Effect of bismuth (III) chloride on the dealloying of Cu binary alloys in acid solution: Dezincification

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ABSTRACT

The inhibition effect of 70-30 α brass using inorganic bismuth (III) Chloride (BiCl$_3$) in 0.1 M HCl at 30°C has been assessed by Tafel plots, potentiostatic polarization and scanning electron microscopy (SEM). The addition of very low concentrations of BiCl$_3$ decreased the cathodic current only which indicate that BiCl$_3$ behaves as cathodic inhibitor. The decrease in the corrosion rate beside the high efficiency achievement which reached up to 97.3% was attributed to the deposition of Bi metal at zinc locations on the alloy surface. This deposited film is highly persistence as examined in an acid solution without inhibitor by potentiostatic polarization measurements and consequently its suppress the selective leaching of zinc from the alloy surface. © 2008 Trade Science Inc. - INDIA

KEYWORDS

INTRODUCTION

Electrochemical dealloying is a phenomenon of much interest both scientific reason and because of its industrial importance. Two main theories explain the dealloying of single phase homogeneous binary alloys. One of them proposes the simultaneous dissolution of both constituent metals where after that the more noble metal redeposit from the solution[1-7]. The other proposes the selective dissolution of the less noble metal from the alloy to leave a porous residue rich with the more noble metal[6-15]. The dezincification of 70/30 α-brass is one of the most important phenomenon of the dealloying. It is well known that brass dezincification starts by the selective dissolution of Zn which is fundamental process of the alloy dissolution.

A good deal of work has been carried out on the inhibition of brass 70/30 using specific inhibitor for the dissolution of Cu such as BTA and other derivatives. All the inhibitors cited in the literature has been overlooked the role of Zn in the selective dissolution mechanism. This inhibitor was chosen from the view point that the α-brass behaves as Cu metal in aqueous solution.

On the other hand, several corrosion inhibitors are reported in the literature to inhibit the dissolution of zinc. For example inorganic bismuth (III) compounds were subjected to a study by Armaki et al.[16-19] to evaluate its role in the corrosion inhibition of various metal like Fe, Zn, Ni and Co in different acid solutions. In their work very low concentration of Bi (III) compounds (10^{-7} M to 10^{-4} M) are used to give high inhibition efficiency as a result of the formation of a protective layer of metallic bismuth on the metal surface[20-22].

In the present work the effect of BiCl$_3$ on the se-

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lective dissolution of Zn from 70/30 α-brass is examine using electrochemical and scanning electron microscopy techniques.

EXPERIMENTAL

Cold worked α brass coupons (with the composition Cu-30Zn-0.02Pb-0.02Fe) were cleaned and pretreated following the standard procedures already described[23]. The brass test coupons were in the form of rectangles of side $1 \times 0.5 \times 0.1$ cm. $BiCl_3$ inhibitor and HCl were all of reagent grade and were used as supplied. All measurements are carried out in deaerated 0.1 M HCl solutions with and without the inhibitor at 30^0C. The deaeration was made by bubbling pure nitrogen gas for one hour and then a continuous deaeration was made for all time of the experiment over the surface of the solution to put the cell under nitrogen atmosphere.

The corrosion rate of the test coupons was determined from Tafel plots of the polarization curves. Details on the corrosion rate and inhibitor efficiency (I.E) are cited elsewhere[24]. To estimate the resistance of the protective film formed as a result of the deposition of Bi metal on the brass surface, the current was followed against time at constant potential ± 400 mV in 0.1 M HCl free from $BiCl_3$ inhibitor. The changes occurring on the brass surface after treatment in 0.1 M HCl free from and contaminating 10^{-6} M $BiCl_3$ under free condition were followed by scanning electron microscopy (Jeol. TSM T20 Japan, accelerating voltage 19 KV, magnification X35-X1000).
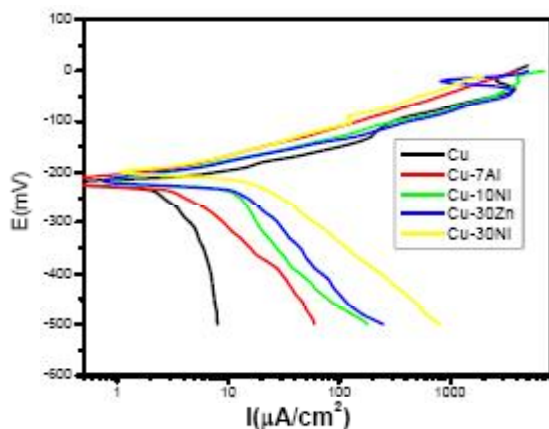

Figure 1: Tafel plots for Cu metal and different copper base alloys in 0.1 M HCl

RESULTS AND DISCUSSION

Relationships between the potential and current density in 0.1M HCl at 25^0C for Cu, brass (Cu/30Zn), (Cu/10Ni), (Cu/30Ni) and Al-Bronz (Cu/7Al) are shown in figure 1. The curves of this figure show that there are a similarity in the anodic branch while the cathodic branch represent two interesting features, first for pure Cu, a minimum cathodic current density was recorded. Second in case of the alloy, as increasing the concentration of the active metal in the alloy the cathodic current density increases. This is due to selective dissolution of the active metal (Zn, Ni or Al). This interpretation is in agree with the previously reported by Heidersbach and Verink[25,26] which show that, in the alloys which are rich in one component like Cu/30Zn or Cu/10Ni. The potential domain between 0.0V and -0.940 V (SHE), the immune region of copper, selective dissolution of Zn from α brass should be prevailing. Furthermore, at potential more positive than 0.00 V (SHE), both copper and zinc in α brass should dissolved simultaneously. Another confirmation was gained recently by Ateya et al[27,28] which shows that for a homogeneous binary alloy (AB), below the critical potential $(E_c) \approx 0.0V$(SHE) selective dissolution of more active component (B) proceeds while above (E_c) the term dealloying was used.

(1) Effect of $BiCl_3$ on the dissolution of copper in 0.1M HCl solution

The corrosion current densities (i.e the corrosion rate) of Cu in 0.1M HCl free from and containing different additions of $BiCl_3$ were determined from the anodic and cathodic Tafel plots. The corrosion currents densities were estimated as the points of intersection of the extrapolated linear segments of the E-logI curves at the free corrosion potential. As the study is of a comparative nature, the corrosion currents are expressed as μAcm^{-2}. It is clear from the curves of figure 2 and TABLE 1 that the cathodic current density and the corrosion rate is

TABLE 1: Cu in 0.1M HCl and different concentrations of $BiCl_3$

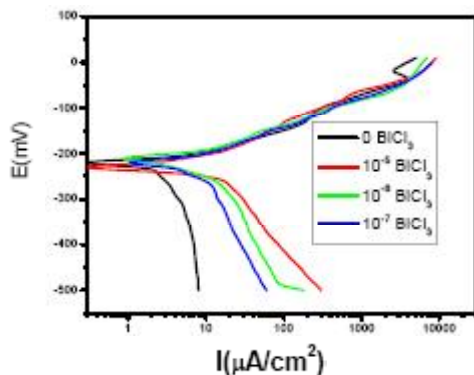| Concentration	$I_{corr.} (\mu A/cm^2)$
0	2.5
10^{-7}	7
10^{-6}	10
10^{-5}	20

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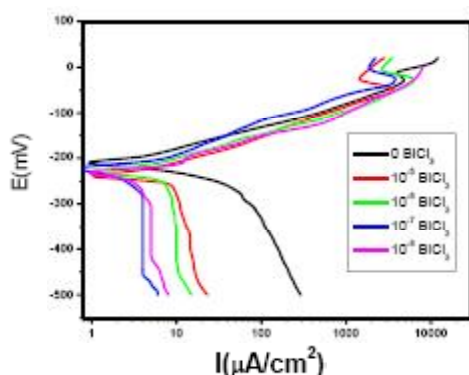**Figure 2 : Tafel plots for Cu metal in 0.1 M HCl and different additives of BiCl₃**

Figure 3 : Tafel plots for brass (Cu-30Zn) in 0.1 M HCl and different additives of BiCl₃

increased with increasing the concentration of $BiCl_3$. This was attributed to the increase in the cathodic reaction where in this case, Cu can not displace H_2 to proceeds the cathodic reaction by the reduction of H_2. So the only cathodic reaction is

$$Bi^{3+} + 3e \rightarrow Bi \tag{1}$$
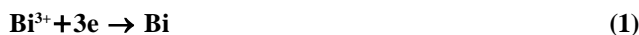
It was found that the corrosion inhibition of a metallic cation depends mainly on the reduction of metal cation to form a deposited layer of metal which covered the corroded surface[29]. This dose not occur for Cu in the presence of $BiCl_3$ where the reaction (1) depends on the equilibrium potential difference between Bi deposition and copper dissolution which can not allow to the deposition of Bi on Cu surface. Therefore, Bi metal can not be deposited to inhibit the dissolution of Cu metal but in contrast it increases the cathodic reaction rate.

(2) Effect of BiCl₃ on the dissolution of brass (Cu/30Zn) in 0.1M HCl solution

The effect of $BiCl_3$ inhibitor on the dissolution of brass in 0.1 M HCl was examined. The concentration

TABLE 2: Brass (Cu/30Zn) in 0.1 M HCl and different concentrations of BiCl₃

Concentration	$I_{corr.}(\mu A/cm^2)$	I.E
0	40	0
10^{-5}	8	80%
10^{-6}	6	85%
10^{-7}	1.1	97.3%
10^{-8}	2.2	94.5%

I.E %=[I°$_{corr}$ - I$_{corr}$/I$_{corr}$] ×100

of the inhibitor studied varied between(10^{-5}M to 10^{-8} M) beside the inhibitor free solutions(curve 0), the results are shown in figure 3. The above diluted concentration makes Bi(III) compound is applicable for industrial uses where its toxicity become negligible[18]. Different Bi(III) compound are used in medicine, for example orally as an antiacid and topically for skin irritation[19,30,31].

As an evidence from the curves of figure 3, $BiCl_3$ effect on the cathodic branch only which retards the dissolution of brass and the cathodic current decreases with the decrease of its concentration. The corrosion potential (E_{corr}) was shifted towards more negative potential with decreasing the concentration of the inhibitor. At the same time the corrosion rate decrease and the inhibition efficiency increase with the additive content as shown in TABLE 2. The inhibition efficiency was above 97% in the presence of a very small concentration of the additive (10^{-7} M $BiCl_3$).

These results can be confirmed from the current time curves of figure 4, where the brass test coupon was immersed in 10^{-1} M HCl containing different additives of the inhibitor (10^{-5}M to 10^{-8}M) for one hour and after that only the solution was changed by 0.1M HCl solution free from the inhibitor to show the persistence of the deposited film. After that the change of current with time was followed at constant potential vs SCE, one time at -400 mV, figure 4a, and the second at +400 mV, figure 4b. Observation of the curve of figure 4a reveals that the curve for zero concentration inhibitor i.e. 0.1 M HCl, the current decreases to its half value within≈10 min. and after that become nearly stable. The decrease the current is due to the selective dissolution of zinc from the alloy surface (dezincification). On the other hand, the stability of the current with time after≈10 min can be interpreted due to the dissolution of zinc from the surface where the colour of the alloy surface because the same metallic copper colour visible by the naked eye. The stability of the current density
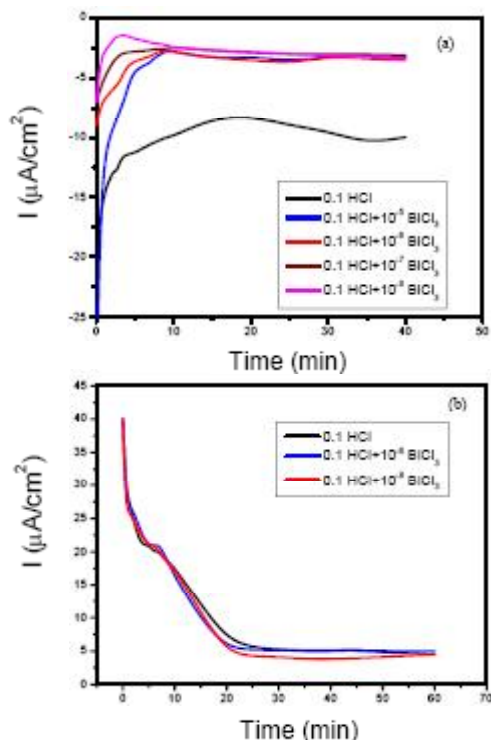
Figure 4 : Potentiostatic current-time curves at constant potential for brass in 0.1 M HCl free from and containing different concentrations of BiCl₃ (a) at -400 mV; (b) at +400 mV

at≈10 μA does not mean that the concentration of zinc on the surface become zero that there are a traces of zinc still dissolved. The only source of this traces of zinc is due to its diffusion from the inner to the outer layer of the surface. This is confirmed from the curves of the inhibitor addition which shows a more decrease in current at the same corresponding time.

On the other hand figure 4a show the effect of addition of different concentration of the inhibitor which have varied between 10^{-5}M up to 10^{-8}M. As is evident from the curves, the same two features at (0) concentration of the inhibitor are recorded but with different manner. First, there is a decrease in the current density at zero time by decreasing the concentration of the inhibitor. Second, there is a decrease in dissolution of zinc by decreasing the inhibitor concentration. This is due to the increase in the persistence of the deposited film of the inhibitor. This is clear from the curves where the time required to reach the stability of current decreases by decreasing the inhibitor concentration. As shown at 10^{-5}M it takes nearly 9 min. while this time decreases to reach less than one minute at 10^{-8} M.

This trend agree with a previous published data[16] which has indicated that at concentrated solution the deposited film become thick and can belled of from the surface to produce a new uncovered area of zinc. These areas takes more time to deposit another film of Bi which is depends on the concentration of BiCl₃ added. Third, after 10 min of immersion for all the concentrations of the inhibitor added, the curves show the same values of current density which is stable and has reached nearly to zero. This can interpreted as a result of the following (1) the surface became dezincified as in case of free solution (0 inhibitor). (2) Some of area on the surface is not covered with Bi metal where, it is dissolved to become dezincified area as in case of (10^{-5} M) inhibitor. (3) Zn on the surface become completely covered with Bi which almost stopped its dissolution as in case of (10^{-7} M, 10^{-8} M inhibitor. This confirms the above result of figure 3 and TABLE 2 which represent that the deposition of Bi decrease the corrosion rate and increase the I.E to amount≈97.3% at 10^{-7} M BiCl₃.

On the other hand the same experiment was studied also at +400 mV vs SCE as in figure 4b. At this potential the dissolution of the brass occurs with simultaneous dissolution[27,28]. The result of figure 4b show that at all the concentrations studied from 0 up to 10^{-8}M there is no change in the current-time curves which show that the current decrease with time from the moment of the run and there are two peaks formed within the first 10 minutes which are due to the oxidation of Cu/Cu^+ and Cu^+/Cu^{++}[33-37] systems and after that within 20 minutes a passive current recorded.

The above results can further be confirmed using SEM technique. Surface examination of the brass specimens after equilibrated for one hour in deareated solution of 0.1 M HCl free from and containing different additions of BiCl3 are shown in figure 5. Figure 5a shows scanning electron micrographs of the surface of sample immersed in deareated solution of 0.1 M HCl for one hour. The surface shows that the attack spread over nearly all the sample with different degrees which concentrated on the depression regions and the other on a spot, this depends on the behaviour of the alloy dissolution. Previous data[23] studied by the same author indicated that at the same condition, leaching of Zn from brass surface was occur to produce a dezincfied surface. This was attributed to the acid medium is nonoxidizing,
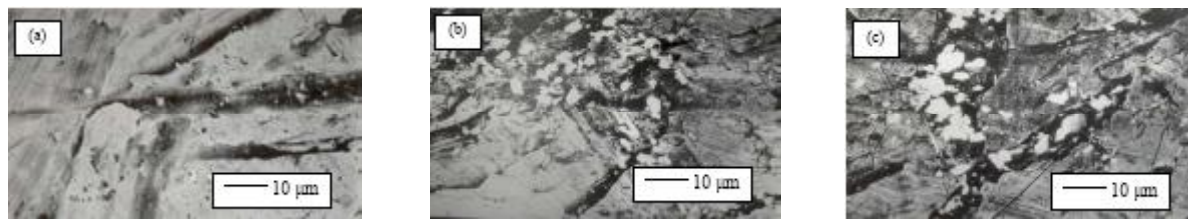
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Figure 5 : Scanning electron micrographs showing the surface of brass in solution of : (a) 0.1 M HCl ; (b) 0.1 M HCl containing 10^{-7} M BiCl$_3$ which represent the major part of the surface; (c) 0.1 M HCl containing 10^{-7} M BiCl$_3$ which represent the minor part of the surface

their aggression towards Zn[32] should be more sever than toward Cu. This confirms that most of the attacked areas are due to the dezincification of the brass surface.

On the other hand, examination of the alloy surface after treated in the test deareated solution of 0.1 M HCl containing different concentrations of BiCl$_3$(10^{-5} M to 10^{-8}M) for one hour was also studied. Observation of this surface shows that there is no any definite variation with all the concentrations studied. Figure 5 (b,c) show scanning electron micrographs of the surface of samples immersed in deareated solution of 0.1 M HCl in presence of 10^{-7} M BiCl$_3$ which was shown as an example for all the treated concentrations where figure 5b represent the major part of the surface while figure 5c indicate definite area of minor part on the surface. It can be seen from figure 5b which represent the major part of the surface, that there are different features. First, the deposition of Bi on the surface is observed. This confirms previous accepted results[17] which represent the deposition of Bi on the surface of Zn metal. Second, the concentration of Bi metal deposited on the surface occurs with a non homogeneous distribution. This occurs as a result of the change in concentration of Zn on the alloy surface. This change is produced during cleaning the surface using Sic paper after treatment[23]. Further in sight into the above two features could be gained form figure 5c which shows the deposition of Bi was concentrated at the down area (depressions) on the surface which are formed during the mechanical cleaning of the surface using SiC paper where the mechanical polishing can remove Zn from some regions to leave it at cavities and depression on the surface.

It is well known that the corrosion inhibition using metallic cations can be performed by reduction of the cation to form a deposited metal layer on the corroding metal surface[29]. The reduction of the cation depends on the equilibrium potential difference between the metal deposition and the dissolution of the metal substrate. Previously[16-19], inorganic bismuth (III) compounds have been used as corrosion inhibitor for various metals such as Fe, Zn, Ni and Co in different acid solutions.

In the present study to confirm the above results we must represent the standard equilibrium potentials of the two half cells of zinc in the test medium at 25^{0}C where, BiCl$_3$ affect as cathodic inhibitor to prevent the selective dissolution of Zn while Cu is not dissolved at this negative potential. This occur as a result of the deposition of Bi on Zn and not on Cu depending on the standard equilibrium potentials, where

Zn = Zn^{2+}+ 2e   E$_1$= -0.76V   vs SHE   (2)
Bi^{3+}+3e=Bi   E$_2$=-0.317V   vs SHE   (1)
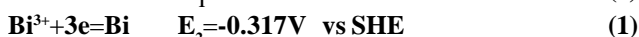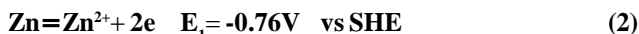
It is clear that E$_2$ is less negative than E$_1$ so that in the solution the following reaction will occur

3Zn+ 2Bi^{3+} = 2Bi+3Zn^{2+} (3)

Bi^{3+} adsorbed on the cathodic regions which was reduced to metallic Bi on the surface at the Zn location of the alloy surface. This confirmed previously by using SEM technique, where the test solution is 0.1 N HCl

Zn=Zn^{2+}+2e   (4)
2H$^+$+2e=H$_2$ (5)
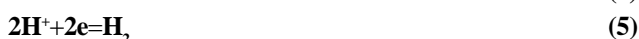
However, Bi had a high over potential for H$_2$ evolution. So that the deposition of Bi metal at Zn location on the alloy surface hindered H$^+$ from the solution to reach to Zn which eliminate the cathodic process of represented by equation (5). The rate controlling step[38] was

H$^+$+e=H$_{ads}$ (6)

H$_{ads}$ represents H$_{atoms}$ adsorbing on the Zn location at the alloy surface. Therefore, BiCl$_3$ inhibited the selective dissolution of Zn from brass 70/30Zn in HCl solution by controlling the cathodic reaction rate.

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CONCLUSIONS

1. The selective dissolution of zinc from α-brass is the fundamental process of the alloy dissolution where in 0.1 M HCl (inhibitor free) depletion of zinc from brass surface, leading to dezincification.

2. $BiCl_3$ was an effective inhibitor of cathodic reaction associated to brass corrosion in 0.1 M HCl solution.

3. The high inhibition efficiency was attributed to the deposition of a protective film of Bi metal on the brass surface at zinc locations which raised the hydrogen overpotential.

4. The loss of the inhibition of $BiCl_3$ in 0.1 M HCl under anodic polarization (+400 mV SCE) was due to the dissolution of both zinc and copper of the alloy along the anodic branch while as mentioned above during the cathodic branch zinc was only dissolved and the deposition of Bi occurs at Zn locations which control the dissolution of the alloy as a whole.

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