Effect of Pretreatment with Benzotriazole on the Corrosion of Copper in

Sulfide Polluted Salt Water

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Abstract

Copper undergoes extensive general and intergrannular corrosion (IGC) in sulfide polluted salt water. On the other hand, when copper was pretreated for one hour in the presence of 10 mM benzotriazole (BTAH) under a mild oxidizing potential, only localized corrosion occurred at the grain boundaries while the grain surfaces remained well protected. Under this condition, sulfur was detected using energy dispersive spectroscopy (EDS) at the grain boundaries, but not on the grain surfaces. X-ray photoelectron spectroscopy revealed the presence of sulfide ions and BTAH on the corroded surface. This pretreatment resulted in a protection efficiency of about 92%.

Key words: Intergranular corrosion, copper, salt water, sulfide, SEM, XPS, benzotriazole

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Introduction

Copper and many of its alloys are manufactured in various forms and utilized in many industries, particularly in marine environments. The corrosion of copper and many of its alloys in such environments has been extensively studied.[1-4] Sulfide ions are known to promote the corrosion of copper.[5-10] This is believed to occur via an initial adsorption step, i.e.

$$HS^- + Cu = Cu : HS^-_{(ads)} \qquad\qquad [1]$$

$$Cu : HS^-_{(ads)} = CuS_{(s)} + H^+ + 2e^- \qquad\qquad [2]$$

where $Cu : HS^-_{(ads)}$ refers to an adsorbed HS^- ion on the copper surface. Sulfide attack on copper and its alloys is particularly relevant to the proposed use of copper canisters for the disposal of Swedish, Finnish and Canadian high level nuclear waste deep in granite environment,[8,9] the rapid failure of copper nickel condenser tubes in wet hydrogen sulfide atmosphere[11] and the extensive use of copper and its alloys in sulfide polluted environments.

Benzotriazole ($C_6H_5N_3$, BTAH) has long been known as an inhibitor for the corrosion of copper and many of its alloys. The remarkable inhibiting efficiency of BTAH is attributed

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to the formation of a protective film of Cu(I)BTA on the surface, which inhibits the anodic corrosion reaction.[12-19]. The mechanism of inhibition involves adsorption of BTAH, which can be represented by:

$$Cu_{(s)} + BTAH_{(aq)} = Cu:BTAH_{(ads)} \qquad [3]$$
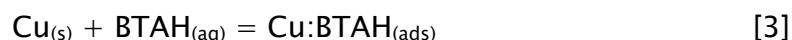
where $Cu:BTAH_{(ads)}$ refers to BTAH adsorbed on the copper surface.   Under anodic potentials, this adsorbed species can be oxidized to give the complex Cu(I) BTA,[19] i.e.

$$Cu : BTAH = Cu \, (I) \, BTA + H^+ + e^- \qquad [4]$$
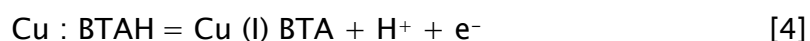
The above mechanisms of inhibition are well accepted in unpolluted media. It is now widely recognized that many natural water bodies and industrial waste water streams are polluted. For example, formation waters in sour oil and gas wells are heavily contaminated with hydrogen sulfide which promotes metallic corrosion.[20] In such environments, copper and its alloys serve in media that are inhibited by BTAH and polluted with sulfide ions.

The objective of this work is to assess the efficiency of pretreatment of copper with BTAH on its resistance to sulfide attack.

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2. Experimental

Electrodes were prepared from electrolytic copper (99.9 %) in the form of rods having 0.96 cm diameter. The working electrode was the cross sectional area of the rod while the immersed length of the rod was coated with a protective adhesive so that only the cross sectional area is exposed to the solution. Electrical contact to the external circuit was made through the rod. The working electrodes were polished using SiC papers successively down to 2400 grits, followed by 0.3 micron alumina to acquire a mirror-like finish. Measurements were performed using a Gamary potentiostat and software. A conventional three-electrode cell was used with a Ag/AgCl reference electrode, E = 0.197 V SHE, and a Pt sheet counter electrode. Solutions were prepared using deionized water, AnalaR Na_2S and NaCl from Fluka, BTAH from Aldrich. Measurements were performed at 25 $\pm$ 1°C in 3.5 wt. % NaCl solution which was open to air and stirred using a magnetic stirrer. The surfaces of the electrodes were examined using JSM– 6300 JEOL scanning electron microscope (SEM) and XPS, VG SCIENTIFIC 200 Spectrometer (UK), using MgK_α radiation (1253.6 eV) operating at 300W, 13 kV and 23 mA.

Results and Discussion

Polarization tests

Fig.1 illustrates the effects of BTAH and of sulfide ions on the polarization curves of copper, measured at 5 mV s^{-1}.　Curve (a) refers to the blank solution (3.5% NaCl), curve (b) was measured after the electrode was pretreated in the presence of 0.01 M BTAH for 1 h while curve (c) was measured after injection of 10^{-3} M HS$^-$ following the above pretreatment. Curve (d) was obtained in the presence of 10^{-3} M HS$^-$ in the blank electrolyte.　It is added for the sake of comparison with curve c which was measured after　pretreatment with　BTAH.
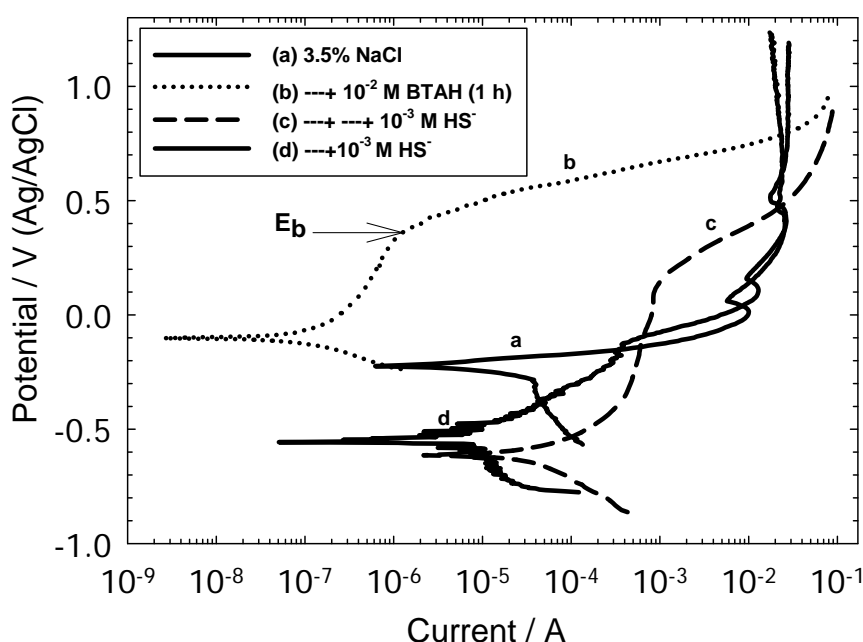

Fig. 1: Effect of sulfide ions on the polarization curves of copper in 3.5%NaCl with and without pretreatment in 10^{-2} M BTAH at 25°C, see text.

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The presence of BTAH decreases the rate of anodic dissolution of copper by about four orders of magnitudes (compare curves a and b). A passive region appears in the anodic branch of the curve, which is attributed to the formation of a protective film of the Cu(I)BTA complex, Eq.4. It extends for about 500 mV and ends at the break down potential, E_b, beyond which the current increases rapidly with potential. The sulfide ions diminish the passivity caused by BTAH by increasing the current in the passive region by about three orders of magnitude (compare c and b). They also shift the polarization curve much closer to that of the unprotected copper. Furthermore, they lower both the breakdown potential E_b, and the free corrosion potential by hundreds of mV.

Potentiostatic current transients were measured in the BTAH inhibited electrolyte at a potential of 0.0 V (Ag/AgCl), before and after injection of sulfide ions. This potential was chosen to be in the passive region. Fig.2 illustrates some of the results. The remarkable
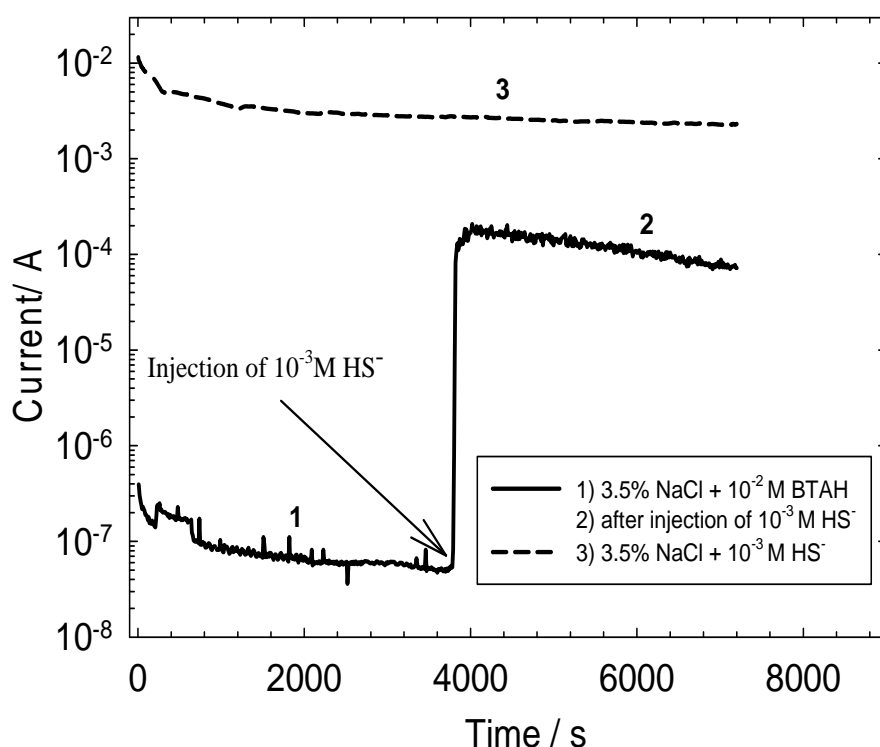
Fig. 2: Potentiostatic current transients of copper at 0.0 V under different conditions:

1)   In the presence of 10^{-2} M BTAH.

2)   After injection of 10^{-3} M HS$^-$.

3)   In the sulfide polluted salt solution.

inhibiting efficiency of BTAH is reflected in a passive current of less than 0.1 µA cm^{-2} in the

presence of 10^{-2} M BTAH after one hour (curve 1). Upon injection of 10^{-3} M HS$^-$, a rapid

increase in current to about 200 µA was obtained (curve 2). The magnitude of this sudden

increase in current upon injection of sulfide ions is taken as a measure of the intensity of

sulfide attack. Curve (3) was measured in the presence of 10^{-3} M HS$^-$, without pretreatment

in BTAH, for the sake of comparison. The current obtained upon injection of the sulfide

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ions (2) is much less than the current obtained under the same conditions without pretreatment without BTAH (3). This indicates clearly that the pretreatment of copper in the presence of BTAH improves its resistance to sulfide attack. The efficiency of an inhibitor (%P) can be calculated from the following equation:

$$\%P = 1 - i_2 \,/\, i_1 \qquad\qquad\qquad [5]$$

where i_2 and i_1 are the currents with and without inhibitor treatment, respectively. These results indicate that the above pretreatment with BTAH achieves a protection efficiency of about 92% against sulfide attack.

It is shown below that the high currents obtained without pretreatment in BTAH (curve 3 in Fig. 2) result from general corrosion of the metal at the grain surfaces and from localized intergranular attack. On the other hand, the exceedingly low currents (~ 0.1 µA) before injection of sulfide ions (curve 1) point to a well protected surface, while the current jump seen after injection of sulfide (2) is due to localized intergranular corrosion only at the grain boundaries.

Scanning electron microscopy (SEM)

Figs. 3a–c show the morphology of copper surfaces that were potentiostated for 1 h in the salt solution at 0.0 V (Ag/AgCl). While the surface treated with BTAH is well protected (3a),

extensive corrosion appears with more visible grain boundary attack on the surfaces that were not pretreated in 10^{-2} M BTAH (3b). On the other hand, only localized intergranular corrosion occurred at the grain boundaries of the surfaces that were pretreated with BTAH (3c). A closer look at the topography of the corroded surfaces is given in Figs.4a and b at a greater magnification. Fig.4a was obtained on samples corroded in the sulfide polluted medium without pretreatment in the presence of BTAH. It reveals extensive corrosion on the grain surfaces in addition to the grain boundary attack. This explains the higher currents seen in Fig.2 for the electrodes that were not pretreated in 10^{-2} M BTAH (curve 3). On the other hand, the topography of the surface that was pretreated in the presence of 10^{-2} M BTAH shows much less general corrosion at the grain surfaces. However, there is still a moderate degree of intergranular attack due to the sulfide ions, which explains the increase in current upon injection of HS^- ions (curve 2).
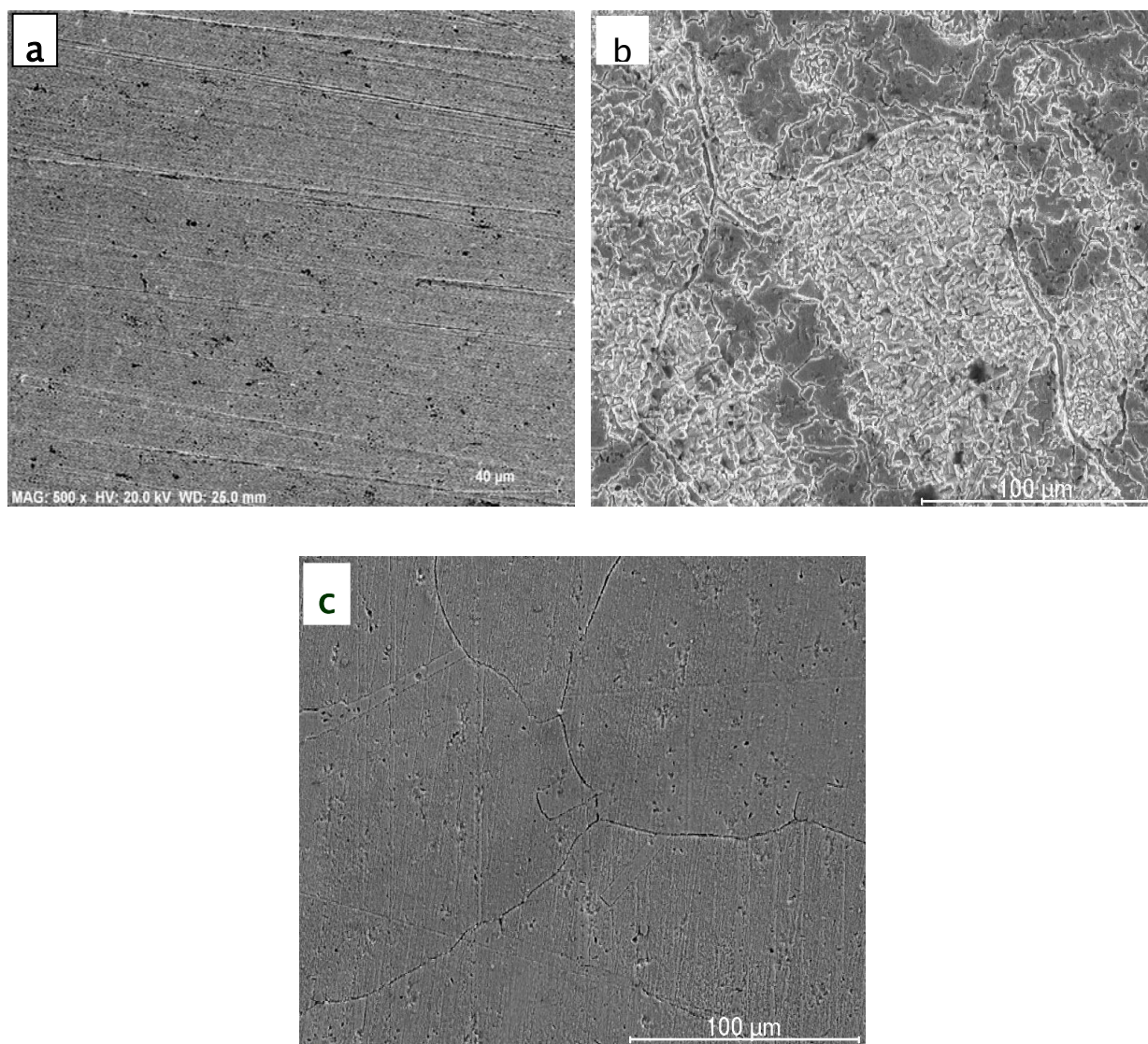
Figs. 3 SEM micrographs of copper potentiostated for 1 h at 0.0 V (Ag/AgCl) in 3.5% NaCl under the following conditions:

a) In the presence of 10^{-2} M BTAH.

b) In the presence of 10^{-3} M HS$^-$.

c) In the presence of 10^{-2} M BTAH followed by injection of 10^{-3} M HS$^-$ and further potentiostating for another hour.
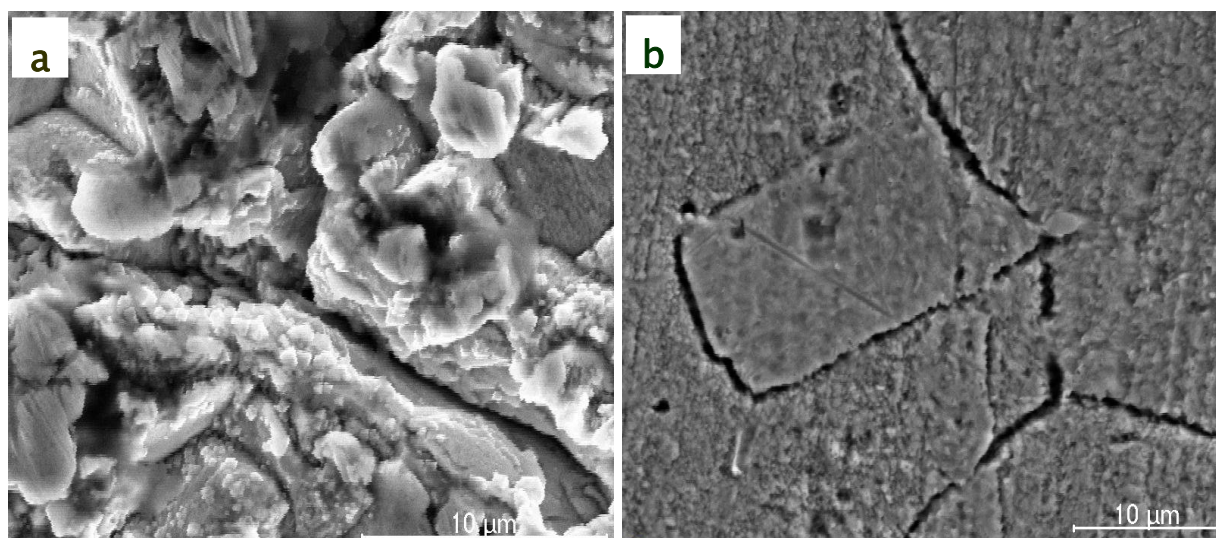
Fig. 4: SEM micrographs of copper potentiostated for 1 h at 0.0 V (Ag/AgCl) under the following conditions:

a) In the presence of 3.5% NaCl+10^{-3} M HS$^-$.

b) In the presence of 3.5% NaCl+10^{-2} M BTAH followed by injection of 10^{-3} M HS$^-$ and further potentiostating for another hour.

Characterization of the corrosion products

The corrosion products were characterized using energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). While EDS can analyze selected regions, it requires a fairly thick layer and provides no indication of oxidation states. On the other hand, XPS can analyze several atom layers and reveal oxidation states. However, the XPS technique samples the entire surface. Both techniques complemented each other towards the objectives of this work.

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EDS results were obtained from regions inside and outside the grain boundaries in Fig.4b. Fig.5 shows EDS spectra of spots shown in Fig.4b on the grain surface (a) and inside the grain boundary (b). A weak sulfur signal appears in the EDS spectrum recorded off the grain boundary while no sulfur signals were detected on the grain surface.
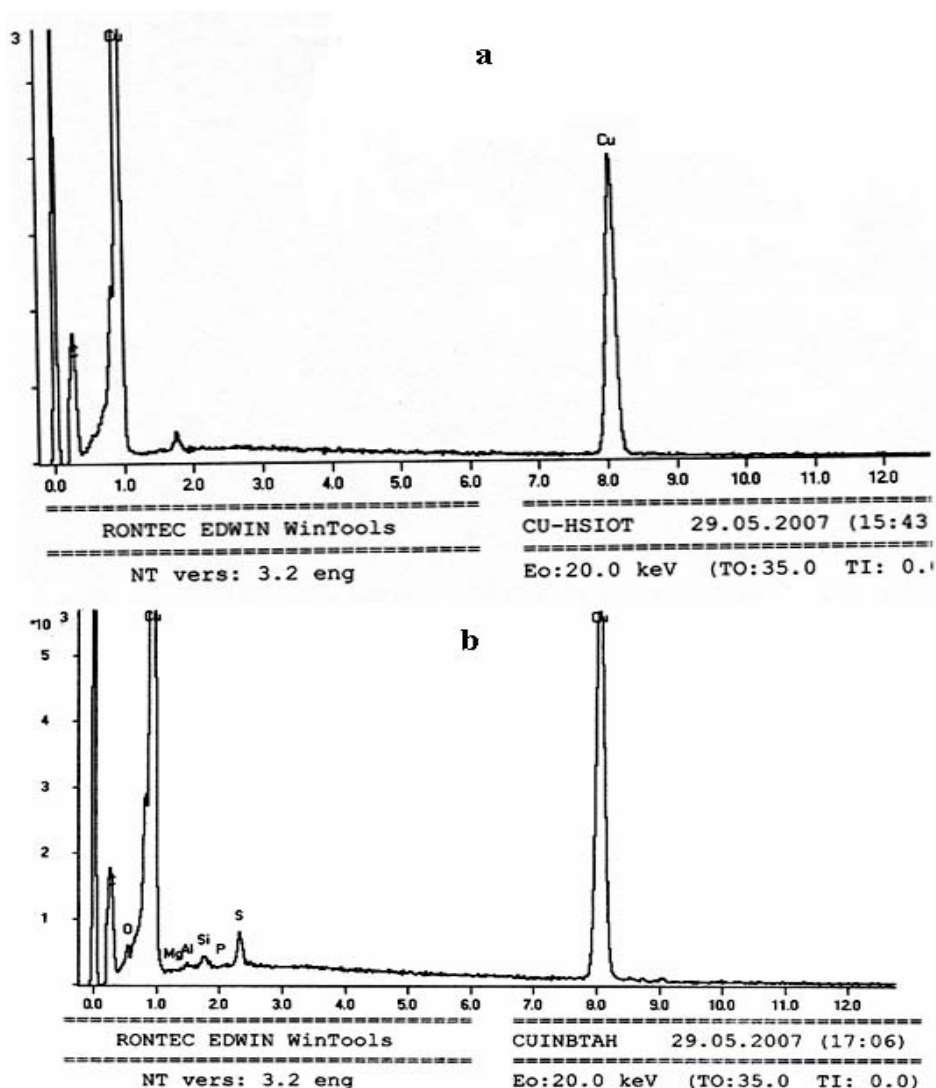

Fig. 5: EDS spectra of regions in Fig.4b. (a) on the grain surface and (b) at the grain boundary.

Fig.6 illustrates parts of the XPS spectra obtained from the copper surface that was imaged in Fig.4b. The spectra show a strong S_{2p} peak at a binding energy of 162.8 eV (referred to C1s at 284.6 eV). This is characteristic for copper sulfide.[4,21]. Fig. 6 shows also an XPS signal of nitrogen at a binding energy of 400.5 eV. It reveals the presence of BTAH on the corroded surface, even after injection of sulfide ions.
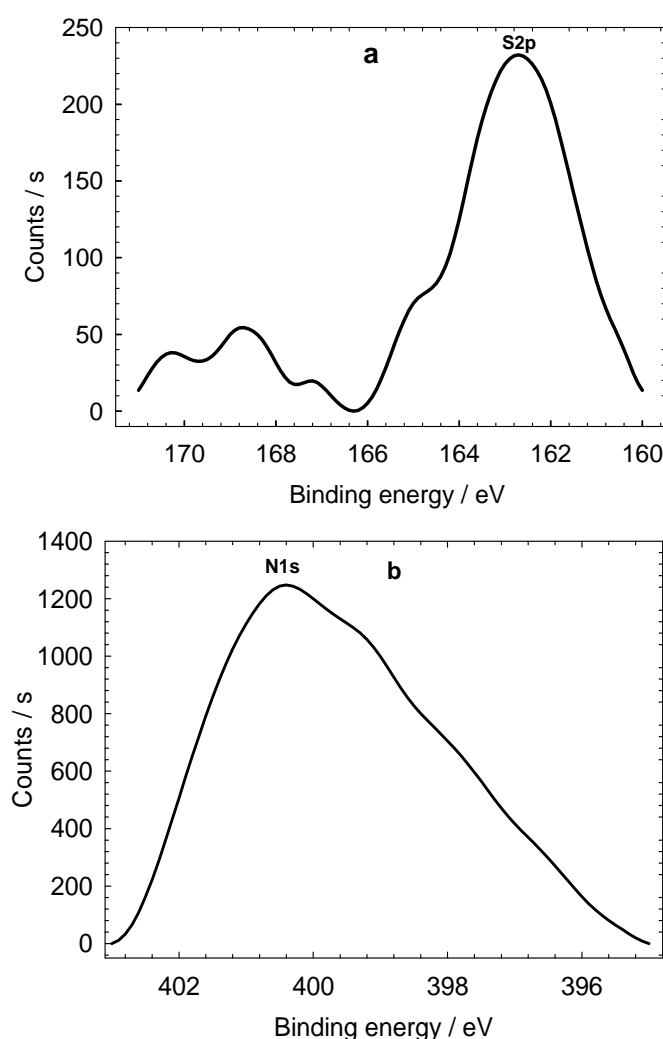

Fig. 6: XPS spectra of copper potentiostated for 2 h at 0.0 V (Ag/AgCl) in 3.5% NaCl+10^{-2} BTAH before the injection of 10^{-3} M HS$^-$ and further potentiostating for an hour.

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Conclusions

The present work provides three well documented conclusions:

1- The intensity of sulfide attack on copper is considerably diminished upon pretreatment of copper in the presence of 10^{-2} M BTAH.

2- Pretreatment of copper in the presence of BTAH provided a much higher protection efficiency on the grain surface and relatively lower efficiency at the grain boundary.

3- After sulfide attack on the pretreated copper; copper sulfide was detected only at the corroded grain boundaries while some BTAH remain on the surface.

Pretreatment in the presence of BTAH leads to the development of a Cu(I)BTA film on the copper surface, according to Eq.4.   The grain boundary region is often less homogeneous and more rich in impurities than the grain surfaces. This is often attributed to segregation of impurities to the grain boundaries.[22-24] The results indicate that the Cu(I)BTA film on the grain surface is much stronger than that which forms at the grain boundaries.   The breakdown of the protective film at the grain boundary is attributed to the strong tendency of copper to form copper sulfide, i.e.
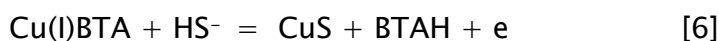
$$Cu(I)BTA + HS^- = CuS + BTAH + e \qquad [6]$$

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Acknowledgements

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