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The effect of a surface-active additive on the dissolution efficiency and surface finish in ECM

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For the electrochemical machining of mild steel in 2·5 M NaCl electrolyte, the effect of a polyacrylamide surface-active additive on the dissolution efficiency and on the surface finish was studied. The current efficiency was found to be slightly lowered by the additive, although in the low current density region of the cell on the inlet side where the electrolyte was fresh, the additive had a greater effect. Crystallographic etching (faceting) was used as a qualitative indication of the effect of the additive on surface finish, and it was found that even under the high-flow, fast-dissolution conditions of ECM, a certain amount of electropolishing could be observed.

1. Introduction

The need for the generation of an anodic film during electrochemical machining, ECM, has been discussed in depth [1]. Classical electropolishing theory acknowledges that bright surface finish occurs where the dissolution process is controlled by diffusion polarization and films are generally now regarded as compact dissolution intermediate or precipitated product. However viscous-films also undoubtedly lead to polishing and 'standard' electropolishing solutions usually involve 'a viscous layer forming additive' [2]. The thickness of the diffusion layer due to the concentration gradient of the dissolving material has been classically related to the electrolyte flow velocity by the Navier–Stokes, relationships [3]. The effect of additions of surface-active materials on the diffusion layer, however, cannot be so rigorously defined, although they certainly generate a relatively thick, viscous layer at the metal surface. An exploratory study of the effect of viscous-layer forming surface-active polyacrylamides in ECM electrolytes was made [4]. One such additive, Decapol A33, was found to suppress etching of mild steel in NaCl electrolyte under certain conditions, although it was suggested that the efficiency of the dissolution process might be lowered.

In the work reported here some further efficiency studies have been made, both with and without the additive, for the dissolution of mild steel in 2·5 M NaCl (15%) aqueous electrolyte, including the effect that this suppression would have on stray current attack [5]. Further, a survey has been carried out of the conditions under which the generation of a surface-active film of polyacrylamide will lead to electropolishing.

2. Experimental

Laboratory reagent grade chemicals (purity greater than 99%) were used to make the electrolytes. The polyacrylamide used was Decapol A33 (Fospur, Ltd, Alfreton, Derbyshire) and the steel was normalized mild steel (0·07% carbon).

The electrolytes were pumped around a QVF glass rig using a Stuart–Turner pump and through a cast-araldite cell. The anode holder was easily removable to enable quick detachment of the anode; the surface size of the electrodes was 50 × 12·5 mm, and the inter-electrode gap was 0·5 mm. A Rotameter flow meter was included in the electrolyte circuit. Because of the 'ageing' characteristics of the surface-active additive [4], which causes the material to lose its activity after prolonged periods of mechanical agitation, the electrolytes with the Decapol additions were not recirculated. Electrical power was supplied from a Hirst 3000a rectifier; current was passed for a fixed period of time at a predetermined value and the anode weighed dry before and after dissolution for the purpose of calculating the efficiency, after which slices were removed in order to make a scanning electron microscope study.

For the stray current attack study, the same equipment was used with the exception of the electrode arrangement which consisted of a segmented anode and a smaller cathode [5]. The nine segments were each 12·5 x 2·5 mm and the cathode, 12·5 x 12·5 mm in surface size, was positioned directly opposite the middle five of the segments. The segments were all polished flat and individually weighed before dissolving at a fixed current for a fixed period of time, after which time they were washed, dried and reweighed. For the ideal case of infinitely poor throwing power, the segments numbered 1, 2, 8 and 9 should suffer zero weight loss.

Flow was recorded in terms of the Reynolds Number, (Re), which is defined by

$$(Re) = \frac{Ud\rho}{\eta}$$

where U is the electrolyte velocity, ρ and η the density and viscosity of the electrolyte, and d is the hydraulic diameter of the tube through which the electrolyte flows. For a small-gapped cell of rectangular section, this diameter approximates to twice the gap. For all the experiments reported ρ and η were taken as $1\ \text{g cm}^{-3}$ and $0{\cdot}01\ \text{g cm}^{-1}\ \text{s}^{-1}$ respectively. These approximations are estimated to introduce a maximum uncertainty into (Re) of ± 10%.

3. Results

3.1. *The effect of additive on the dissolution efficiency*

Fig. 1 shows the slight reduction in efficiency obtained for 2·5 M NaCl with 100 ppm additive compared with that without. At the electrolyte velocity used $[(Re) \sim 15\,000]$, the additive serves to reduce the dissolution efficiency slightly for measurements made over a wide range of current density. The uncertaintities shown arise mainly from the difficulty in passing precise currents for short times (30–120 s).

The effect of the additive in reducing the efficiency is also displayed in Fig. 2. The significant finding is that the additive reduces the metal dissolution in the stray current areas, i.e. from those segments which are not directly opposite the cathode, more so at the inlet than at the exit. The stray dissolution at the exit side of the cell appears to be quite small for mild steel in NaCl even without the Decapol. The electrolyte velocity for this study was $30\ \text{m s}^{-1}$ $[(Re) \sim 30\,000]$.

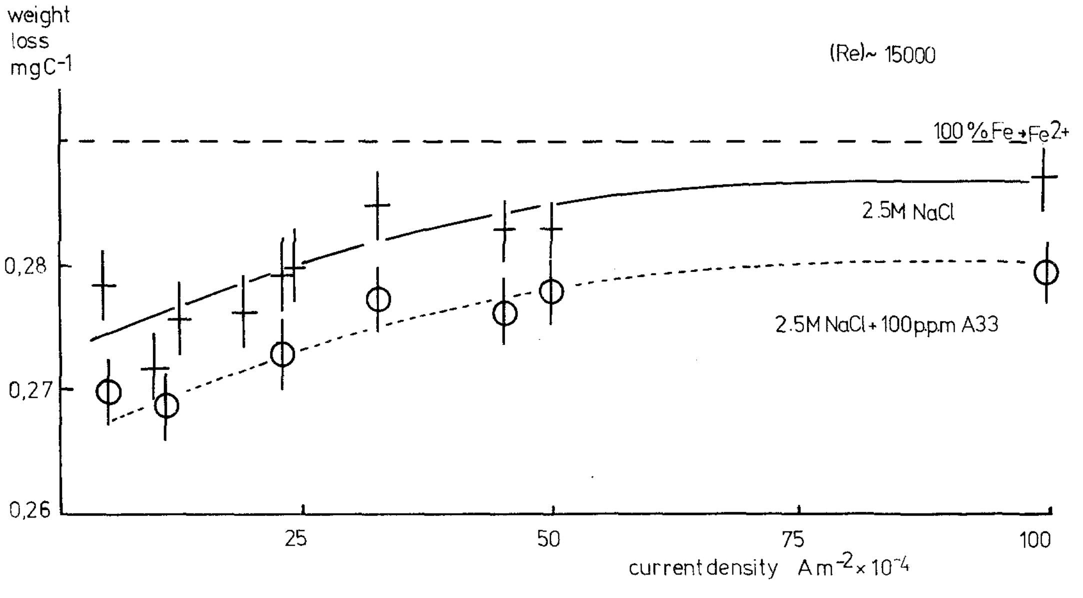

Fig. 1. Efficiency of dissolution for mild steel in 2·5 M NaCl.

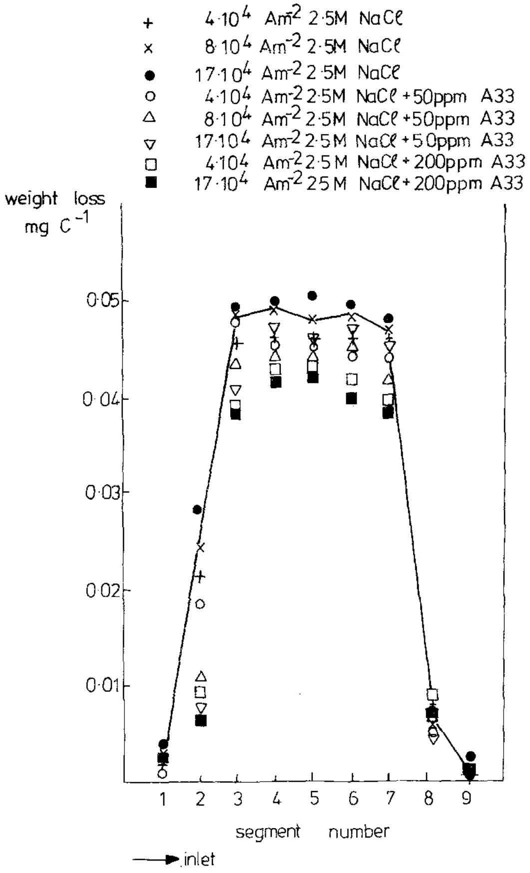

Fig. 2. Stray current attack on mild steel.

3.2. *The effect of additive on surface finish*

Intragranular, crystallographic, etching (faceting) was chosen as a microscopic feature by which to judge qualitatively the effect of the additive in bringing about polishing. A survey of the conditions under which crystallographic etching could be obtained on machining mild steel was carried out. The variables were current density, electrolyte velocity and amount of additive–Decapol A33. The electrolyte used throughout was 2·5 M NaCl. The findings are displayed in Table 1 and a selection of the scanning electron micrographs shown in Fig. 3. Figs. 3a–c show the effect of flow of electrolyte without additive and Figs. 3d–f are similar but with 100 ppm of Decapol A33 added to the electrolyte. Figs. 3g–i show the effect of increasing the quantity of additive at constant current density and constant flow, Figs. 3j–l show the effect of increasing current density at constant flow without additive.

4. Discussion

The efficiency results suggest that the polyacrylamide has an effect in generating an anodic film, which, as it apparently reduces the efficiency of the metal dissolution, probably encourages to a slight extent a secondary anodic process such as oxygen evolution,

$$2H_2O \rightarrow O_2 + 4H^+ + 4e.$$

The very slight rise in metal dissolution efficiency observed in Fig. 1, for both systems, with increase in current density, supports this suggestion. Increase in current density for a fixed flow would tend to increase the local acidity due to the oxygen evolution reaction and hence the corrosive nature of the electrolyte. A limit to this rise would be attained when supersaturation of the electrolyte in the vicinity of the anode would produce a precipitated film. This effect would be flow-dependent and was observed by Chin and Wallace [6] for lower flows than those employed in the present work. Up to that limit, however, those workers also observed a slight rise in efficiency for mild steel in NaCl. On the other hand the generation of acid conditions due to the oxygen evolution reaction would be expected to be reflected in poor stray attack at the cell outlet compared with the inlet. This was observed for the case of Ti in bromide electrolyte [5] but is not apparent for the present studies shown in Fig. 2. There is apparently more stray current at the inlet where the electrolyte is fresh than at the outlet where the electrolyte is diluted by reaction products. The polyacrylamide eliminates this activity at the inlet. Clearly film formation is slight, particularly in the absence of the additive, and hence acid generation is also slight.

The survey of surface finsih obtained on mild steel under the influence of variable current density, electrolyte velocity and amount of additive, is displayed in Table 1 and in Fig. 3. Earlier work [4] had suggested that polyacrylamides under certain circumstances might have a considerable smoothing effect on mild steel during electrochemical machining. It is seen from the work presented here that although this improvement is very real, it appears that the features occur only in a specific range of flow and of current density. Crystallographic etching, Figs. 3a–c, occurs at medium flow [$(Re) \sim 15\,000$] but not at low flow [$(Re) \sim$

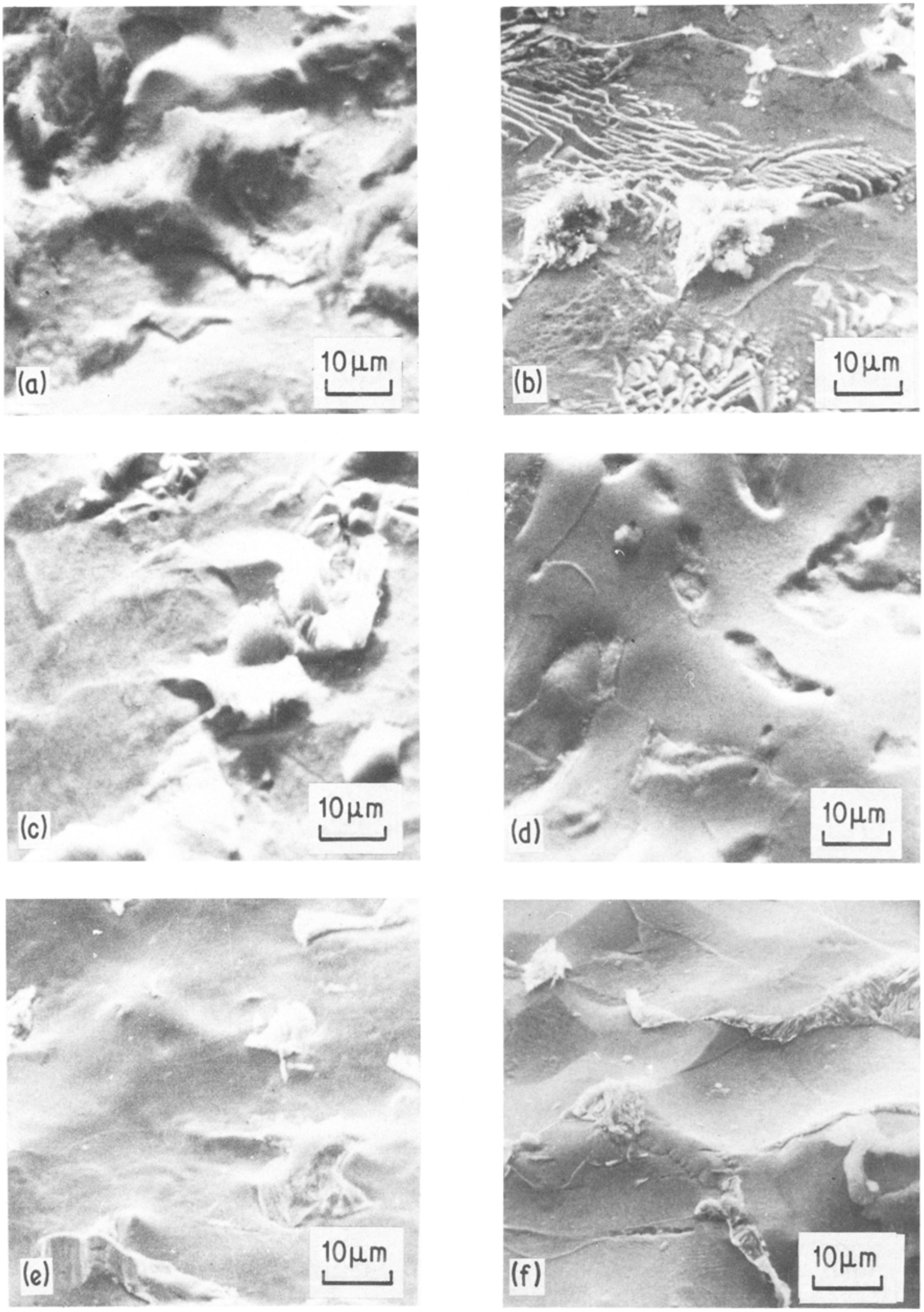

Fig. 3. Scanning electron micrographs of mild steel surfaces. (*Re*) = Reynolds number; J = current density in 10^4 A m^{-2}; A33 denotes amount of additive in ppm, respectively. (a) 7000; 40; 0 (b) 15 000; 40; 0 (c) 30 000; 40; 0 (d) 7000; 40; 100 (e) 15 000; 40; 100 (f) 30 000; 40; 100

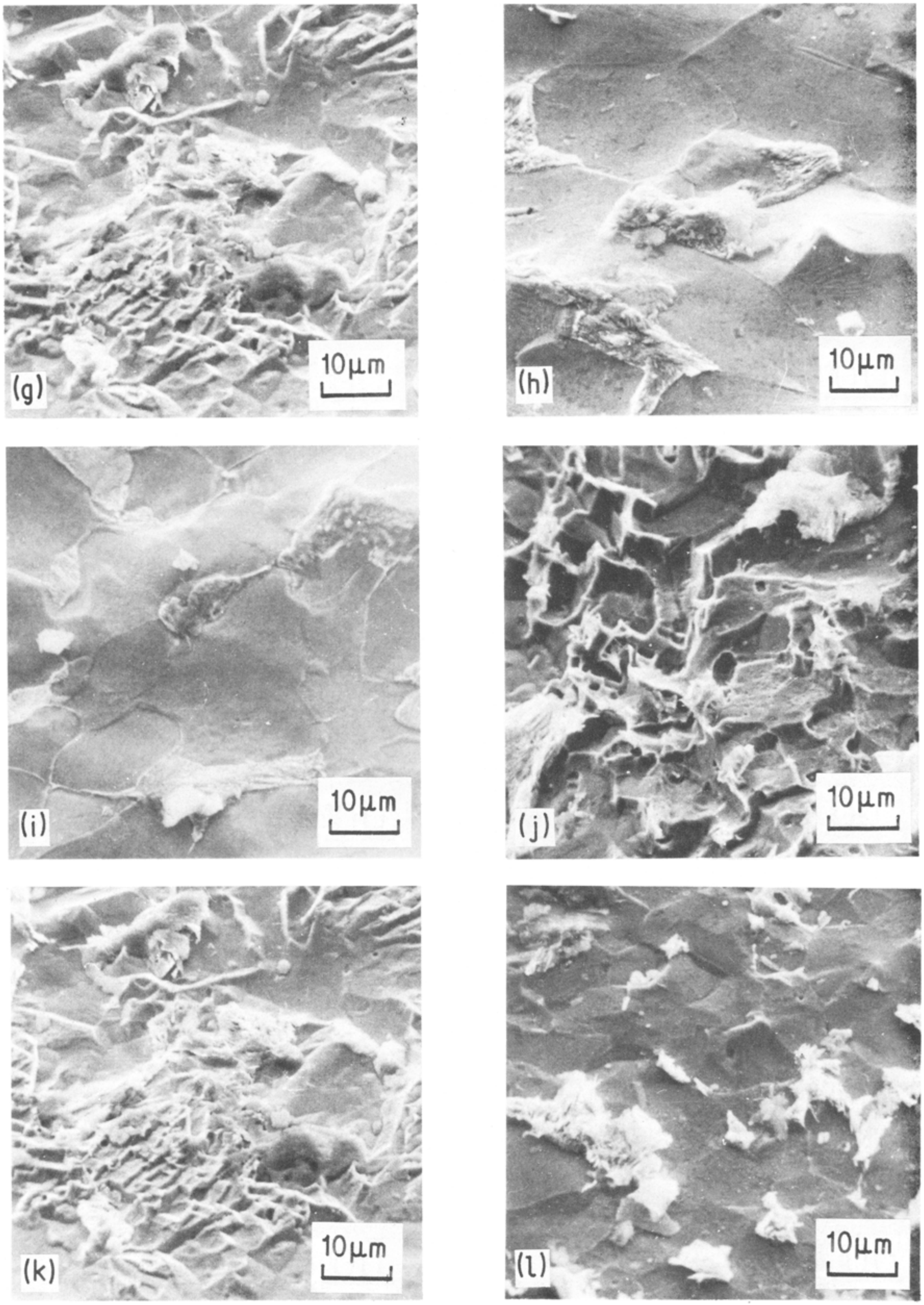

Fig. 3. (g) (*Re*) 30 000; *J* 17; A33 0 (h) 30 000; 17; 50 (i) 30 000; 17; 200 (j) 30 000; 4; 0 (k) 30 000; 17; 0 (l) 30 000; 30; 0.

Table 1. Classification of mild steel surfaces after ECM

Decapol A33 (ppm)	*Flow* (m s^{-1})	*(Re)* (± 10%)	*Current density* × 10^{-4} (A m^{-2})	*No. of samples*	*Appearance*
0	30	30 000	4	4	Crystallographic etch and pitted (Fig. 3j)
50	30	30 000	4	2	Slightly etched
200	30	30 000	4	2	Surface film
0	40	40 000	6·2	1	Slightly etched
50	40	40 000	6·2	1	Slightly etched
0	30	30 000	8	1	Etched
50	30	30 000	8	1	Slightly etched
0	30	30 000	17	3	Some crystallographic etch (Figs. 3g and k)
50	30	30 000	17	3	Slightly etched (Fig. 3h)
200	30	30 000	17	2	Very slight etched (Fig. 3i)
0	7	7 000	25	1	Slightly etched
100	7	7 000	25	1	Smooth
0	10	10 000	25	2	Etched; some crystallographic etch
0	15	15 000	25	2	Crystallographic etch
100	15	15 000	25	1	Slightly etched
0	18	18 000	30	2	Crystallographic etch
50	18	18 000	30	1	Etched
100	18	18 000	30	2	Only slightly etched
0	30	30 000	30	3	Etched (Fig. 3l)
100	30	30 000	30	2	Only slightly etched
0	7	7 000	40	4	Etched; porous film (Fig. 3a)
100	7	7 000	40	3	Smooth (Fig. 3d)
0	10	10 000	40	2	Etched; Some crystallographic etch
0	15	15 000	40	5	Etched; occasionally crystallographic (Fig. 3b)
100	15	15 000	40	3	Smooth surface (Fig. 3e)
0	30	30 000	40	3	Slightly etched (Fig. 3c)
100	30	30 000	40	2	Smooth (Fig. 3f)
0	40	40 000	100	1	Etched
50	40	40 000	100	1	Etched

7000] and only to a small extent at high flow [$(Re) \sim 30\,000$] at a current density of 40×10^4 A m^{-2}. With the additive present the surfaces are much smoother at all flows. The series in Figs. 3g–i show the effect of the additive used under conditions in which the crystallographic etching would otherwise be obtained, and the series, Figs 3j–l indicate that crystallographic etching occurs at medium current densities. It may be concluded that this type of etching occurs at $\sim 17 \times 10^4$ A m^{-2} for high flow and at higher current density for lower flows, but not at all with the surface-active additive present. The earlier study [4] was undertaken with conditions [current density 25×10^4 A m^{-2}, (Re) 20 000] in this etching range. It will also be seen from the series in Fig. 3 that the smoothing effect occurs on a somewhat more macroscopic scale than has hitherto been discussed; the pearlite phase which stands proud of the ferrite when mild steel is machined in NaCl has been somewhat smoothed in the presence of the additive. This feature was particularly evident for a concentration of additive of 200 ppm. Above this concentration very little additional effect was observed.

The surface finish results can be explained simply in terms of the film-forming properties of the surface-active additive. In Fig. 3a, at low electrolyte velocity and high current density, product precipitation occurs as noted by Chin and Wallace

[6]. If this surface were mechanically scrubbed free of the film it would be quite bright although intergranular etching would be in evidence. At the higher flow (Fig. 3b) less precipitation would occur and the edges of crystal planes would become actively dissolved. At even higher flow most of the surface would become simultaneously active. The effect of 100 ppm of Decapol A33 (Figs. 3d–f) is to generate a dissolution-controlling film. In a similar manner dissolution at low current density occurs at selected spots or at active crystal edges, to produce etching (Figs. 3j and k), but at higher current density the anode is active over most of its surface (Fig. 3l). The series in Figs. 3g–i shows that surfaces obtained under conditions of the worst occurrence of the crystallographic effect are significantly modified by the additive.

This work serves to show that on a microscopic level the generation of a viscous film by the addition of a surface-active polyacrylamide helps to bring about a certain amount of electropolishing, even at the high dissolution rates encountered in ECM.

Acknowledgements

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