Anodic Polarization During Electrobrightening and Electropolishing of Aluminium

D. R. Gabe

Department of Metallurgy, University of Sheffield

SUMMARY—The polarization characteristics of six established electropolishing and electrobrightening solutions for aluminium have been determined. It is suggested that the distinction between electropolishing and electrobrightening can be made in terms of activation energies for dissolution and transitional temperatures establishing a threshold condition for satisfactory performance. The advantages of a 20% perchloric acid in methanol solution are pointed out, this solution giving excellent mirror-bright finishes.

INTRODUCTION

THE distinction between electrobrightening and electropolishing, particularly relevant in the case of aluminium, has never been completely clarified. The former is a term widely applied to metal finishing operations and the latter in metallography, but this is certainly not exclusive. We may define electrobrightening as a process for increasing the lustre of a metal but not necessarily improving the levelling or smoothing, whereas electropolishing increases lustre but also the smoothness of the surface. In terms of reflectivity the former increases specular reflectivity while the latter improves the reflected image quality, that is the mirror property. In practice, electrobrightening solutions frequently yield a surface on which a residual bulky oxide film is present and which must be dissolved in a 'desmudging' operation to produce the lustrous surface finish. By contrast, electropolishing yields a polished surface directly and without need for any post-treatment.

Aluminium, being amphoteric, may in principle be electropolished or electrobrightened in either alkaline or acid solutions. In practice alkaline conditions are usually used for etching to produce matt appearances and only one solution has found wide application for brightening— a carbonate-phosphate solution[1-3] typified by the *Brytal* process (see Table I). The acid solutions may be classified in four categories: a mixed sulphuric-chromic acid solution[4,7] similar to the *Aluflex* process, a sulphuric-phosphoric acid solution[6] in which nitric acid is the oxidant, and a phosphoric acid based solution containing chromic acid as oxidant typified by the Battelle patent[9] and also known

TABLE I. INDUSTRIAL-SCALE ELECTROBRIGHTENING PROCESSES FOR ALUMINIUM

Solution type	Composition †	Commercially recommended conditions					
		Temp, °C	CD, mA/cm² *	Voltage, V	Time, min	Cathode material	
Brytal	150 g/l Na₂CO₃ 50 g/l Na₃PO₄	70–95	20–45	10–18	2–12	iron	
Sulphuric-chromic ...	1450 g/l H₂SO₄ 30 g/l CrO₃	70–80	75–150	10–20	2–5		
Sulphuric-phosphoric ...	150 g/l H₂O 280 g/l H₃PO₄ 1280 g/l H₂SO₄ 15 g/l HNO₃ 5 g/l Al	70–80	100–150	12–18	1–8		
Battelle	120 g/l H₂O 935 g/l H₃PO₄ 65 g/l CrO₃ 550 g/l H₂SO₄	75–85	50–150			stainless steel	
Alzak	270 ml H₂O 560 ml 40% HBF₄ ie 27% HBF₄	24	23	25	5–8	copper	

* 1 mA/cm² ≡ 1·1 A/ft²
† In order of make-up

TABLE II. PERCHLORIC ACID SOLUTIONS FOR ELECTROPOLISHING ALUMINIUM

$HClO_4$ %	$(CH_3CO)_2O$ %	CH_3COOH %	CH_3OH %	C_2H_5OH %	Voltage, V	CD mA/cm^2	Temp, °C	Ref
53	47				20–70	8–25	35	13, 14
33	67				18–20			15, 16
5		95						17–19
2·5			97·5				−70	20, 21
10			90		20	1000	20	22
5–20			95–80				20	23, 24
20				80	15–20	200	30	19, 25–27

as the *G5* process. (The last two solutions also appear to have been widely used in Russia.[10]) The fourth acid solution, known in its original form as the *Alzak* process,[11] is based upon fluoboric acid but modifications include hydrofluoric acid in the composition.[12] Solutions in each of these five categories have been examined in this investigation, details of composition used and commercially recommended conditions are given in Table I. Proprietary additives, for example cellosolve, have not been used because it was hoped to discriminate between basic solution types.

Metallographic electropolishing is conventionally a small-scale laboratory operation; while phosphoric-sulphuric-chromic acid types of solutions can be used, perchloric acid based solutions have found wide acceptance for over thirty years but the explosive hazards associated with the original 'Jacquet' solutions,[13-18] in which acetic anhydride acts as solvent, have made them unacceptable on a large scale. Replacing the anhydride with acetic acid makes them safer but less satisfactory in performance, but the recent interest in methanol or ethanol as solvent for perchloric acid and its possible application as a "universal" electropolishing solution[20, 23] suggested that a fresh approach might be useful. The composition of perchloric acid solutions is given in Table II; recent work suggests that 5-20% perchloric acid in methanol offers valuable flexibility in the case of steel.[24]

Particular ambiguity is associated with these solutions because in general a cell voltage is quoted as a criterion of optimum performance, ambiguity arising because the main factor affecting cell voltage in these solutions is usually solution resistance rather than the anode reactions. High solution resistance is caused by large anode-cathode distances and gives rise in turn to large heating effects, the cause in turn of further ambiguity in the temperature requirements. Previous investigations have emphasized the need to consider anode potential rather than cell voltage to obtain the truly optimum conditions, for both copper in orthophosphoric acid, which exhibits classical 'polishing plateau' features,[28] and also mild steel in perchloric acid/methanol solutions, which exhibits limiting current characteristics.[24] It is believed that the critical temperature range can be established by examining transitions in the activation energy for dissolution,[24, 28] and in view of the rather sketchy polarization data available for aluminium this approach has been used to examine a range of both electrobrightening and electropolishing solutions.

In order to obviate voltage ambiguities in this investigation a potentiostatic technique has been employed in order to establish the anode potential unequivocally and enable the anode current density to be measured accurately (this is particularly important for the phosphoric acid solutions

when a potential 'plateau' may be observed). The over-potentials recorded therefore refer to the anode and no attempt has been made to measure cell voltages or solution resistivities.

EXPERIMENTAL

Six solutions were selected for detailed examination, representing the six main types reviewed earlier; the exact solution compositions are given in Table I and Table II (5 and 20% perchloric acid in methanol). Each solution was used to electropolish or electrobrighten aluminium of 99·8% purity, during which treatment potentiodynamic anodic polarization curves were determined for the range 0-3 V overpotential at 200 mV, min scanning rate using an *Amel* potentiostat and *Servoscribe* potentiometric recorder. (NB. All polarization curves have been plotted as overpotential rather than electrode potential against current density in order to make comparisons between various solutions at various temperatures rather easier.) Temperatures were varied over a wide range, from −10°C to +120°C where appropriate. Once polarization curves were established, the bright polishing regions were identified in terms of the overpotential [*] and potentiostatic measurements of the polishing current I_p were made at a large number of temperatures throughout the selected range, thereby enabling activation energies for dissolution to be determined. The Arrhenius relation is:

$$I_p = const \exp(-Q/RT)$$

or $$\log I_p = \log const - Q/2·303\,R\,.\,1/T$$

where T is the temperature (°K), R is the gas constant (8·31 J/°K mol) and Q is the activation energy (J/mol). A graph of $\log I_p$ against $1/T$ results in a straight line of slope $(-Q/2·303\,R)$ when dissolution takes place by a common mechanism for that temperature range.

The perchloric acid solutions, being relatively new in the field, were used also to electropolish three aluminium alloys—Al-3·2% Fe, Al-3·26% Cr and Al-2·55% Mg—the first two being duplex and non-commercial and the last one a commercial single phased alloy.

Distinction has been made between electrobrightened surfaces in which the specular reflectance was improved and electropolished surfaces in which the total reflectance and image quality was improved. No attempt has been made at this stage to compare reflectivities but it is hoped later to compare susceptibilities to anodizing and sealing.

---

[*] For uniformity 2·8 V overpotential was selected in each instance except the Battelle solution, when 1·5 V was considered to be more appropriate.
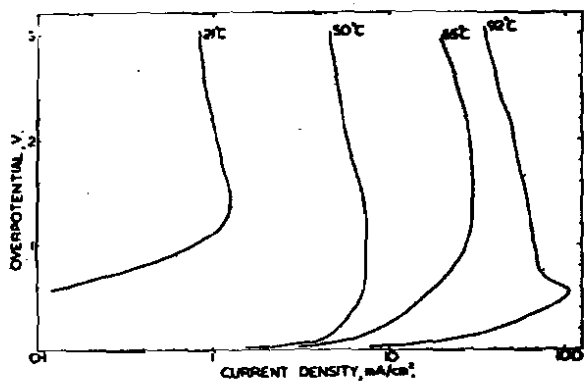
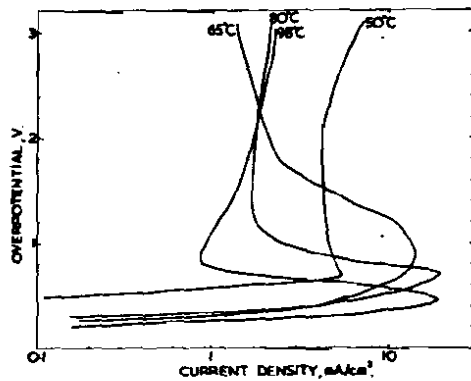Fig 1. Polarization curves for aluminium in *Brytal* solution.

Fig 3. Polarization curves for aluminium in sulphuric-chromic solution.
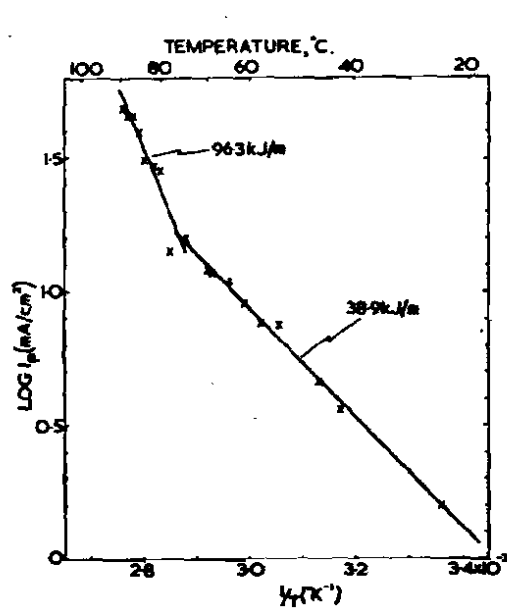

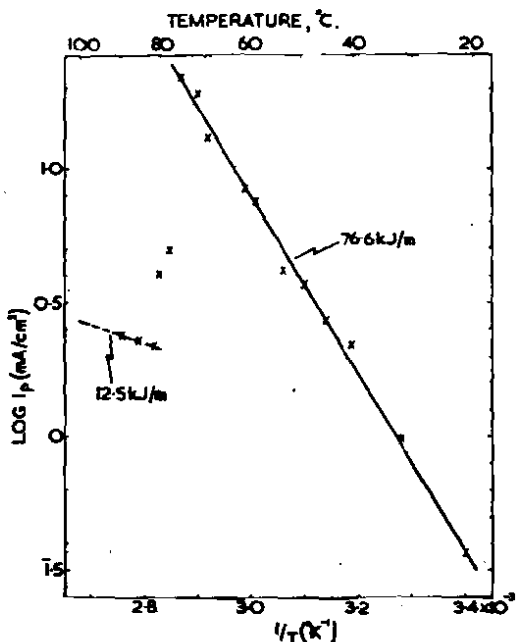Fig 2 Activation energy graph for electropolishing in *Brytal* solution.

Fig 4. Activation energy graph for electropolishing in sulphuric-chromic solution.

TABLE III. ACTIVATION ENERGY DATA FOR ELECTROPOLISHING ALUMINIUM

Solution type	Activation energy, kJ/mol		Transition temp. °C	Polishing c.d at recommended temp.* mA/cm²
	Low temp	High temp		
Brytal	38·9	96·3†	76	35–60
Sulphuric-chromic	76·6	12·5†	77	1–2
Sulphuric-phosphoric	64·0	28·8†	58	30–40
Battelle	73·6	26·3†	43	90–110
Alzak	28·0†	68·6	10	15–30
20% Perchloric in methanol ...	20·5†			20–30
Cu in 67% H₃PO₄	24·7†	17·6	37	
Fe in 5% Perchloric-methanol ...	8·8†	38·5	28	
Fe in 20% Perchloric-methanol ...	38·5†	20·9	22	

* see Tables I and II   † optimum polishing condition

RESULTS

BRYTAL SOLUTION

Potentiodynamic polarization curves are shown in Fig 1, from which it may be seen that the 'passive' limiting current density increases progressively with temperature. However, the potentiostatic values of I_p (Fig 2) show that a change in behaviour occurs at about 76°C with a much higher activation energy for dissolution apparent at temperatures above this transitional value. The activation energy values, transition temperature and polishing current density found by polarization measurements for the temperature commercially recommended are collated in Table III.

SULPHURIC-CHROMIC SOLUTION

Below about 60°C a systematic increase in I_p was found but instability existed in the range 65-80°C (the commercially recommended temperature range), as shown in Fig 3 and the dramatic change shown in the activation energy graph (Fig 4). Within this temperature range the current/time relation, at constant potential, showed oscillatory features attributable to uneven, incomplete or spasmodic film formation.

SULPHURIC-PHOSPHORIC SOLUTION

A wholly systematic polarization behaviour was apparent (Fig 5) with a change in dissolution character occurring at about 58°C (Fig 6).

BATTELLE SOLUTION

This solution showed many of the classical electropolishing characteristics often associated with phosphoric acid based solutions, for example systematic polarization behaviour (Fig 7) with a fall in current density at the critical current/ Flade potential region, and a highly polished metal surface. Rapid polishing occurs above about 80°C but above about 100°C pitting was evident. The visible polishing transition seemed to occur at about 75°C but the activation energy graph (Fig 8) indicates a transition at 43°C; however, this could be associated with the low solubility of chromium trioxide at low temperatures, solution of the requisite amount only being achieved above about 70°C.

ALZAK SOLUTION

Systematic polarization behaviour was observed (Fig 9) with a transition in behaviour apparent at 10°C (Fig 10). Brightening appeared to take place at temperatures below

about 20°C and above 25°C a matt-satin finish was usual. The commercially recommended temperature of 23°C therefore perhaps represents the highest temperature (or fastest dissolution rate) commensurate with brightening, although this investigation suggests that lower temperatures would be preferable.

PERCHLORIC-METHANOL SOLUTIONS

Together with the Battelle solution these easily gave the highest degree of polish. Polarization measurements showed that the curves had the same form at both 5% and 20% $HClO_4$ concentration (Figs 11 and 12) but that the 5% solution had somewhat higher dissolution rates at higher overpotentials, showed less marked limiting current density and offered inferior polishing ability. The activation energy graph showed no transition over the temperature range investigated (Fig 13). Observation suggests that for the 20% solution the minimum overpotential for electropolishing was 2·1 V at 25°C and 1·8 V at 5°C.

The effect of acid concentration could be seen more clearly in the polishing of some dilute aluminium alloys. For both the Al-2·55% Mg (Fig 14) and Al-3·26% Cr (Fig
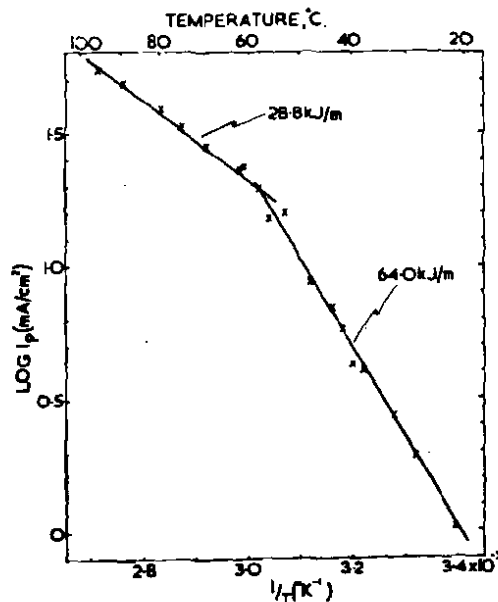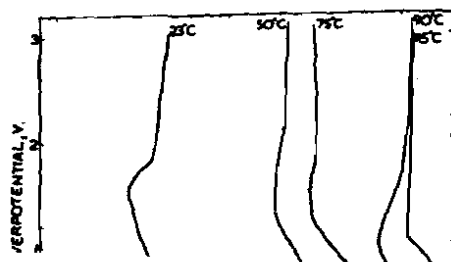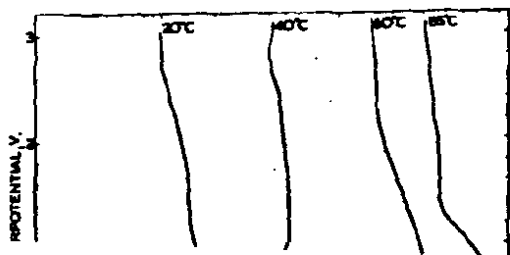
Fig 6. Activation energy graph for electropolishing in sulphuric-phosphoric solution.
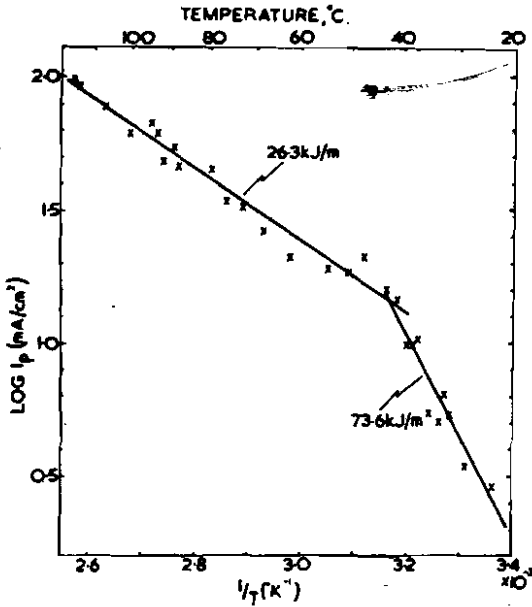
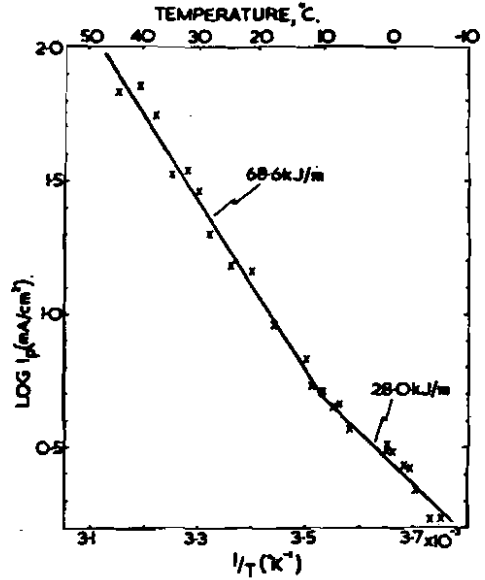Fig 8. Activation energy graph for electropolishing in Battelle solution.

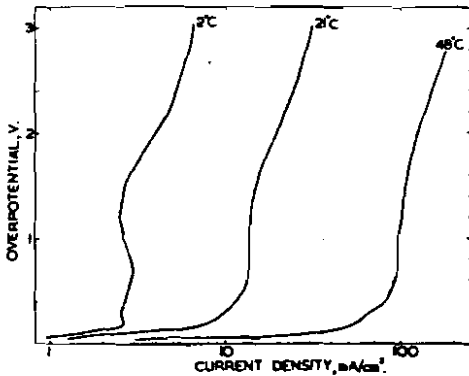Fig 10. Activation energy graph for electropolishing in *Alzak* solution.

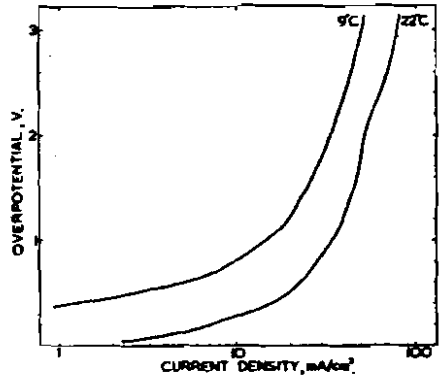Fig 9. Polarization curves for aluminium in *Alzak* solution.

Fig 11. Polarization curves for aluminium in 5% perchloric-methanol solution.

15) alloys the higher concentration improved polishing and the polarization curves showed a more marked fall-back in current density at polishing potentials. This same effect may be seen for an Al-3·2% Fe alloy in 5% solution by lowering the temperature from 22°C to 6°C (Fig 16).

DISCUSSION

It has long been apparent that distinction ought to be made between electropolishing and electrobrightening of aluminium in the context of metal finishing, and some attempt has been made to do this.[29] As was emphasized in the Introduction, instinctively one attempts to do this in terms of levelling ability and reflectivity but also in terms of the need to subject the metal surface to a post-treatment—the so-called desmudging treatment—which may be necessary to remove relatively massive thicknesses of oxide film, thereby revealing the brightened metal surface. Despite the comparatively good understanding of electropolishing of some other metals in terms of polarization behaviour (polishing 'plateau', diffusion-limited dissolution etc), little has been done for aluminium in this respect. In fact, some

analogies drawn with the classical behaviour of copper in orthophosphoric acid where the 'plateau' has a small and finite potential range can be misleading.[29,30]

Shenoi and Indira[31] have shown, for example, that the oxygen evolution reaction which limits the upper potential range by virtue of its diffusion layer disruption and side effect of surface pitting commonly has an overvoltage of 10 V or more associated with it in both acid and alkaline aqueous solutions, while for essentially non-aqueous perchloric acid solution it would be even higher (the equivalent value for copper would be ~1·5 V). Furthermore, ambiguity commonly arises because operating conditions tend to include cell voltages as criteria and unfortunately these merely reflect the resistive nature of the electrolyte and the variable anode-cathode electrode spacings which arise. It is in fact fortunate that the oxygen overvoltage is as high as 10 V, otherwise polishing might not be possible with such a vaguely defined anode potential. The consequence of using such high voltages is that solution heating is marked; while this can be advantageous for the solutions used at 70-90°C, in the case of the low temperature solutions it can be a problem. In this context the frequently quoted requirement for perchloric acid solutions of a
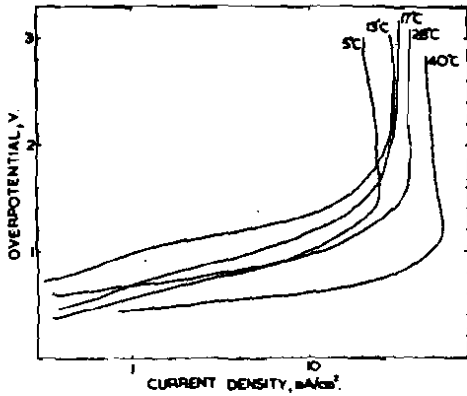
Fig 12. Polarization curves for aluminium in 20% perchloric-methanol solution.

temperature as low as $-70°C$ is primarily as a heat sink for the excessive heat generated below the critical temperature, which may be as high as $20°C$.[23,24]

Of the solutions examined in this investigation, observation in terms of the need to post-treat by desmudging places the *Brytal* and *Alzak* solutions and possibly the sulphuric-chromic solution as electrobrightening processes, the perchloric acid, methanol and Battelle solutions and possibly the sulphuric-phosphoric solution as electropolishing solutions. On this basis it should be possible to classify them by other criteria also involving the mode of dissolution and the build up or absence of massive surface films. The critical electropolishing condition may be characterized in most cases by the appearance of a current 'plateau' on the polarization curves and for the *Brytal*, sulphuric-phosphoric, Battelle and perchloric acid solutions $I_p \simeq 50$-100 mA/cm², although for the other two solutions the value is an order of magnitude lower.

In Table III the activation energy values and transition temperature data have been collated, together with similar data for copper[25] and mild steel,[24] both of which are well defined electropolishing systems. Inspection suggests that if the activation energy decreases with increase of temperature across the transition value electropolishing takes place, otherwise electrobrightening occurs. However, it cannot be quite as simple as that, because of the tendency to form well passivated surfaces whether the film be a phosphate or an oxide-hydroxide type such as may be found typically after anodizing and sealing. Thus in solutions like the alkaline *Brytal* electrolyte dissolution may
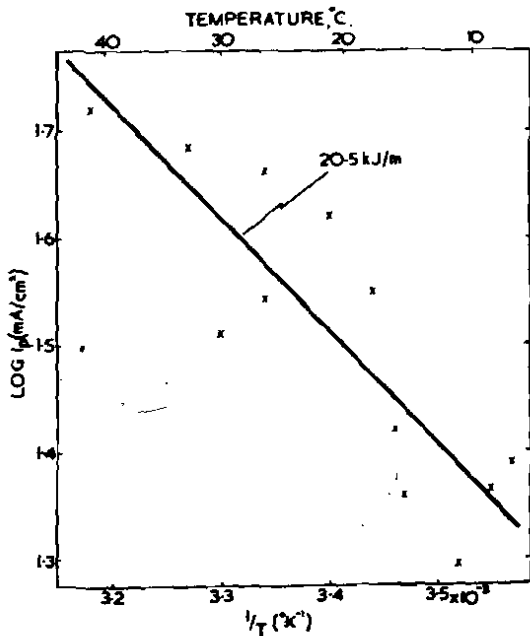

Fig 13. Activation energy graph for electropolishing Al in 20% perchloric-methanol solution.
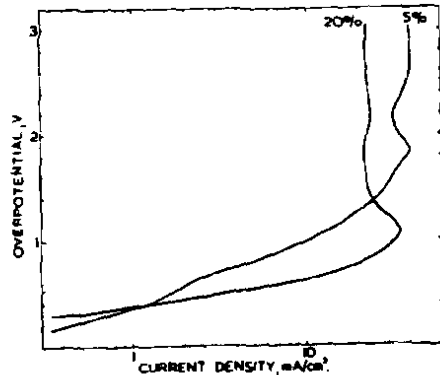

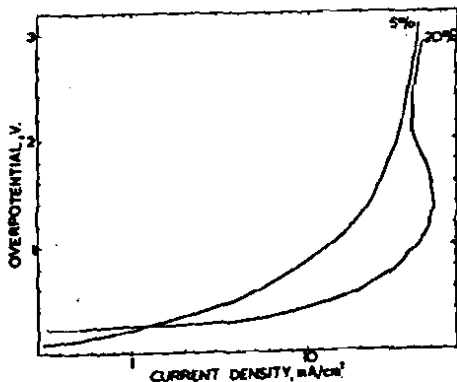Fig 15. Polarization curves for Al-3·26% Cr alloy in 5% and 20% perchloric-methanol solution at 22°C.

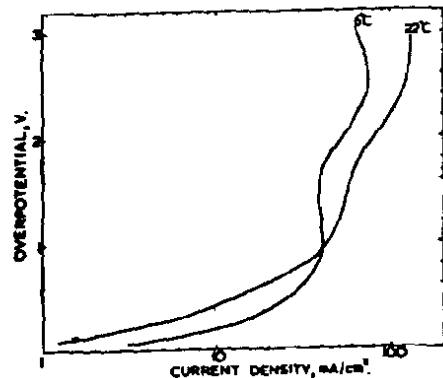Fig 14. Polarization curves for Al-2·55% Mg alloy in 5% and 20% perchloric-methanol solution at 22°C.

Fig 16. Polarization curves for Al-3·2% Fe alloy in 5% perchloric-methanol solution at 6° and 22°C.

be rapid and easy at low temperatures but more difficult at higher temperatures when the monohydrated oxide (böhmite) may be more stable—the optimum temperature being said to be 70-80°C,[32] which coincides exactly with the transition temperature found here (76°C). By contrast, the Battelle solution which is phosphoric acid based behaves rather more conventionally, offering a phosphate-passivated state at lower temperatures but electropolishing above the transition temperature as the film becomes less stable, and at temperatures above 100°C pitting develops quite rapidly. This may be interpreted in terms of a decreasing a_m/a_{H_2O} ratio in the electrode diffusion layers as the temperature is increased as suggested by Hoar.[33] In the case of the perchloric acid solutions it seems likely that the complex film is only stable at relatively low temperatures and higher concentrations (20% polishes better than 5% solution), while for the *Alzak* solution (fluoboric acid based) it may become too thick at temperatures above 25°C thus necessitating desmudging to obtain even a satin-matt finish. The sulphuric-chromic and sulphuric-phosphoric solutions behave more like the Battelle solution, but by modifying the solution composition the film constitution and its stability at various temperatures are modified.

Without direct evidence it is not possible to do more than speculate about the film compositions. The characteristic presence of phosphoric acid usually suggests a phosphate-type film, but it is really unlikely to be stoichiometric $AlPO_4$ as has been suggested.[29] Similarly, perchloric acid solutions give rise to a white, predominantly perchlorate film but which is known to contain C, O, S, Cl and N as trace elements.[34,35] Both the Al-Cr (Fig 15) and Al-Fe (Fig 16) alloys were duplex and the polarization curves indicate that selective etching of the two phases occurs. In the case of Al-Mg (Fig 14) increase of $HClO_4$ concentration from 5% to 20% clearly promotes film formation and illustrates this critical change in behaviour which was found also for mild steel.[24]

If the history of electropolishing is traced it may be seen that perchloric acid plays quite an important rôle,[14] but until recently almost entirely with acetic acid or anhydride as solvent (see Table II). The notoriety of this latter solution is in view of its explosive hazard, primarily during mixing but also in operation if allowed to overheat. There is no evidence that the perchloric acid/methanol solutions suffer from this same hazard, although they are of course inflammable and toxic but not to an abnormal extent. They have the advantage of being used cold rather than hot, are not highly concentrated like the sulphuric acid based solutions, no desmudging is necessary and they give excellent polishes. Therefore, the methanol-based solution deserves some consideration in view of possible saving in unit process demand and power consumption for external heating. The large IR drop and consequent electrolysing current heating can be minimized by careful jigging, but refrigeration and circulation are obviously desirable. The perchloric-methanol and Battelle solutions give the best

polished surfaces both in about 5-10 min, but owing to the lower current density employed in the former case (25 compared to 100 mA/cm²) the dissolution rate is slower and the amount of metal removed less (0·0038 compared to 0·015 mm/min).

REFERENCES

1 Brit Pat 449, 162 (1935).
2 N. D. Pullen, *J Inst Met*, 1936, **59**, 151.
3 A. W. Brace, *Proc Amer Electropl Soc*, 1959, **46**, 211.
4 Fr Pat 984. 863 (1951).
5 R. Pinner. *Electropl and Met Fin*, 1956. **6** (11), 401.
6 Brit Pat 743, 692 (1953).
7 R. Lattey, *Proc Amer Electropl Soc*, 1959, **46**, 233.
8 Fr Pat 940. 698 (1948).
9 US Pat 2,550,544 (1951).
10 N. P. Fedot'ev and S. Ya. Grilikhes. Electropolishing. Anodizing and Electrolytic Pickling of Metals, Draper. 1959.
11 US Pat 2,108.603 (1938), Brit Pat 433,484.
12 US Pat 2,040,617-8 (1936).
13 P. A. Jacquet. *Met Corr Usure*, 1943, **18**, 198.
14 P. A. Jacquet, *Met Rev*, 1956, **1**, 157.
15 P. A. Jacquet. *Compt Rend*, 1937, **205**, 1232.
16 P. Lelong and J. Herenquel. *Rev Met*, 1961, **58**. 587.
17 P. A. Jacquet, *Compt Rend*, 1948. **227**, 556.
18 P. A. Jacquet. *Rev Met*, 1949, **46**. 214.
19 H. M. Tomlinson, *Phil Mag*, 1958. **3**, 867.
20 E. N. Hopkins *et al*, Iowa State Univ Conf—650414-3 (21 June 1965).
21 A. T. Davenport and B. Belyakov, *J Iron & Steel Inst*, 1968. **206**, 610.
22 G. W. Briers *et al*, *J Inst Met*, 1964-5, **93**, 87.
23 D. R. Gabe, *Metallography*, 1972. **5**, 415.
24 D. R. Gabe. *Corr Sci*, (to be published).
25 E. C. W. Perryman and J. C. Blade. *J Inst Met*, 1950, **77**, 263.
26 R. B. Nicholson, G. Thomas and J. Nutting, *Brit J Appl Phys*, 1958, **9**, 25.
27 G. Thomas, *J Inst Met*, 1961, **90**, 57.
28 D. R. Gabe. *Corr Sci*, 1972, **12**, 113.
29 A. W. Brace and J. M. Kape, Proc Int Conf on Anodizing, Nottingham 1961, 167.
30 S. Wernick and R. Pinner, The Surface Treatment and Finishing of Aluminium and its Alloys, Draper, 1964.
31 B. A. Shenoi and K. S. Indira, *Met Fin*, 1963, **61** (11), 52.
32 B. A. Shenoi, K. Vijayalakshmi and K. S. Indira, *Met Fin*, 1963, **61** (12). 50
33 T. P. Hoar, *Corr Sci*, 1967, **7**, 341.
34 C. G. Dunn and L. A. Harris, *J Electrochem Soc*, 1970, **117**, 81.
35 J. Plateau *et al*, *Met Corr Ind*, 1951, **26**, 235.