STABILITY OF ANTIMONY AND ITS ANODIC OXIDE FILM AGAINST CORROSION IN AQUEOUS SOLUTIONS

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Abstract

The open circuit potential and impedance measurements were used to investigate the corrosion behavior of antimony in 0.1M citric acid solution made to various pH values. The results showed that the antimony surface undergoes spontaneous corrosion in the citrate solutions. Also the properties of the anodic oxide film on antimony were examined by impedance technique. It was found that the antimony surface becomes more passive as the thickness of the anodic oxide film formed on antimony increase. The anodic oxide film on antimony behaves like a non- ideal capacitor. The stability of the anodic oxide film in the aqueous solutions was found to depend on the concentration of the formation medium for the anodic oxide.

Keywords: Antimony, oxide film, corrosion.

Introduction

AC impedance techniques have been recommended and employed for investigation of the corrosion reactions for a large number of metal/ electrolyte systems [1, 2]. Yun *et al.* [3] have used capacitance method in a study of the properties of oxide films. One of the important electrochemical parameters of metal oxide electrode that responds to pH is the open circuit potential. Tourky and Moussa [4,5] have investigated the behaviour of the antimony electrode in buffer solutions. A straight line potential-pH relationship based on the steady state potential values was obtained. Antimony oxide electrodes have been used as pH indicator electrode [6-8]. Dutta and Batrua [9] have studied the dielectric properties of anodized antimony in a frequency range of 100 to 20,000 Hz and the dependence of capacitance of Sb_2O_3 films on the oxide thickness.

Previously we have studied the currentless dissolution of the anodic oxide films on antimony in different aqueous solutions [10-13] and the kinetics of the metal dissolution in phosphate solutions of different pH values [14]. The aim of the present investigation is to study the reactivity of the antimony surface in buffer solutions using potential and impedance measurements. The effects of frequency and

the concentration of the formation medium on the properties of the anodic oxide films on antimony will also be discussed.

Experimental

The antimony electrode was made from 99.99% antimony rod (BDH, England).'A stout copper wire was used as the electrical contact. The electrode was fixed in a glass tube with Araldite resine leaving surface area of 0.274 cm^2 in contact with the test solution. The solutions were prepared using Analar grade reagents and triply distilled water. The measurements were carried out at 25 ± 0.5 °C in naturally aerated and unstirred solutions.

The electrode was abraded using successively finer grades of metallographic emery papers down to 4/0 until a mirror-bright surface was obtained, then rubbed with a soft cloth and immersed in the test solution. The electrode impedance, i.e. the capacitance, C_m, and the resistance, R_m, was measured by means of a high precision standardized bridge of the Wien type. The bridge and electrolytic cell were essentially the same as those described elsewhere [15,16]. The input ac voltage to the bridge was always 10 mv. The normal working frequency was 1000 Hz unless otherwise stated. The potential of the antimony electrode was measured vs a saturated calomel electrode (SCE) by a valve voltmeter (Electronic Instruments Ltd., UK) and then referred to the normal hydrogen electrode (NHE).

Results and Discussion

Potential and Impedance Measurements of Antimony Surface:

The open circuit potential E_h of the mechanically polished antimony surface was followed with time for 3h in 0.1M citric acid made to various pH values by appropriate addition of 0.2M Na_2HPO_4. Figure 1 shows the variation of the initial (after one minute of immersion) and the steady state potential values with pH of the buffer solutions. The relationship is a straight line with a slope amounts to-49 mV/pH for each of the initial and final potentials. Therefore, the pre-immersion oxide film on antimony surface does not affect the pH response of the antimony electrode.

As can be seen from Fig.1, the open circuit potential exhibits a very small decrease in value during the time of electrode immersion in test solutions. This indicates thinning of the pre-immersion oxide film on antimony surface. Such small decrease in potential is almost the same in all buffer solutions (Fig.1) and reveals to the low of surface reactivity of antimony in these solutions. Previously it was found

that in NaOH of concentrations more than l.0 M the potential of abraded zirconium drifts to more negative values indicating dissolution of the air-formed oxide [17]. Also bismuth was exhibited spontaneous corrosion in 0.025 M solutions of Na_2SO_4 and H_2SO_4 and a 0.05 M solution of NaOH [18].

The complex plane (Cole-Cole plot) analysis has been used for studying electrode reactivity [19]. The variation of the electrode impedance, i.e. the capacitance, C_m, and the resistance, R_m, with frequency in all buffer solutions were measured when more stable values of C_m and R_m are reached, after 3hrs. The frequency range of 200 to 5000 Hz is employed. The impedance spectra are shown in the Cole-Cole plot in Fig. 2, in which l/WC_m (where $W = 2\pi f$ and f is the frequency) is plotted against the resistance R_m. Extrapolation of the lines to intersect the R_m axis at $l/WC_m = 0$ gives the resistance values of the buffer solutions.

The line slope (Fig. 2) represents the tangent of an angle, which depends upon the surface state [20]. The angle amounts to 39° for all buffer solutions and corresponds to Warburg behaviour which indicates diffusion of some species in the pre-immersion oxide on Sb during its dissolution. Hampson and Latham [21] from their studies on the charge transfer reaction at polycrystalline cadmium electrodes in NaOH pointed out that the Warburg behaviour supports a very fast charge transfer reaction. The small value of the angle gives further evidence for the surface reactivity of antimony towards oxide thinning which is a diffusion-controlled process. Therefore, the impedance results (Fig. 2) are in good agreement with those of potential (Fig. 1) and all indicate approximately the same reactivity of Sb in the test solutions.

Impedance Measurements for Anodic Oxide Films:

In this section, an anodic oxide film was formed at a current density of 5 x 10^{-3} A cm^{-2} in 0.I N H_2SO_4 at polarization intervals up to 5, 10, 15, 20, 30, 40 and 50V. After reaching the specified formation voltage, the applied current was interrupted and the impedance (C_m and R_m) of the formed surface oxide film was measured at different frequencies ranging from 500 to 10,000 Hz.

Figure 3 (a and b) represents the variation of the reciprocal capacitance, l/C_m, with the frequency f. The relation is a linear one and 0bey the following equation:

$l/C_m = A - B \log f$ (1)

where B is the slope of the straight line and A is the intercept at f = l. The breaks which appear in the straight lines in Fig. 3 are associated with two values of B. The

decrease in the value of B with increasing the frequency is consistent with the series connection of the capacitance C_m and the resistance R_m of the electrode impedance. It can be seen from Fig. 4 (a and b) that the reciprocal capacitance (l/C_m), which is proportional to the oxide thickness [22], increases linearly with formation voltage at the different frequencies used.

As shown in Fig. 5 (a and b), the variation of the resistance R_m with the reciprocal frequency is a linear relationship following the equation [23].

$$R_m = R°_m + z /f \qquad\qquad (2)$$

Where $R°_m$ is the resistance of the electrolyte. The value of $R°_m$ equals to 35 ohm. The resistance decreases with increase of frequency (Fig.5) which may be attributed to the variation of resistance along the oxide layer. Previously it was found that incorporation of the electrolyte ions into the passive layer cause deviation from stoichiometry and producing a variation of the resistance along the length of the passive layer [24].

The impedance diagrams for the oxide films formed at different formation voltages are shown in the Cole-Cole plot in Fig. 6. The plots intercept the R_m axis at the electrolyte resistance which equals to 35 ohm. Therefore, the value of electrolyte resistance obtained from Figs. 5 and 6 is the same. The slope of the linear part of the plot (Fig.6) represents the tangent of an angle which increases with increase the formation voltage. This means that the antimony surface becomes less reactive or more passive as the oxide thickness increases. Experimental results on tantalum [25] and titanium [26] electrodes showed that the angle increases with decrease of surface reactivity. Also it was reported that the angle increases with increase the insulating properties of the passive layers formed on zinc [27]. The values of the angle lie between 73° and 78°. Such deviation of the angle from 90° indicates that the passive oxide film formed on antimony behaves like a non-ideal capacitor[28].

Influence of the Formation Medium Concentration on the Oxide Film Dissolution Rate:

In order to clarify the influence of H_2SO_4 as a formation medium on the dissolution rate of the oxide film, the latter was formed on the mechanically polished antimony surface till 40 V at a current density of 5 x $l0^{-3}$ A cm^{-2} in H_2SO_4 solutions with concentrations ranging from 0.1 to 3.0 N. The electrode was then withdrawn from the polarization cell, washed with distilled water and immersed in the

dissolution medium. The latter was 0.1 N H_2SO_4. The capacitance C_m of the formed surface oxide film was observed with time until complete dissolution of this oxide.

The results are shown in Fig. 7. From this Figure, it is clear that the reciprocal capacitance decreases with time indicating dissolution of the oxide film. The variation of l/C_m with the dissolution time (Fig. 7) is a linear relationship following the first order equation.

$$-d\,(l/C_m)/\,dt = K\,(l/C_m) \qquad\qquad (3)$$

Where C_m is the measured capacitance at time t and k is a constant. The inflections which appear in the dissolution curves (Fig. 7) indicate that the oxide film is composed of two layers. The outer layer dissolves faster than the inner one.

Besides the possibility of chemical difference between the two layers [29], they may have some physical difference, i.e. in the type and concentration of defects within each layer. Therefore, the outer layer seems to have more structural and mechanical defects since it is more susceptible to dissolive. The duplex nature was observed for the anodic oxide films on antimony [12,13], aluminium [30], tungsten [31,32], bismuth [33], zirconium [34-37] and lnconel alloy 600 [38].

The average rate constant for dissolution of the entire oxide film K, was calculated on the basis of the length of each segment of the dissolution curves in Fig. 7. The dependence of K on the concentration of the formation medium (H_2SO_4) is shown in Fig. 8. A linear increase in the average dissolution rate occurs with increase of acid concentration. This may be due to the more defective character of the oxide film formed in the concentrated H_2SO_4 solution. The results obtained here are in good agreement with those previously reported by Di Paola *et al.,* [39]. It was found that the film formed is spongier as the formation medium become more concentrated and mechanical disruption occurs earlier.
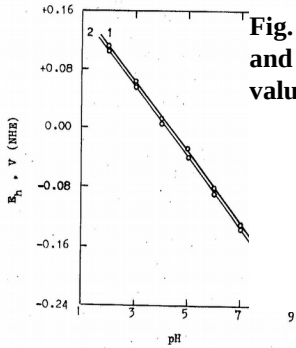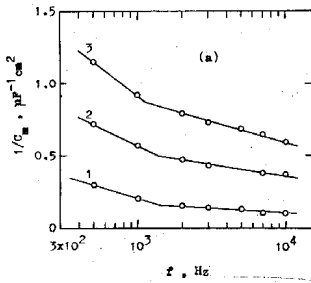
Fig. 1 :   Variation of the initial and final open circuit potential values with
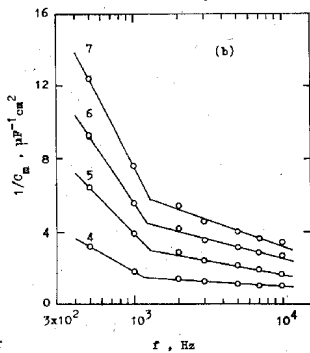   **pH. (1) Initial (2) Final.**
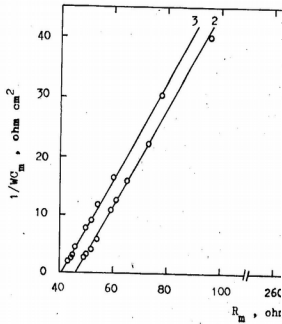
Fig. 2 :   Complex plane analysis of antimony electrode at different pH
         values. (1) 2 (2) 7 (3) 8.

iation of l/C$_m$ with
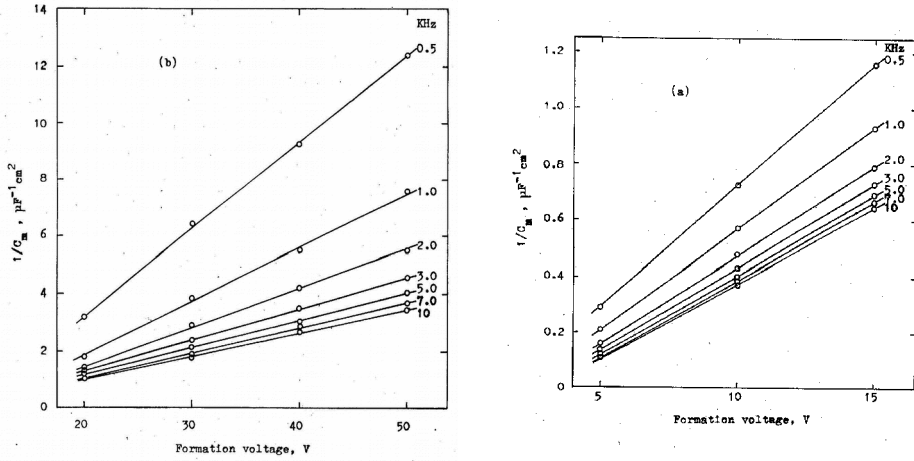r films formed (a)

3) 15V; (b) at: (4)20
7)50V.

Fig·3

Fig. 4: Variation of l/C_m with the formation voltage at different frequencies (a) from 5 to 15 V (b) from 20 to 50 V.
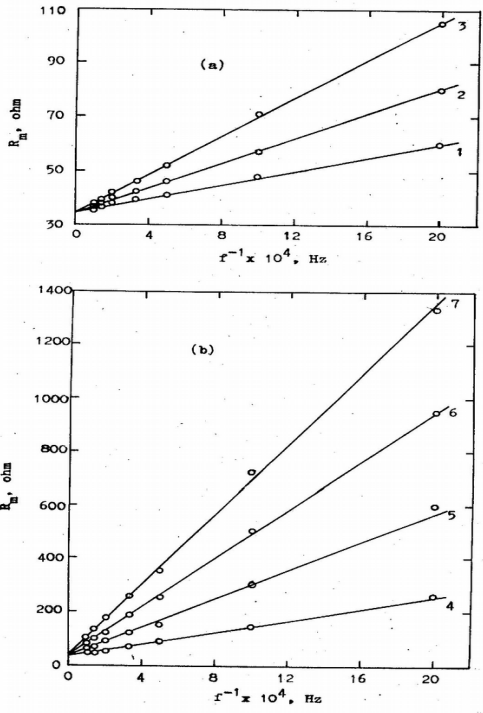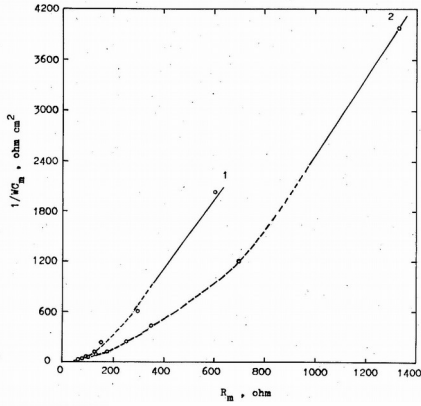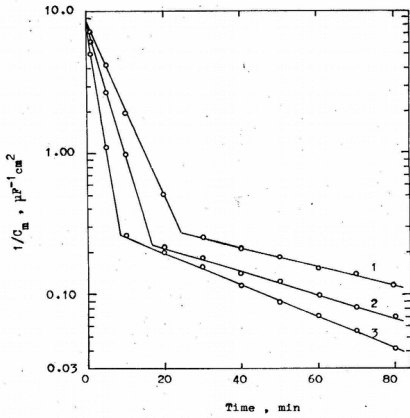

Fig. 5 : Variation of R_m with reciprocal frequency for films formed (a) at:(l) 5 (2) 10 (3) 15 V; (b) at: (4)20 (5)30 (6)40 (7)50 V.
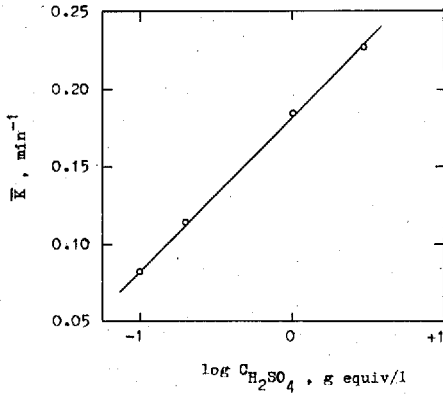
Fig. 6 :   Complex plane analysis for the films formed at different formation
voltages (1) 30 (2) 50 V.

Fig. 7

riations of log l/C_m
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$_2SO_4$ concentrations
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fferent H_2SO_4

Fig. 8

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