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TECHNICAL NOTE

Effect of flow on the dissolution efficiency of mild steel during ECM

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1. Introduction

The generation of a controlling anodic film during electrochemical machining, ECM, plays a part in determining both the dimensional control of the cutting and the type of surface finish obtained. It was suggested by Hoare [1] that a transition over a narrow potential range from passivation to transpassive dissolution is necessary in order that the electrolyte gives good dimensional cutting, and this is found for Fe (and mild steel) in $NaClO_3$. In NaCl a passivating film is not generated and the dimensional control is accordingly poor, i.e. there is a considerable amount of stray current attack. Subsequent work has, however, indicated that the electronically-conducting nature of the film is the important characteristic. Mao [2] measured the current efficiencies for mild steel in NaCl, $NaNO_3$ and $NaClO_3$ for the anodic reactions: metal dissolution or oxygen evolution; and for the cathodic hydrogen evolution. He concluded that the maximum dissolution efficiency achieved in $NaNO_3$, 70–80%, was low because the controlling film happens to be somewhat electronically conducting which leads to the occurrence of anodic reactions other than metal dissolution. In the case of $NaClO_3$ the electronically-conducting film exists only at low current densities, but at higher current densities the film becomes porous in nature and allows the efficiency to approach that of NaCl, 100% [3]. Plots of current efficiency against current density for mild steel in $NaClO_3$ solutions have been made [3, 4], and this type of study has been extended to 4 M NaCl and $NaNO_3$ solutions. However it is more usual in commercial plant to use 15% solutions of these latter two electrolytes (2·5 and 1·8 M respectively), and these concentrations were studied for the work reported here. For comparison with earlier work 3·7 M $NaClO_3$ ($\sim$ 40%) was also studied. Very few determinations of the effect of flow have been reported, and it was the main purpose of this work, using a range of electrolyte velocities, to determine the efficiency of dissolution of mild steel at a fixed current density, 25×10^4 A m^{-2}, again in 2·5 M NaCl, 1·8 M $NaNO_3$ and 3·7 M $NaClO_3$.

The apparatus consisted of a QVF flow rig with Stuart–Turner centrifugal pumps. The cell assembly consisted of a mild steel anode (12·5 × 50 mm) placed opposite a copper cathode in an Araldite casting. It has previously been described [5]. The electrolytes were made using technical grade chemicals (purity greater than 99%) and the steel was normalized mild steel (0·07% carbon). The geometry of the cell was fixed, with a gap of 0·5 mm, and the velocity, U, was therefore directly related to this geometry via the Reynolds number, (Re) defined by $(Re) = Ud\rho/\eta$ where d is the hydraulic diameter of the cell, which for a narrow-gapped cell of rectangular section is approximately equal to twice the gap; ρ and η are respectively the density and viscosity of the electrolyte and were taken as 1 g cm^{-3} and 0·01 g cm^{-1} s^{-1} respectively under the conditions of the experiments.

2. Results and discussion

The efficiency for the dissolution in 2·5 M NaCl at varying current density is shown in Fig. 1, and for 1·8 M $NaNO_3$ and 3·7 M $NaClO_3$ in Fig. 2. The effect of electrolyte velocity on the efficiency for all three electrolytes at a current density of 25×10^4 A m^{-2} is shown in Fig. 3. The dashed lines in the figures represent 100% efficiency for the two-valent dissolution. Uncertainty bars are contained within the symbols except in the cases for NaCl

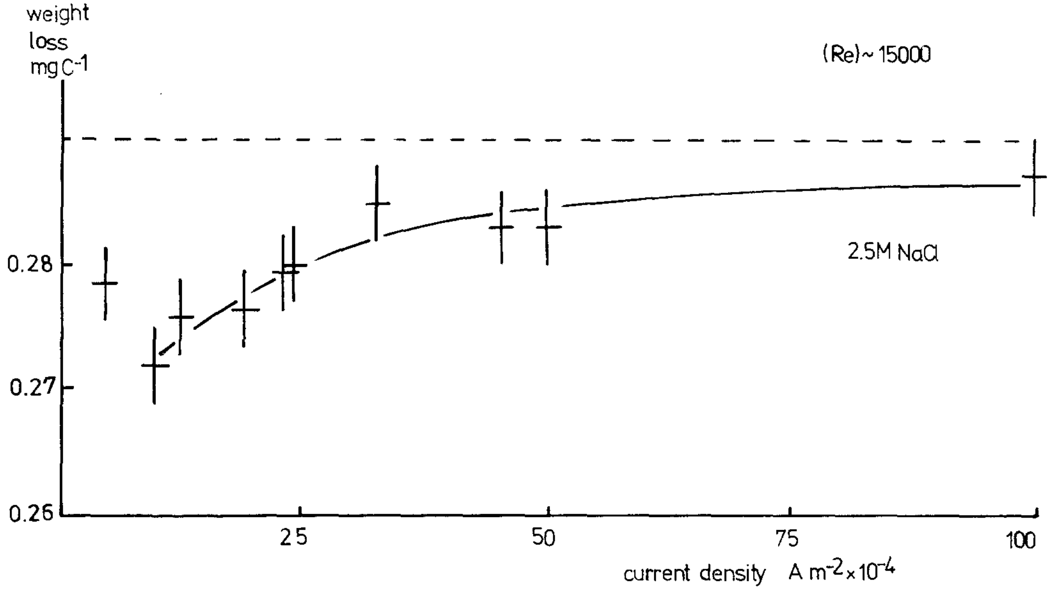

Fig. 1. Efficiency of dissolution for mild steel in 2·5 M NaCl.

where they are given. The possible errors arise principally from the measurement of current over short periods of time (30–120 s).

At all values of current density displayed in Fig. 1, the efficiency for the dissolution in NaCl lies just below 100%, with a probable dip at the lower current densities. This finding is slightly different from that of Chin and Wallace [4] who obtained values slightly greater than 100% although the flow obtained [(*Re*) of 8000] by these authors was lower than that presented in Fig. 1. However the values obtained here are in good agreement with the few measurements made by Mao [2]. The drop in efficiency recorded by Chin and Wallace

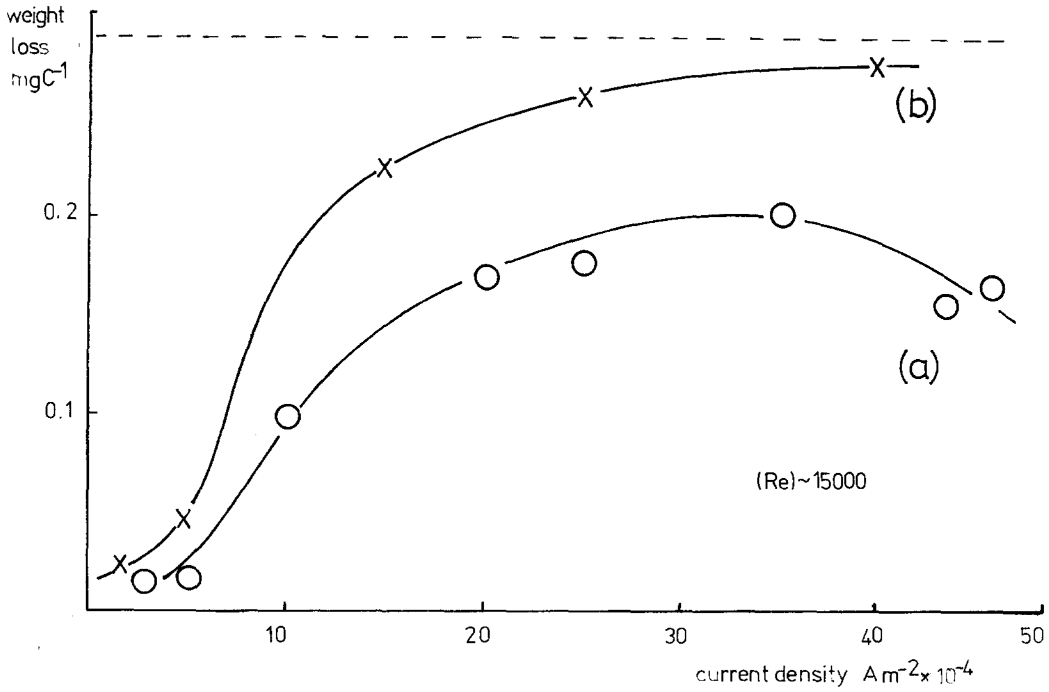

Fig. 2. Efficiency of dissolution for mild steel in (a) 1·8 M $NaNO_3$ and (b) 3·7 M $NaClO_3$.

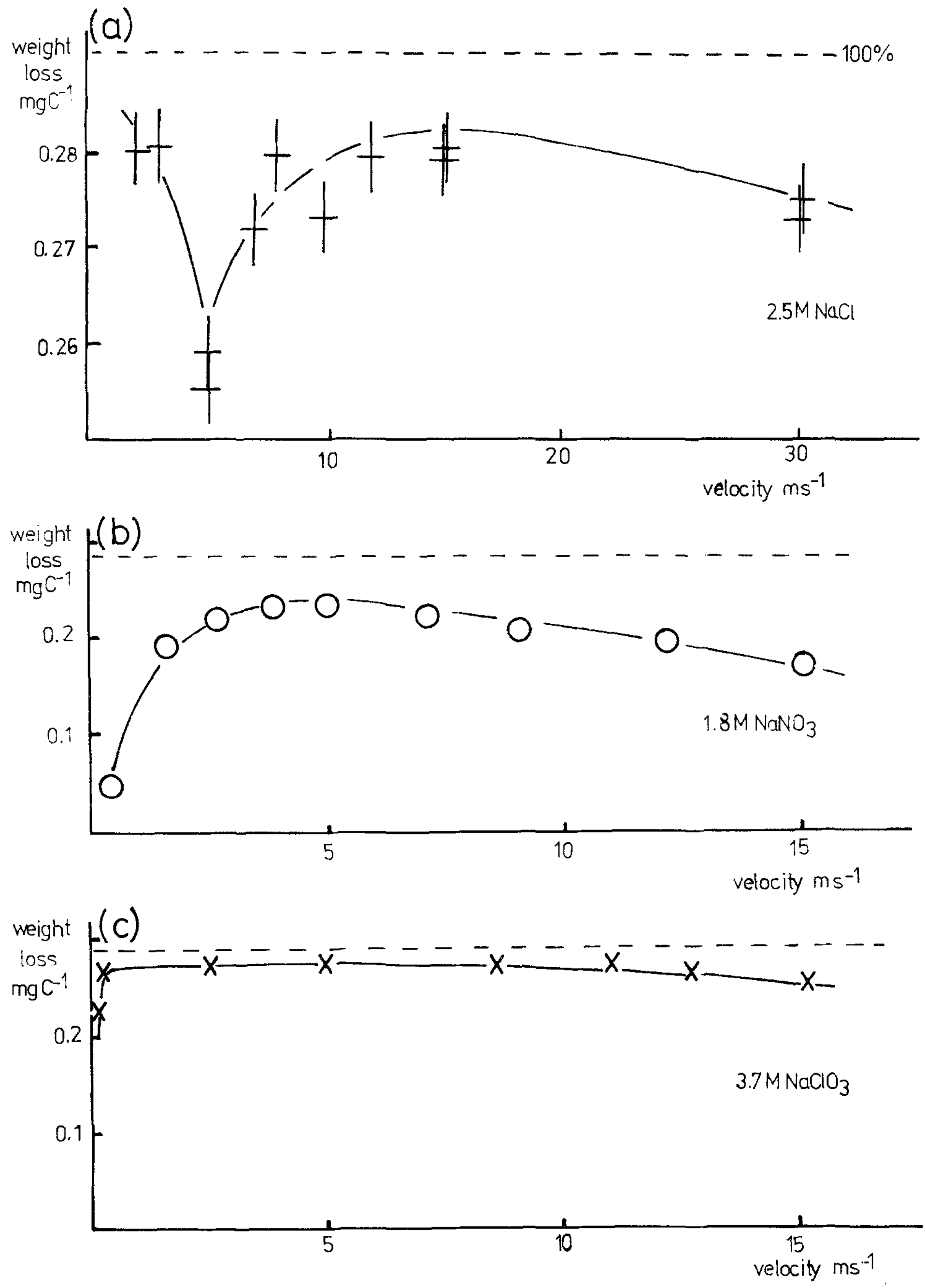

Fig. 3. Effect of electrolyte flow on efficiency at 25 × 10^4 A m^{-2}.

[4] to ~ 80% at a current density between 20 and 50 x 10^4 A m^{-2} was not observed under the conditions of the present work (although see effect of flow later), and it seems from the results obtained here that any film that may arise from dissolution/precipitation, whilst possibly inhibiting the kinetics, does not affect the efficiency and is therefore not electronically conducting. On the other hand the lower overall efficiencies for dissolution in $NaNO_3$ and $NaClO_3$ given in Fig. 2, indicate that considerable electronic conductance occurs, particularly at the lower current densities. The maximum current efficiency achieved in $NaNO_3$ in the present work is given in Fig. 2 as about 70% and this figure is considerably higher than that reported by Mao [2] for a similar concentration of

solution at a similar current density (11·5% at 47×10^4 A m^{-2}). The very low values at the low current density are however in agreement. The reason for the disagreement probably lies in the different flow characteristics between the two studies; flow markedly affects the efficiency in $NaNO_3$ (see Fig. 3). Mao, however, reported much higher values of efficiency at higher electrolyte concentrations and the drop in Fig. 2 at the higher current densities is possibly a reflection of this effect; for a fixed flow rate, the electrolyte will be effectively diluted at the high current densities by the reaction products. Conversely, as the cathodic process in nitrate is a nitrate reduction to numerous species including NH_2OH [2], this drop in efficiency could be associated (for both the current density effect and the concentration effect) with the oxidation of cathodic reduction products. The variance with the nitrate of results of Chin and Wallace [4] will also be due to the different flows. $NaClO_3$ and NaCl showed no such tendency to a drop in efficiency and this is supported by the fact that their efficiencies vary little from 100% with change in electrolyte velocity, Fig. 3. Nevertheless Mao commented on the observed increase in efficiency with increase in concentration of $NaClO_3$ and explained it as an increase of the proportion of ClO_3^- in the film, and hence increased ionic conductivity, with increased concentration. It is possible that a drop in efficiency for $NaClO_3$ might occur for the same reasons as those explained for $NaNO_3$ but at higher current densities than those studied here. The evidence available suggests that mild steel in these two electrolytes has similar films attached which are very porous and which break up under the influence of high flow rates. The drop in efficiency with increased flow for $NaNO_3$ may be associated with a secondary anodic process, $2H_2O \rightarrow O_2 + 4H^+ + 4e$, in which the local change in pH serves to control film thickness. Increased flow will tend to sweep away the acidic solution and reduce this effect. This was not observed to any great extent for NaCl or for $NaClO_3$, although Hoare and Wiese [6] reported efficiencies for the dissolution of pure iron in 4 M $NaClO_3$, with much experimental scatter, but with a hint that increased flow would cause a fall in efficiency. Chin and Wallace [4], on the other hand, for two electrolyte velocities within the range reported here, observed no such fall.

The dip in efficiency for mild steel in 2·5 M NaCl over a range of electrolyte velocity at about 5 m s^{-1} [$(Re) \sim 5000$] appears to be reproducible. Furthermore, the drop in efficiency recorded by Chin and Wallace [4] was for a velocity in this range [(Re) of $4000 \approx 4$ m s^{-1} in Fig. 3] and the results are therefore in agreement. If dissolution product precipitation were to occur at low velocities, this might account for the fall in efficiency. This fall would occur at higher velocities for higher current densities, as observed by Chin and Wallace.

The higher efficiencies at the lowest velocities (Fig. 3a) are probably a result of increased electrolyte agitation caused by boiling. A heat-balance calculation shows that boiling would in fact occur at these very low velocities, although the velocity cannot be estimated precisely due to the complication of 'dilution' effects of electrolysis products on the electrical conductance of the electrolyte.

The specific conductance for 2·5 M NaCl at room temperature [7] would be $\sim 0{\cdot}14\ \Omega^{-1}\ \text{cm}^{-1}$, producing an inter-electrode resistance of $\sim 0{\cdot}06\ \Omega$ and generating 1·35 kJ s^{-1} for a current of $25{\cdot}10^4$ A m^{-2}. In order to remove this heat and avoid boiling an electrolyte velocity of over 1 m s^{-1} would be required. However hydrogen is being produced at the rate of 34·8 cm^3 s^{-1} which will more than double the inter-electrode resistance. Boiling might therefore be expected at anything below 3 m s^{-1}. A similar rise in efficiency does not occur for nitrate (3b) or chlorate (3c).

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