ORIGINAL PAPER

F.H. Assaf

Anodic polarization of Al-Sn alloy in H₃PO₄ solutions

Abstract The anodic polarization behaviour of Al-Sn alloy (5.6% Sn) was studied in aerated 1, 1.5 and 2 M H_3PO_4 acid solutions using potentiodynamic and potentiostatic techniques. Anodic behaviour of Al and Sn metals was investigated for comparison. The results show that the alloy exhibits active-passive transition behaviour. The passivation of the examined alloy is due to the formation of oxide film for both Al and Sn incorporated with their phosphates. In general, at constant concentration of PO_4^{3-} ion, the passive current density (I_{pass}) is decreased with increase of pH in the range 2.5–5. Further, the influence of Cl^- ions on the passivity of the given alloy was studied. It was found that the aggressive effect of Cl^- ions on the passive film is inhibited with increase in phosphate concentration and pH. However, the addition of organic compounds (2- and 3-picoline and 2-aminopyridine) shows that only 2-aminopyridine inhibited the attack of Cl^- ions.

Key words Anodic polarization · Aluminium-tin alloy · Passivation · Chloride · Phosphoric acid

Introduction

Aluminium is one of the elements which has a high capacity to form alloys with other elements. Tin is one of the elements which are added to increase the fluidity of casting alloys [1]. Aluminium-tin alloy bearings are extensively used for automobiles to give high speed and load service [2]. A considerable amount of data on the corrosion and electrochemical behaviour of aluminium and its binary and tertiary alloys with e.g. Fe, Cu, Mn, Mg, Zn, and Li in different media, using various techniques, have been reported in the literature [3–10].

However, few investigations into the electrochemical behaviour and corrosion of Al-Sn alloy have been carried out. The passivity of high-resistance Cu-Al 10-Sn 5 alloy was studied by Virtanen et al. [11]. They found that the pH dependence of the passivation of the photocurrent behaviour of the alloy clearly indicates that the passivity of this alloy in neutral solutions is due to the formation of passive film enriched with aluminium oxide.

Recently, Kliškic et al. [12] studied the effect of tin content on the electrochemical behaviour of Al-Sn alloys in NaCl solution. They found that at high Sn content ($>0.2\%$) the cathodic behaviour of pure Al is affected. Cyclic voltammetric studies showed that at all pH values (except pH 1) the presence of tin affects the anodic process as well as the corrosion potential. They concluded that the presence of tin tends to stabilize the oxide film and that the stability is increased with increase of the tin content in the alloy.

Because of the wide application of aluminium alloys for technological purposes, the present study deals with the anodic polarization behaviour of Al-Sn alloy in H_3PO_4 solutions. In addition, the aggressiveness of Cl^- ions was investigated. In view of this aggressive behaviour, 10^{-2} M solutions of several organic compounds in 1 M H_3PO_4 (pH 2.5) were added to inhibit this effect of Cl^- ions.

Experimental

Aluminium-tin alloy was prepared by alloying (99.99%) tin and (99.99%) aluminium. The alloying elements were added per weight of both Al and Sn. The mixture was melted at 700 °C in a grey iron mould provided with openings to make rods of the desired diameter, and this was followed by air cooling. The alloying process was conducted at the Aluminium Company of Egypt. The composition of the alloy was determined using an Atomic Absorption Spectrophotometer 850. The tin content was found to be 5.6%.

Working electrodes 5 mm in diameter were mounted in Teflon so that only the flat surface was in contact with the solution. Before every run the electrode was polished with different grades of emery

F.H. Assaf (✉)
South Valley University, Faculty of Science,
Chemistry Department, Qena, Egypt

paper, degreased in ethanol and cleaned with distilled water. Electrolytes were made from Analar grade chemicals. The pH of the solutions was adjusted by adding NaOH pellets and measured using a Fisher Scientific pH meter, Model 800.

The electrolytic cell was made from Pyrex glass with openings for fitting a platinum sheet counter-electrode and a saturated calomel electrode (SCE) as a reference electrode in separate compartments. The end of the reference electrode compartment was elongated in the form of a Haber-Luggin capillary. To minimize the IR drop, the tip of the Luggin capillary was kept at 0.1 mm close to the surface of the working electrode (at a distance of 0.1 mm). All electrode potential values were measured with respect to SCE.

Potentiodynamic and potentiostatic techniques were performed using a computerized EG&G potentiostat/Galvanostat, model 273A. In the potentiodynamic experiments, the potential of the working electrode was varied automatically by software (Model 352). The sweep rate was 5 mV/s. Representative results were recorded at different sweep rates ranging from 0.5 to 5 mV/s. Potentiostatic current-time transients were produced by imposing a constant potential on the Al-Sn alloy at +500 mV (passive region). The variation of current as a function of time was recorded automatically. The measurements were conducted in aerated solutions at 25 ± 0.5 °C. Most of the experiments were carried out twice and the reproducibility was found to be satisfactory.

Results and discussion

Comparative behaviour of Al, Sn and Al-Sn alloy

Figure 1 shows the potentiodynamic anodic polarization curves for Al, Sn and their alloy in aerated 1 M H_3PO_4 solution at pH 4. Although pure Al did not exhibit ac-

tive-passive transition, a steady anodic current of $\sim$75 $\mu A/cm^2$ is exhibited by the metal over a wide potential range (up to +1600 mV) . This may indicate the formation of a porous Al_2O_3-containing aluminium phosphate film just on dipping Al metal in H_3PO_4 solution (pH 4). It can be seen from these curves that Sn and Al-Sn alloy exhibited active-passive transition. The anodic peak at $\sim$−450 mV is related to the formation of SnO_2. The thermodynamic potential of the system SnO/SnO_2 (−336 mV) is more positive than the experimental value at the given pH value. The fact that the shift is negative compared to thermodynamic value may be ascribed to an overpotential associated with oxide (hydroxide) formation or pH change in the vicinity of the electrode surface. It is probable that, in this solution, this passivity is due to the formation of an SnO_2 film incorporated with tin phosphate [13]. These results indicated that passivation of the alloy is associated with the formation of oxide film of both Al and Sn incorporated with their phosphates. The steady anodic current I_{pass} of the Al-Sn alloy $\sim$61 $\mu A/cm^2$, is less than I_{pass} of pure Al metal, indicating that Sn enhances the stability of the oxide film formed on the alloy surface [12]. Faiza et al. [5] studied the passivation of Al and Al-Si alloys in aerated H_3PO_4 solution. They found that the electrochemical behaviour of Al-Si alloy was very similar to that of pure Al. They also concluded that the oxide film formed on Al consists of two layers. Similar results were obtained for Cu-Al 10-Sn 5 alloy in neutral solution [11]. These studies

Fig. 1 Potentiodynamic anodic polarization curves in 1 M H_3PO_4, pH 4 at scan rate 5 mV/s of (○): Al; (△): Sn; (●): Al-Sn alloy
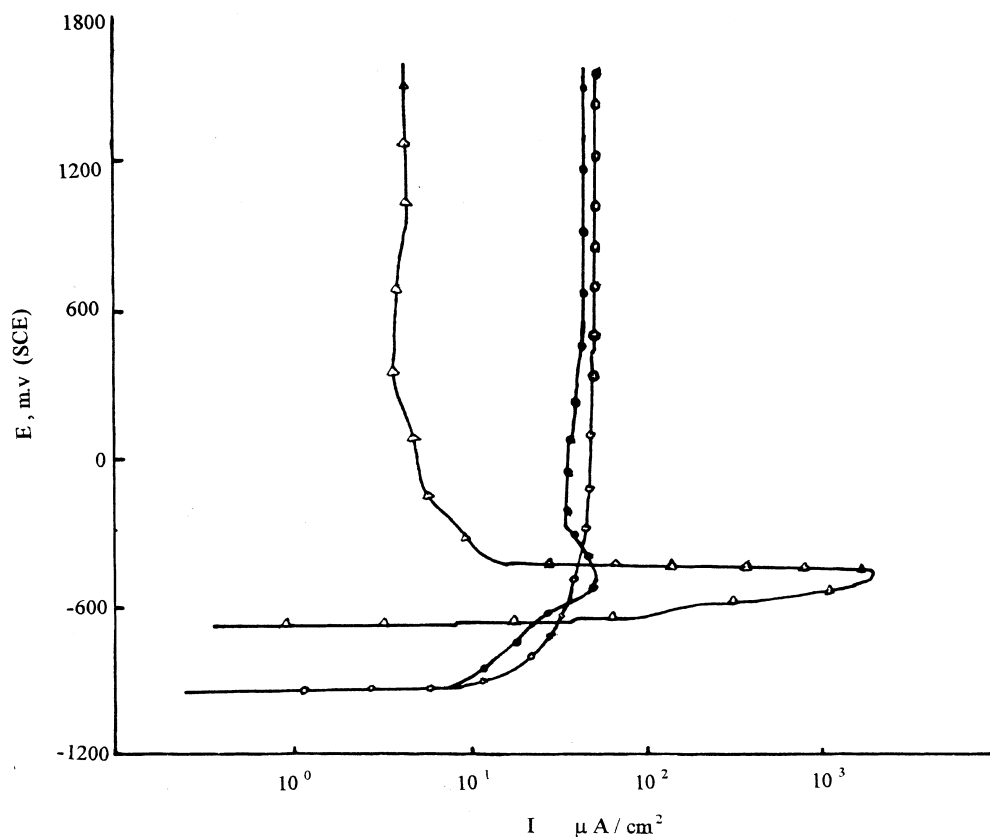
emphasize that the passivity of this alloy is due to the formation of a passive film enriched with aluminium oxide.

The influence of scan rate, v, on the anodic polarization behaviour of Al-Sn alloy in 1 M H_3PO_4 acid at pH 5, is shown in Fig. 2. Similar curves were recorded for other H_3PO_4 solutions (1.5 and 2 M). The data imply that an increase in scan rate in the range (0.5–5 mV/s) enhances the primary passive current I_p of the anodic peaks as well as I_{pass}, and the peak potentials are shifted to more noble potential values. Additionally, the relationship between I_p and $v^{1/2}$ was plotted for Al-Sn alloy in 1, 1.5 and 2 M H_3PO_4 at pH 5, Fig. 3. These curves show a linear variation of I_p with $v^{1/2}$. These findings suggest that the anodic process is under diffusion control and may be underlying the following relation [14],

$$I_p \rightarrow abCz^{3/2}D^{1/2}v^{1/2}$$

where a and b are constants, D is the diffusion coefficient of the diffusive species, C is the concentration of the diffusive species, z is the number of exchanged electrons, and v is the scan rate. A similar mechanism was proposed for the passivation of Fe in phosphate solutions [15].

Effect of pH

The potentiodynamic polarization curves of Al-Sn alloy in 1 M H_3PO_4 solutions of pH values 2.5, 3, 3.5, 4, 4.5 and 5 are shown in Fig. 4. Similar curves were observed for 1 and 1.5 M H_3PO_4 concentrations of H_3PO_4 solution. These curves show active-passive transition, which is more pronounced at high pH values (4 and 5). Increase of passive current, I_{pass}, at low pH values may attributed to the adsorption of phosphate ions at places where the passive film is not satisfactory. This suggests that the phosphate ions interfere with the alloy electrooxidation process and that the anodic layer provides less

Fig. 3 Linear dependence of I_p on $v^{1/2}$ for Al-Sn alloy in different H_3PO_4 acid concentrations solutions (pH 5) (○): 1 M; (●): 1.5 M; (△): 2 M

protection against the electrolyte. In the present study, this phenomena is more pronounced at low pH (2.5) in 1, 1.5 and 2 M H_3PO_4 solutions. Rajagopalam and Venu [16] have reported that the stronger metal-anion bonds are in the order phosphate > hydroxide. The surface of the Al-Sn alloy was found to be covered with a gelatinous layer, probably of phosphate salt [15].

Olik [8] found that the passive film destruction of Al-Zn-Mg alloy in neutral solution and hence the corrosion rate are increased with increase in the acidity (decreasing pH value) of the medium.

Figure 5 shows the pH-log passive current (I_{pass}) of the Al-Sn alloy in 1, 1.5 and 2 M H_3PO_4 solutions at + 600 mV. It can be seen that the log of passive current decreases linearly with increasing pH in the range 2.5–5.

Fig. 2 Potentiodynamic anodic polarization curves of Al-Sn alloy in 1.5 M H_3PO_4, pH 5 at the given scan rates, mV s^{-1} (○): 5; (●): 4; (△): 2.5; (▲): 1; (□): 0.5
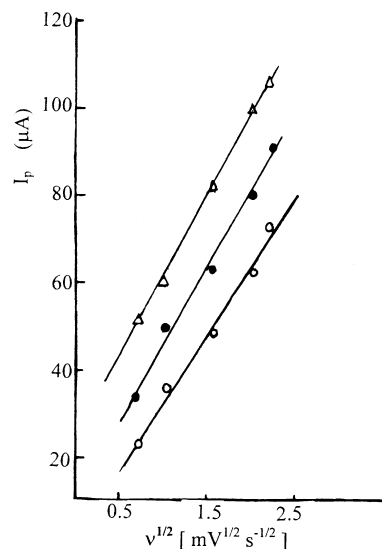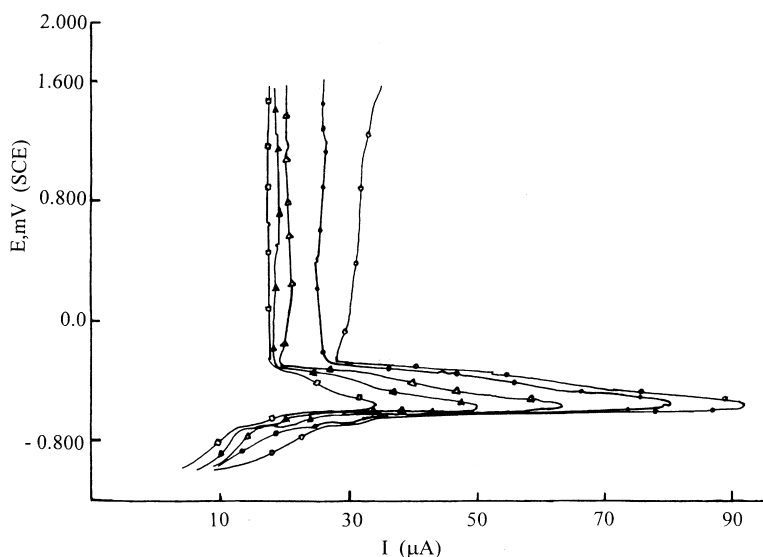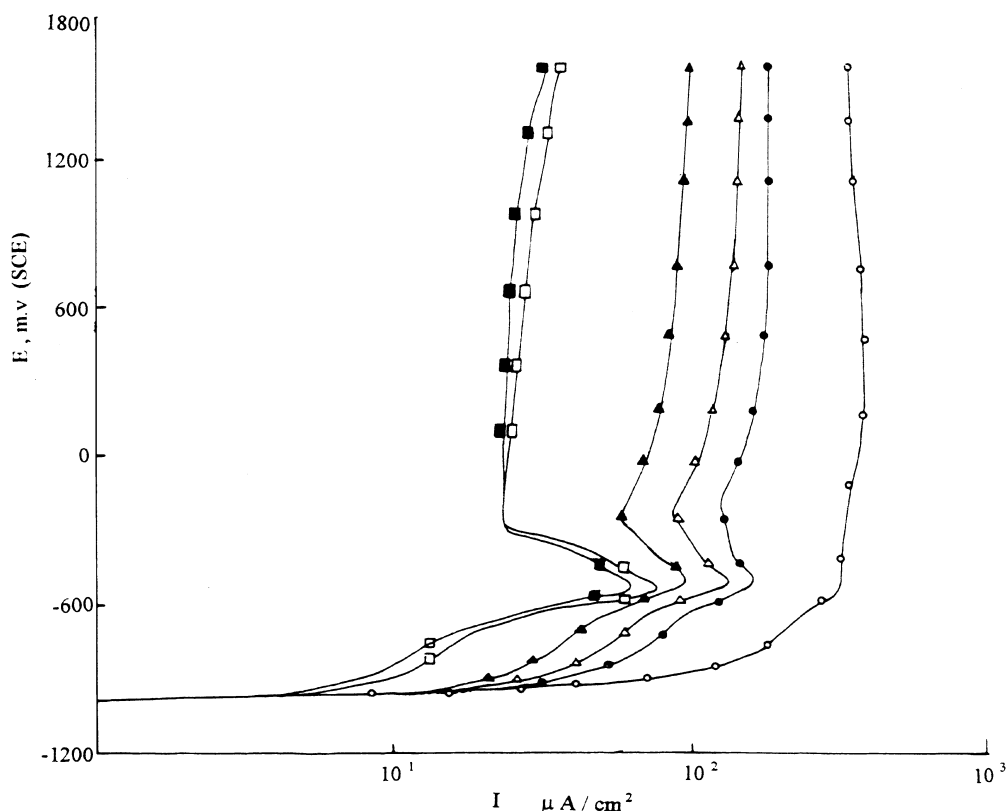
Fig. 4 Potentiodynamic anodic polarization curves for Al-Sn alloy in 1 M H_3PO_4 solutions at scan rate 5 mV/s and various pH values: (○): 2.5; (●): 3; (△): 3.5; (▲): 4; (□): 4.5; (■): 5

To clarify these results, a study of potentiostatic current-time transients of Al-Sn alloy in 1.5 M H_3PO_4 solutions of different pH was carried out by imposing a constant potential in the passive region (see experimental section). The curves are represented in Fig. 6. This was repeated for 1 and 2 M H_3PO_4 solutions. These curves show that the steady-state current is decreased on increasing the pH. Moreover, these results indicated that the corrosion of the alloy is retarded on increasing the pH.

Effect of acid concentration

At constant pH (3.5), the effect of various H_3PO_4 concentrations on the potentiodynamic anodic polarization behaviour of Al-Sn alloy is presented graphically in Fig. 7. These curves show regular increase of active dissolution currents of Al-Sn alloy as well as the passive current density with increasing H_3PO_4 concentration in the range 0.5–2 M at pH 3.5. Similar results were recorded for Fe in H_3PO_4 solutions [15]. From Fig. 7, the values of I_p for Al-Sn alloy in 1, 1.5 and 2 M H_3PO_4 at the same pH increased with increasing concentration of H_3PO_4. This confirms the formation of phosphate salt at some sites of the passive film [16]. Figure 8 shows the potentiodynamic polarization curves of the examined alloy in both unstirred and stirred solutions of 1 M H_3PO_4 (pH 4). It can be seen that in stirred solutions the entire anodic polarization curve is displaced to higher currents, though its shape remains the same [15]. This is probably because loose phosphate salt does not provide protection of the passive film formed on the alloy surface.
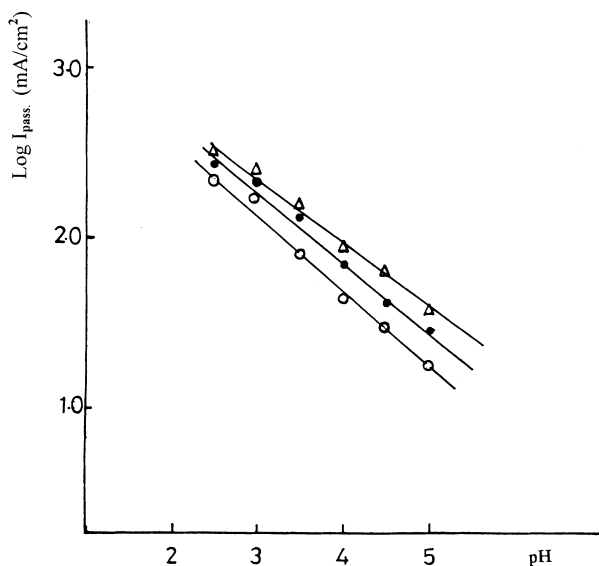
Potentiostatic current-time transient measurements at 500 mV for Al-Sn alloy in different H_3PO_4 concentrations at a constant pH of 3.5 was recorded. The resulting

Fig. 5 Passive current I_{pass} vs pH for Al-Sn alloy in different H_3PO_4 concentrations at +600 mV (○): 1 M; (●): 1.5 M; (△): 2 M

Fig. 6 Potentiostatic current-time transient curves for Al-Sn alloy at +500 mV in 1.5 M H_3PO_4 solutions of different pH values (——): 2.5; (----): 3; (—·—·—): 3.5; (—··—··—): 4; (—···—···—):4.5; (······):5
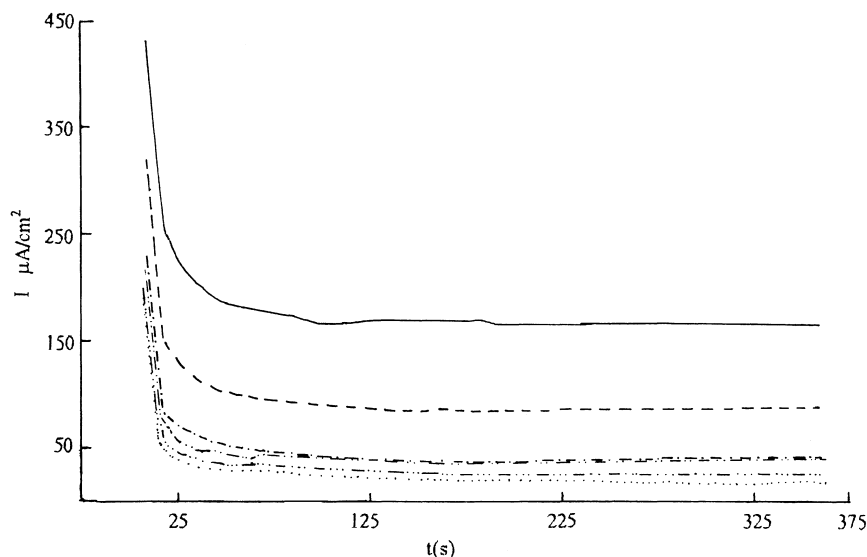
curves show that the steady-state current increases with increasing acid concentration, so that there is a good agreement between potentiodynamic and potentiostatic results.

Effect of Cl⁻ anion

The anodic polarization curves of Al-5.6% Sn alloy in aerated 1, 1.5 and 2 M H_3PO_4 solutions at different pH values (2.5–5) in the absence and presence of Cl⁻ ions in the concentration range 10^{-4}–10^{-2} M was carried out. The results show, at low concentrations of Cl⁻ ions (10^{-4}, 10^{-3} and 5×10^{-3} M) in all studied solutions, the potentiodynamic curves are slightly displaced to higher currents, with no change in the curve features. This suggests that in the presence of such Cl⁻ ion concentrations the anodic film hindered the extent of attack by Cl⁻ ions.

The attack of Cl⁻ ions on the passive film of Al and Al-alloys has been the subject of several investigations

Fig. 7 Potentiodynamic anodic polarization curves for Al-Sn alloy in different H_3PO_4 concentrations at scan rate 5 mV/s and pH 3.5 (○): 0.5 M; (●): 1 M; (△): 1.5 M; (▲): 2 M
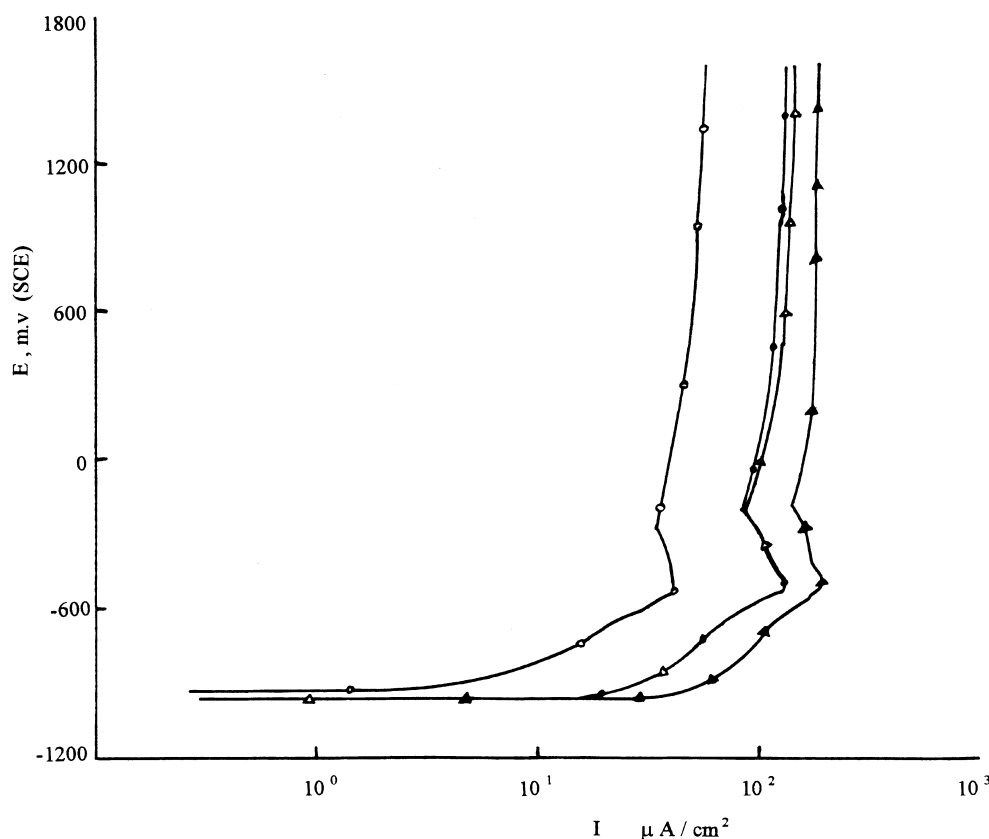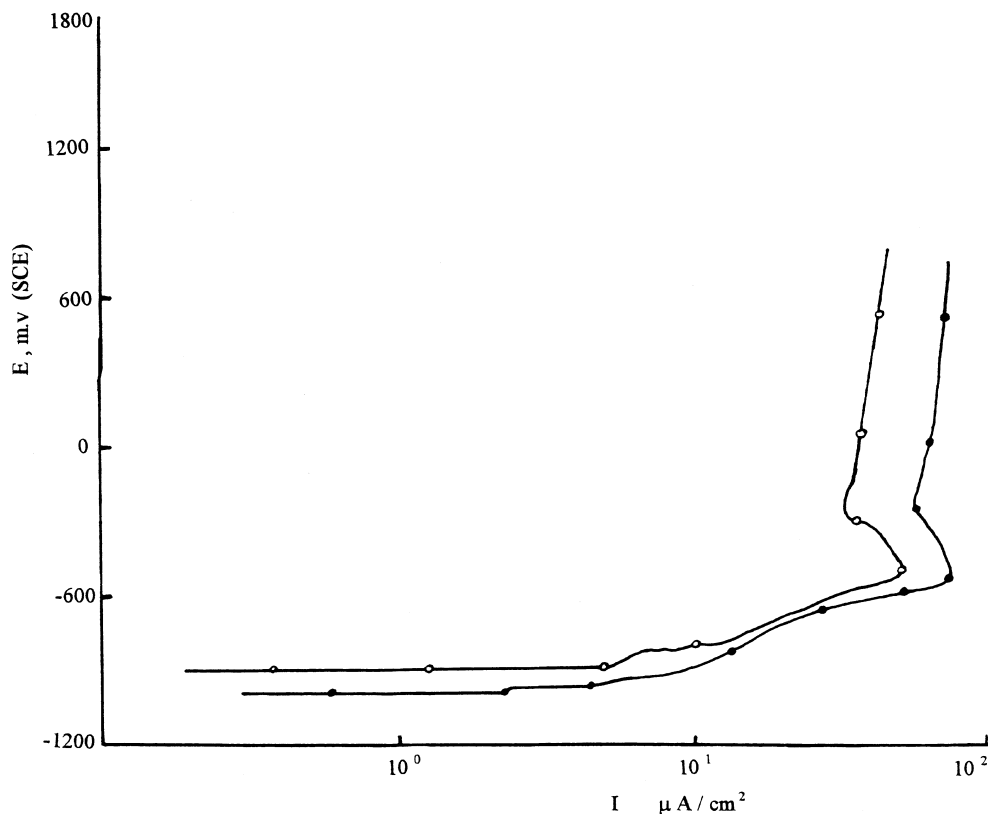
[4, 5, 7, 17–19]. Some of these studies have shown that the effect of Cl$^-$ ions is dependent on both pH and Cl$^-$ ion concentration. The pitting potential of pure Al (99.99%) was found to be less as the pH increased [19]. The higher values (more positive) of the pitting potentials of Al-Mn-Cu alloy in 0.3 M NaCl solution at pH 3 were attributed to low Cl$^-$ ion concentration [20].

Figures 9 and 10 represent the influence of 10^{-2} M Cl$^-$ ions on the potentiodynamic curves of Al-Sn alloy in 1 M and 2 M H$_3$PO$_4$ solutions at different pH values respectively. From these curves, it can be observed that in 1 M H$_3$PO$_4$ at pH 2.5 early breakdown of the passive film takes place, while in 2 M H$_3$PO$_4$ solution of the same pH this breakdown did not occur. This indicates that the anodic dissolution reaction is displaced to a higher rate by addition of Cl$^-$ ions, suggesting that Cl$^-$ ion allows Al-Sn alloy to dissolve.

Usually a sharp increase in current density in the form of current oscillation through the passive region (pitting attack) occurs in chloride-containing solutions [21]. It is important to mention that in aerated solutions, the competitive adsorption of Cl$^-$ ions and oxygen-containing species on the alloy surface led to the absence of pitting attack by such ions. The same observations were recorded for Al–1%Si–0.5%Cu alloy in Na$_2$SO$_4$ solution containing Cl$^-$ ions [22].

In the presence of 10^{-2} M Cl$^-$ ions and at pH 2.5, the breakdown of the passive film can be attributed to the increase in Cl$^-$ ion concentration, which increases their attack on the passive film. This leads to the loss of its

protective action. Excessive adsorption of the Cl$^-$ ions results in creating a negative charge, which in turn creates an equal and opposite charge on the metal side of the oxide film [23]. The effect of the presence of chloride ion on the extent of the attack by HNO$_3$ solutions upon the oxide film on Al and Al-Si alloy formed by anodic passivation in 1 M H$_3$PO$_4$ was studied by Fiaza et al. [5] using impedance measurements. They found that with increase of Cl$^-$ ion concentration the extent of attack of ions on the oxide film increased leading to the loss of its protection, and a new non-protective oxyhalide layer formed. Loose white deposits (probably oxychloride precipitate) on some sites of the Al-Sn alloy appeared at the end of the experiment. Increasing the pH of the solution may increase the formation of oxychloride film. As a result, the layer blocks off and isolates the alloy surface from the solution.

On the other hand, the potentiodynamic polarization curves (Fig. 10), of Al-Sn alloy in 2 M H$_3$PO$_4$ solutions over the whole pH range studied (2.5–5) show that the effect of Cl$^-$ ions is inhibited. Similar results showing the inhibitive effect of phosphate ions in chloride-containing solutions were reported for iron [24] and tin [25].

Potentiostatic current-time transient measurements were conducted for Al-Sn alloy in 1, 1.5 and 2 M H$_3$PO$_4$ solutions containing 10^{-2} M Cl$^-$ ion at different pH values by imposing a constant potential (500 mV). A similar trend was shown to that in Fig. 6, showing that the steady-state current values decrease with increasing the pH and acid concentration. This shows that the
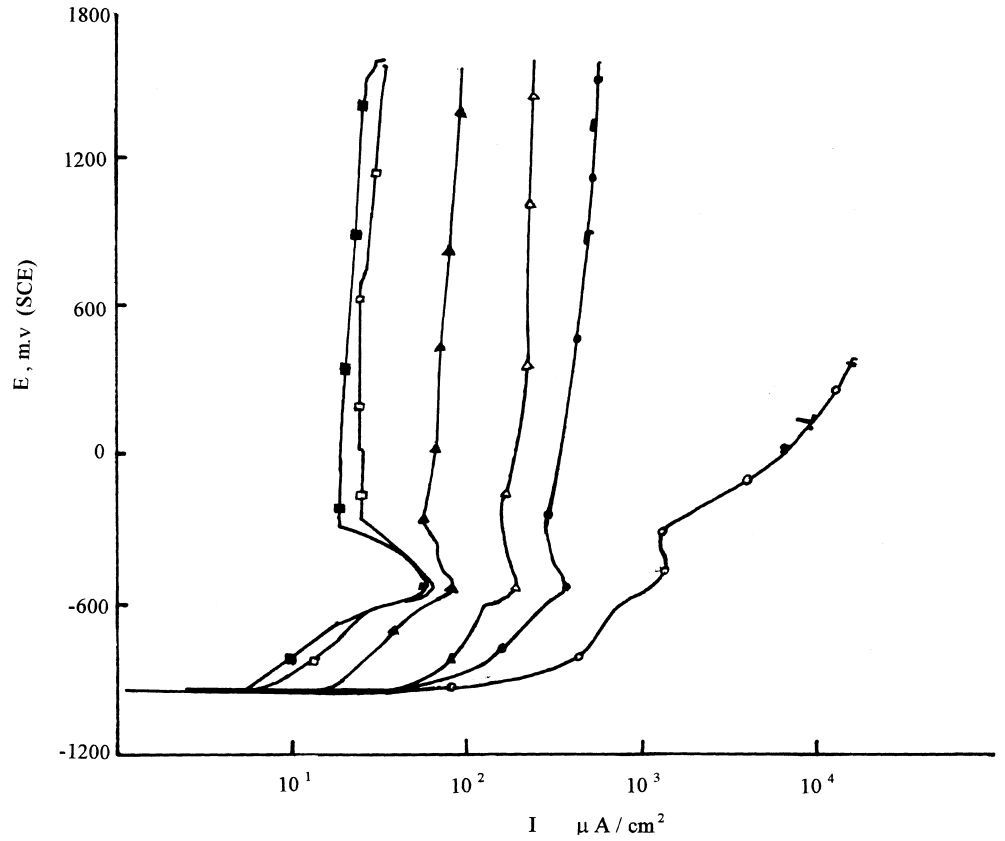
Fig. 9 Potentiodynamic anodic polarization curves for Al-Sn alloy in 1 M H_3PO_4 solutions at scan rate 5 mV/s and in the presence of 10^{-2} M Cl^- ions at different pH values: ($\bigcirc$): 2.5; ($\bullet$): 3; ($\triangle$): 3.5; ($\blacktriangle$): 4; ($\square$): 4.5; ($\blacksquare$): 5

Fig. 10 Potentiodynamic anodic polarization curves for Al-Sn alloy in 2 M H_3PO_4 solutions at scan rate 5 mV/s and in the presence of 10^{-2} M Cl^- ions at different pH values: ($\bigcirc$): 2.5; ($\bullet$): 3; ($\triangle$): 3.5; ($\triangle$): 4; ($\square$): 4.5; ($\blacksquare$): 5
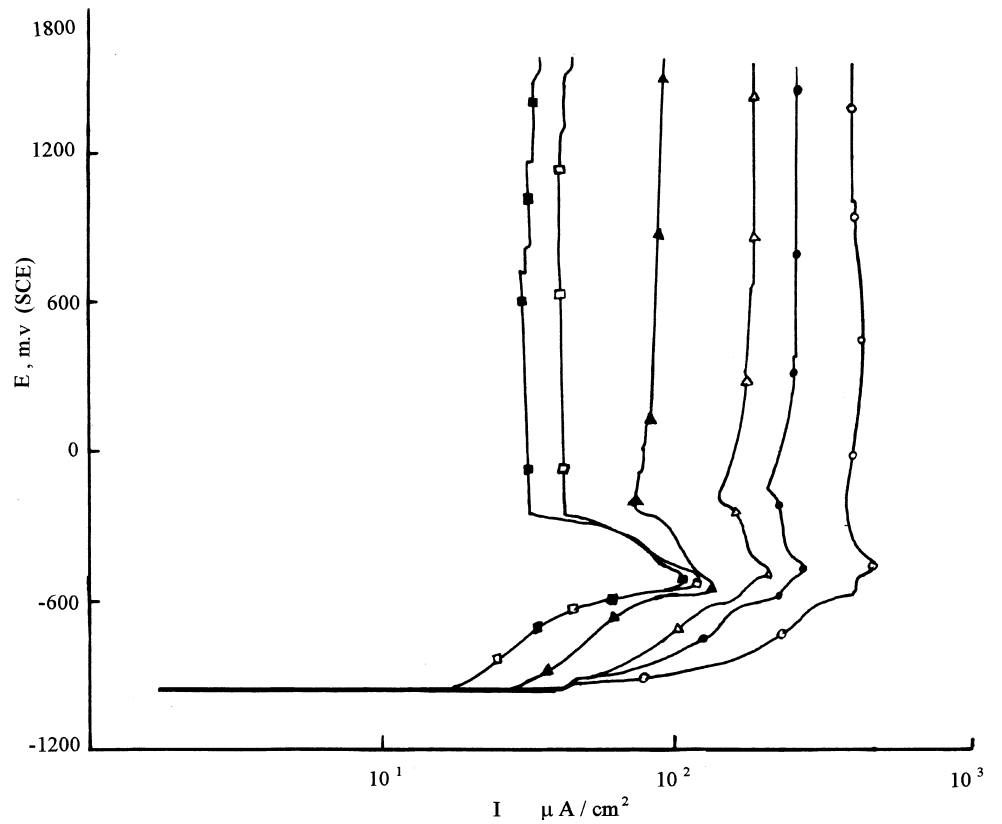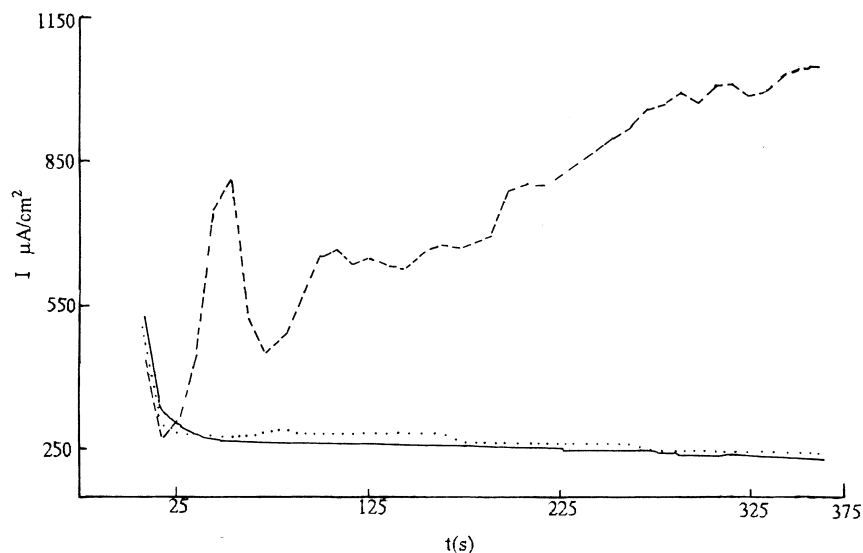
Fig. 11 Potentiostatic current-time transient curves for Al-Sn alloy at +500 mV in different H_3PO_4 concentrations containing 10^{-2} M Cl$^-$ ions, pH 2.5 (- - - -): 1 M; ($\cdots$):1.5; (——): 2 M

aggressive effect of Cl$^-$ ions is inhibited by increasing both pH and H_3PO_4 concentration, which confirms the results obtained by the potentiodynamic technique.

The unusual course of a potentiostatic current-time transient shown in Fig. 11, for Al-Sn alloy in 1 M H_3PO_4 containing 10^{-2} M Cl$^-$ ion at pH 2.5 demonstrated the attack of Cl$^-$ ions upon the alloy surface. These findings show alloy dissolution, resulting in increasing current. This reveals that the aggressive effect of Cl$^-$ ions occurs at low pH (2.5) and acid concentration (1 M), which confirms the results obtained by potentiodynamic measurements (Fig. 9).

Effect of organic inhibitors

The effect of organic inhibitors on the anodic polarization curves of Al-Sn alloy in 1 M H_3PO_4 (pH 2.5) solutions containing 10^{-2} M Cl$^-$ ions is illustrated in Fig. 12. These curves show that in the presence of 10^{-2} M of 2- and 3-picoline the passivity breakdown occurred at a potential (−20 ± 5 mV) which is more positive than that obtained in the absence of such compounds (−350 mV), while in the presence of 2-aminopyridine the breakdown did not occur. Thus, the magnitudes of the passivation effects are in the following order:

2- aminopyridine > 2- picoline > 3- picoline

It is assumed that, in acid media, the compounds used are present in the form
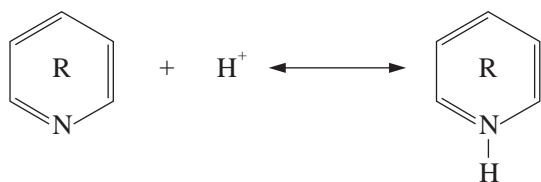
where R represents −CH$_3$ or −NH$_2$ substitutions. A methyl group substituted in the 2 position increases the electron density on the N atom of the pyridine ring more than in the 3 position through the inductive effect. Thus the −NH$_2$ group in the 2 position is expected to increase the electron density on the N atom via the mesomeric effect and induction. Further, from the pK_b values [26] of such compounds (2-aminopyridine 7.18, 2-picoline 8.03, 3-picoline 8.32), it is evident that the basicities of those inhibitors are in the same order as that of their magnitudes of passivation.

The results obtained for tin and cadmium metal in H_2SO_4 solution in the presence of these compounds revealed that the inhibition efficiencies are in the same order [27]. Similar views were reported for an Al-Cu alloy in HCl solutions in the presence of inhibitors such as pyridine, piperidine, 2- and 3-picoline, revealing that the inhibition efficiences of such compounds are in the order mentioned [28]. This suggests that the positive charge on the N atom promotes physical adsorption of such compounds on the alloy surface [29].

Heavy corrosion of the alloy surface was observed at the end of the experiment in the presence of 2- and 3-picoline.

Conclusions

The results obtained for the anodic polarization behaviour of Al-Sn alloy in H_3PO_4 acid solutions show that

1. The formation of SnO/SnO$_2$ incorporated with phosphates of both metals (Al and Sn) leads to a highly stable passive film.
2. The pitting attack of Cl$^-$ ions did not occur because of the competitive adsorption of Cl$^-$ ions and oxygen-containing species in aerated solution.

Fig. 12 Potentiodynamic anodic polarization curves for Al-Sn alloy in 1 M H_3PO_4 solutions at scan rate 5 mV/s, pH 2.5, in the presence of 10^{-2} M Cl$^-$ ions and the presence 10^{-2} M of (a): 0; (b): 3-picoline; (c): 2-picoline; (d): 2-aminopyridine
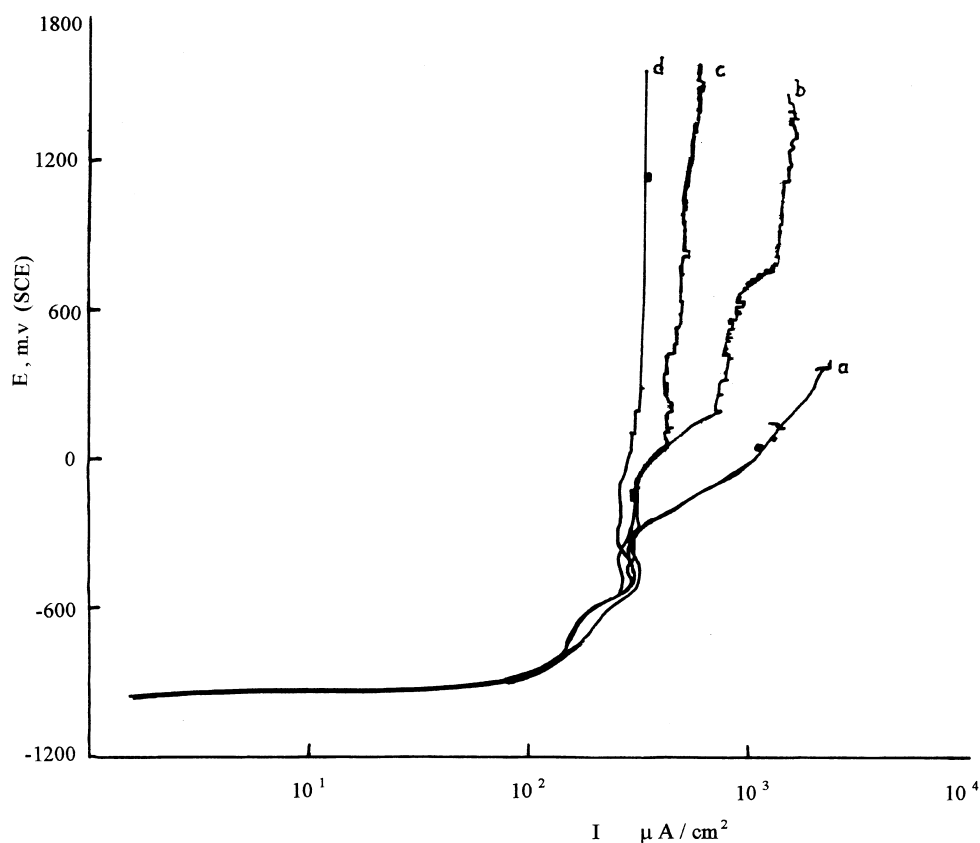
3. The presence of Cl$^-$ ions cause passivity breakdown at low acid concentration and low pH (1 M and pH 2.5), while at high acid concentration and high pH breakdown of the passive film did not occur.
4. The retarding effect of alloy dissolution was more effectively achieved by increasing both acid concentration and pH than the addition of the organic additives.

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