Role of Transition Metal Sulphates in the Corrosion of 1100 Aluminium in Hydrochloric Acid

P.N.S. YADAV† and A.K. SINGH*

Department of Chemistry
Kendriya Vidyalalya-2, O.C.F., Shahjahanpur-242 001, India

The corrosion behaviour of 1100 aluminum in 10% hydrochloric acid has been studied in the presence of transition metal sulphates such as iron. cobalt, nickel, copper and zinc sulphate using galvanostatic and weight loss methods. The concentrations of added metal sulphates were 50, 100 and 500 ppm. It has been observed that iron and zinc sulphates retard the corrosion at all concentrations whereas nickel and copper inhibit the reaction of aluminium in hydrochloric acid up to 100 ppm concentration. Cobalt sulphate accelerates corrosion at all studied concentrations. Polarisation studies reveal the fact that iron and zinc are effective on cathodic sites.

INTRODUCTION

Various metal sulphates have been reported as inhibitor for corrosion of aluminium in hydrochloric acid[1-3]. It has also been reported that copper ions increase the attack of sulphuric acid on aluminium by forming local pits[4]. The present paper deals with the role of transition metal sulphates, *viz.*, iron, cobalt, nickel, copper and zinc sulphates in the corrosion characteristics of aluminium in 10 per cent hydrochloric acid.

EXPERIMENTAL

The composition of aluminium (1100) sheets (24 S.W.G.) supplied by M/s HINDALCO, Renukoot, Sonbhadra (India) was Si = 0.130, Fe = 0.520, Mn = 0.068, Mg = 0.021, Cu = 0.010 and Al = 99.251%. Preparation, testing and cleaning procedures for specimens were the same as described elsewhere[5]. All the chemicals used were of AR grade and solutions were prepared in triply distilled water. The rectangular specimens of size $3'' \times 2''$ were completely immersed in 300 mL of of test solution in 500 mL capacity corning glass beakers. After 2 h exposure period the corrosion product was removed by dipping the aluminium sulphate in 70% nitric acid for 5 min followed by mechanical rubbing with a rubber stopper. Galvanostatic studies were carried out using the specimens with a side tag of length 4 cm having a working area of 2 cm^2 with 100 mL test solution in pyrex glass cell. The specimen is made either the anode or cathode and the change in potential was measured against SCE using precision potentiometer and a galvanometer. Liquid junction potential was minimised by keeping the tip of salt bridge very close to the aluminium surface. The procedure described by Gatos[6] was employed in the present investigation. Weight loss as well as galvanostatic experiments were carried out at 50, 100 and 500 ppm concentrations

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†Department of Chemistry, Kendriya Vidyalaya, Mughalsarai, Chandauli, India.

of transition metal sulphates in 10% hydrochloric acid in an electronically controlled air thermostat at a 35 ± 0.2°C.

TABLE-1

RELATIVE PERCENTAGE LOSS (RPL) OF 1100 ALUMINIUM IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF TRANSITION METAL SULPHATES AT 35 ± 0.2°C

Immersion period = 2 h

Composition of solution	Relative percentage loss		Steady state corrosion potential (mV)
	By weight loss method	Galvanostatic method	
10% HCl	100	100	802
10% HCl + NiSO$_4$			
50 ppm	32.33	35.24	802
100 ppm	49.98	52.45	806
500 ppm	165.20	160.23	801
10% HCl + FeSO$_4$			
50 ppm	32.37	35.42	801
100 ppm	35.27	40.22	802
500 ppm	39.67	46.34	795
10% HCl + ZnSO$_4$			
50 ppm	43.24	52.33	808
100 ppm	43.11	52.40	806
500 ppm	38.51	46.25	808
10% HCl + CuSO$_4$			
50 ppm	39.08	43.28	798
100 ppm	65.65	70.04	802
500 ppm	146.33	140.32	790
10% HCl + CoSO$_4$			
50 ppm	176.77	174.54	800
100 ppm	178.01	174.80	802
500 ppm	185.04	183.12	800

RESULTS AND DISCUSSION

The relative percentage loss shown in Table-1 was calculated using the relation.

$$RPL = a/b \times 100$$

For galvanostatic studies:

a = corrosion current in 10 per cent hydrochloric acid in the presence of transition metal sulphate.

b = corrosion current in 10 per cent hydrochloric acid.

For weight loss studies:

    a = weight loss in 10 per cent hydrochloric acid in the presence of transition
        metal sulphate.

    b = weight loss in 10 per cent hydrochloric acid.

    It is seen from Table-1 that in the case of zinc sulphate relative percentage loss decreases with concentration. In all other metal sulphates corrosion rate of 1100 aluminium increases by increasing concentration of transition metal ions. Cobalt sulphate shows a vulnerable effect and in the presence of all concentration of this sulphate it becomes approximately twice as compared to the 10% hydrochloric acid. The corrosion of aluminium is of pitting type in the presence of chloride ions. The pit formation on the aluminium surface in the presence of chloride ions has been attributed to the disruption of the protective oxide film present on aluminium surface by the chloride ions forming a metastable $AlCl_4^-$ complex. It has been reported that $AlCl_4^-$ is hydrolysed to $Al_2O_3 \cdot 3H_2O$[7] and above mechanism of different chloride complexes, *e.g.*, $2AlOCl$, $Al(OH)_2Cl$, $Al(OH)Cl_2$ etc., may also be formed by reacting oxide film and chloride ions. Hence it may be suggested that chloride ion which disrupts the formation of protective oxide film is a cause of initial pitting attack on aluminium.
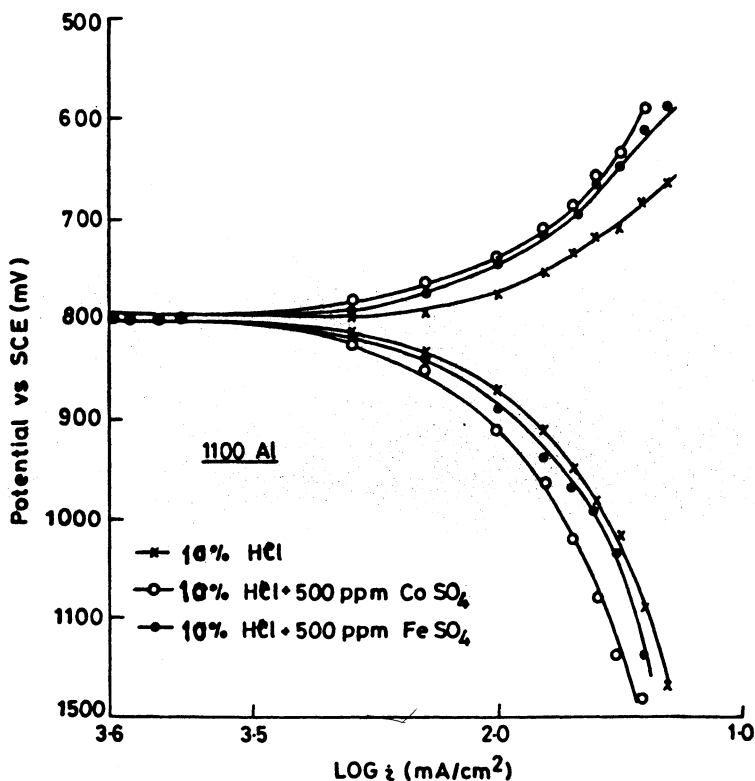

Fig. 1. Effect of current density on the cathodic and anodic potential

It was observed during weight loss experiment that a porous metallic copper film was deposited in spongy form on aluminium surface. It may be suggested that when copper is in the solution it is more noble than aluminium. Consequently it will plate out on the surface of aluminium. Thus a local galvanic cell with the aluminium as anode can be created. It is due to this reason that the corrosion rate of aluminium increases. The deposited metallic copper may act as active site for cathodic reaction because of the lower hydrogen overvoltage on copper as compared to that of aluminium[8, 9]. The same mechanism may also be proposed for the enhanced corrosion rate of aluminium at 500 ppm $NiSO_4$ and at all concentrations of cobalt sulphate.

The galvanostatic measurements were shown in Fig. 1. The plots for 10% hydrochloric acid and for two metal sulphates are given. Polarisation studies show that the corrosion of aluminium is inhibited by metal sulphate (except copper and cobalt) due to their action on local cathodes. No correlation between the values of steady state corrosion potential and corrosion rate could be obtained.

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