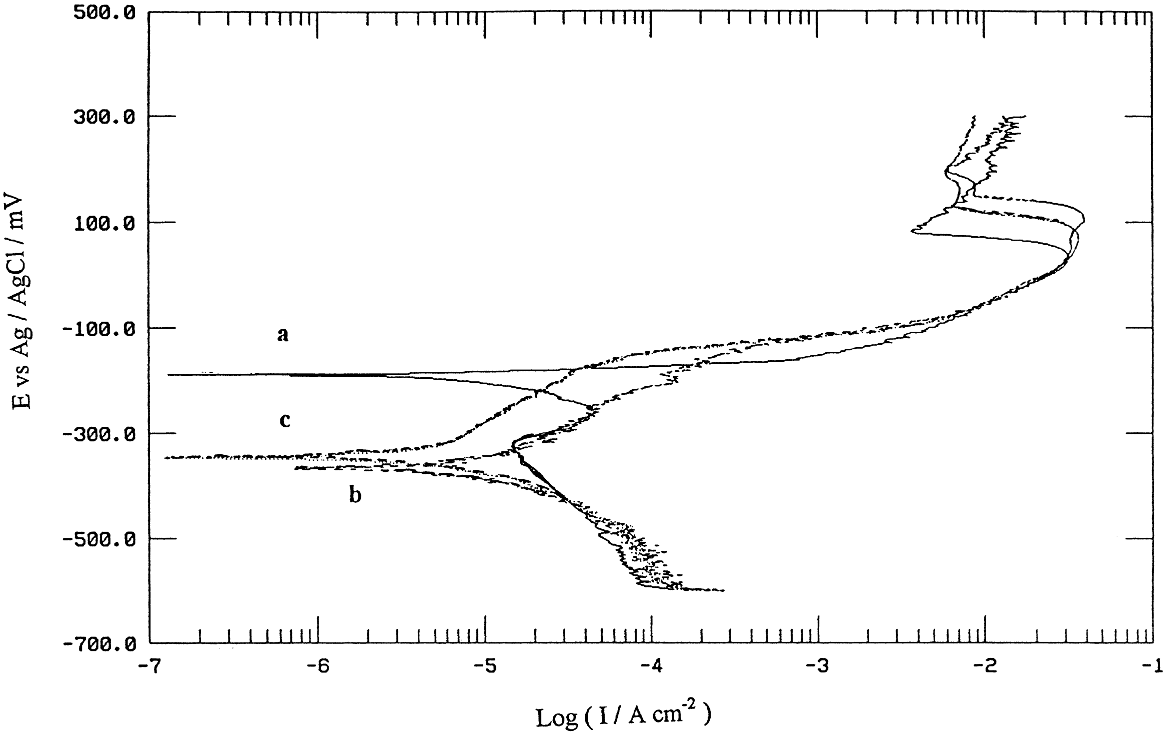

Fig. 6. Polarization curves of alpha brass in (a) 0.58 M NaCl, (b) 0.58 M NaCl + 0.625×10^{-4} M (2 ppm) sulfide and (c) same as (b) + 10^{-3} M BTAH.

effects of sulfides on the rates of the anodic and cathodic partial reactions [21–29]. In presence of both HS^- and BTAH in the same medium, the above results suggest that BTAH competes with HS^- for adsorption on the same active sites on the brass surface, that is,

$$BTAH_{(aq)} + HS^-{:}Cu = BTAH{:}Cu + HS^-_{(aq)} \qquad (10)$$

Reaction 10 is shifted more in the forward direction with increase in the concentration of BTAH in the medium, $BTAH_{(aq)}$. For such a competitive adsorption process and assuming the applicability of the Langmuir isotherm, it can be readily shown that the degree of coverage of the surface with each species is given by

$$\theta_{HS^-} = K_{HS^-}[HS^-]/(1 + K_{HS^-}[HS^-] + K_{BTAH}[BTAH]) \qquad (11)$$

$$\theta_{BTAH} = K_{BTAH}[BTAH]/(1 + K_{HS^-}[HS^-] + K_{BTAH}[BTAH]) \qquad (12)$$

where K refers to the equilibrium constant of the adsorption of the particular species (see Equation 4). Equations 11 and 12 indicate that an increase in the concentration of BTAH in the medium decreases θ_{HS^-} and hence decreases the rates of Reactions 5–7.

4. Conclusions

Benzotriazole (BTAH) decreases the extent of localized corrosion of alpha brass in sulfide contaminated salt water. This may be attributed to competitive adsorption of benzotriazole and sulfide ions on the surface of alpha brass. The presence of BTAH leads to a decrease in the surface coverage of alpha brass with HS^- and hence in the rates of the partial anodic and cathodic reactions and the overall corrosion reaction. It is noteworthy that this effect of BTAH was observed when its concentration was much greater than that of sulfide ion. BTAH was unable to stop the localized corrosion of alpha brass induced by sulfide ions even when the concentration ratio of BTAH:HS^- was 40:1. This fact points to the detrimental effects of sulfide ions on the efficiency of BTAH, which is most commonly used to protect copper and its alloys. The subject calls for more systematic studies at various concentrations of BTAH and HS^- using techniques with higher resolution to gain more insight into the mechanisms involved.

References

1. R. Babic and M. Metiokas-Hukovic, *Thin Solid Films* **359** (2000) 88.
2. J.M. Maciel and S.M.L. Agostinho, *J. Appl. Electrochem.* **30** (2000) 981.
3. N. Huyanh, S.E. Bottle, T. Notoya and D.P. Schweinsberg, *Corros. Sci.* **42** (2000) 259.
4. F. Ammeloot, F. Fiuad and E.M.M. Sutter, *Electrochim. Acta* **44** (1999) 2549.
5. A. Frignani, L. Termmesani, G. Brunoro, C. Monticelli and M. Fogagnolo, *Corros. Sci.* **41** (1999) 1205.
6. C. Jes-Hua, L. Zhi-Cheng, C. Shu, N. Li-Hua and Y. Shou-Zhuo, *Electrochim. Acta* **43** (1998) 265.

7. M.R. Vogt, R.G. Nichol, O.M. Magnussen and R.J. Behm, *J. Phys. Chem.* **102B** (1998) 5859.
8. D. Tromans, *J. Electrochem. Soc.* **145** (1998) L45; D. Tromans and J.C. Silvia, *Corrosion* **53** (1997) 16; D. Tromans and R.H. Sun, *J. Electrochem. Soc.* **138** (1991) 3235.
9. E.A. Ashour, S.M. Sayed and B.G. Ateya, *J. Appl. Electrochem.* **25** (1995) 137.
10. R. Alkire and A. Cangellari, *J. Electrochem. Soc.* **136** (1989) 913.
11. R. Youda, H. Nishihara and K. Aramaki, *Electrochim. Acta* **35** (1990) 35.
12. Zhi Xu, Sharon Lau and P.W. Bohn, *Langmuir* **9** (1993) 993.
13. J.B. Cotton and I.R. Scholes, *Br. Corros. J.* **2** (1967) 1.
14. R. Walker, *Corrosion* **29** (1973) 290.
15. G.W. Poling, *Corros. Sci.* **10** (1970) 359.
16. F. Mansfeld, T. Smith and E.T. Parry, *Corrosion* **27** (1971) 289.
17. T. Hashemi and C.A. Hogarth, *Electrochim. Acta* **33** (1988) 1123.
18. P.G. Fox, G. Lewis and P.J. Boden, *Corros. Sci.* **19** (1979) 457.
19. Y. Ling, Y. Guan and K.N. Han, *Corrosion* **51** (1995) 367.
20. M. Metikos-Hukovic, R. Babic and A. Marinovic, *J. Electrochem. Soc.* **145** (1998) 4045.
21. S. Jacobs and M. Edwards, *Water Research* **34** (2000) 2798.
22. M. Vazquez and S.R. De Sanchez, *J. Appl. Electrochem.* **28** (1998) 1383.
23. H.C. Xu, G. Seshadri and J.A. Kelber, *J. Electrochem. Soc.* **147** (2000) 558 and **146** (1999) 1762.
24. J.N. Alhajji and M.R. Reda, *J. Electrochem. Soc.* **142** (1995) 2944.
25. H.M. Shalaby, A. Al-Hashem and K. Al-Muhanna, *Br. Corr. J.* **31** (1996) 199.
26. J.P. Gudas and H.P. Hack, *Corrosion* **35** (1979) 67.
27. C. Kato, H.W. Pickering and J.E. Castle, *J. Electrochem. Soc.* **131** (1984) 1225.
28. R. Sanchez and D.J. Schiffrin, *Corros. Sci.* **22** (1982) 585.
30. E.A. Ashour, H.S. Hegazy and B.G. Ateya, *J. Electrochem. Soc.* **147** (2000) 1767. D.D. Macdonald, B.C. Syrett and S.S. Wing, *Corrosion* **35** (1979) 367 and **35** (1979) 409.