JOURNAL OF APPLIED ELECTROCHEMISTRY 11 (1981) 253–259

Electrochemical machining as a method of preparing grained aluminium surfaces

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Received 25 October 1977; in revised form 1 August 1980

Aluminium, usually in sheet form, is often subjected to a graining process prior to further treatment. This is normally a batchwise acid pickle. A study was carried out on a laboratory scale to show that electrochemical machining can be used to produce grained aluminium surfaces by a continuous, high-rate process using non-acid electrolytes.

1. Introduction

There is widespread and growing demand for aluminium sheets to be treated to produce a real surface area which is 10 to 50 times the apparent surface area. This need arises in two major fields of modern technology: in the electrolytic capacitor field [1] and in the preparation of lithographic printing plates. This demand has prompted a search for methods whereby this 'graining' process may be accelerated. Existing techniques use electroetching which requires an etching time of up to several minutes, the rate determining process being the diffusion of reaction product away from the dissolving anodic aluminium sheet. The electrolyte used is usually an acidic aqueous solution, which raises problems of reduction in electrolyte lifetime due to dissolved metal in solution. The aim of the present work was to solve these problems using existing experience in the field of electrochemical machining.

Though the aluminium is used for quite different purposes by each industry, the surface-finish requirements are similar. The surface must be:

(a) homogeneous (in terms of 'pore size' distribution),

(b) very reproducible,

(c) mechanically robust, so that it can withstand further treatment without damage.

It is usual to anodize the sheet after graining, to form an oxide film which can act, for example, as the ink reservoir on a printing plate. The homogeneous nature of aluminium sheet etched by conventional processes in HCl solution is shown in Fig. 1. It was hoped to reproduce as near as possible this surface finish.

Electrochemical machining (ECM) is performed by the passage of high currents across a narrow inter-electrode gap in an electrolytic cell, in which the workpiece is made the anode. Metal removal is achieved solely by electrolytic dissolution of the workpiece. In this latter respect, ECM would not act very differently from conventional electrolytic graining processes, but advantages may accrue from the fact that the small inter-electrode gap used in ECM will lead to smaller *iR* drops in potential, and hence provide capacity to use higher currents. Also, as will be discussed later, ECM can be performed using neutral salt solutions rather than HCl or HNO_3, which are usually used in conventional graining baths.

The ECM process may be automated easily, by moving the anode and cathode relative to each other. ECM methods can produce a wide range of surface textures on metals, ranging from polished to deep pitting [2]. The finish obtained can be varied by controlling:

(a) the potential at which anodic dissolution is occurring (and hence the current density flowing through the anode);

(b) the composition of the electrolyte, and

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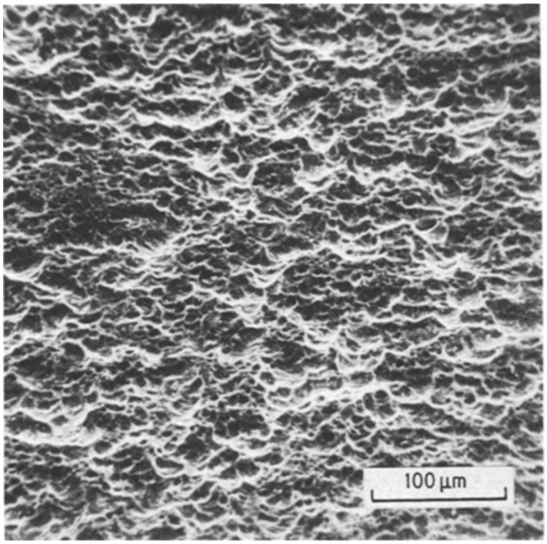

Fig. 1. Commercially produced grained Al sheet.

(c) the electrolyte flow conditions.

ECM is therefore potentially applicable to continuous graining of aluminium sheet at higher production rates than currently available. The programme of experiments reported here was designed to show this applicability. The experiments showed that a satisfactory surface finish can be produced by controlling the variables listed below. Conditions were varied so that their effects on the surface could be assessed by scanning electron microscopy.

2. Cell design

Two cells were used in this study. The smaller of these was a simple, rigid cell built from perspex and steel, and had a fixed cathode and removable anode. The aluminium samples (50 mm x 12 mm) were attached to this anode, care being taken to ensure good electrical contact. The gap between the two plane electrodes was set before each experiment, and the electrolyte was pumped lengthwise along this gap. By using this cell it was possible to examine the effects of inter-electrode gap, current density, time of machining, electrolyte flow rate and temperature.

The second cell used a fixed anode, past which moved a cathode at a speed which could be varied up to a maximum of 25 mm min^{-1}. This gave a shortest possible residence time (i.e. time of point on anode opposite cathode in the cell) of 22 s for the 9 mm deep cathode used in the experiments. The geometry in the plane of cathode movement was fixed rigidly, to maintain a constant inter-electrode gap. The effective cathode dimensions were 9 mm x 115 mm, and the area of aluminium machined in each sweep of cathode past anode was 205 mm x 115 mm. The cathode (Fig. 2) had the electrolyte delivered through a slit (1.5 mm x 110 mm). Extreme care was needed, especially in keeping the slit from becoming partially blocked and in sample pre-treatment, as both of these factors caused 'flow marks' due to uneven electrochemical attack.

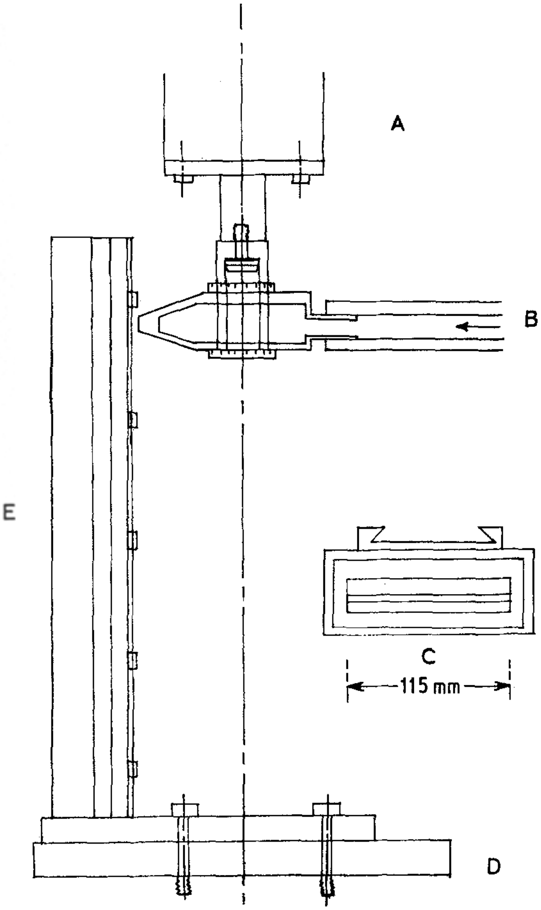

Fig. 2. The travelling-cathode apparatus. A, ram; B, electrolyte flow path; C, end view of the cathode; D, stainless steel bed; E, rigid welded support.

3. Experiments

The aluminium sheets used in this study had been

Table 1. Experiments using the small cell

(a) Electrolyte	2.7 M NaCl
Gap	0.5 mm
Flow rates	1.7 to 6.2 $dm^3 min^{-1}$
Machining times	5 to 30 s
Currents	10, 40, 50, 100, 150 A
Temperature	288 ± 1 K
(b) Electrolytes	2.7 M NaCl; 3.5 M $NaClO_3$
Gaps	0.5, 1.0, 2.0 mm
Flow rates	1.2, 4.1, 6.2 $dm^3 min^{-1}$
Currents	15, 60, 100 A
Machining time	15 s
Temperature	288 ± 1 K
(c) Electrolytes	2.7 M NaCl; 3.5 M $NaClO_3$
Gap	1.0 mm
Flow rates	1.2, 6.2 $dm^3 min^{-1}$
Currents	15, 60 A
Machining time	15 s
Temperature	313 ± 1 K
(d) Electrolytes	0.9 M NaCl; 1.4 M HCl; 0.8 M HNO_3
Gap	1.0 mm
Flow rates	1.2, 6.2 $dm^3 min^{-1}$
Currents	15, 30 A
Machining time	15 s
Temperature	288 ± 1 K

rolled to a thickness of 0.5 mm, and were of 99.7% purity. The chemicals used in preparation of electrolytes were of commercial or L.R. grade. Table 1 summarizes the experiments using the small cell in which variations of temperature, current density, electrolyte and electrolyte flow rate, time of machining and inter-electrode gap were examined with respect to their influence on surface finish. Following the preliminary studies in (a), study (b) was made at a fixed machining time and temperature. The effect of increased temperature was studied in part (c) and in part (d) the effect of using acid electrolytes was examined. All the samples were pretreated by immersion for 120 s in 0.5 M NaOH at 308 K.

Further experiments were performed with the larger cell. This cell was designed to resemble more closely the likely cell conditions to be used in industry in having the aluminium and the cathode move relative to each other. The effect of orientation of the rolling direction with respect to the machining direction was examined, and was found to be very small. Since, in mass production, machining would be possible only along the rolling direction, almost all samples were prepared in this configuration. The effect of wire-brushing before machining, which was considered as a possible industrial pretreatment to break up existing oxide layers, was examined. This process was found to have little beneficial effect; it was, in fact, injurious to the surface finish obtained using nitrate-based electrolytes, in that the metal removal was so small that the brush marks were not removed.

Hunter [3] has described the process of preparation of aluminium foil for use in capacitor manufacture, and has explained the necessity of solution pretreatment of aluminium (using NaOH or some similar solution) before electrolytic etching. This is performed primarily to remove most of the naturally-formed oxide film existing on the aluminium sheet. In the present study, samples were either totally degreased by immersion in trichloroethylene (C_2HCl_3) before machining, or treated by immersion in 0.5 M NaOH (which might be expected both to degrease the specimen and remove oxide films, as suggested by Hunter [3]). There was a definite detrimental effect on surface finish if the time of immersion in NaOH solution exceeded 180 s, and the usual time used was 120 s. This effect took the form of enhanced deep-pit formation, rather than uniform graining of the surface, during the machining process. No similar problems were encountered using trichloroethylene.

Table 2 summarizes the large number of experiments performed using the moving cell assembly. The $NaNO_3$/NaCl system appeared to be the most promising of the electrolytes studied, and so was used for further experiments using larger electrode separation (i.e. 2.5, 6 and 12.5 mm). These were examined because it was felt that there would be problems during industrial-scale processes in maintaining the 0.8 mm separations which had been used earlier. Throughout the experiments with the larger cell, the area opposite the cathode at the time of commencement of machining was observed to have a much more homogeneous surface finish than the rest of the sheet. This effect was totally reproducible, and was assumed to be due to potential variations at the anode during the period whilst the electrodes were polarizing. Cell voltages and aluminium anode potentials were measured (with respect to a saturated calomel electrode introduced to the machining cell) during this period, and recorded. The electrolyte used for

Table 2. Experiments using the travelling-cathode cell. Current density 30 kA m^{-2}; cathode speed 25 mm min^{-1}

Sample	*Pretreatment*	*Electrolyte*	*Flow rate* (dm^3 min^{-1})	*Temperature* (K)	*Gap* (mm)	*Observation*
1	a	0.9 M NaCl	8	288	1	Angular pitting
2	b		8	288	0.8	Angular pitting
3	b	3.5 M $NaClO_3$	6	288	0.8	Angular pitting
4	b	2.4 M $NaNO_3$ + 0.8 M HNO_3	11	288	0.8	Good pitting but patchy
5	c		11	288	0.8	Macroscopic pitting
6	d		11	288	0.8	Approaching the required topography
7	b	2.4 M $NaNO_3$	11	288	0.8	Macroscopic pitting; some original surface remaining
8	b	2.4 M $NaNO_3$ + 0.5 M NaCl	11	288	0.8	Good etch
9	d	2.4 M $NaNO_3$ + 0.3 M NaCl	11	288	0.8	Good etch
10	b	2.4 M $NaNO_3$ + 0.15 M NaCl	11	313	12.5	Macropitting; some original surface
11	b		6	313	12.5	Macropitting; some original surface
12	b		11	313	6	Fair etch
13	b		6	313	6	Fair etch; some original surface
14	b		11	313	2.5	Fair etch
15	b		6	313	2.5	Fair etch
16	b		11	288	2.5	Good etch
17	b		6	288	2.5	Ideal etch (Fig.7)

a, Mechanical brushing followed by degrease in 0.5 M NaOH solution.
b, Immersion for 120 s in 0.5 M NaOH.
c, Immersion for 240 s in 0.5 M NaOH.
d, Immersion for 240 s in C_2HCl_3.

these experiments was 2.4 M $NaNO_3$ + 0.8 M HNO_3, the flow rate was 11 dm^3 min^{-1}, and the inter-electrode gap 0.8 mm. Current densities used were 30 and 40 kA m^{-2}, and the experiment was carried out at 288 K. Specimens which appeared to the naked eye to have suitable surface finishes were examined using a scanning electron microscope.

4. Results

The surface finishes which were obtained using the small cell were encouraging in that they showed that a desirable size of pit could be obtained over a wide range of conditions. These results showed, however, that both NaCl- and $NaClO_3$-based electrolytes tended to produce crystallographic etching, as opposed to the required rounded pits. Figs. 3 and 4 show typical results.

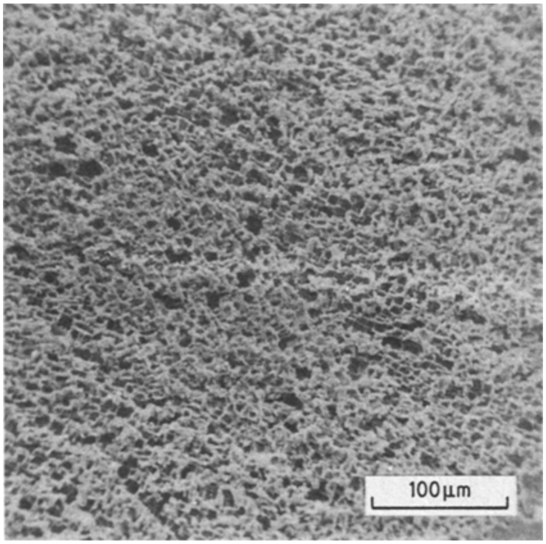

Fig. 3. Al surface grained in NaCl electrolyte.

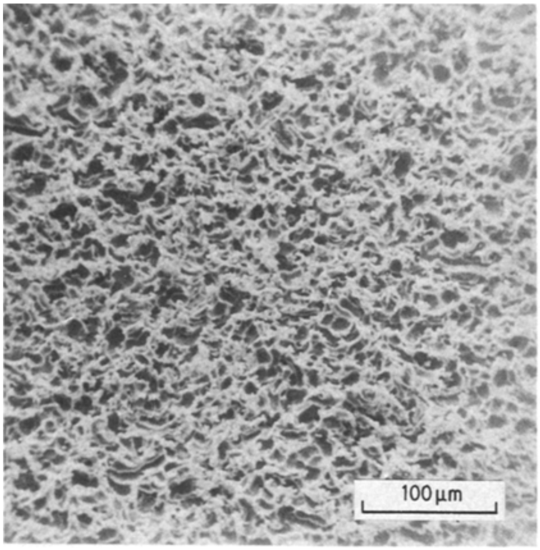

Fig. 4. Al surface grained in $NaClO_3$ electrolyte.

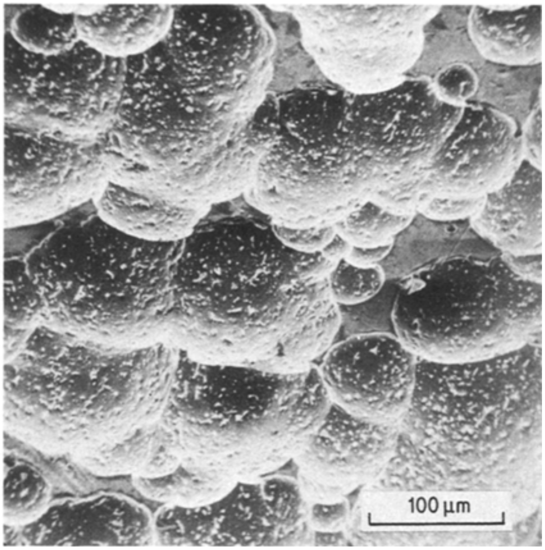

Fig. 5. Al surface grained in nitrate electrolyte (sample 7).

The conventional industrial method of electrolytic etching of aluminium involves the use of baths of HCl or HNO_3 as electrolyte. The use of such acids in the ECM process, however, appears to yield no advantages over salt solutions. In the experiments carried out there was little apparent difference between samples machined in 0.9 M NaCl and 1.4 M HCl solutions, whilst there was no visible graining of samples machined in 0.8 M HNO_3. In the case of samples machined in 0.8 M HNO_3 + 2.4 M $NaNO_3$, or in 2.4 M $NaNO_3$ alone, similar macropitted surfaces were obtained (Fig. 5), although the start-up zone was quite homogeneous (Fig. 6). These samples are rather more promising than those prepared in chloride or chlorate because the texture is even and does not appear to be influenced markedly by crystallographic features. Samples machined in $NaNO_3$ with small additions of NaCl (~ 0.3 M) produced surfaces approaching the desired topography (see description of surfaces, Table 2).

The results from the experiments in which large gaps (> 2.5 mm) were used were rather mixed. The best results using these larger separations were obtained using Cl^- concentrations of 0.15 to 0.25 M, Fig. 7 shows such a surface finish. This should be compared with Fig. 1. Because of the increased *iR* drop across the 6 and 12.5 mm electrode gaps, temperatures of 313 K were used to raise the conductivity of the electrolyte. However, this increased the tendency to remove metal by pitting rather than graining.

Fig. 8 shows the plot of measured potential versus time during the initial period of machining. There is a clear variation in potential during this time. This plot appears to confirm that the different surface finish in this area is probably due to potential fluctuations, and this suggests that etching might be possible without the need for full rectification of the power.

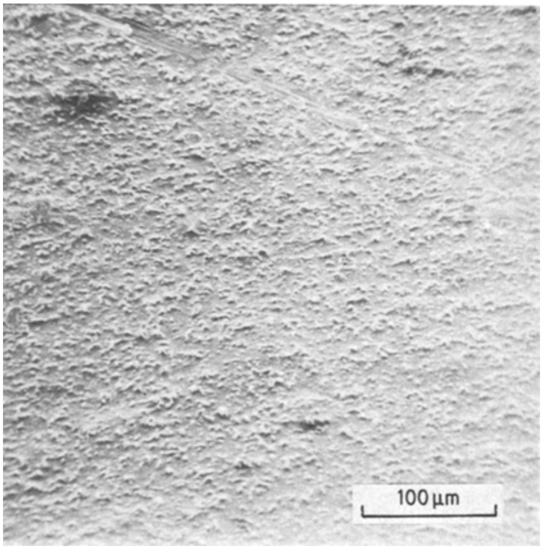

Fig. 6. Start-up zone of nitrate sample.

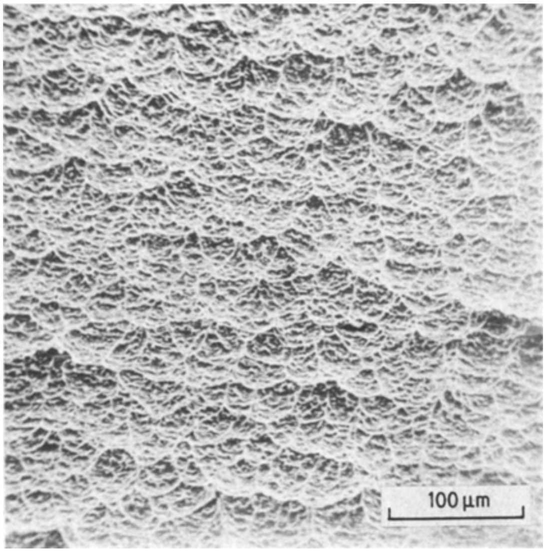

Fig. 7. Al grained in 2.4 M $NaNO_3$ + 0.15 M NaCl (sample 17).

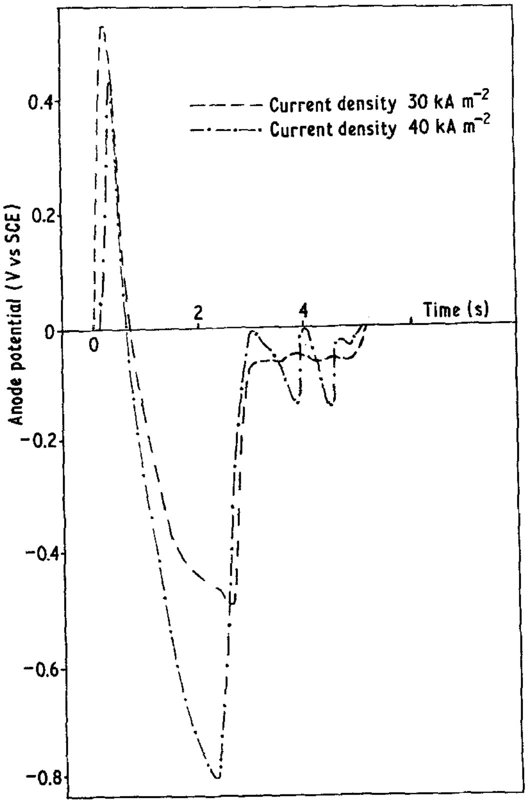

Fig. 8. Potential–time characteristic during start-up for Al in 2.4 M $NaNO_3$ + 0.8 M HNO_3.

5. Discussion

The mechanism of chloride-ion attack on aluminium oxide layers, particularly with respect to pitting of the aluminium substrate, has long been studied, and appears to be via formation of $AlCl_4^-$ ions, or a similar complex ion species, or via formation of a readily soluble basic salt such as $Al(OH)_2Cl$ [4–6]. In using a composite electrolyte, a balance is sought between the promotion of oxide-film growth by nitrate ions and disruptive action by chloride ions. It has been shown [7] that there are specific ratios of $NO_3^-:Cl^-$ ion concentrations which produce maximum and minimum pitting corrosion of aluminium. In the investigation, we are seeking a specific point in this range. The idea of antagonistic action by components of a composite electrolyte is not new: Davydov *et al.* [8] have suggested this type of action during ECM, and there has been a recent report [9] of a study of the effects of electrolyte components on the dimensions of pits formed on aluminium. It should be pointed out that one usually contrives in using ECM to produce an electropolished surface and indeed this is possible for Al in chloride electrolytes. However, this occurs only at very high current density, when the controlling mechanism is presumably via a dissolution/precipitation film and is thus a random process, as opposed to the localized pitting through the insulating oxide film at lower current densities.

The action of H^+ ions in the electrolytic etching can also be discussed fairly quantitatively. Consideration of the Pourbaix diagram [10] for the $Al–H_2O$ system at room temperatures shows Al^{3+} ions to be stable with respect to precipitation of aluminium hydroxide at values of pH less than 3 to 4. In other words, an acidic electrolyte should be capable of dissolving the passivating film on aluminium, to allow attack on the metal. Brook [11] has recalculated the Pourbaix diagram for elevated temperatures, and has shown how the stability of the oxide layer (with respect to pH and potential) will change as the temperature rises.

It has been shown [6] that the critical potential for pitting of aluminium immersed in a chloride-containing solution becomes more negative as the temperature is increased. This is one possible explanation for the increased degree of deep pitting in the $NaNO_3$/NaCl electrolyte as the temperature is raised. It is envisaged that the tendency to passivity at the higher temperatures could be counteracted by an increase in the chloride concentration in the electrolyte. Because of the amphoteric character of aluminium hydroxide, the oxide film is unstable with respect of AlO_2^- ion formation at $pH > 9$. This is the apparent reason for the detrimental effect of pretreatment of the aluminium sheet in 0.5 M NaOH for more than 180 s; i.e. there is local pitting of the oxide layer which leads to exaggerated pitting at such points during ECM. Because $Al(OH)_3$ is insoluble in the range $4 < pH < 9$, it will be precipitated from an approximately neutral electrolyte solution and might be filtered out. This is an advantage over acid electrolytes; the neutral electrolyte will have a much longer lifetime.

The use of ECM as a method of graining aluminium sheets in a continous process thus seems viable, though it still requires proving under industrial conditions. For example, the throughput of 25 mm min^{-1} would need to be increased, but this could be achieved by using a bigger cathode (tool) when the required residence time could be maintained. Clearly, also, it would be more appropriate on a large scale to have the sheet of aluminium move relative to the fixed tool.

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