

Anodisation of Aluminium in Aqueous Sodium Oxalate and Sodium Sulphate Media

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Abstract

An investigation was conducted on the anodisation of commercial grade aluminium in aqueous sodium sulphate and sodium oxalate solutions. The parameters investigated were anodisation potential and electrolyte composition. Degree of anodisation was evaluated by visual observation of the anodised surface, analyses of current-concentration graphs at constant potential and current-potential characteristics, and measurement of corrosion rate of the anodised surface. Anodisation potential played an important role on the degree of anodisation. The optimum potential was 400 mV and 800 mV wrt saturated Ag/AgCl (SSE) reference electrode for sodium sulphate and sodium oxalate solutions respectively. Below and above the optimum potential poor anodisation was due to insufficient production of Al^{3+} to form anodic film and surface breakdown respectively. Anodisation increased with the increase of oxalate concentration. Sulphate concentration was less effective on the degree of anodisation. Between the two electrolytes sodium oxalate was more suitable than sodium sulphate for aluminium anodisation.

Introduction

Anodisation is an important technique for the formation of barrier oxide film on the substrate surface. It improves hardness and abrasion and corrosion resistance. Only Al, Ta, Ti, Nb, Zr and Si, among all metals, are suitable for anodisation [1]. The parameters which influence anodisation are concentration and pH of the electrolyte, current density, applied anodic potential, duration of anodisation and temperature [2]. The condition for anodisation of aluminium influences many surface properties such as hardness, absorption ability, electronic property and adhesion ability [3, 4]

Aluminium is the most widely used metal after steel and copper. It is also the cheapest among all anodisable metals. The oldest and perhaps the most general application of anodisation is the protection of Al and its alloys used in aircraft construction. It is applied for Al and its alloy used in window frames, refrigeration ice trays, machine parts, pistons and reflectors etc. Anodised Al is

also used in electronics industry. The unidirectional current carrying characteristics of the anodised film has made possible the Al electrolytic condenser and rectifier. The porous anodic oxide film has application in ultrafiltration or reverse osmosis usages as well as in nanotechnology to produce nanowires and nanotables [5].

K. Watanabe et al [6] studied the formation of Al-Zr composite oxide films on Al by sol-gel coating and anodising. W. J. Bernard et al [7] investigated the formation of anodic oxide film on Al in aqueous borate solution. It has been reported that the condition of anodisation has substantial influence on the properties of anodic oxide film on Al. G. E. Thompson [9] investigated anodisation of Al in sulphuric acid media and observed irregular film growth surrounding intermetallic particles. Zahavi et al [10] observed a steady state porous anodic film growth in the vicinity of intermetallic particles on Al-Fe alloys.

In the present work anodisation of aluminium was carried out in aqueous sodium oxalate and sodium sulphate solutions using constant potential anodisation technique.

Experimental

One mm thick and 3 cm x 5 cm commercial grade aluminium sheet (composition-99% Al, 0.20% Cu, 0.25-0.60% Fe, 0.15 to 0.44% Si [11]) was used in the experiment after mechanical polishing on a polishing wheel followed by chemical polishing using phosphoric acid and nitric acid mixture. Anodisation was carried out at constant potential technique using a potentiostat [Model DT11005 HI-TEK, INSTRUMENTS, ENGLAND) against satd. Ag/AgCl (SSE) reference electrode and Pt foil as the counter electrode. The current change due to anodisation was followed by a digital multimeter (model 3236 DIGITAL HI TESTER, HOIKI, JAPAN). Aqueous solution of 1 % to 3.4 % $\text{Na}_2(\text{COO})$ and 1% to 5 % Na_2SO_4 was prepared from analytical grade reagents. The applied potential ranges were 0 to 1.2 V for oxalate and 0 to 1.6 V for sulphate solutions wrt SSE reference electrode for 10, 20 and 30 minutes durations. Corrosion test of anodised specimen was made in aggressive chloride media by weight loss method based on spectrophotometric analysis.

Results and Discussions

Fig. 1 represents the relationship between the anodisation current and sodium oxalate concentration after 10, 20 and 30 minutes of anodisation at 400 mV wrt SSE anodic potential. Anodisation current decreased slowly with the increase of oxalate concentration up to 3% and then steeply decreased to a minimum at 3.4% (max. sodium oxalate conc.).

Anodisation produces non-conductive, honeycomb aluminium oxide on the aluminium surface. In this situation film thickening only takes place by electrolytic conduction through the honeycomb pores of the oxide. Decrease of anodic current indicates film thickening process. The figure shows that increased film thickening was produced for anodisation in 3.4% sodium oxalate solution. Anodisation time does not have significant role on this film thickening process for 10, 20, and 30 minutes anodisation. However, 10 minutes anodisation is preferable for 3.4% sodium oxalate solution.

Fig.2 shows the effect of sodium sulphate concentration on anodic current at 400mV constant applied anodic potential. Concentration and time both have less effect on the anodisation current, and anodisation current is considerably higher than that in sodium oxalate solution. A decrease of anodisation current is observed for 5% sodium sulphate solution. This suggests more effectiveness of sodium oxalate solution over sodium sulphate solution for anodisation of Al. The dependence of anodisation on the anodic potential is shown in Fig. 3 for 3.4% sodium oxalate solution. The results for 10, 20 and 30 minutes anodisation have minimum anodisation current at 400 mV wrt SSE applied anodic potential. Thus, this is the optimum potential for anodisation in sodium oxalate solution. High current at higher anodisation potential may be due to higher rate of surface breakdown.

The results also show minimum anodisation current for 10 minutes of anodisation among the three anodisation durations. From the dependence of anodisation current on the anodisation potential graphs in sulphate media, as shown in Fig. 4, no valley was observed up to 1500 mV wrt SSE. Also duration of anodisation does not have visible effect on the anodisation current in this potential range. However, interference colour was observed on this surface after anodisation by visual observation. This is an indication of non-uniform surface film formation during anodisation. All of these suggest that there is no good anodisation potential for sodium sulphate media and the anodisation does not take place uniformly over the whole Al surface.

For better understanding about the anodic film formation due to anodisation corrosion tests of anodised Al was performed after 3 days immersion in aqueous solution containing 500 ppm chloride at pH 8. The results after anodisation in sodium oxalate and sodium sulphate solutions are shown in Figs. 5 and 6 respectively. In sodium oxalate anodisation the corrosion rate was almost zero when anodisation was made up to 400 mV for 2% sodium oxalate solution. In the case of 3% and 3.4% sodium oxalate solutions the rate was zero up to 600 mV anodisation potential. The best corrosion resistance was observed for anodisation in 3.4% sodium oxalate solution.

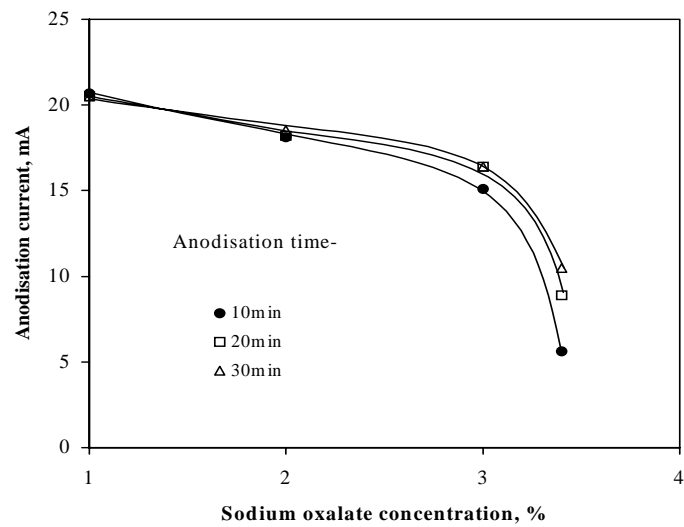


Fig. 1: Effect of sodium oxalate const. on the anodisation current at 400 mV const. anodisation potential, Surface area, 0.25 dm^2 ; temperature, $(30 \pm 2)^\circ\text{C}$

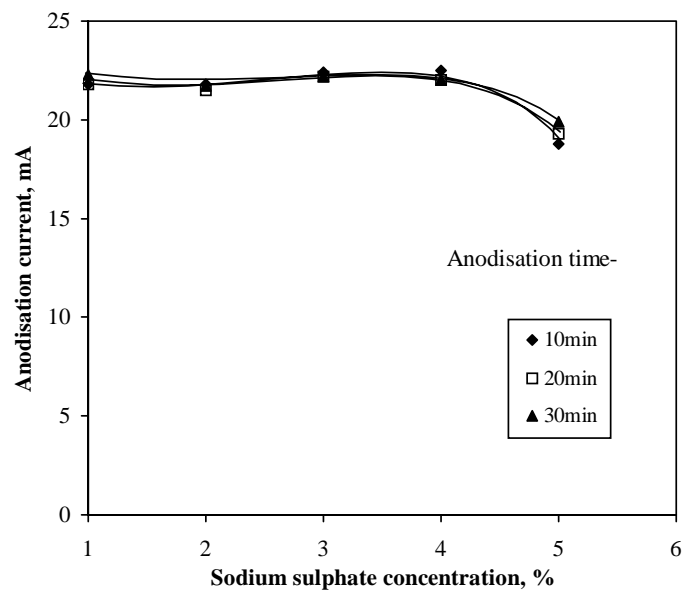


Fig. 2: Effect of sodium sulphate const. on the anodisation current at 400 mV const. anodisation potential, Surface area, 0.25 dm^2 ; temperature, $(30 \pm 2)^\circ\text{C}$.

However, significant corrosion was observed for all anodisation potentials when anodisation was carried out in 1% sodium oxalate solution. This substantiates the earlier result of the best anodisation from 3.4% sodium oxalate solution at 400 mV wrt SSE. Fig. 6 shows that the corrosion rate of the anodised Al decreases with the increase of anodisation potential up to 800 mV for anodisation at all concentrations of sodium sulphate between 2% to 5%. Afterwards the anodisation current increased. Like sodium oxalate solution the higher concentration of sodium sulphate has a beneficial effect in this case. However, unlike anodisation in sodium oxalate solution significant corrosion was observed in sodium sulphate solution. For anodisation in latter solution pitting types of corrosion attack was observed after 3 days immersion in chloride solution. The number of pits of the non- anodised surface was on an average 6 per cm², and the average diameter was between 0.1 mm to 0.5 mm. On the other hand sodium sulphate anodised surface had 1.5 pits per cm² with a similar diameter to that of the non-anodised surface. Pitting type corrosion attack normally takes place at defects of the surface. This suggests that anodisation in sulphate media is not good for aluminium because of non-uniform and poor aluminium oxide film formation.

Conclusion

The following are conclusions of this work:

1. Anodisation of aluminium in aqueous sodium sulphate solution produces non-uniform aluminium oxide on the surface, which is vulnerable to the pitting type corrosion attack in aggressive chloride media.
2. In sodium oxalate media the best anodisation is obtained at 400 mV wrt SSE anodic potential. At higher potential the anodisation is not good. So potential control is an important factor for good anodisation.
3. Anodisation in 3.4% sodium oxalate solution (maximum conc. used in the work) produces very good and uniform anodic aluminium oxide film on the surface.
4. Anodisation time after 10 minutes is less effective on the anodisation process in sodium oxalate solution.

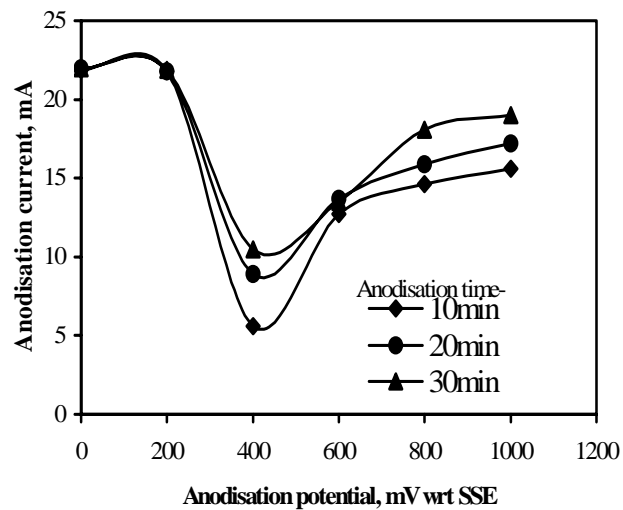


Fig. 3. Effect of anodisation potential on the anodisation current in 3% sodium oxalate solution. Surface area, 0.25 dm^2 ; temperature $(30 \pm 2)^\circ\text{C}$

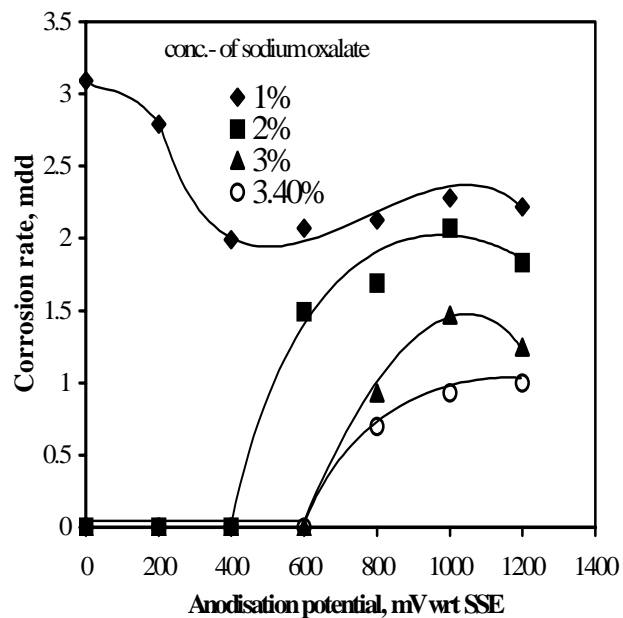


Fig. 4. Effect of anodisation potential on the corrosion rate in 500 ppm chloride medium at pH 8 for sodium oxalate anodisation. Soaking period, 3 days; surface area, 0.25 dm^2 ; temperature, $(30 \pm 2)^\circ\text{C}$.

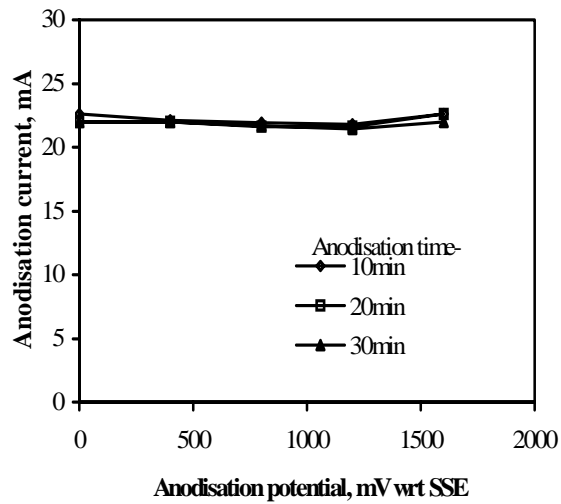


Fig. 5. Effect of anodisation potential on the anodisation current for sodium sulphate anodisation. Surface area, 0.25 dm^2 ; temperature, $(30 \pm 2)^\circ\text{C}$

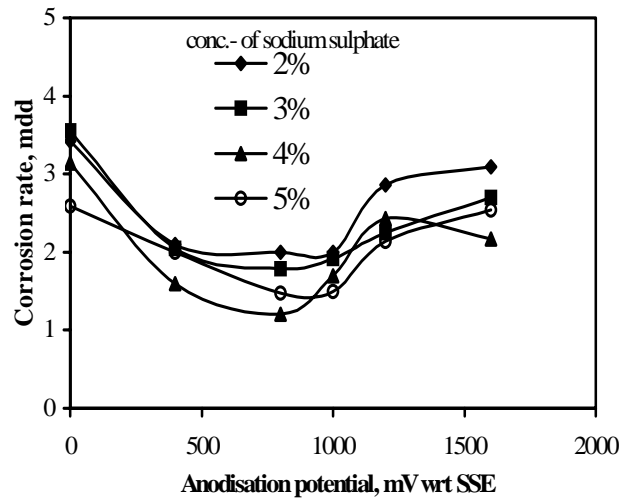


Fig. 6: Effect of anodisation potential on the corrosion rate in 500 ppm chloride medium at pH 8 for sodium sulphate anodisation. Soaking period, 3 days; surface area, 0.25 dm^2 ; temperature, $(30 \pm 2)^\circ\text{C}$.

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