Corrosion inhibition of Al–bronze in acidified 4% NaCl solution

A. A. EL-WARRAKY, H. A. EL-DAHAN
Department of Electrochemistry and Corrosion, National Research Centre, Dokki, Cairo, Egypt

The synergistic effect between either benzotriazole (BTA) or thiourea (TU) and iodide ion are used to retard the dissolution of Al–bronze alloy in deaerated solution of acidified 4% NaCl of pH 1.8–2 at 60 °C; this is shown by the weight loss and polarization techniques. Iodide ion alone has no effect on the dissolution of the alloy but addition of 100 p.p.m. KI to 300 p.p.m. of both BTA and TU improved the inhibition efficiency to 92% and 78.8%, respectively, and also decreased the anodic current density in both media.

1. Introduction
Copper-based alloys have long enjoyed commercial popularity as condenser and heat exchanger materials. Among them, the Al–bronzes exhibit excellent mechanical and chemical properties [1–9].

The corrosion of copper-based alloys and their inhibition by organic inhibitors in acid solution have been studied by several authors [10–15]. Acid solutions are widely used in industry, the most important fields of application being acid pickling, industrial cleaning, acid descaling and oil-well acidizing.

Corrosion inhibition by benzotriazole (BTA) has been extensively studied, especially because of its high efficiency in the corrosion protection of copper and copper alloys exposed to a variety of attacking media [16–21]. It is generally assumed that BTA forms a polymeric cuprous complex on the metal surface which prevents further copper dissolution.

The effect of dibutyl thiourea (DBTU) on the corrosion of the copper–nickel alloy in acidified seawater was examined at 60 °C [22]. The results indicate that the compound (DBTU) is decomposed at the brass surface.

Potassium iodide (KI) improves the efficiency of some inhibitors against iron corrosion [23–25]. A recent study [26] shows that a synergistic effect exists between BTA and iodide ions in the case of corrosion of copper in sulphuric acid.

In the present study two different acid inhibitors BTA and TU are evaluated towards corrosion inhibition of Al–bronze in acidified 4% NaCl of pH ≈ 1.8–2.0. Addition of KI to both inhibitors are essentially studied to show the nature of the chemisorbed layer on the alloy surface.

2. Experimental procedure
2.1. Chemicals and materials
The inhibitors, acid NaCl were reagent grade and were used as supplied. Solutions were prepared using doubly distilled water.

Each experiment was performed using deaerated solution of 4% NaCl in the presence of 10⁻² M HCl of pH 1.8–2, stirred by a magnetic stirrer.

The source of the aluminium bronze alloy is the same as that of Ateya [9], with the following composition: 7 Al, 0.04 Fe, 0.01 Ni, 0.04 Si, 0.0006% Mg, and the remainder is Cu.

2.2. Weight-loss test
The corrosion rate (CR) of Al–bronze was determined by the weight loss method as mg cm⁻² h⁻¹. The Al–bronze test coupons were in the form of rectangles of sides 1.4 x 0.1 cm thick. The procedure followed was similar to that reported previously [27].

The corrosion rates of the test coupons immersed in deaerated solution of acidified 4% NaCl of pH 1.8–2 were determined over several temperature settings of 25, 30, 40, 50 and 60 °C.

The effect of both BTA and TU inhibitors on the dissolution kinetics was measured at 60 °C in absence and presence of different concentrations of KI additives.

2.3. Electrochemical measurements
The polarization measurements were recorded using a Wenking potentiotstat (model POS 73). Briefly, tests were conducted on the test electrodes with sides 1.2 x 1 x 0.1 cm thick after cleaning. The anodic polarization scans were conducted in deaerated solutions of acidified 4% NaCl at 60 ± 2 °C using a Pt counter electrode and an external saturated calomel reference electrode (SCE) interfaced to the test solution via a salt bridge assembly and luggin capillary. The test solution was continuously stirred, and before use the Al–bronze electrodes were pretreated as in the case of weight loss measurements. Prior to commencing the polarization measurements the samples were kept at −600 mV versus SCE for 30 min in the test
environment, to reduce the oxides (mainly copper oxide) on the sample surfaces before carrying out the measurement [26]. After that the inhibitor was injected into the electrolyte and the potential was then scanned from $-600$ to $+600$ mV versus SCE at a scan rate of $10$ mV min$^{-1}$.

3. Results and discussion

3.1. Weight-loss results

The curves of Fig. 1 represent the variation of the weight loss with time of Al–bronze immersed in deaerated solutions of acidified 4% NaCl of pH 1.8–2 at temperatures varying between 25 and 60 °C. The curves show two rates of dissolution, which have been reported previously [27] in the case of brass in the same medium; a linear relation started at a limited value of copper concentration of the corrodent due to the autocatalytic effect on the formation and dissolution of cuprous chloride (CuCl).

The effect of BTA and TU on the dissolution of Al–bronze in the test solution was examined at 60 °C, which is the temperature commonly adopted during the acid cleaning of the distillers. The measurements were carried out in the usual manner in which the test coupons were exposed to test solution containing a definite inhibitor concentration. At increasing time intervals the specimens were withdrawn, washed, dried, weighed and reintroduced into the same solution for subsequent evaluation.

Fig. 2 shows the effect of increasing BTA concentration on the dissolution of Al–bronze in acidified 4% NaCl solution. The curve for 0 p.p.m. represents the inhibitor-free solution. Observation of the curves of this figure reveals that BTA causes slight inhibition effect between 100 and 600 p.p.m. By increasing the concentration of the inhibitor to above 800 p.p.m. retards the dissolution of alloy till 20 h and after that the dissolution is almost completely stopped due to the formation of a more protective film of BTA, which prevents the adsorption of anions. On the other hand, the corrosion rate (CR) which was calculated during the linear relation is very low, and the inhibition efficiency amounts to above 99.5% (Table I).

The effect of TU additives on the dissolution of Al–bronze in the test solution was also examined at 60 °C. The concentration of the inhibitor added varied between 100 and 300 p.p.m. (Fig. 3). As is evident from the curves, TU extended the first dissolution period of Al–bronze (to about 50 h at 300 p.p.m.) but increased the CR with respect to the TU-free solution (Table I). This behaviour has been reported previously for dibutylthiourea [22] and can be attributed to its decomposition at 60 °C on the electrode surface (70 Cu/30 Ni alloy) and the products of decomposition are either inactive or weaker inhibitors than the mother substance.

3.2. Electrochemical measurements

The anodic polarization behaviour of Al–bronze in the test solutions containing different additives of BTA is shown in Fig. 4. In all cases except the inhibitor free curve (●), the initial active region is followed by passivation behavior and two anodic current peaks are observed, I and II. The two peaks in each curve are followed at higher potentials by a slight decrease in the current density. Several studies [28–31] suggest that peak I is associated with oxidation of copper to Cu$^+$ and peak II is associated with oxidation of Cu$^+$ to Cu$^{2+}$ state.

Solutions containing increasing amounts of BTA shift the positions of the active peaks I and II to more negative values and decrease the time of its formation.

Figure 1 Weight loss–time curves of Al–bronze in acidified 4% NaCl solution of pH 1.8–2.0 at different temperatures. (●) 60 °C; (○) 50 °C; (■) 40 °C; (□) 30 °C; (×) 25 °C.