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Inhibition Of The Sulfide Induced Pitting Of Copper Nickel Alloy Using Benzotriazole

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ABSTRACT

Benzotriazole (BTAH) affects the localized corrosion of Cu10Ni alloy in 3.4% NaCl salt water containing 2 ppm sulfide ions. BTAH concentrations > 5 x 10^{-4} M imparted corrosion inhibiting efficiency that increased with its concentration. On the other hand, a concentration of 10^{-4} M BTAH acted as a promoter of pitting corrosion of the alloy in the above medium. The results of optical and scanning electron microscopy could be rationalized on the basis of competitive adsorption of BTAH and sulfide ions on the alloy surface and the formation of copper oxide and copper sulfide. The presence of the above phases was identified in the x-ray diffraction spectra of the corrosion products.

KEYWORDS

Copper- nickel alloy;
Seawater,
pitting;
Benzotriazole;
Inhibitor;
Sulfide;
Competitive adsorption.

INTRODUCTION

Copper-nickel alloys are extensively used in marine environments because of their high resistance to corrosion and biofouling [1,2]. Although pipes made from stainless steel or titanium alloys have higher erosion corrosion resistance than copper alloys, they have lower heat transfer coefficients, suffer from biofouling and are more costly. Thus ship designers and many land-based power plants [1,3] prefer to use copper nickel alloys.

The corrosion resistance of Cu-Ni alloys is attributed to their ability to form protective films of corrosion products on their surfaces. Among these corrosion products, Cu_2O plays a vital role in the corrosion protection of Cu-Ni alloys in seawater [4-10]. The inner Cu_2O layer is able to incorporate foreign cations that affect its protective properties [11]. Some authors [7,8] suggested that the incorporation of nickel ions in the defective lattice of Cu_2O decreases its ionic and electronic conductivity and hence increases its corrosion resistance. Conversely, sulfide ions may affect the integrity and hence the protective characters of the Cu_2O layer. Eiselstein [12] reported that in aerated sulfide-polluted seawater the accelerated corrosion of copper-nickel alloys appears to be the result of the sulfide preventing the formation of a protective oxide corrosion product layer. Instead a relatively hard and porous Cu_2S layer is formed which has poor protection efficiency against corrosion. The similarity between the oxide and sulfide ions suggests the possibility of incorporation of sulfide ions in the Cu_2O lattice (see below).

On the other hand, the Cu_2O layer is also important for the adsorption of benzotriazole (BTAH), which is a well known inhibitor for the corrosion of copper and its alloys, and is a source of Cu^+ ions which are used in the formation of the protective Cu(I)-BTA complex[13]. The incorporation of sulfide ions in the defective lattice of Cu_2O is bound to affect the protective properties of the film and hence the corrosion behavior of the alloy and its response to the use of BTAH(see below).

The objective of this paper is to study inhibiting effect of BTAH on the corrosion of Cu10Ni alloy in sulfide polluted salt water. The importance of this work stems from the following: (a) BTAH has been widely studied as a corrosion inhibitor for copper and its alloys in non-polluted media, (b) Many natural and industrial water streams are polluted with sulfide ions which are well known corrosion promoters, and (c) The simultaneous presence of sulfide ions and BTAH raise some basic questions about their tendency to interact with the alloy surface.

EXPERIMENTAL

The copper-nickel alloy was supplied by abu-Keer power station, Alexandria, Egypt containing 87.6% Cu, 10.7% Ni, 1.2% Fe and 0.55% Mn. Rectangular coupons (3x2x0.1cm) were polished successively down to 2000 grade SiC papers, degreased with ethanol and finally washed with distilled water. Each coupon was suspended in a 100ml beaker using glass hooks through holes in the corners of the specimens and allowed to corrode for varying lengths of time, from 5 to 120 h at room temperature(24±2 °C). At the end of the run, the specimens were removed from the solution and rinsed with distilled water. The corroded alloy surfaces were examined using a scanning electron microscopy (SEM, JOEL, JSM-T 20, Japan), an optical microscope (Wild M 50, Herbrugg, Switzerland), and an x-ray diffractometer philips (pw-1390) with Cu tube (Cu $K\alpha_1$, $\lambda = 1.54051$ A°).

Solutions were prepared with reagent grade chemicals and doubly distilled water. Na_2S was obtained from Ridel-de Haën and benzotriazole was obtained from Aldrich Chemical Co. Ltd. All measurements were performed in a solution containing 3.4% NaCl which has a comparable salt level to that of seawater. In view of the value of pK_1 of H_2S ($pK_1 \approx 7$), one concludes that the predominant sulfide species in the polluted medium is HS^-

RESULTS AND DISCUSSIONS

Corrosion reactions

Figsures 1 and 2 display optical micrographs of the corroded alloy surfaces after 5 h of immersion in unpolluted (3.4% NaCl) and in polluted (3.4% NaCl + 2 ppm HS^-) media, respectively. The cor-

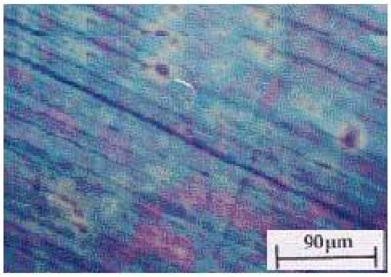


Figure 1 : Optical micrografh of the Cu 10Ni alloy surface after 5 hours of immersion in 3.4% Nacl under free corrosion conditions

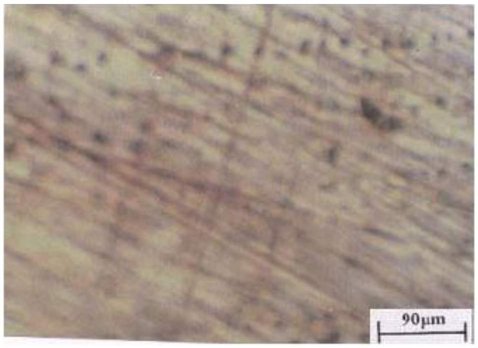


Figure 2 : Optical micrografh of the Cu 10Ni alloy surface after 5 hours of immersion in 3.4% Nacl under free corrosion conditions

TABLE 1: Summary of XRD results obtained on: a) fresh alloy, b) an alloy corroded for 35 days in 3.4% NaCl and c) an alloy corroded for 35 days in 3.4% NaCl + 2 ppm HS$^-$.

Peak No.	Fresh surface			Measured in unpolluted medium			Measured in polluted medium			On PDF file		
	2θ, degree	d, A°	% I	2θ, degree	d, A°	% I	2θ, degree	d, A°	% I	d, A°	% I	Phase
1	90	1.089	49	90.4	1.086	100	90.2	1.087	95	1.090	33	Cu
2	42.6	2.120	68	43.4	2.083	53	43.3	2.088	93	2.088 2.080	100 50	Cu Cu-Ni
3	50.2	1.816	70	50.4	1.809	81	50.1	1.819	24	1.810 1.820	15 30	$Cu_2(OH)_3Cl$ $Cu_2(OH)_3Cl$
4	74.1	1.279	100	74.2	1.277	85	74.2	1.277	75	1.278	33	Cu
5							39.9	2.257	6	2.240	50	Cu_2S
6							32.3	2.769	12	2.764 2.765	7513	Cu_2S CuS
7							16.1	5.501	33	5.500	65	$Cu_2(OH)_3Cl$
8							10.8	8.19	51	8.18	8	CuS
9							22	4.037	10	4.05	60	$CuCl_2.2H_2O$

rosion reaction in the unpolluted medium is believed to proceed through the following partial reactions[17].

$$2Cu + H_2O = Cu_2O + 2\,H^+ + 2\,e \qquad (1)^-$$
anodic

$$1/2\ O_2 + 2\,H^+ + 2\,e^- = H_2O \qquad (2)$$
cathodic

with an overall corrosion reaction represented by

$$2\,Cu + ½\,O_2 = Cu_2 \qquad (3)$$

The formation of Cu_2O is in agreement with the results of earlier works which identified Cu_2O in the corrosion products of some copper alloys after immersion in salt water for 1 h[15]. The resulting Cu_2O passivates the surface of the alloy and hence progressively decreases its corrosion rate.

On the other hand, in the presence of sulfide ions, competing partial anodic reactions involving HS^- ions contribute to the corrosion reaction[16, 17], i.e.

$$HS^-_{(aq)} + Cu = HS^-{:}\,Cu \qquad (4)$$

Where HS^-:Cu refers to an HS^- ion adsorbed onto the alloy surface. The adsorbed HS^- ions promote the anodic dissolution reaction, i.e.

$$HS^-{:}Cu = CuS + H^+ + 2\,e^- \qquad (5)$$
$$2\,HS^-{:}Cu = Cu_2S + H_2S + 2\,e^- \qquad (6)$$

Combination of the competing partial anodic reactions (Eq. 5 and 6) with the partial cathodic reaction (Eq.2) leads to the following alternate overall corrosion reactions:

$$HS^- + Cu + ½\,O_2 = CuS + OH^- \qquad (7)$$
$$HS^- + 2\,Cu + ½\,O_2 = Cu_2S + OH^- \qquad (8)$$

Both Cu_2S and CuS are known to be nonprotective[12] or even corrosion promoters[18, 19]. These phases were detected in the x-ray diffraction (XRD) spectra of the alloys corroded in the sulfide polluted medium. Figure 3 illustrates the measured XRD spectra measured on alloys corroded for 35 days in the polluted and in the unpolluted media. TABLE 1 summarizes the results. The XRD spectra mea-

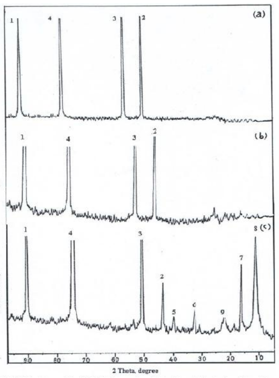
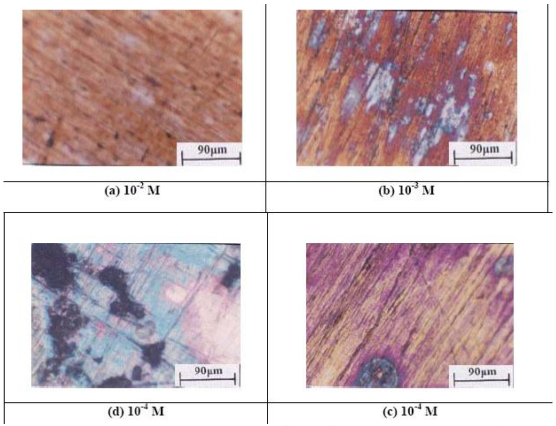


Figure 3: XRD patterns of the Cu10Ni alloy surface obtained on : (a) fresh ally, (b) an alloy corroded for 35 days in 3.4% NaCl and (c) an alloy corroded for 35 days in 3.4% NacCl = 2 ppm HS, see TABLE 1.



(a) 10^{-2} M (b) 10^{-3} M

(d) 10^{-4} M (c) 10^{-4} M

Figure 4 : Optical micrografh of the Cu 10Ni alloy surface after 5 hours of immersion in 3.4% Nacl + 2 ppm S^{2-} with different conectrations of BTAH under free corrosion conditions

sured after 5 days of immersion(not shown here) did not reveal the presence of these phases, presumably because their quantities on the surface were too small to be detected. The presence of the sulfide ions leads to an increase of several folds in the corrosion rate of the alloy. For instance, the integral weight loss after 35 days of immersion was 1.90 and 0.93 mg in the polluted and in the unpolluted media, respectively. This agrees with the findings of Jacobs and Edwards [18] who reported that the presence of sulfides increased copper corrosion rates. At a given oxygen/sulfide ratio, Cu_2O, Cu_2S and CuS will all tend to form on a competitive basis[20]. Because these compounds have different crystal structures, a significant mismatch is likely to occur where one growing crystal impinges on a neighboring crystal of a different structure. The resulting structural defects render the corrosion product film less protective[20].

The deterioration of the protective characters of Cu_2O may also be caused by the incorporation (doping) of the sulfide ions into the defective lattice structure of Cu_2O, which is known to be anion deficient [21]. The ionic radii of the oxide, O^{2-}, and sulfide, S^{2-}, ions are 1.32 and 1.84 A°, respectively[22]. Consequently, the incorporation of the (larger) sulfide ion in the(smaller) oxygen vacancy generates considerable strain in the Cu_2O lattice. In the event these strains are generated, one expects the resulting(doped) Cu_2O to be less coherent, more brittle and hence less protective.

Effects of BTAH

The effects of BTAH are shown in Figures.4a-d for: (a) 10^{-2}, (b) 10^{-3} and (c and d) 10^{-4} M BTAH (c and d representing different regions of the corroded surface). Figure.4a shows a well protected surface indicating that BTAH at 10^{-2} M inhibits the corrosion of the alloy efficiently under these conditions. The mechanism of inhibitive action of BTAH has been extensively studied [23-28]. It is believed to include an adsorption step followed by an electrochemical reaction, i.e.

$$BTAH_{(aq)} + Cu = BTAH{:}Cu \quad (9)$$

Where BTAH:Cu refers to BTAH adsorbed on the copper surface. This is followed by an electrochemical reaction, i.e.

$$BTAH{:}Cu = Cu(I)BTA + H^+ + e^- \quad (10)$$

here Cu(I)BTA is a polymeric complex that forms a protective film[23-28] on the alloy surface. Alternatively, the Cu(I)BTA complex may form directly from BTAH and Cu^+ ions coming from Cu_2O or from the dissolution of the metal, i.e.

$$BTAH + Cu^+ = Cu(I)BTA + H^+ \quad (11)$$

An increase in the concentration of BTAH in the electrolyte promotes reactions(9-11) in the forward direction, that is towards more coverage of the alloy surface with adsorbed BTAH and/or with the protective complex Cu(I)BTA.

On the other hand, Figure.4b shows some mild localized attack within protected regions indicating a lower inhibiting efficiency of BTAH(at 10^{-3} M) than that seen with the 10^{-2}M BTAH. Figures. (4 c and d) represent different regions of the surface of the alloy that was inhibited by 10^{-4}M BTAH. Both reveal various degrees of general and localized attack on the alloy surface. Figure 4c shows a region that

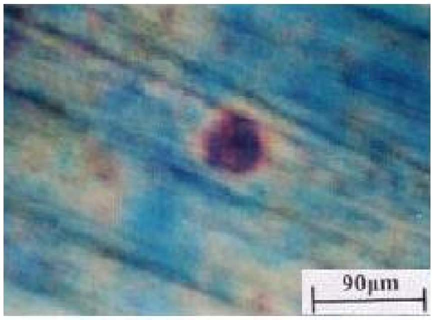


Figure 5 : Optical micrografh of the Cu 10Ni alloy surface after 24 hours of immersion in 3.4% Nacl under free corrosion conditions

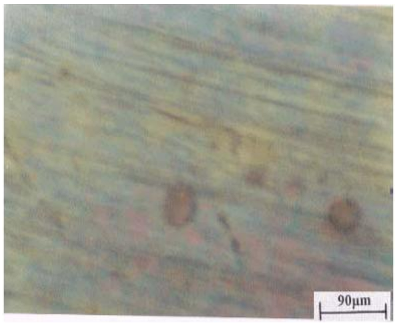


Figure 6 : Optical micrografh of the Cu 10Ni alloy after 24 hours of immersion in 3.4% Nacl + 2 ppm S^{2-} under free corrosion conditions

suffered much more damage than that shown in Figure4d.

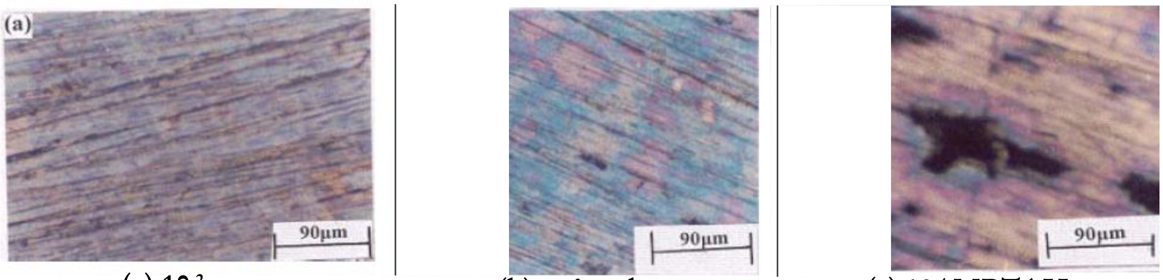
The noteworthy feature here is the extensive pitting in the presence of 10^{-4} M BTAH, which is much more than that observed in the unprotected media, see Figures 1 and 2. We have observed that BTAH at this concentration inhibits the corrosion of the alloy in the unpolluted medium. This indicates that at this low concentration of BTAH (10^{-4}M) and in the presence of 2ppm sulfide ions, BTAH promotes the localized corrosion of the alloy. A similar phenomenon was observed by Walker [29] who found that BTAH promoted the corrosion of Cu in a medium containing ammonium hydroxide and ferric chloride. This finding adds to the evidence that insufficient levels of anodic inhibitors promote localized corrosion [30-32].

The corresponding results obtained after 24 h of immersion are shown in Figures. (5 and 6) for unpolluted and polluted media, respectively. The effects of BTAH on the morphology of the alloys corroded in the polluted medium are shown in Figures 7a, b and c for 10^{-2}, 10^{-3} and 10^{-4} M BTAH, respectively. Figures 7a and b show uniform changes of the surface, whereas Figure 7c at 10^{-4} M BTAH shows evidence of localized attack. While the alloy surface shown in figure 7a appears to be well protected, the surface in figure 7b underwent corrosion to a greater extent than that in Figure 4b obtained after 5 h of exposure and otherwise the same conditions. This evidence indicates that the 10^{-3}M BTAH concentration is gradually losing its efficiency in protecting the surface against the corrosive attack of the polluted medium.

Similar measurements were performed after 72 and 120 h. The results are shown in figures 8(a,b,c) and 9(a,b,c), respectively. Both sets of figures reveal that 10^{-2}M BTAH imparts good protection of

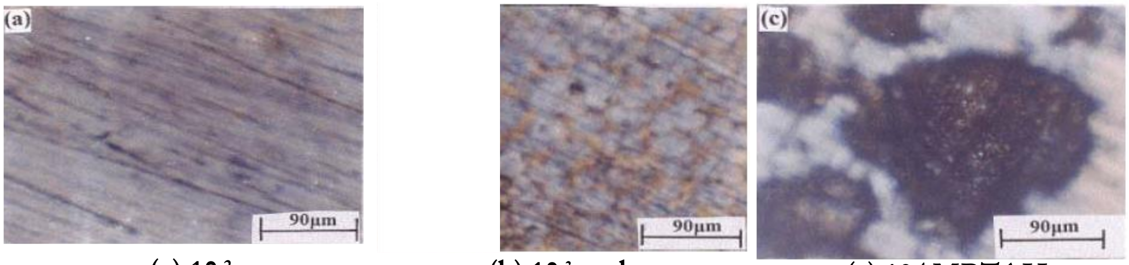
(a) 10^{-2} M (b) 10^{-3} M (c) 10^{-4} M

Figure 7 : Optical micrografh of the Cu 10Ni alloy after 24 hours of immersion in 3.4% Nacl + 2 ppm S^{2-} with different concentrations of BTAH under free corrosion conditions



(a) 10^{-2} (b) 10^{-3} and (c) 10^{-4} MBTAH

Figure 8 : Optical micrografh of the Cu 10Ni alloy after 72 hours of immersion in 3.4% Nacl + 2 ppm S^{2-} with different concentrations of BTAH under free corrosion conditions.



(a) 10^{-2} (b) 10^{-3} and (c) 10^{-4} MBTAH

Figure 9 : Optical micrografh of the Cu 10Ni alloy after 120 hours of immersion in 3.4% Nacl + 2 ppm S^{2-} with different concentrations of BTAH under free corrosion conditions.

the surface while 10^{-3} M BTAH does not prevent general corrosion, although it decreases its rate. On the other hand, 10^{-4} M BTAH leads to extensive pitting.

SEM micrographs

The corroded surfaces were also inspected using a scanning electron microscope. The effect of exposure time in the polluted medium on the morphology of the corroded alloy surface is shown in figures 10-13 for exposure times of 5, 24, 72 and 120 h, respectively. They clearly reveal the dangerous growth of localized corrosion with the time of exposure. On the other hand, figure 14 (a,b,c) shows the morphologies of the alloy surfaces which were corroded for 120 h in the polluted medium in the presence of (a)10^{-2}, (b)10^{-3} and (c)10^{-4} M BTAH, respectively. Figure 14a, for 10^{-2} M BTAH, shows a well protected surface after 120 h of exposure. On the other hand, Figure 14b, for 10^{-3} M BTAH, shows evidence of general corrosion while Figure 14c shows localized corrosion.

Inspection of the above micrographs reveals that sulfide ions cause severe attack on the surface of the Cu10Ni alloy in 3.4% NaCl that increases with the time of immersion. On the other hand, the use of BTAH at concentrations $\geq 5\times10^{-4}$M decreases the extent of corrosion damage on the surface of the alloy. While BTAH at 10^{-2}M BTAH retains its high inhibiting efficiency against the corrosive attack in the polluted medium for the duration of the test, an inhibitor level of 10^{-3}M BTAH gradually loses its efficiency. On the other hand, BTAH at 10^{-4}M is clearly a promoter of localized corrosion in the polluted medium while it was shown to protect the alloy in the unpolluted medium.

Competitive adsorption

The above results can be rationalized on the basis of competitive adsorption of HS^- and BTAH [17] on the alloy surface and the promoting effects of sulfides on the rates of the anodic and cathodic partial reactions[18,33]. In the presence of HS^- and BTAH in the same medium, BTAH competes with HS^- for adsorption on the active sites of the surface[17], i.e.

$$\mathbf{BTAH\,aq + HS^{-}{:}Cu = BTAH{:}Cu + HS_{aq}} \qquad (12)$$

Reaction (12) is shifted more in the forward

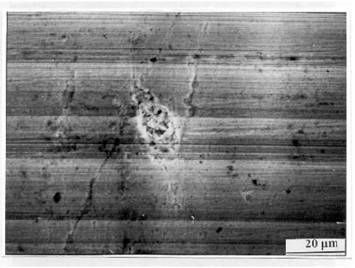


Figure 10 : Sem micrografh of the Cu 10Ni alloy after 5 hours of immersion in 3.4% Nacl+2 ppm S^{2-} under free corrosion conditions.(a) and (b) represent two different regions of the alloy surface

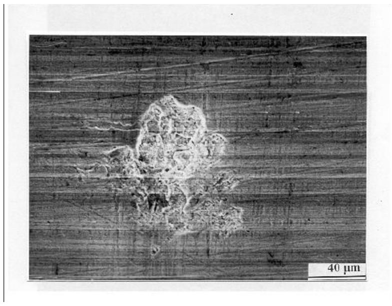


Figure 11 : Sem micrografh of Cu10Ni alloy after 24 hours of immersion in 3.4% Nacl+2 ppm S^{2-} under free corrosion conditions.

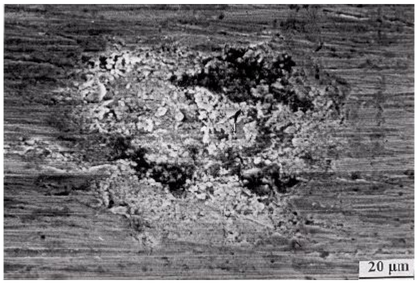


Figure 12 : Sem micrografh of Cu 10Ni alloy after 72 hours of immersion in 3.4% Nacl + 2 ppm S^{2-} under free corrosion conditions

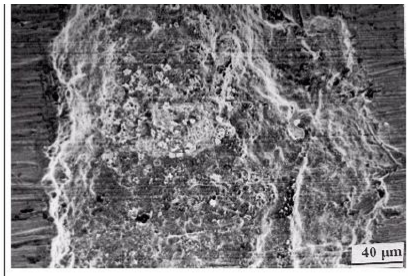


Figure 13 : Sem micrografh of Cu 10Ni alloy after 120 hours of immersion in 3.4% Nacl + 2 ppm S^{2-} under free corrosion conditions

direction with increase in the concentration of BTAH in the medium. Consequently, the formation of Cu(I)BTA on the surface is favored (see Eq. 9-11). In this case, the coverage of the alloy surface with adsorbed HS^- ions decreases. Hence, the rates of reactions (5-8) decrease.

For such a competitive adsorption process and assuming the applicability of the Langmuir isotherm, it can be readily shown that the degrees of coverage of the surface with HS^-(θ_{HS^-}) and with BTAH($_{BTAH}$) are given by[17]:

$$\theta_{HS^-} = K\,HS^-[HS^-] / (1 + K\,HS^-[HS^-] + K\,BTAH\;BTAH]) \qquad (13)$$

$$\theta_{BTAH} = K\,BTAH[BTAH] / (1 + K\,HS^-[HS^-] + K\,BTAH\;[BTAH]) \qquad (14)$$

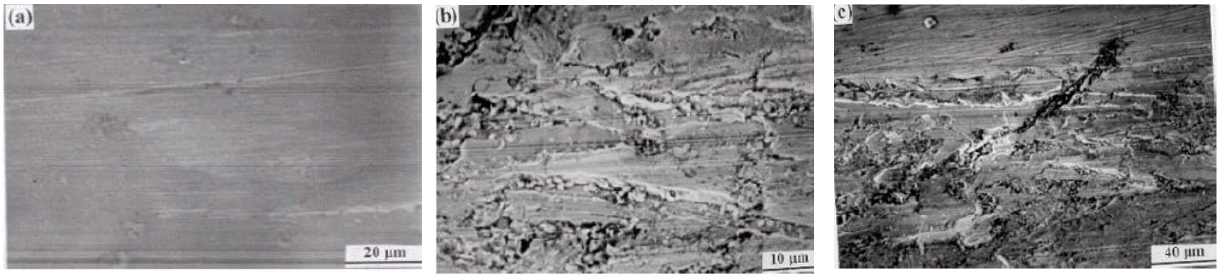
where K refers to the equilibrium constant of adsorption of the particular species, i.e. reactions 4 and 9 for HS^- and BTAH, respectively. Equations (13) and (14) indicate that an increase in the concentration of BTAH in the medium decreases θ_{HS^-} and increases θ_{BTAH} and hence decreases the rates of reactions (5-8). The formation of the protective Cu(I)BTA film may be represented by Eqs. (9-11). Conversely, an increase in the concentration of HS^- in the medium increases θ_{HS^-}(and the rates of Eqs. 5-8) and decreases θ_{BTAH} and hence the rates of Eqs.9-11, resulting in more aggressive attack and lower inhibiting efficiency of BTAH [34].

SUMMARY AND CONCLUSIONS

The present work reveals the effects of sulfide ions (at 2ppm) and benzotriazole (BTAH) (10^{-4}– 10^{-2}M) on the corrosion of Cu10Ni alloy in 3.4% NaCl at room temperature. The following points represent major conclusions:

Sulfide ions alter the composition and hence properties of the corrosion product film which normally protects the alloy during its corrosion in unpolluted 3.4% NaCl.

The presence of 2 ppm sulfide ions in the medium promotes localized attack on the alloy surface. The nucleation of pits was detected during the first few hours of immersion. They grow rapidly with exposure time causing extensive damage to the alloy. Benzotriazole (BTAH) inhibited localized corrosion of Cu10Ni alloy in sulfide polluted salt water provided that its concentration remains $\geq 10^{-3}$M BTAH. A concentration of 10^{-3} M BTAH was not enough to prevent general corrosion of the alloy in the pol-



(a) 10^{-2} (b) 10^{-3} and (c) 10^{-4} M

Figure 14 : SEM micrografh of Cu 10Ni alloy after 120 hours of immersion in 3.4% Nacl+2 ppm S^{2-} under free corrosion conditions in presence of different conditions

luted medium up to exposure times of 120 h. However, the same level of BTAH concentration showed very high efficiency against general corrosion of the alloy in the unpolluted 3.4% NaCl over much longer exposure times.

The presence of low concentration (10^{-4} M) of BTAH accelerates localized corrosion in the polluted medium at early times of exposure while it inhibits corrosion in the unpolluted 3.4% NaCl.

As the concentration of BTAH decreases, its inhibiting efficiency in the polluted medium decreases and the alloy undergoes general corrosion. Further decrease in the concentration of BTAH leads to localized corrosion. This sequence remains to be rationalized.

The subject calls for more systematic studies at various concentrations of both BTAH and HS^- using techniques with higher resolution to gain more insight into the prevailing mechanisms.

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