STUDIES ON THE BEHAVIOUR OF ZINC-ALLOYS AND ZINC-COMPOSITES IN ALKALINE KOH SOLUTION

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Abstract : Polarisation behaviour of primary alloys and composites of zinc with aluminium, magnesium, cadmium, Al_2O_3, and TiO_2 have been studied in KOH solutions of various concentration. The Rockwell hardness of the binary alloys and binary composites are greater than that of pure zinc. Aluminium and Al_2O_3 addition to zinc, appear to increase the corrosion current of these alloys in 30%-40% KOH solution while the addition of Mg and TiO_2 decreases the corrosion current. The aspect of surface degradation of these electrodes in terms of surface roughness, pitting and anodic growths, in dilute KOH solutions have also been studied.

INTRODUCTION

It has been a long practice to use zinc-electrodes as anodes [1-9] for cathodic protection and in alkaline batteries. However, the dissolution of zinc appear to be a problem in these types of applications, particularly during the idle period when no current is drawn. To counteract this self-corrosion, zinc is amalgamated with 0. 5% of Hg or alloyed with Pb and Sn. Dendritic crystalline growth on zinc, during charging, is also a problem for battery industry. Alloying (and amalgamation) of zinc with suitable alloying elements may improve the corrosion and oxidation resistance of zinc [5-9] to a certain extent. Nevertheless the exchange current density remains as an important criterion for use of zinc and its alloys and composites for battery applications. These electrodes should not get passivated during use and dissolve at an optimum rate in a particular electrolyte, which does not necessarily show a faster rate of corrosion. Moreover the hardness and strength of these electrodes are also important.

In this investigation, the polarization behaviour, corrosion-rate, self-dissolution and hardness of zinc alloys and composites for use in batteries and as corrosion resistant materials has been reported.

EXPERIMENTAL

Materials :

Electrolytically pure zinc, aluminium, cadmium and magnesium, Al_2O_3 and TiO_2 were used in preparing the binary zinc alloys, e. g. Zn-Al, Zn-Cd, Zn-Mg and binary zinc composite electrodes, namely, Zn-Al_2O_3, and Zn-TiO_2. Analytical grade chemical were used.

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Physical properties :

Hardness values have been obtained in Rockwell-scale and then expressed in B. H. N. scale. Micro-structure of the surfaces of the binary alloys and composites were studied in Neophot-21 metallurgical microscope and ZEOL 35C8 Scanning Electron Microscope at 200° × and 500° ×.

Electrochemical properties :

Potentiodynamic anodic and cathodic polarization have been carried at a scan rate of 1 mV/sec, with a PAR model 173 system. The chemical composition of the binary alloys have been determined, using Perkin Elmer atomic absorption spectrophotometer Model 380. Corrosion rates have been calculated from wight loss measurements in 30% KOH solution for a period of 30 minutes.

RESULTS AND DISCUSSION

Table I shows the composition, corrosion rate (weight loss basis) and microstructure of zinc and its binary alloys and composites. The addition of Al and Mg to zinc, improves the hardness values, while it is only marginally improved by the addition of Cd, Al_2O_3 and TiO_2. Photomicrographs revealed the dispersion of Al_2O_3 and TiO_2 particulates throughout the matrix, in the case of zinc-composites. The alloying addition like Al, Cd and Mg have been done within their solid-solubitity limit and in the case of zinc-composites, 3% addition of Al_2O_3 and TiO_2 have been carried out. The self corrosion behaviour of all these alloys appear to be higher than that of pure zinc in KOH solution.

Table II reveals the OCP values of the zinc and its binary alloys and composites in different concentrations of KOH solutions. As the concentration of KOH is increased the potential shifts in the more noble direction in the case of zinc and its alloys and composites.

Table II also shows the current values at constant overpotential (cathodic) for KOH solutions of 20%, 30% and 40% concentration. These values have been obtained from the anodic and cathodic polarization plots at a scan rate of 1mV/sec. Maximum polarization was observed for Zn + TiO_2 and Zn + Mg, while the polarization effect was found to be minimum for Zn + Al and Zn + Al_2O_3 electrodes (Fig. 1). These electrodes have been polarized within a current range of 1 mA to 100mA/cm². It is already seen from the values of Table III that the current values of Zn-Al and Zn-Al_2O_3 are higher in all concentrations of KOH solutions. It is well known from the Tafel equation [10] that at a constant overpotential, the changes in the current i, is reflected in the changes in the exchange current density, i_o. The electrodes Zn-Mg and Zn-TiO_2 on the other hand reveals lower current values and dissolve to a comparitively less extent. Table II further shows the overpotential values at a constant current of 2 mA for 20%, 30% and 40% KOH solutions. It is observed that Zn-Al and Zn - Al_2O_3 have a comparitively lower overpotential than other systems. Such lower polarization tendency may be an indicator of the higher i_o. Table III shows that the i_{corr} for zinc alloys and composites increase with increase in the concentration of KOH solution, in the case of pure zinc. The E_{corr} values are affected marginally by the increase in the concentration of KOH solution. The i_{corr} values of Zn-Al and Zn-Al_2O_3 systems are higher than the other systems for all concentrations of KOH solution, while Zn-Mg and Zn-TiO_2 reveal lower i_{corr} values. The i_{corr} values of these electrodes are in conformity with the weight-loss corrosion rate values as reported in Table I.

TABLE I

COMPOSITION, HARDNESS, CORROSION RATE AND MICRO-STRUCTURE OF BINARY ZINC-ALLOYS AND COMPOSITES

Material	Properties		
	Corrosion rate (g/sq cm) 30% KOH	Hardness (BHN)	Microstructure
Pure Zinc	0.32×10^{-3}	76	Equiaxed columnar grains
Zn + Al (3%)	1.39×10^{-3}	713	Circular pattern
Zn + Cd (3%)	0.39×10^{-3}	80	Smaller grains uniformly distributed throughout the matrix
Zn + Mg (3%)	1.33×10^{-3}	107	Segregation of micro-consitituents
Zn + Al_2O_3 (3%)	1.81×10^{-3}	71.5	Uniform distribution of Al_2O_3 particulates in the matrix
Zn + TiO_2 (3%)	0.59×10^{-3}	68.5	Uniform distribution of TiO_2 particulates in the matrix

TABLE II

ELECTROCHEMICAL PROPERTIES OF ZINC ALLOYS AND COMPOSITES IN KOH SOLUTIONS OF VARIOUS CONCENTRATIONS

Material	Open circuit potential (V)			Current at 30mV cathodic over-potential (mA)			Cathodic over-potential at 2mA current (mV)		
	20%	30%	40%	20%	30%	40%	20%	30%	40%
Pure Zinc	−1.541	−1.550	−1.590	4.2	1.6	13.6	30	40	50
Zn+ Al	−1.530	−1.552	−1.580	3.5	7.4	2.6	0	5	25
Zn+Cd	−1.535	−1.552	−1.554	3.0	3.8	4.6	10	20	15
Zn + Mg	−1.597	−1.537	−1.591	6.5	3.1	0.7	5	22	84
Zn + Al_2O_3	−1.563	−1.540	−1.560	3.4	12.0	4.7	0	5	15
Zn+ TiO_2	−1.544	−1.552	−1.594	2.3	2.8	1.1	60	20	65

TABLE III

E_{corr} AND I_{corr} VALUES IN DIFFERENT CONCENTRATIONS OF KOH SOLUTION FOR ZINC AND ITS BINARY ALLOYS AND COMPOSITES

(SCAN RATE = 1mV/SEC)

Material	20% KOH soln.		30% KOH soln.		40% KOH soln.	
	E_{corr} (mV)	i_{corr} (mA/cm²)	E_{corr} (mV)	i_{corr} (mA/cm²)	E_{corr} (mV)	i_{corr} (mA/cm²)
Pure zinc	−1.571	2.25	−1.580	4.40	−1.620	5.75
Zn+Al	−1.560	10.50	−1.582	4.60	−1.610	2.10
Zn+Cd	−1.565	10.70	−1.582	4.80	−1.584	3.40
Zn+Mg	−1.567	5.10	−1.567	2.80	−1.621	0.54
Zn+Al_2O_3	−1.543	17.00	−1.570	8.0	−1.590	4.40
Zn+TiO_2	−1.574	1.90	−1.572	1.70	−1.624	0.80

Fig. 1 gives the polarization curves (anodic and cathodic) of zinc binary alloys and composites in 30% KOH solution. It is seen that the electrodes Zn-Al and Zn-Al_2O_3 polarizes minimum, revealing higher corrosion currents at comparable overpotential values, while those of Zn-Mg and Zn-TiO_2 reveal much higher polarization effect.

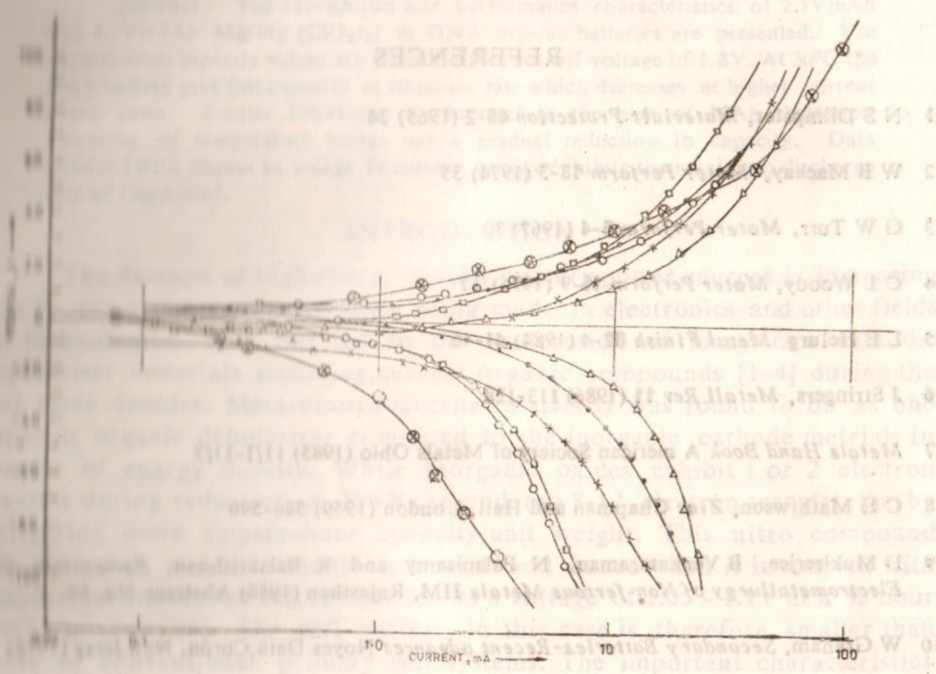

Fig. 1. Anodic and cathodic polarisation of pure zinc and its binary alloys and composites in 30% KOH

⊗ —— ⊗ Pure Zn ● —— ● Zn-Al × —— × Zn-Cd

□ —— □ Zn-Mg △ —— △ Zn-Al_2O_3 ○ —— ○ Zn-TiO_2

It has been further observed after the exposure of these electrodes in 30% KOH solution that addition of Al_2O_3 particulates in zinc-matrix results in uniform corrosion of the surface, while the addition of Al to zinc resutls in a circular pattern, while that of Mg produces segregation. In the case of Zn-Al_2O_3 and Zn-TiO_2 composites, the microstructure reveal uniformly distributed particulate materials in the zinc-matrix.

CONCLUSIONS

Addition of Al and Al_2O_3 to zinc improves the hardness of pure zinc. The corrosion-current of the alloy Zn-Al and composite Zn-Al_2O_3 appear to be higher than other systems like Zn-Mg, Zn-Cd and Zn-TiO_2 in 20%, 30%, and 40% KOH solution. Zinc-Al, Zinc-Al_2O_3 composite electrode after amalgamation with traces of Hg, may be useful in zinc - alkaline batteries.

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