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Effect of sulfide pollution on the stability of the protective film of benzotriazole on copper

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Abstract

Benzotriazole (BTAH) is an excellent inhibitor for the corrosion of copper and many of its alloys in unpolluted media. Protection is attributed to the formation of a film of Cu(I)BTA. Injection of sulfide ions into a benzotriazole inhibited salt water damages the protective Cu(I)BTA film very rapidly, increases the corrosion rate and leads to the formation of copper sulfide. This effect is quite marked at a sulfide concentration as low as 10^{-5} M (about 0.3 ppm sulfur) in the presence of 10^{-2} M BTAH, which is 1000-fold greater than that of the sulfide ion. The intensity of sulfide attack increases with its concentration.

Prolonged pre-passivation of copper in the BTAH protected medium even at high concentration does not markedly improve the resistance of the protective film to sulfide attack. This finding is contrary to a well-documented phenomenon in unpolluted media where the inhibiting efficiency of BTAH increases with the time of immersion and the concentration of the inhibitor. X-ray photoelectron spectroscopy (XPS) reveals the presence of both sulfide and BTAH on the corroded surface indicating that sulfide attack is localized.

1. Introduction

Benzotriazole ($C_6H_5N_3$ BTAH) is widely used as a corrosion inhibitor for copper and its alloys in many industries, for example, chemical mechanical polishing [1–5], desalination [6], petrochemical industries [7], refrigeration [6,8], and in gliding arc plasma in humid air [9]. Many aspects of the process have been studied in efforts to reveal the mechanisms involved and the nature of the interaction between the metal, the inhibitor and/or the environment [10–26]. Two mechanisms have been proposed to explain the high inhibiting efficiency of BTAH. One mechanism attributes it to the formation of a protective film of Cu(I)BTA on the surface, which inhibits the anodic dissolution reaction, that is,

$$Cu_{(aq)}^+ + BTAH_{(aq)} = Cu(I)BTA_{(s)} + H_{(aq)}^+ \qquad (1)$$

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The other mechanism postulates an adsorbed layer of BTAH, that is,

$$Cu_{(s)} + BTAH = Cu : BTAH_{(ads)} \qquad (2)$$
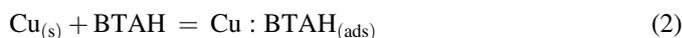
where $Cu:BTAH_{(ads)}$ refers to BTAH adsorbed on the copper surface. Under oxidizing conditions, this adsorbed species can be oxidized to give the complex Cu(I)BTA [16], that is,

$$Cu : BTAH = Cu(I)BTA + H^+ + e^- \qquad (3)$$

Eq. (3) indicates that the complex Cu(I)BTA is favored at more anodic potentials in less acidic media, while the adsorbed species is formed in more acidic media under cathodic potentials. It has also been well substantiated that the inhibiting efficiency increases with the concentration of BTAH and time of immersion of the metal in the inhibited medium.

The above mechanisms are well accepted in clean (unpolluted) media. It is now widely recognized that many of the service environments of copper and its alloys are polluted. For example, formation waters in sour oil and gas wells are heavily contaminated with dissolved sulfides, which are mostly in the form of HS^- ions in nearly neutral media. In

such environments, these metallic components serve in media that are inhibited by BTAH and polluted with sulfide ions. Sulfide ions are known to promote the corrosion of copper [27–37]. The process involves an adsorption step, that is,

$$HS^- + Cu = Cu : HS^- \qquad (4)$$

where Cu:HS$^-$ refers to an adsorbed HS$^-$ ion on the copper surface. This adsorbed species is oxidized to give CuS, that is,

$$Cu : HS^- = CuS + H^+ + 2e^- \qquad (5)$$
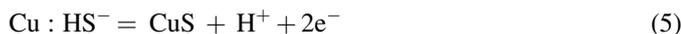
Hence, copper and its alloys face service environments containing corrosion promoting sulfide ions and corrosion protecting benzotriazole. This raises questions regarding the potential interaction of HS$^-$ and BTAH on the copper surface and the ensuing effects on the protection efficiency of BTAH against the corrosion of copper.

The objective of this paper is to study the interaction of benzotriazole and sulfide ions on the surface of copper.

2. Experimental

Electrodes were prepared from Cu (99.9%) obtained from Goodfellow. The electrodes were 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. 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, BTAH from Aldrich, AnalaR Na$_2$S and NaCl from Fluka.

Potentiodynamic polarization curves were measured on the Cu electrodes at a voltage scan rate of 5 mV s^{-1} in 3.5% NaCl solution containing various concentrations of sodium sulfide and BTAH. Potential scanning started from the less to the more anodic potentials. The potential was controlled using a Gamry potentiostat. Polarization resistance (R_p) of the electrodes was measured using electrochemical impedance spectroscopy (EIS) under different conditions of BTAH and sulfide concentrations. EIS experiments were also performed using the Gamry potentiostat. The values of R_p were calculated from the EIS spectra using the Gamry software. Measurements were performed at 25 ± 1 °C while the electrolyte was stirred using a magnetic stirrer. The surfaces of the electrodes were examined using XPS, VG SCIENTIFIC 200 Spectrometer (UK), using Mg Kα radiation (1253.6 eV) operating at 300 W, 13 kV and 23 mA.

3. Results and discussion

3.1. Polarization curves

Fig. 1 shows the effect of the concentration of BTAH on the polarization behavior of copper. The presence of BTAH
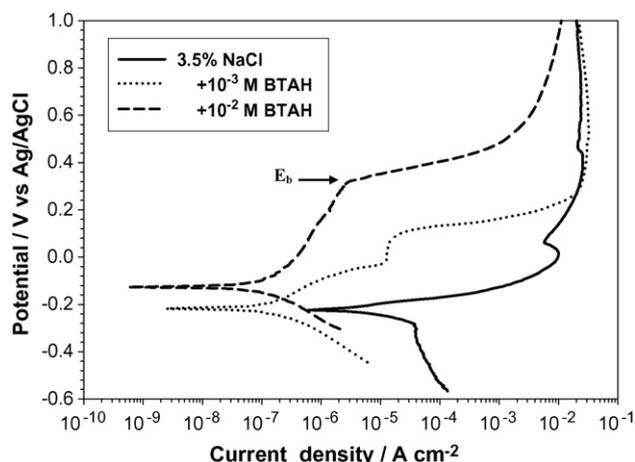
Fig. 1. Polarization curves of copper in 3.5% NaCl solution containing various concentrations of BTAH.

decreases the rate of anodic dissolution by 3–4 orders of magnitudes, depending on its concentration. A passive region appears in the anodic branch which is attributed to the formation of a protective film of the Cu(I)BTA complex (Eqs. (1)–(3)). This passive region ends at the break down potential, E_b, beyond which the current increases rapidly as the potential becomes more anodic. The rapid increase in current above E_b is caused by localized corrosion as a result of the breakdown of the protective film [38]. As the concentration of BTAH increases, the breakdown potential, E_b, becomes more positive and the current in the passive region decreases indicating that the film becomes more protective.

The effect of sulfide ions on the polarization curve of copper in the BTAH inhibited solution is illustrated in Fig. 2. The sulfide ions have strong detrimental effect on the passivity caused by BTAH. The increase in the concentration of HS$^-$ ions has the following effects:

(a) It lowers the breakdown potential, by hundreds of mV depending on its concentration;
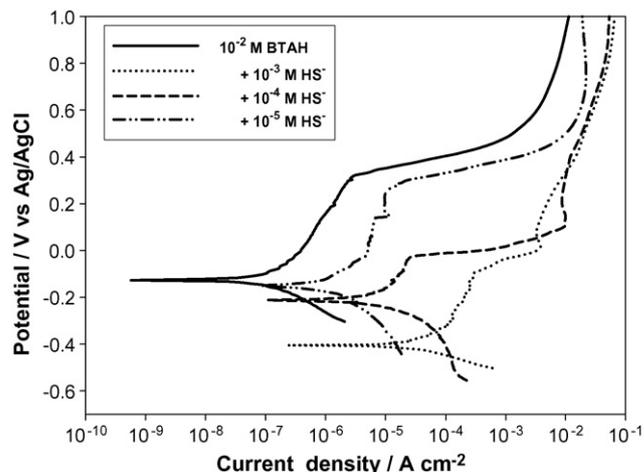
Fig. 2. Effect of the concentration of sulfide ions on the polarization curves of copper in the presence of 3.5% NaCl and 10^{-2} M BTAH.

(b) It increases the current in the passive region and the rate of anodic dissolution by orders of magnitude;

(c) It shifts the free corrosion potential in the cathodic direction by hundreds of mV.

Note that a sulfide ion concentration as low as 10^{-5} M (0.32 ppm sulfur) increases the current on the polarization curve of copper by about 10-fold in the presence of 10^{-2} M BTAH. This concentration of BTAH (10^{-2} M) is 1000-fold greater than that of the sulfide ions. However, it was not able to prevent the sulfide attack.

3.2. Current transients

Potentiostatic current transients were measured on copper electrodes in the presence of various concentrations of BTAH at potentials in the passive region. Fig. 3 illustrates the current transients measured in the presence of 10^{-3} and 10^{-2} M BTAH at a potential of 0.05 V versus Ag/AgCl (within the passive region). Note the initial rapid decrease of current with time before the current tends to level off toward a steady value. After 1 h the currents were 50 and 0.7 μA cm^{-2} for the 10^{-3} and 10^{-2} M BTAH, respectively. An order of magnitude increase in the concentration of BTAH results in about 70-fold decrease in the steady current under the present experimental conditions. This is an illustration of the remarkable efficiency of BTAH against the dissolution of copper within the passive region. Under this potential, corrosion protection is attributed to the formation of Cu(I)BTA complex, see Eqs. (1) and (3). The decrease of current with time is an illustration of progressive increase of the inhibiting efficiency of the Cu(I)BTA film with time of immersion (see also Fig. 8 below). The corresponding currents at the same potential (0.05 V versus Ag/AgCl) in the potentiodynamic polarization curves (Fig. 1) are about 12 and 0.5 μA cm^{-2} for 10^{-3} and 10^{-2} M BTAH, respectively. While the two currents in the presence of 10^{-2} M BTAH are fairly close, the steady state current in the presence of 10^{-3} M BTAH (50 μA cm^{-2}) is about fourfold greater than the current obtained from the potentiodynamic polarization curve

(12 μA cm^{-2}). This might be attributed to the tendency of copper to undergo localized corrosion in the presence of low concentrations of BTAH [38].

Similar experiments were performed to find out whether the pre-immersion of copper in the BTAH inhibited electrolyte would also improve its resistance to sulfide attack. In each experiment a certain concentration of sulfide ions was injected into the electrolyte after various times of contact of copper with BTAH under potentials in the passive region. The copper surface was polarized for 1, 5 and 17 h in the presence of 10^{-2} M BTAH before the injection of 10^{-3} M HS$^-$, Fig. 4a–c, respectively. Note the rapid increase in current upon injection of sulfide ions that appear in all cases, which indicate that the duration of the Cu(I)BTA film growth process does not improve its resistance to sulfide attack. This is contrary to the well-documented finding in unpolluted media where the inhibitor efficiency increases with the immersion time [10,13,37]. The magnitude of this sudden increase in current upon injection of sulfide ions is taken as a measure of the intensity of sulfide attack.
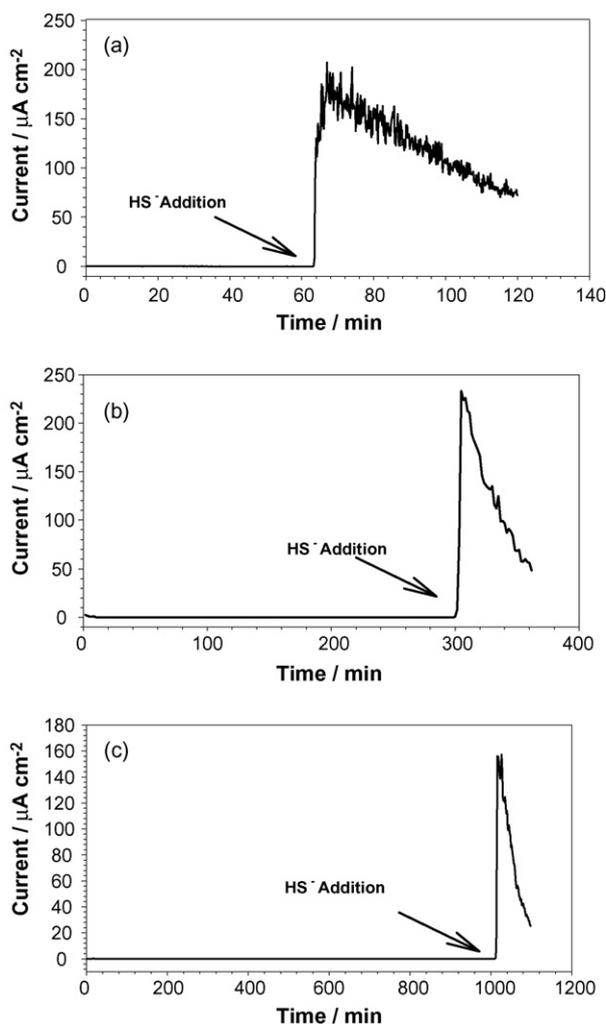
Fig. 4. Current transients of copper electrodes polarized at 0 V vs. Ag/AgCl in a solution of 3.5% NaCl + 10^{-2} M BTAH for various times: (a) 60 min, (b) 300 min and (c) 1020 min before injection of 10^{-3} M sulfide ions.

Fig. 3. Potentiostatic current transients produced by the copper electrode in the presence of (a) 10^{-3} and (b) 10^{-2} M BTAH at 0.05 V (Ag/AgCl) in the passive region.
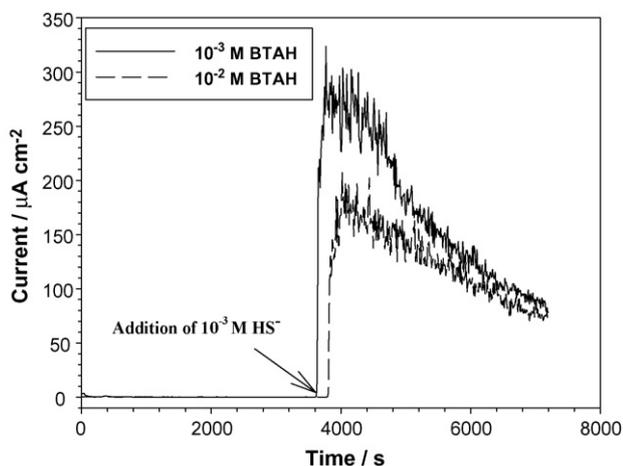
Fig. 5. Effect of the concentration of BTAH on the current transients of copper upon injection of 10^{-3} M HS$^-$ ions into the electrolyte. The electrode was polarized at 0 V vs. Ag/AgCl in an electrolyte of 3.5% NaCl and BTAH.

Fig. 5 displays another set of results to reveal the effect of the concentration of BTAH on the response of current transient to the sulfide attack. One electrolyte was inhibited by 10^{-3} M BTAH while the other was inhibited by 10^{-2} M BTAH. Note the rapid increase in the current upon the addition of sulfide ions in both media. Note also that the increase in the current is more pronounced in the presence of 10^{-3} (about 260 μA cm^{-2}) than in the case of 10^{-2} M BTAH (about 170 μA cm^{-2}). This indicates that an order of magnitude increase in the concentration of BTAH does not prevent sulfide attack but only lowers its intensity rather modestly (by about one third).

The effect of the concentration of the injected sulfide ions on the current transients is shown in Fig. 6 for sulfide concentration of 10^{-3} and 10^{-4} M HS$^-$ in the presence of 10^{-2} M BTAH. Upon the addition of 10^{-4} M HS$^-$ the current increases by only about 20 μA cm^{-2} compared to 270 μA cm^{-2} upon injection of 10^{-3} M HS$^-$.

A question arises here regarding the source of the increase in current after injecting the sulfide ions; that is, whether it is due
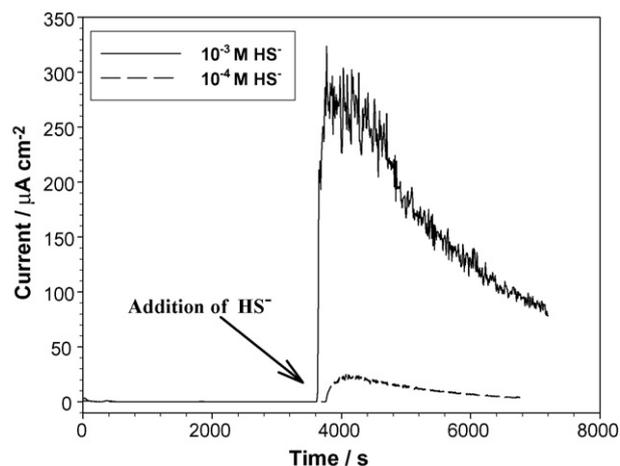
Fig. 6. Effect of the concentration of injected sulfide ions on the current transients of copper polarized at 0 V vs. Ag/AgCl in an electrolyte of 3.5% NaCl and 10^{-2} M BTAH.
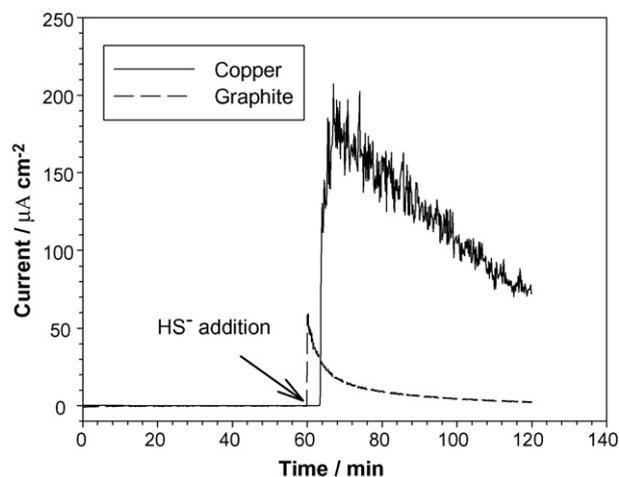
Fig. 7. Effect of sulfide addition on the current transients of copper and graphite electrodes in 3.5% NaCl in the presence of 10^{-2} M BTAH. Each electrode was potentiostated at 0 V vs. Ag/AgCl for 1 h in the inhibited electrolyte before injecting 10^{-3} M sulfide ions.

to the oxidation of sulfide ions or to an increase of the rate of corrosion of Cu. Sulfide ions can be oxidized to give several possible products including elemental sulfur [39], that is,

$$HS^- = S + H^+ + 2e^- \qquad E^\circ = -0.065 \, V(SHE) \qquad (6)$$

$$2HS^- = S_2^{2-} + 2H^+ + 2e^- \qquad E^\circ = 0.298 \, V(SHE) \qquad (7)$$

$$2HS^- + 3H_2O = S_2O_3^{2-} + 8H^+ + 8e$$
$$E^\circ = 0.200 \, V(SHE) \qquad (8)$$
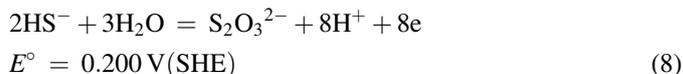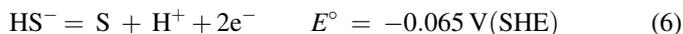
To answer the above question, similar experiments were performed on graphite and copper electrodes under the same conditions. Fig. 7 shows the current transients produced by the copper and the graphite electrodes that were polarized at 0 V versus Ag/AgCl in an electrolyte containing 3.5% NaCl + 10^{-2} M BTAH. Upon injection of 10^{-3} M HS$^-$ ions, the current produced by the copper electrode jumps to a value of about 170 μA cm^{-2} and subsequently decreases with time. However, it remains fairly high after 1 h (about 70 μA cm^{-2}). On the other contrary, the current of the graphite electrode jumps to about 50 μA and decreases rapidly to a negligibly small value. Graphical integration of the charges passed under the curves (for 1 h) yields values of 418.3 and 34.6 mC for the copper and graphite electrodes, respectively. This indicates that the oxidation of the sulfide ions (Eqs. (6)–(8)) contributes only a small fraction of about 8% of the charge passed upon injection of the sulfide ions while the rest of the charge is due to enhanced corrosion of copper (Eq. (5)).

3.3. Polarization resistance

The progressive decrease of current with time (Fig. 3) reveals that the inhibiting efficiency of benzotriazole increases with time. Electrochemical impedance spectra were measured after various times of immersion of copper in the BTAH inhibited medium, before and after injection of the sulfide ions.
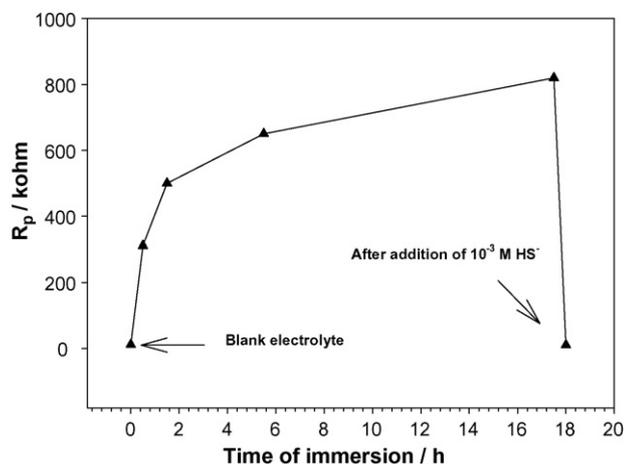
Fig. 8. Effect of immersion time on the polarization resistance (determined using EIS technique) of copper electrode immersed in a solution of 3.5% NaCl + 0.01 M BTAH. Note the sudden decrease of R_p upon injection of 10^{-3} M sulfide ions.

Analysis of these spectra was performed as shown before [39]. The analysis yields the polarization resistance (R_p) which is inversely proportional to the corrosion rate [40], that is,

$$R_p = \frac{K}{i_{corr}} \tag{9}$$

where K is a constant for each system. The variation of R_p with the time of immersion is shown in Fig. 8. Note the gradual increase of R_p with the time of immersion before injection of the sulfide ions, in agreement with results of earlier work [10,13,37]. Note also the remarkable detrimental effect of the sulfide ions in decreasing R_p (and hence increasing the corrosion rate). The effect of sulfide ions is extremely rapid.

3.4. X-ray photoelectron spectroscopy (XPS)

Fig. 9 illustrates parts of the XPS spectrum obtained from the corroded copper surface. The electrode was polarized at 0 V versus Ag/AgCl for 17 h in the presence of 10^{-2} M BTAH before injection of 10^{-3} M HS$^-$, which remained in contact with the copper surface for 1 h. The XPS spectrum reveals the presence of N1s peak at a binding energy of 400 eV and S 2p at 162.0 eV, referred to the peak of C1s at 284.6 eV [41]. The N1s peak reveals the presence of some BTAH on the copper surface that was corroded in the presence of sulfide ions. Furthermore, the S 2p at a binding energy of 162.0 eV reveals the presence of sulfide ions in the form of copper sulfide. The absence of an S 2p at 164.0 eV reveals the absence of elemental sulfur on the corroded copper surface [41]. This is another proof that the increases in current in Figs. 2 and 4–7 are caused by the dissolution of copper under the effect of the sulfide ions (Eq. (5)), rather than the oxidation of the sulfide ions (Eqs. (6)–(9)).

3.5. Mechanism of film breakdown

A rationale for the observed effect of sulfide ions can be found in the relative stabilities of copper sulfide and the
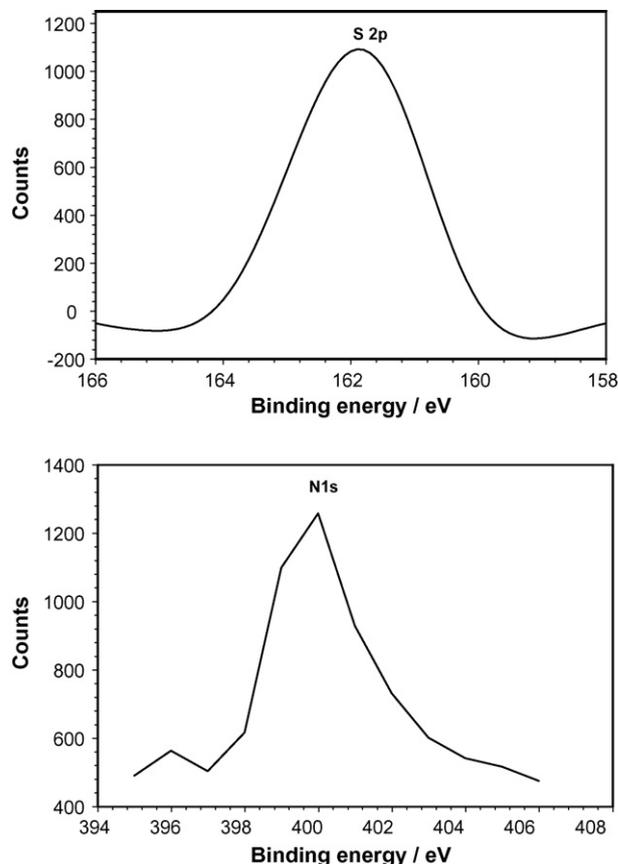
Fig. 9. Parts of the XPS spectra of copper immersed in 3.5% NaCl + 10^{-2} M BTAH solution to which 10^{-3} M HS$^-$ was added after 17 h. The electrode remained in contact with the medium for 1 h after injection of sulfide.

protective Cu(I)BTA complex. While Cu$_2$S has a stability constant [42] of about 10^{47}, the stability constant of Cu(I)BTA complex [43] is about 10^2. This indicates that sulfide ions compete for Cu(I) ions under a much stronger driving force than BTAH [35]. Consequently, sulfide ions can extract the Cu(I) ions from the Cu(I)BTA complex. The first step is the break down of the protective Cu(I)BTA film under the effect of the sulfide ions, that is,

$$Cu(I)BTA + HS^- = CuS + BTAH + e^- \tag{10}$$
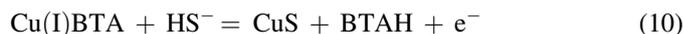
This reaction leads to the disappearance of some of the protective Cu(I)BTA film and the appearance of copper sulfide [27–37]. Once the protective film breaks down, corrosion occurs on the bare surface.

4. Conclusions

Sulfide ions decrease the inhibiting efficiency of benzo-triazole against the corrosion of copper in chloride media. The extent of this effect depends on the relative concentrations of both species (Figs. 5 and 6). The current transients reveal interesting interactions between the injected sulfide ions and the BTAH on copper surface. An order of magnitude increase in the concentration of sulfide ions (at a certain concentration of BTAH) increases the intensity of sulfide attack by more than one order of magnitude (Fig. 6). On the contrary, an order of

magnitude increase in the concentration of BTAH decreases the intensity of sulfide attack by only about one third (Fig. 5). Extended pre-passivation of the copper surface in the presence of BTAH does not improve its resistance to sulfide attack.

Acknowledgement

References

[1] A.T. Al-Hinai, K. Osseo-Asare, Electrochem. Solid St. 6 (2003) 23.
[2] T.H. Tsai, S.-C. Yen, Appl. Surf. Sci. 210 (2003) 190.
[3] S. Hegde, S.V. Babu, Electrochem. Solid St. 6 (2003) 126.
[4] A. Beverina, H. Bernard, J. Palleau, J. Torres, F. Tardif, Electrochem. Solid St. 3 (2000) 156.
[5] Q. Luo, S.V. Babu, D.R. Campbell, Langmuir 12 (1996) 3563.
[6] C.J. Korpics, Mater. Performance 21 (1974) 11.
[7] S.T. Keera, E.A. Eissa, A.R. Taman, Anti-Corros. Method. M. 45 (1998) 252.
[8] T.C. Wen, S.-M. Lin, J. Chin. Inst. Chem. Eng. 22 (1991) 311.
[9] N. Bellakhal, M. Dachraoui, Mater. Chem. Phys. 85 (2004) 366.
[10] F. El Taib Heakal, S. Haruyama, Corros. Sci. 20 (1980) 887.
[11] K. Mansikkamaki, C. Johans, Electrochem. Soc. 153 (1) (2006) B22.
[12] P.G. Cao, J.L. Yao, J.W. Zheng, R.A. Gu, Z.Q. Tian, Langmuir 18 (2002) 100.
[13] M. Metikos-Hukovic, R. Babic, A. Marinovic, J. Electrochem. Soc. 145 (1998) 4045.
[14] H. Yeung, H. Chan, M.J. Weaver, Langmuir 15 (1999) 3348.
[15] W. Polewska, M.R. Vogt, O.M. Magnussen, R.J. Behm, J. Phys. Chem. B 103 (1999) 10440.
[16] R. Youda, H. Nishihara, K. Aramaki, Electrochim. Acta 35 (1990) 1011.
[17] C. Jin-Hua, L. Zhi-Cheng, C. Shu, N. Li-Hua, Y. Shou-Zhuo, Electrochim. Acta 43 (1998) 265.
[18] Z.D. Schultz, M.E. Biggin, J.O. White, A.A. Gewirth, Anal. Chem. 76 (2004) 604.
[19] Z. Xu, S. Lau, P.W. Bohn, Surf. Sci. 296 (1993) 57.
[20] W. Qafsaoui, C. Blanc, N. Pebere, H. Takenouti, A. Srhiri, G. Mankowski, Electrochim. Acta 47 (2002) 4339.
[21] A. Frignani, M. Fonsati, C. Monticelli, G. Brunoro, Corros. Sci. 41 (1999) 1217.
[22] Y. Jiang, J.B. Adams, D. Sun, J. Phys. Chem. 108 (2004) 12851.
[23] F. Zucchi, G. Trabanelli, C. Monticelli, Corros.Sci. 38 (1996) 147.
[24] F. Zucchi, G. Trabanelli, M. Fonsati, Corros. Sci. 38 (1996) 2019.
[25] L. Tommesani, G. Brunoro, A. Frignani, C. Monticelli, M. Dal Colle, Corros. Sci. 37 (1997) 1221.
[26] D.-Q. Zhang, L.-X. Gao, G.-D. Zhou, Corros. Sci. 46 (2004) 3031.
[27] D.D. Macdonald, B.C. Syrett, S.S. Wing, Corrosion 35 (1979) 367.
[28] J.P. Gudas, H.P. Hack, Corrosion 35 (1979) 67.
[29] S.R. de Sanchez, D.J. Schiffrin, Corros. Sci. 22 (1982) 585.
[30] C. Kato, H.W. Pickering, J.E. Castle, J. Electrochem. Soc. 131 (1984) 1225.
[31] J.N. Alhajji, M.R. Reda, J. Electrochem. Soc. 141 (1994) 1432.
[32] J. Smith, Z. Qin, F. King, L. Werme, D.W. Shoesmith, Corrosion 63 (2007) 135.
[33] M. Vazquez, S.R. De Sanchez, J. Appl. Electrochem. 28 (1998) 1383.
[34] K. Rahmouni, M. Keddam, A. Srhiri, H. Takenouti, Corros. Sci. 47 (2005) 3249.
[35] E.A. Ashour, H.S. Hegazy, B.G. Ateya, J. Electrochem. Soc. 147 (2000) 1767.
[36] N.K. Allam, E.A. Ashour, H.S. Hegazy, B.E. El-Anadouli, B.G. Ateya, Corros. Sci. 47 (2005) 2280.
[37] F.M. Al-kharafi, B.G. Ateya, J. Electrochem. Soc. 149 (2002) 206.
[38] A.M. Abdullah, F.M. Al-kharafi, B.G. Ateya, Scripta Mater. 54 (2006) 1673.
[39] B.G. Ateya, F.M. Al-Kharafi, A.S. Al-Azab, Electrochem. Solid St. 6 (2003) C137.
[40] M. Stern, A.L. Geary, J. Electrochem. Soc. 104 (1957) 56.
[41] C.D. Wagner, Practical Surface Analysis, in: D. Briggs, M.P. Seath (Eds.), second ed., Auger and X-Ray Photoelectron Spectroscopy, vol. 1, John Wiley and Sons, New York, 1990, p. 595.
[42] J.A. Dean, Lange's Handbook of Chemistry, forteenth ed., McGraw Hill, Inc., New York, 1992, Section 8, pp. 808.
[43] D. Tromans, G. Li, Electrochem. Solid St. 5 (2002) B5.