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Galvanostatic polarizations of some Sn-Cd alloys in some carboxylic acids

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The anodic and cathodic polarization of three Sn–Cd alloys in solutions of acetic, succinic and malic acids was investigated. Corrosion potentials of the three alloys did not vary appreciably with the concentration of the acid or its nature. Anodic polarization of the 65% Sn–Cd alloy revealed one arrest before the potential of O_2 evolution and corresponds to the SnO/SnO_2 system. Two arrests were manifested by the anodic curves in the case of the 50 and 35% Sn–Cd alloys; these correspond to the Cd/Cd^{++} and SnO/SnO_2 systems respectively. Cathodic Tafel slopes (b—) for the h.e.r. on the three alloys range from −130 up to 202 mV. Values of the exchange current densities (i_0) range from $1{\cdot}1 \times 10^{-7}$ up to $1{\cdot}4 \times 10^{-10}$ A cm^{-2}.

1. Introduction

Alloy coatings of Sn–Cd have been claimed to be resistant to both vapour corrosion and atmospheric exposure [1–4]. Recent studies by Donovan and Strenger [5] on the effect of organic acid vapours on the corrosion of some metals and alloys revealed that coatings of Zn–Ni, Mn–Se and Sn–Cd alloys on steel give a useful degree of resistance to attack much superior to Zn or Cd coatings. The corrosion of some tin-base binary alloys in various acid solutions was examined by Endo and Yokoyama [6]. They found that the addition of cadmium to tin increased its resistance to acids. The same general trend was found by Cohen [4] for electrodeposited Sn–Cd alloy in the presence of acetic acid vapours.

El-Din and Abdelwahab [7] studied the cathodic and anodic behaviour of Sn, Cd and some Sn–Cd alloys in NaOH and Na_2SO_4 solutions. They found that the Sn–Cd alloys exhibited upon cyclic polarization features common to both alloying metals.

Although these researches have provided a basis for speculations on the electrochemical behaviour of some Sn–Cd alloys, they have been mainly concerned with solutions of strong acids or bases and some organic acid vapours. The present investigation is devoted to the study of the electrochemical behaviour of some electrodeposited Sn–Cd alloys in solutions of some carboxylic acids.

2. Experimental

The chemicals were A.R. grade (B.D.H. or Merck) and all solutions were prepared from bidistilled water.

The electrolytic cell was made of pyrex glass without any rubber connection. It consists of a vessel ~300 ml capacity. The male joint of the vessel (B 54) is provided with five openings, two of these are used for fitting the working and the counter electrode. The latter is a Pt sheet of area 5 cm^2 and separated from the main bulk of electrolyte by means of a (G 4) sintered glass disk. The potential of the working electrode was measured relative to a standard calomel electrode via a salt bridge whose tip was drawn in a capillary form which was placed at a distance of ~0·1 mm from the surface of the working electrode.

The solution in the electrolytic cell was deaerated by bubbling pure nitrogen gas through it for a period of 4 h. The working electrodes were prepared by electrodeposition of the Sn–Cd alloy as a coating 0·005 in thick on Pt sheet having a surface area of 1 cm^2. The electrolytic bath was essentially similar to those described by Antropov and Lebedeva [8].

Depending upon the bath composition, current

Table 1. Corrosion potentials of some Sn–Cd alloys in carboxylic acids

Alloy	*Acid concentration* ($\mathrm{ml\,l^{-1}}$)	*Acetic* (E mV corr.)	*Succinic* (E mV corr.)	*Malic* (E mV corr.)
65% Sn–Cd	0·50	−287	−294	−298
	0·10	−290	−288	−308
	0·05	−282	−278	−311
50% Sn–Cd	0·50	−481	−481	−480
	0·10	−496	−483	−489
	0·05	−501	−479	−487
35% Sn–Cd	0·50	−504	−495	−496
	0·10	↔506	−499	−501
	0·05	−498	−492	−496

density (c.d.) and cell potential, the following electrodeposited Sn–Cd alloys were obtained.

(1) 65% Sn–Cd alloy. In this case, the bath was made up of $SnSO_4$, 4·7 $\mathrm{g\,l^{-1}}$ $CdSO_4$, $8H_2O$ 3 $\mathrm{g\,l^{-1}}$, 20 $\mathrm{ml\,l^{-1}}$ concentration H_2SO_4, p–toludine 0·5 $\mathrm{g\,l^{-1}}$ and gelatin 2 $\mathrm{g\,l^{-1}}$. The deposition was performed at 60°C, using a c.d. of 0·5 $\mathrm{A\,dm^{-2}}$ and a cell voltage of 1·2 V. The electrolysis was carried out in a two compartment cell separated by a sintered glass disk (G 4). The anode was a 90% Sn–Cd alloy and electrolysis was continued for 30 min. Stirring of the solution was maintained during the period of deposition.

(2) 50% Sn–Cd alloy. An alloy of this type and composition was deposited from a bath containing 1·25 $\mathrm{g\,l^{-1}}$ $SnSO_4$, 10 $\mathrm{g\,l^{-1}}$ $CdSO_4$, $8H_2O$, 20 $\mathrm{ml\,l^{-1}}$ concentrated H_2SO_4 and 1·5 $\mathrm{g\,l^{-1}}$ gelatin. The deposition was carried out at 60°C, the c.d. was 1 $\mathrm{A\,dm^{-2}}$ and the cell voltage was 1·6 V. The period of electrolysis as well as the anode material was similar to those in the case of alloy 1.

(3) 35% Sn–Cd alloy. This alloy was deposited from a bath containing 0·7 $\mathrm{g\,l^{-1}}$ $SnSO_4$, 15 $\mathrm{g\,l^{-1}}$ $CdSO_4$, 20 $\mathrm{ml\,l^{-1}}$ concentrated H_2SO_4 and 1·5 $\mathrm{g\,l^{-1}}$ gelatin. The electrolysis was carried out at 60°C, the c.d. was 1 $\mathrm{A\,dm^{-2}}$ and the cell voltage 1·5 V. The period of deposition and the anode material were similar to those in the previous two cases. The alloys were analysed by determining the percentage of Cd and Sn gravimetrically by the methods outlined in Vogel [9]. The electrodes were thoroughly washed with bidistilled water till the washing solution became sulphate free. After rinsing they were transferred immediately to the cell containing the electrolyte solution.

Electrolytes: 0·05, 0·10 and 0·5 M solutions of acetic, succinic and malic acids were prepared by dissolving the appropriate amount of the A.R. acid in bidistilled water. The currents were supplied from a self-made galvanostat and the potentials measured with a high precision potentiometer (Muirhead D-972. A England). All measurements were carried out at 35 ± 0·5°C and the potentials were referred to the reversible hydrogen electrode.

3. Results and Discussion

3.1. *Corrosion potentials*

Corrosion (open circuit) potentials measured after an immersion time of 20 h in the deaerated acid solutions are given in Table 1. The corrosion potential values of the 65% Sn–Cd alloy are approximately the same, irrespective of the nature of the acid or its concentration. These values are comparable to the calculated [10] potential value of the SnO/SnO_2 system at the corresponding pH values of the examined solutions.

Corrosion potentials of the 50 and 35% Sn–Cd alloy do not vary appreciably with the acid concentration and their values are ~ 100 mV more negative than the equilibrium potential of the system Cd/Cd^{++}.

3.2. *Electrochemical behaviour under galvanostatic conditions*

3.2.1. *Anodic polarization.* The electrodeposited alloys were anodically polarized at various current densities (c.ds.) ranging from 50–250 $\mu\mathrm{A\,cm^{-2}}$.

(1) *Behaviour of the 65% Sn–Cd alloy.*

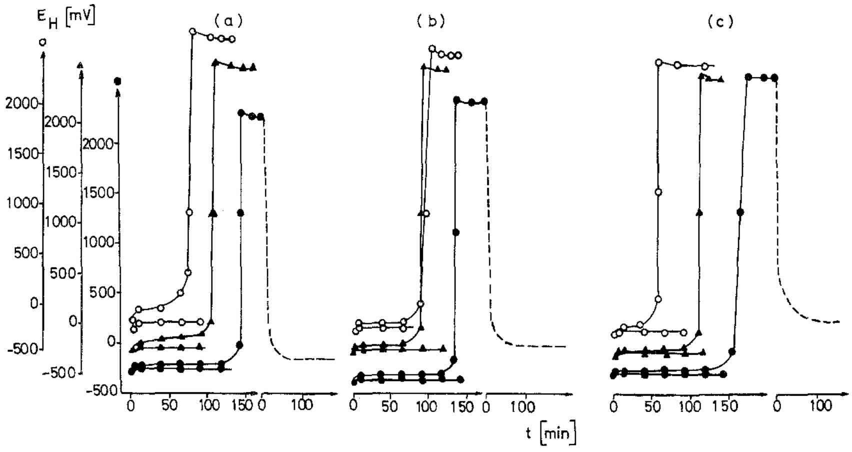

Fig. 1. Anodic potential-time and anodic decay curves for 65% Sn–Cd alloy in (a) acetic (b) succinic and (c) malic acids. ● 0·5 M; ▲ 0·1 M; ○ 0·05 M.

Representative anodic charging curves at 50 μA cm^{-2} and those at which O_2 evolution occurs (passivating c.ds.) are shown in Fig. 1. These curves show one arrest before the potential of O_2 evolution. The potentials of these arrests have values ranging from −240 up to −270 mV. These values agree closely with the equilibrium potential of the system SnO/SnO_2 at the corresponding pH's of the examined solutions and may be correlated to the following electrode reaction.

$$SnO + H_2O = SnO_2 + 2H^+ + 2e. \quad (1)$$

These results suggest the rapid formation of an SnO film on the surface of the alloy (even when anodic polarization is preceded by cathodic currents of up to 500 μA cm^{-2}). This behaviour resembles that of Sn–Ni and $FeSn_2$ in 0·1 M citric acid [11].

(2) *Behaviour of 50% Sn–Cd alloy.* Fig. 2 shows the representative anodic polarization curves at 50 μA cm^{-2} and those at which O_2 evolution occurs. From these curves it can be observed that the alloy exhibits practically the same general features in the three examined acids. The anodic charging curves manifest two arrests before the potential jumps to the O_2 evolution value. The first arrest has potential values ranging from −410 up to −460 mV which agree satisfactorily with the

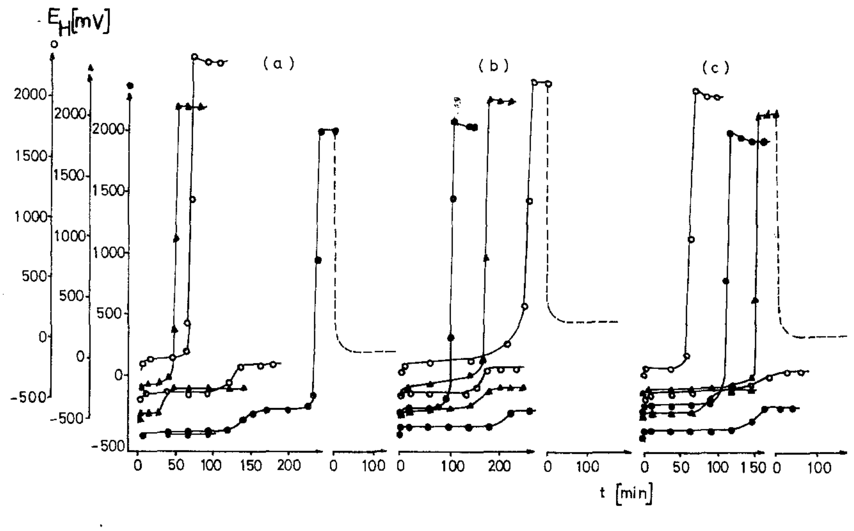

Fig. 2. Anodic potential-time and anodic decay curves for 50% Sn–Cd alloy in (a) acetic (b) succinic and (c) malic acids. ● 0·5 M; ▲ 0·1 M; ○ 0·05 M.

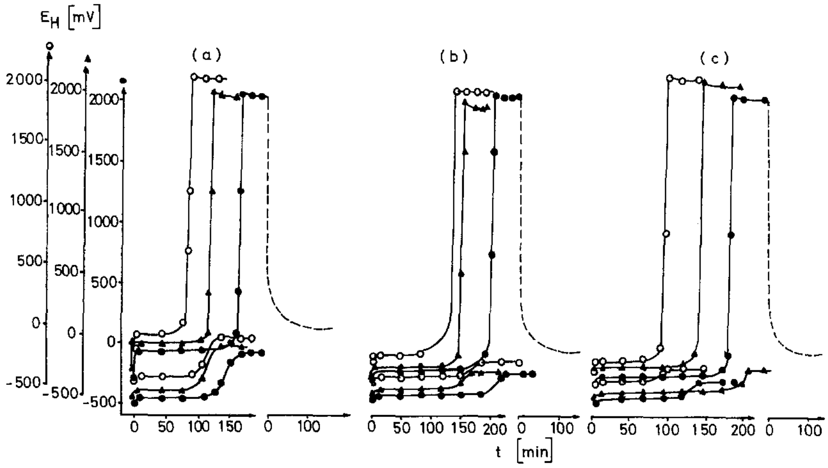

Fig. 3. Anodic potential-time and anodic decay curves for 35% Sn–Cd alloy in (a) acetic (b) succinic and (c) malic acids. ● 0·5 M; ▲ 0·1 M; ○ 0·05 M.

equilibrium potential of the system Cd/Cd^{++} (E^0 = −404 mV). The second arrest occurs at potentials ranging from −230 up to −275 mV and corresponds mainly to the oxidation of SnO to SnO_2 according to the electrode reaction [1].

(3) *Behaviour of 35% Sn–Cd alloy.* Representative anodic polarization curves at 150 $\mu A\,cm^{-2}$ and those obtained with the passivating currents are shown in Fig. 3. These curves show two arrests, the first of which has potential values which lie within the range −450 up to −480 mV and compare satisfactorily with the values of the equilibrium potential of the system Cd/Cd^{++}. These arrests are followed by second ones having the potential values −115 ± 10 mV in acetic acid and −290 ± 20 mV in both succinic and malic acid solutions. In the case of acetic acid, the potential values of the second arrest are comparable with the equilibrium potentials of the systems $Sn(OH)_2/Sn(OH)_4$ ($E^0 = -97$ mV) and Cd/CdO ($E^0 = -107$ mV), according to the following electrode reactions.

$$Sn(OH)_2 + 2H_2O = Sn(OH)_4 + 2H^+ + 2e \quad (2)$$

$$Cd + H_2O = CdO + 2H^+ + 2e. \quad (3)$$

The equilibrium potentials for Reactions 2 and 3 are close enough for the reactions to occur spontaneously. The potential values of the second arrest in the anodic polarisation curves of the 35% Sn–Cd alloy in both succinic and malic acid solutions agree closely with the calculated values for the system SnO/SnO_2 at the corresponding pH's and range from −241 up to −288 mV. At the passivating c.ds. the second arrests manifested by the anodic polarization curves of the three alloys in all examined solutions occur at potentials more positive than those obtained at low c.ds. The potentials of these arrests are ~100 mV more positive than the equilibrium potential of the system SnO/SnO_2 at the same pH's. This positive shift may be ascribed to the simultaneous oxidation of $SnO \rightarrow SnO_2$ and $Cd \rightarrow CdO$. This behaviour indicates that the potential of the passivating step for the three alloys is in fact a mixed potential governed by Reactions 1 and 3 taking place simultaneously. Similar results were obtained by El Din and Abdelwahab [7] with some Sn–Cd alloys in alkaline solutions.

It is also worth remarking that the length of the passivating step measured during anodization increased with the concentration of the electrolyte. In any particular medium, higher currents cause passivity to set in earlier than when low currents are used. Both features can be explained on the basis of the dissolution of part of the anodically formed oxide.

(4) *Anodic decay.* Representative open circuit decay curves ($E-t$) are shown in Figs. 1, 2 and 3 together with the anodic charging curves. The general characteristics of the curves are substantially the same. The potential shifts rapidly during the first few minutes from the O_2 evolution values to less positive ones, then decreases slowly attaining

Table 2. Parameters for h.e.r. on some Sn–Cd alloys in carboxylic acids

Acid	*Concentration* $(ml\,l^{-1})$	*65% Sn–Cd alloy*			*50% Sn–Cd*			*35% Sn–Cd*		
		Slope (mV)	$(i_0$ A cm$^{2})$	α	*Slope* (mV)	i_0 (A cm^{-2})	α	*Slope* (mV)	i_0 (A cm^{-2})	α
Acetic	0·50	−174	$1{\cdot}1 \times 10^{-7}$	0·35	−135	$5{\cdot}1 \times 10^{-9}$	0·44	−148	$9{\cdot}8 \times 10^{-9}$	0·41
	0·10	−177	$9{\cdot}0 \times 10^{-8}$	0·34	−130	$1{\cdot}9 \times 10^{-8}$	0·47	−153	$2{\cdot}4 \times 10^{-8}$	0·40
	0·05	−181	$1{\cdot}1 \times 10^{-7}$	0·34	−133	$2{\cdot}0 \times 10^{-8}$	0·46	−148	$9{\cdot}0 \times 10^{-9}$	0·41
Succinic	0·50	−130	$1{\cdot}1 \times 10^{-8}$	0·46	−137	$8{\cdot}0 \times 10^{-9}$	0·44	−136	$4{\cdot}0 \times 10^{-10}$	0·44
	0·10	−137	$2{\cdot}6 \times 10^{-8}$	0·43	−135	$2{\cdot}3 \times 10^{-8}$	0·44	−140	$8{\cdot}0 \times 10^{-10}$	0·43
	0·05	−134	$6{\cdot}6 \times 10^{-9}$	0·45	−132	$5{\cdot}0 \times 10^{-9}$	0·45	−142	$4{\cdot}0 \times 10^{-10}$	0·42
Malic	0·50	−143	$2{\cdot}1 \times 10^{-7}$	0·42	−144	$4{\cdot}5 \times 10^{-9}$	0·42	−146	$2{\cdot}9 \times 10^{-9}$	0·41
	0·10	−170	$7{\cdot}6 \times 10^{-7}$	0·36	−202	$4{\cdot}5 \times 10^{-7}$	0·28	−155	$9{\cdot}8 \times 10^{-9}$	0·40
	0·05	−136	$6{\cdot}0 \times 10^{-9}$	0·44	−133	$8{\cdot}4 \times 10^{-8}$	0·46	−135	$1{\cdot}4 \times 10^{-10}$	0·44

its steady state value after ~2 h. The potential values of such steady states fall within the range −40 up to +200 mV. These potentials cannot be correlated to one of the redox systems of both tin and cadmium. Probably they correspond to the decomposition of the higher oxides of cadmium formed at the O_2 evolution potential [7].

3.2.2. *Cathodic polarization.* The electrodeposited alloys were cathodically polarized at various current densities ranging from 50 up to 500 μA cm^{-2}. Parameters for the hydrogen evolution reaction (h.e.r.) on the investigated alloys are given in Table 2. Tafel slopes (b−) with values ranging from −130 up to −202 mV were obtained.

The rate determining step in the h.e.r. on the investigated alloys is assumed to be the discharge of hydrogen ions. Similar mechanism was suggested by Ammar *et al.* [12] for similar binary alloys and also for pure tin [12] and pure cadmium [13] in acid solutions. Therefore the folowing reactions are possible:

$$H^+ + e \;=\; H_{ads} \text{ (slow)} \qquad (4)$$

$$2H_{ads} \;=\; H_{2(gas)} \text{ (fast)}. \qquad (5)$$

The relation between applied cathodic current (i_c) and overpotential η is expressed by the equation

$$\eta \;=\; a - \frac{RT}{ZF} \ln i_c \qquad (6)$$

where $a = RT/ZF \ln i_c$. For $Z = 1$, α-values obtained from Equation 6 using the experimental b-values range from 0·28 up to 0·48. The theory of slow discharge predicts $\alpha = 0{\cdot}5$ for a symmetrical energy barrier. However, this ideal symmetry need not be followed in every case, and with a different α, the slow discharge may still be rate-determining. The change in α may indicate a distortion of the potential distribution in the phase boundary as a result of an additional energy barrier due to the adsorption of the carboxylic acid molecules. The chemisorption of organic polar molecules on metal surfaces was discussed earlier by Hackerman and Makrides [14]. Kaesche and Hackerman [15] found that the chemisorption of aniline and aniline derivatives on iron increases the Tafel slope for the h.e.r. from acid solutions. Tafel slopes with values ranging from −140 up to −300 mV were reported by Petrenko [16], while studying the h.e.r. on indium in the presence of some organic cations. High Tafel slopes were also obtained by Conway and Vijh [17] for the study of the mechanism of Kolbe reaction and were ascribed to the formation of a dipole layer film having barrier-like properties.

Values of the exchange current densities (i_c) determined by extrapolation of the cathodic Tafel curves to $\eta = 0$ were found to be of the same order of magnitude as those obtained for tin [12] and cadmium [13, 18] in acid solutions.

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