Inhibitor effects of Tolytriazole on zinc, cupper and brass surfaces to corrosion effect of environment

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Abstract: Electrochemical properties of zinc, copper and brass were comparatively investigated in 0.1 M NaCl and 0.1 M NaCl containing tolyltriazole (TTA) and benzotriazole (BTA).Electrochemical behavior of brass in these medium resembles to copper. TTA hinders corrosion of brass by adsorption and enhancing ZnO formation on the surface. A mechanism is proposed by the help of solution analysis after constant potential electrolysis and potentiodynamic polarization curves.

Keywords: *Tolyltriazole, Benzotriazole, Corrosion, Inhibition, Brass, Copper, Zinc.*

Introduction

In chloride containing media, the corrosion of ordinary brass takes place by the dissolution of zinc in to the solution. There are two types of corrosion here: Layered type and local corrosion. In the first type of corrosion, the corrosion of the surface takes place all over the surface and is generally observed in brass rich in zinc. In local corrosion there are small local pits and holes formed on the surface, and there is very little corrosion on other parts of the surface. The region of the surface where these pits and holes are formed has a porous structure and is highly weakened. The metal is easily broken from these regions. Surface film consists of ZnO and Cu_2O in 0.1 M NaCl [1-11].

One of the most widely used inhibitors for the protection of copper and brass is benzotriazole (BTA) and its derivatives [12-21]. The workers in literature reached a consensus on the fact that the inhibiting effect of BTA stems from the formation of polymeric Cu (I) –BTA complex upon the surface of the metal [12-21]. The structure of this film was investigated by the use of infrared spectroscopy, electron microscopy and scanning electron microscopy [12-16].

It is thought that the presence of a side group upon the benzene ring would increase the efficiency of the inhibitor. That is why the studies on benzene substituted BTA compounds are getting popular [14, 15, 19, 20, 22].

The purpose of this study is the investigation the inhibition mechanism of tolyltriazole (TTA), a derivative of BTA, on brass in chloride containing media and compares the results with those obtained with BTA.

Material and Methods

The brass electrode was prepared from 1 mm-thick brass sheet with a composition of Cu 70% and Zn 30%; it was cut as a strip and sealed with epoxy resin. The copper and zinc electrodes were prepared from electrolitically pure copper wire and a pure zinc strip in the same manner. The electrodes were mechanically polished with fine grain emery paper under water

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flow, washed with distilled water and acetone and dried prior to the experiments. Open surface areas of brass, copper and zinc electrodes were 0.7, 0.06 and 1 cm^2 respectively

The potential of working electrode was measured against a saturated calomel electrode (SCE) with a Luggin Haber capillary tip. The counter electrode was 1 cm^2 platinum plate and all three electrodes were mounted in to a conventional Pyrex glass cell. All the potentials in the text are quoted against to the saturated calomel electrode. All the Volta metric experiments were carried out with VoltaLab 40 (PGZ301Universal potentiostate) system. Constant potential electrolysis was performed in 0.1 M NaCl solutions containing TTA at different concentrations and potentials. The soluble ionic species were detected with PU 9258 Model Atomic Absorption Flame Spectrometer.

Result and Discussion

Current-potential curves obtained in TTA containing 0.1 M NaCl

Figure 1 shows the anodic and cathodic polarization curves of brass and copper obtained in 0.1M NaCl + $1.2x10^{-4}$ M TTA at a scan rate of 1mV/s. All the curves were taken from negative to positive potential values. Current potential curve of brass is very similar to that of copper obtained in 0.1 M NaCl + $1.2x10^{-4}$M TTA solution. One can see anodic formation and reduction peaks of copper compounds are at about the same potential with copper and brass electrodes and highly apparent on the brass curve.
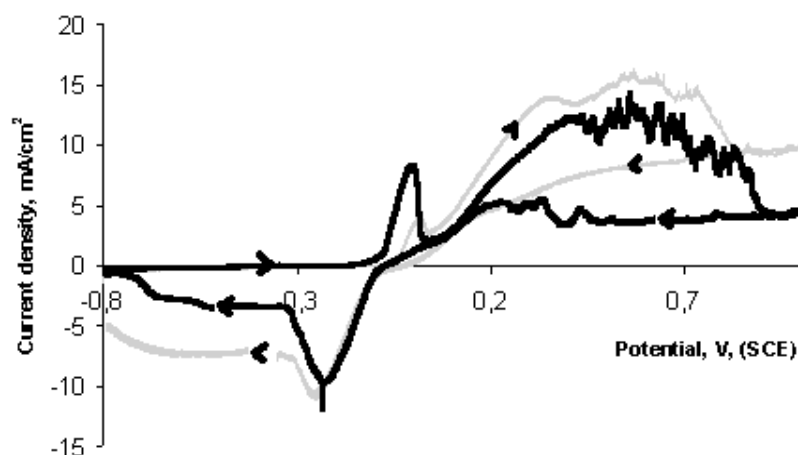

Figure.1 Anodic and then cathodic polarization curve of brass(dark line) and copper (light line)electrodes between -0.8 and +1.0V. Scan rate 1 mV/s

There is no evidence for inhibition. However the inhibiting effect of TTA at this scan rate can only be observed at high TTA concentrations (Figure 2). In 0.1 M NaCl, TTA protects brass surface up to 0.6 V for $1.2x10^{-2}$M and up to 0.8V for $2.7x10^{-2}$M.

Better protection is obtained in $2.7x\ 10^{-2}$M TTA solution .After potential reversal at 1.0 V, anodic current is higher than the forward direction, but it is lower than the curve obtained in 1.2 x 10^{-2}M TTA containing 0.1M NaCl solution.

The amounts of copper and zinc ions diffused in to the solution during constant potential electrolysis between -0.8 V and 1.0 V, in order to see the efficiency of TTA at low and high concentrations and in 0.1 M NaCl were determined with atomic absorption spectroscopy and plotted in Figure 3a and 3b. In Table 1 the values of the chronoamperometrically determined charges in 0.1 M NaCl, 0.1 M NaCl + $2x10^{-4}$M TTA and 0.1 M NaCl + $2.7x10^{-4}$M TTA were tabulated.
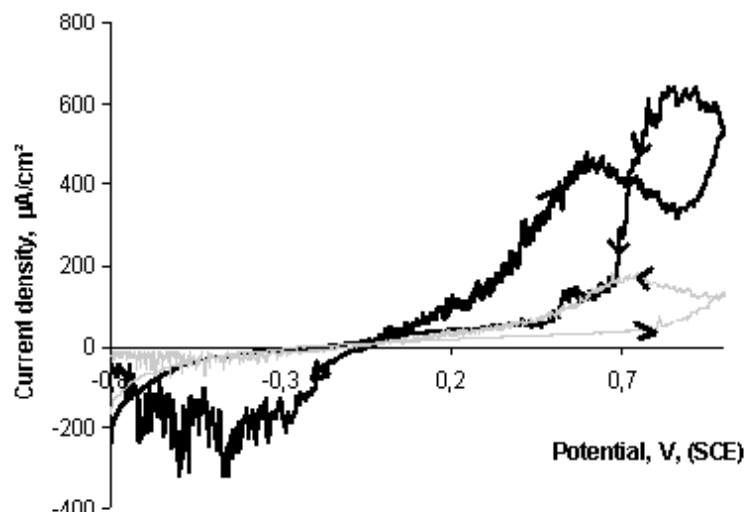
Figure. 2 Anodic and then cathodic polarization curves of brass obtained in 1.2×10^{-2}M TTA (▬▬) and 2.7×10^{-2}M TTA (▬▬) between-0.8 and +1.0V.

The investigation of Figure 3a and 3b show that brass is corroded with the dissolution of zinc and copper ions between -0.6 V and -0 4 V in 0.1 M NaCl in the absence of TTA.
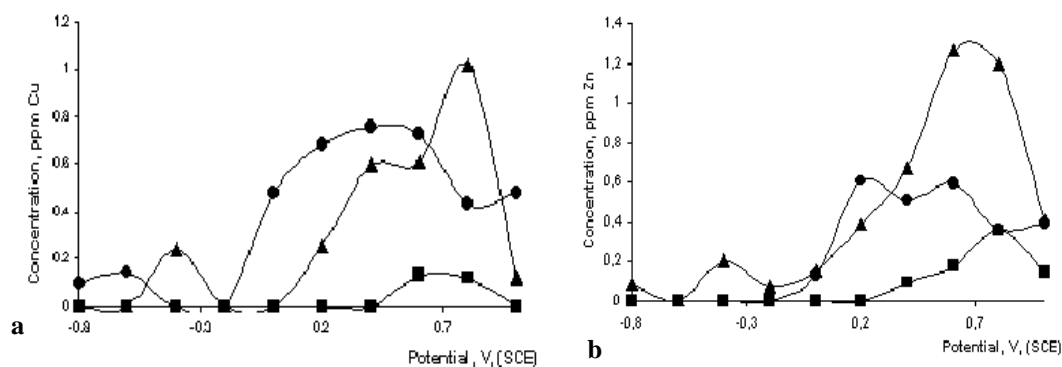

Figure. 3 Copper(a) and zinc (b) ion concentrations after the electrolysis of brass in ▬▲▬ 0,1 M NaCl, ▬●▬0,1 M NaCl + 1,2 x 10^{-4} M TTA , ▬■▬ 0,1 M NaCl + 2,7 x 10^{-2} M TTA solutions for 20 minutes..

Although cathodic charges were measured between -0.8V and 0.0V in 0.1 M NaCl, possible anodic reactions can be occurred by the help of the galvanic effect of the surface zinc atoms at the beginning are:

$$Cu + Cl^- \rightarrow CuCl_{ads} + e \qquad \text{and}$$
$$Cu + 2 Cl^- \rightarrow CuCl_2^- + e$$
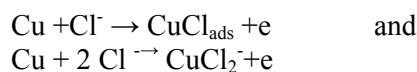
Some of the copper ions can leave but some cannot leave the surface and precipitate upon the surface by giving

$$2 CuCl_2^- + Zn \rightarrow 2 Cu + ZnCl_4^{2-}$$
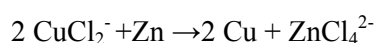
In the region where the negative charge passes the reduction of copper and zinc ions on the electrode not diffused to the solution takes place together with the reduction of oxygen.

The addition of $1.2x\ 10^{-4}$ M TTA to the medium, made the charge passed at -0.2 V maximum. The increase of the cathodic charge with the presence of TTA can be explained by the reduction of soluble or insoluble corrosion products formed upon the surface. That this was actually an insoluble product is apparent by the fact that the amount of zinc and copper ions diffused into the solution was zero with the presence of the TTA. This product is probably a complex structure formed between TTA, zinc and copper. Figure 3a and 3b indicate that this film especially formed upon the zinc atoms on the brass surface. Diffused zinc ion concentration is under the detection limits of AAS between-0.8V and 0.0V, but diffused copper ion concentration is increased in TTA containing 0.1 M NaCl solution from -0.2V to higher potentials.

Figure 4 shows current- potential curves obtained at a scan rate of 500 mV/s in 0.1 M NaCl and 0.1 M NaCl and $1.2x10^{-2}$ M TTA containing solution with zinc electrode. The polarization curves of pure zinc electrode 0.1 M NaCl and 0.1 M NaCl $+1.2x\ 10^{-4}$M TTA indicate that this film can be formed upon the zinc atoms on the brass surface . The addition of TTA shifted the anodic oxidation potential of zinc to positive values and increased the amount of the reducible corrosion products of zinc in the cathodic region at -0.9 V.
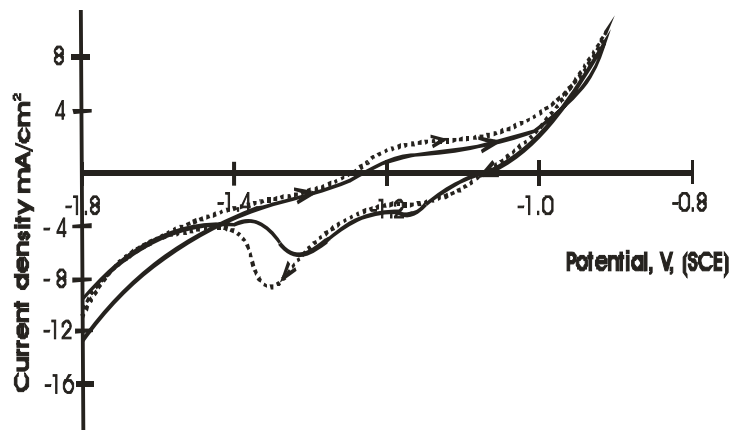

Figure 4. Current –potential curves of zinc electrode obtained in 0.1M NaCl (•••••) and 0.1M NaCl +$1.2x10^{-2}$ M TTA(——) between -1.8V and -0.9V.scan rate 500 mV/s.

The i-t curves obtained $2.7x10^{-2}$M TTA+0.1 M NaCl

In Table 1 the values of the chronoamperometrically determined charges in $2.7x10^{-2}$ M were tabulated against the potential.

The solution analyses and the amount of charge passed in a medium of $2.7x\ 10^{-2}$ M TTA + 0.1 M NaCl reveals that TTA protects the surface quite well up to 0.8 V (Table 1 and Figure 3). Figures 5a-c show the i-t curves of brass obtained   in $2.7x\ 10^{-2}$ M TTA + 0.1 M NaCl. The decreasing trend of the curve in Figure 5a indicates that the surface is in a passive state at -0.2 V. The passage of cathodic current at 0.2 V and 0.4V in Figure 5b is explained by the formation of a film enough to prevent the anodic events to take place. The cathodic charge passed is consumed for the reduction of the surface film (Figure 5b). Figure 5c indicates the formation of a surface covering film with re-dissolution. Currents are thousand times (mA) higher than the currents at 0.4 V and lower then this potential. For $2.7x\ 10^{-2}$M TTA better protection obtained up to 0.4V. At higher potentials decomposition of film structure can be occurred and another less protective layer can be formed.

According to Table 1 the anodic charge passes at these potentials is lower than that of 0.1 M NaCl. Also according to Figure 3a and 3b the film protects the surface up to 1V at this TTA

concentration. However it is not possible to elucidate the structure of the film formed at high TTA concentrations based upon these data.
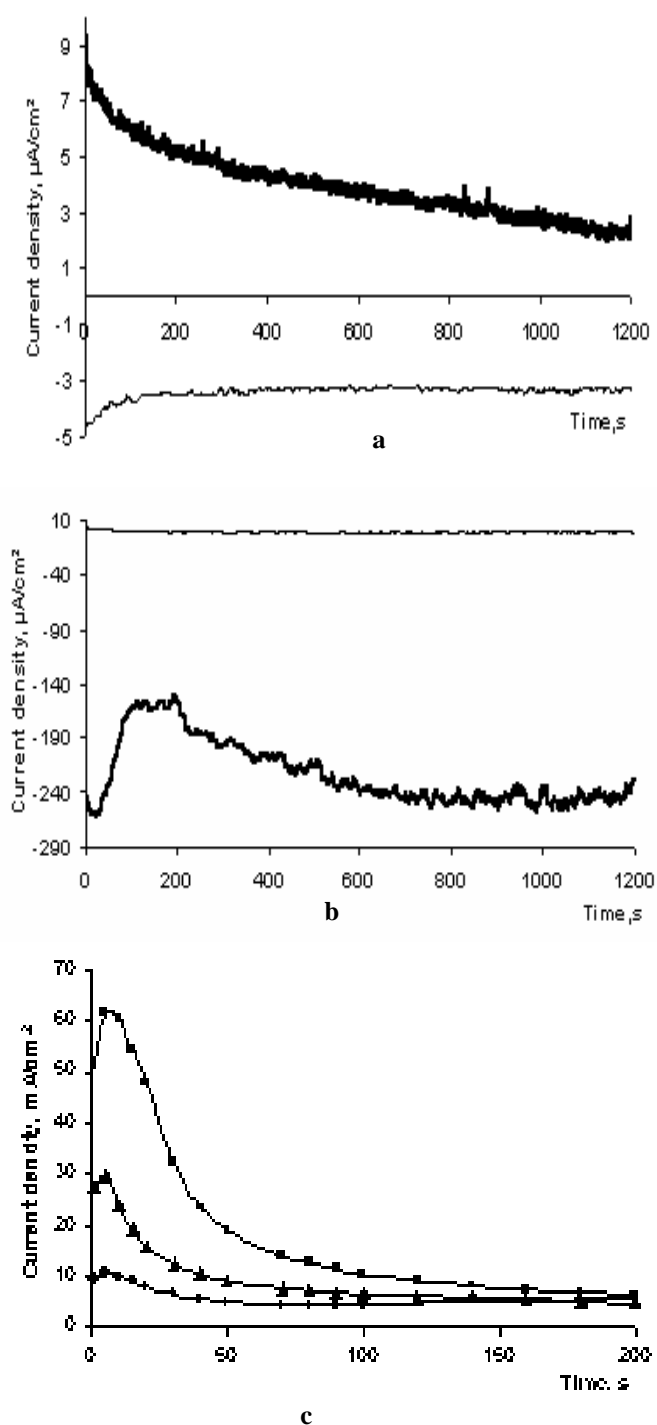

Figure 5 i-t curves obtained in 0.1 M NaCl + 2.7x10^{-2} M TTA with brass electrode
a) at (⎯⎯) -0,2 V and at (⎯⎯) 0,0 V.
b) at (⎯⎯) +0,2 V and (⎯⎯) +0,4 V
c) at ⎯●⎯ +0,6 V,   ⎯■⎯ +0,8 V and ⎯▲⎯ +1,0 V.

Conclusion

TTA can be used as an inhibitor to prevent the corrosion of brass. The addition of small amount of TTA to the medium covers the zinc sites upon the surface and stops the dezincification. This results the diffusion of copper to the solution to be enhanced. At higher TTA concentrations TTA prevents the corrosion by both covering the zinc sites on the surface preventing them to diffuse into the solution and forming an insoluble Cu (I)-TTA complex. The fact that $1.2x\ 10^{-4}$ M TTA is not sufficient can be seen from both current-potential (Figure 1) plots and charge –potential relations (Table 1). At this concentration the formation of CuCl and copper oxide are as distinctive as they are in the solution containing no TTA. At higher the TTA concentrations the film formed upon the surface have better coverage properties. This film resists anodic polarizations up to 1.0V.

The difference between the structures of BTA and TTA is a methyl group. The charge passed with BTA and TTA at different potentials is tabulated in Table 1 in order to compare their respective efficiencies.

Table1. The comparison of the charge passed at different potentials with the use of BTA and TTA.

E,V (SCE)	0.1M NaCl (C/cm^2)	1.2 x10^{-4}M TTA(C/cm^2)	2x10^{-4}M BTA(C/cm^2)	2.7x10^{-2} TTA(C/cm^2)	2.7x10^{-2}M BTA(C/cm^2)
-0.8	-0.103	-0.114	-0.156	-0.035	-0.023
-0.6	-0.108	-0.128	-0.386	-0.0116	-0.000570
-0.4	-0.128	-0.213	-0.403	-0.00784	-0.000267
-0.2	-0.046	-0.484	-0.033	--0.0041	-0.00205
0.0	1.84	2.06	1.79	0.0048	-0.163
0.2	11.43	12.94	10.49	-0.001	0.016
0.4	16.95	16.34	16.94	-0.268	0.0056
0.6	20.6	15.01	12.45	3.1	1.32
0.8	11.98	14.027	11.2	6.66	1.12
1.0	12.26	13.93	12.14	4.04	1.11

The investigation of this table reveals that the potential of highest cathodic charge or the highest amount of reducible compounds on the surface at $2x10^{-4}$ M concentration is -0.2V for TTA and between -0.6V and -0.4 V for BTA. These are the potentials where the amounts of zinc and copper ions diffuse in to the solution are under the detection of AAS. However at higher concentration and potentials TTA is more effective than BTA. One can think that BTA is effective at low potentials, but TTA is effective at high potentials, and obtain better protection with a suitable concentration ratio of BTA and TTA.

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