IMPEDANCE STUDY OF ALUMINIUM SURFACE SUBJECTED TO VARIOUS SURFACE TREATMENTS

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Aluminium surface has been subjected to various treatments like electropolishing, anodising, electropolishing and anodising and chemical etching. Impedance data have been obtained for the above treatments by exposing the samples in 3% sodium chloride for various timings. Data obtained have been analysed and explained with the help of an equivalent circuit. Electropolished and anodised aluminium surface is having better corrosion resistance than bare aluminium, chemically treated and anodised and electropolished aluminium.

Keywords: Aluminium, electrochemical impedance spectroscopy, anodic films

INTRODUCTION

Electropolishing is a controlled electrochemical operation to achieve two distinct purposes namely a very high luster and smoothness over a metal surface by the removal of a thin surface layer [1-2]. This is applicable in instances where mechanical polishing is not practical or a superior finish is required. It is best suited where dimensional tolerance is very stringent [3-4]. Besides, electrodeposits over electropolished surface are more adherent than that over mechanically polished surface. Moreover metallurgically clean surface, free from foreign inclusions due to cold working and abrasive particles can be obtained with ease. Because of these distinct advantages the process is gaining importance in commercial applications.

Considerable amount of work has been carried out for electropolishing of aluminium and its alloys [4-8]. Mostly the electropolishing bath contains a mixture of concentrated phosphoric acid and sulphuric acid with an oxidizing agent like chromic acid or nitric acid [9].

EXPERIMENTAL

The bath is prepared by adding chromic anhydride to phosphoric acid and dissolved by warming if necessary. Then the solution was cooled and sulphuric acid was added slowly with stirring.

Aluminium panels of size 150 mm (100 mm was provided with leads and the sides of the panels were ground to remove the burrs. Then the panels were mechanically polished to smoothen the surface. The buffing compounds adhering over the surface were degreased with acetone. The panels were then deoxidized and washed in warm tap water and dried.

Composition of bath

Orthophosphoric acid	60% v/v
Sulphuric Acid	35% v/v
Chromic Acid	6% v/v
Water	5% v/v
Temperature	343-348 K

A to and fro movement was given to the aluminium panel to be electropolished with a stroke distance of 100 mm to 150 mm and stroke rate of 12 to 16 strokes per minute to avoid streak formation on the surface of the aluminium panel. A current density of 10 A/dm^2 was impressed for a period of 10 minutes and voltage raised upto 25-35 V. Then the panels were removed from the electrical circuit and immediately washed with water. Before anodizing the electropolished panel was again washed in tap water and finally rinsed in demineralised water. The panel was then anodized at a temperature of 298 ± 2 K in 7% V/V sulphuric acid at a current density of 1.2 A/dm^2 for 10 minutes.
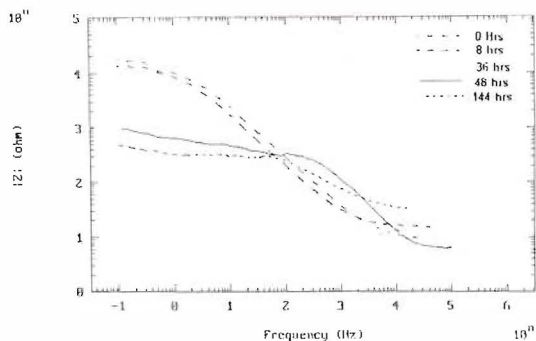
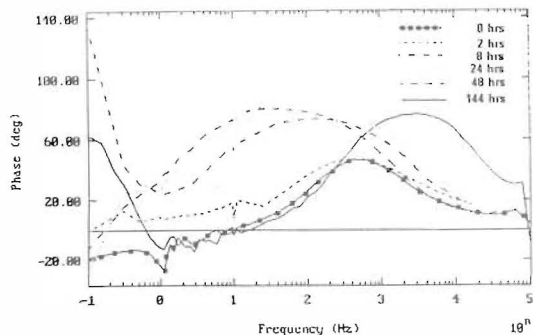*Fig. 1a: Bode Impedance plot for electropolished aluminium with exposure to NaCl for various hours*

Fig1b: Bode Phase angle plot for electropolished aluminium with exposure to NaCl for various hours

Panels were also prepared 1) Degreasing the bare aluminium; 2) Chemically treating the metal surface in phosphatic reagent; 3) Chemically treating the sample in sodium hydroxide solution; 4) Mechanically polished and electropolished

The solution compositions and operating conditions used for the chemical treatments are as follows.

For solution 1

Sodium Carbonate	20 gpl
Trisodium Phosphate	5 gpl
Temperature	333 K
Duration	3 minutes
Desmutting	30 % v/v HNO_3
Desmutting time	2 minutes

For solution 2

Sodium hydroxide	50 gpl
Sodium gluconate	0.5 gpl
Temperature	313 K
Duration	5 minutes
Desmutting	30 % v/v HNO_3
Temperature	303 K
Duration	3 minutes

The impedance spectra were obtained using a Model398 Impedance Analyzer of the Princeton Applied Research (EG & G Instruments Inc). The spectra were analyzed in the frequency range of 100 mHz to 100 KHz. The electropolished, electropolished and anodized samples were then exposed to NaCl media for varying hours of exposure

and the impedance spectra of these samples were also analyzed. The circuit fit model was obtained using the non-linear least square method.

The AC impedance measurement has become a powerful tool for the investigation of aluminium oxide films as well as the electrochemical processes occuring at the electrolyte interface [10]. The impedance data are commonly discussed in terms of various electrical equivalent circuits consisting of series and parallel combination of resistances and capacitances [11-16]

RESULTS AND DISCUSSION

Figs. 1a and 1b are the impedance diagrams (Bode impedance plot and Bode phase angle plot) for various immersion time (in hours) after electropolishing while Figs. 2a and 2b are the same plots for the electropolished and anodized samples. It is clear from the graphs that the corrosion resistance in the case of the electropolished and anodized samples is more compared to electropolished samples. The anodized layer consists of barrier and porous layers successively.Resistance and capacitance values calculated from the diagrams (Bode as well as Nyquist) have been tabulated (Tables I and II). These values refer to the composite capacitances and do not reflect the individual properties of each layer. The bode plots do not contain distinct regions corresponding to each layer and in most cases they overlap. However the capacitance increase indicates the formation of pits or with intergranular corrosion. The maximum capacitance in our case was 112.14 $\mu F/cm^2$ whereas in the case of alloys especially for 2289 (T87) alloy it was 160 $\mu F/cm^2$ after exposure to 144
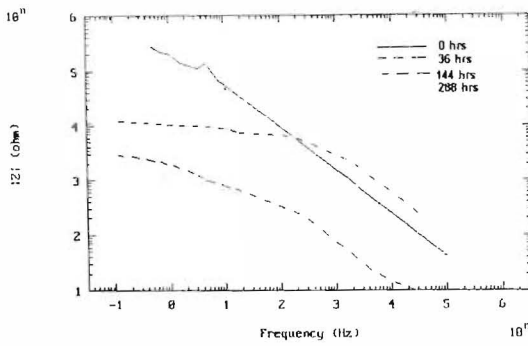
Fig2a: Bode impedance plot for electropolished and anodised aluminium with exposure to Nacl for various hours
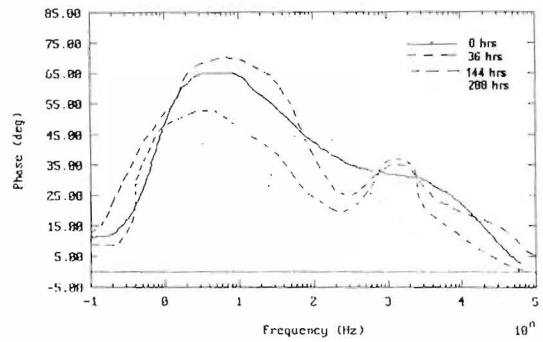

Fig. 2b: Bode phase angle plot for electropolished and anodised aluminium with exposure to NaCl for various hours

hours which is five times lesser than that observed for 2024 alloy. This indicates that a marked difference in the corrosion texture can be expected on this electropolished and anodised aluminium. And even when this is compared with electropolished aluminium from the tables (112.14 $\mu F/cm^2$ and 141.364 $\mu F/cm^2$ electropolished and anodised aluminium will have a marked difference in the corrosion texture as compared with electropolished aluminium. Corrosion texture of electropolished and anodised aluminium is better than bare aluminium, chemically treated aluminium and anodised and electropolished aluminium. The equivalent circuit for the electropolished and anodised samples are given in Schemes 1 and 2. It is known that the capacitance of a

parallel plate capacitor with a dielectric constant ε between its plates is

$$C = \varepsilon \ \varepsilon_0 \frac{A}{d}$$

where ε_0 is the permittivity of empty space , A is the area of the plates and d is the distance between the plates.
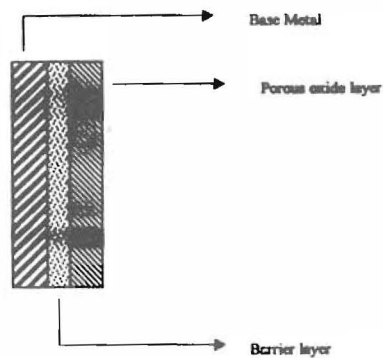
TABLE I: Electropolishing and anodising

Time of exposure (hrs)	R (kΩ)	C (μF)
0	169.500	7.2728
36	6.494	21.5790
144	2.334	81.3520
288	1.092	112.1400

TABLE II: Electropolishing

Time of exposure (hrs)	R (kΩ)	C (μF)
0	10.6300	6.508
8	9.4130	7.405
36	1.1700	31.385
48	0.3580	81.846
144	0.0758	141.364
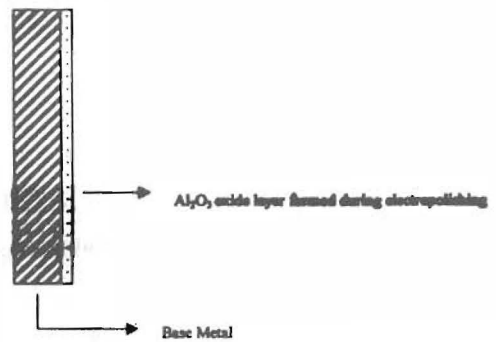
Scheme 1: Layer diagram of the anodised surface

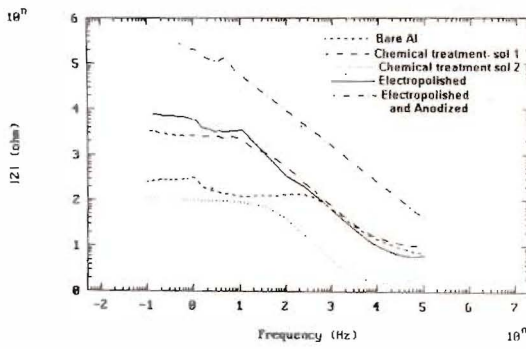*Scheme 2: Equivalent circuit model used for fitting the experimental value*

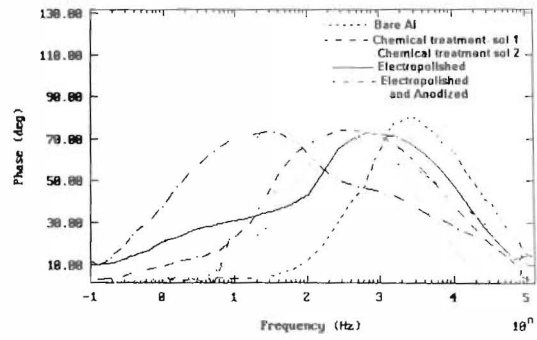*Fig. 3a: Bode impedance plot for various surface treated aluminium*

Fig. 3b: Bode phase angle plot for various surface treated aluminium

The effective dielectric constant of the porous layer has been taken as

$$\varepsilon = 36$$

The individual capacitances can be obtained from the fit model and were found to be 2.36×10^{-6} F/cm^2 and 3.36×10^{-8} F/cm^2. The thickness of the barrier and the porous layer were calculated to be 41 Å and 0.945 µm respectively. For conventionally anodized Al 6061 $Cb = 1.04 \times 10^{-6}$ F/cm^2 and $Cp = 2.94 \times 10^{-9}$ F/cm^2, the thickness was calculated and reported to be 86 Å and for the porous layer 17 µm respectively. The difference in the thickness may be attributed to the low anodising time in the case of electropolished and anodised samples as the principal requirement in these cases is the reflectance which drops as the thickness of the oxide layer builds up.

Figs. 3a and 3b show the impedance diagrams (Bode impedance and Bode phase angle plots) for the bare Al, chemically treated Al, electroplished, electropolished & anodised aluminium. These diagrams clearly indicate that electropolished and anodised Al seems to offer better corrosion resistance compared to electropolished alone or anodised alone or chemically treated or bare aluminium. This is understandable as when bare aluminium is exposed to chloride ions the attack of the ions are much more easier than on a sample treated with phosphate containing treating solution. The phosphate ions form a passive layer and effectively reduce adsorption of chloride ions on the surface. In the case of samples treated with sodium hydroxide solution the thin oxide layer that is formed by exposure to atmosphere on the bare Al is stripped off along with certain

amount of the base metal also. Hence the chloride ions can directly attack the base metal. The drastic reduction in the impedance curve can be attributed to this process.

In the case of electropolished sample the dissolution of metal is found to be uniform and the porous surface oxide layer that is formed (Al_2O_3) is smooth. This surface layer acts as the barrier for against chloride penetration. But the anodized sample offers the best corrosion resistance due to the two-layer formation. The electropolishing prior to anodizing ensures that the barrier layer formed is smooth and defect free which offers better corrosion resistance in addition to the protective porous layer formed during anodising.

The damage function for the samples exposed to corrosive media has been calculated using the formula

TABLE III: Damage function values for both electropolished and electropolished and anodised samples

Time of exposure (hrs)	Electropolished sample	Electropolished and anodised sample
0	----	-----
8	0.046	ND
36	ND	0.91
48	1.16	ND
144	1.714	1.545
288	ND	1.887

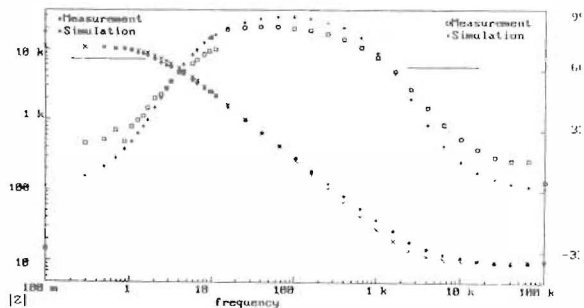Fig. 4a: Simulated and experimental Bode impedance plot for electropolished and anodised aluminium

Fig. 4b: Simulated and experimental Bode Impedance plot for electropolished aluminium

$$D = \log\left(\frac{Z_0}{Z_t}\right)_{t = 0.1 \text{ Hz}}$$

for different exposure durations. The values have been tabulated in Table III. From the table, it is seen that the damage function for electropolished and anodised samples after exposure to 144 hours is low compared to the same electropolished sample. In the other exposure times it is not able to compare due to inaccessible results from the impedance curve at 0.1 Hz..

Figs. 4a and 4b are depicting the experimental values obtained for electropolished and anodised and electropolished aluminium and simulated values assuming the schemes 1 and 2. Electropolished and anodised aluminium has got better corrosion resistance than electropolished aluminium is evident from Figs. 3a and 3b. In the case of electropolished samples only one layer will be present whereas electropolished and anodised samples there will be two layers(viz) a porous outer layer and below which a uniformly covered thin oxide layer . This assumption fits very well with experimental and simulated values.

CONCLUSION

Electropolished and anodised samples of aluminium has got more corrosion resistance compared to electropolished aluminium alone with reaspect to chloride ion attack. Electropolished and anodised Aluminium offers better corrosion resistance compared to electropolished alone or anodised alone or chemically treated or bare aluminium.
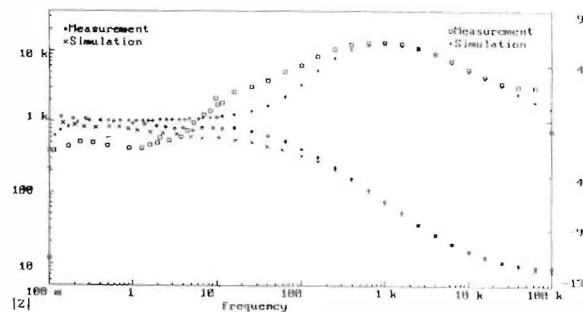
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