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On the influence of electrolyte concentration, pH and temperature on surface brightening of nickel under ECM conditions

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High rate anodic dissolution of nickel in sodium nitrate electrolytes was studied under controlled hydrodynamic conditions in order to investigate the influence of electrolyte concentration, pH and temperature on surface brightening under conditions comparable to electrochemical machining. Dissolution experiments were performed on a rectangular flow channel cell through which the electrolyte was pumped at a constant linear velocity of 1000 cm s^{-1}. Results show that the onset of surface brightening depends on concentration and temperature of the electrolyte but is little affected by pH. The data are consistent with a previously described salt precipitation model for surface brightening.

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1. Introduction

Passivating electrolytes such as sodium nitrate or sodium chlorate are widely used for the electrochemical machining (ECM) of iron and nickel base alloys [1, 2]. Good surface finish, comparable to that of an electropolished surface, can be obtained under suitable operating conditions. In order to learn more about the mechanisms involved in ECM with passivating electrolytes, the transpassive dissolution of nickel in nitrate electrolytes is being studied in this laboratory using a flow channel cell with well-defined hydrodynamic conditions.

In a recent paper [3], a mass transfer model for surface brightening in strongly acidified nickel nitrate and sodium nitrate electrolytes was presented. According to this model, surface brightening is obtained when the limiting mass transfer rate for dissolution products is exceeded causing salt precipitation at the anode. Using binary electrolytes of different nickel nitrate concentration, a quantitative agreement between calculated anodic surface concentration at the onset of brightening and the saturation concentration was obtained. Furthermore, the flow rate dependence of surface brightening in acidified sodium nitrate was found to be well-described by dimensionless relations for convective mass transfer in flow channels.

In technical ECM practice, neutral rather than acidified sodium nitrate solutions are employed and electrolyte concentration as well as temperature vary depending on the application [1]. It was therefore considered to be of interest to extend the previous investigation of surface brightening during high rate nickel dissolution to a wider range of operating conditions. In the present study, the influence of pH, electrolyte concentration and temperature has been investigated using sodium nitrate as electrolyte. The results obtained are discussed in terms of the previously developed salt precipitation model for ECM surface brightening.

2. Experimental

All experiments involved dissolution at constant current in a flow channel cell at an electrolyte velocity of 1000 cm s^{-1}. Current densities employed ranged up to 30 A cm^{-2}. Anode potentials were recorded by means of a digital oscilloscope using a saturated calomel reference electrode connected to the channel by a backside capillary. Details of the apparatus and of the experimental procedure have been given previously [3, 4]. Anodes made of nickel 200 were 1·02 cm long and 0·317 cm wide. They were positioned flush with the channel wall at a distance of 0·05 cm from each other. Before each experiment, the anodes were mechanically polished on 600 carborundum paper, cleaned and cathodically pretreated in 1 M NaOH solution. A constant charge of 60 C cm^{-2} corresponding to a maximum dissolution depth of 20 μm was passed in all experiments. This charge was sufficiently large to allow for gravimetric determination of weight loss resulting from dissolution but it was small enough to avoid appreciable changes in cell geometry during the experiments.

After dissolution, the anodes were removed from the experimental cell, washed, dried and then examined under a microscope in order to determine the fraction of the surface which is bright. In some experiments, dried anodes were weighed before and after dissolution and the current efficiency for nickel dissolution was calculated using Faraday's law with $n = 2$. Analytical grade chemicals were used throughout for preparing solutions. Temperature was maintained at ± 1° C, by means of a thermostat. Unless otherwise indicated, experiments were performed at 25° C.

3. Results

Anodic potential transients resulting from the application of a constant current pulse resembled those described previously [3]: steady state was reached almost immediately at low current densities while typical potential overshoots were observed above a critical current density, the value of which depended on the experimental conditions. Measured steady-state and maximum potential values, respectively, are plotted as a function of current density in Figs. 1–3. Also indicated is the surface appearance i.e. the percentage of total anode surface appearing bright after dissolution. Since the transition from local etching to local brightening was always quite sharp, the percentage of bright surface could be readily estimated. The data given show that in all cases a change in surface appearance is associated with a change in the slope of the corresponding potential current curves. Measured potential values are always higher and slopes are steeper under brightening conditions than under etching conditions. The behaviour has previously been associated with the formation of a salt layer on the anode [3].

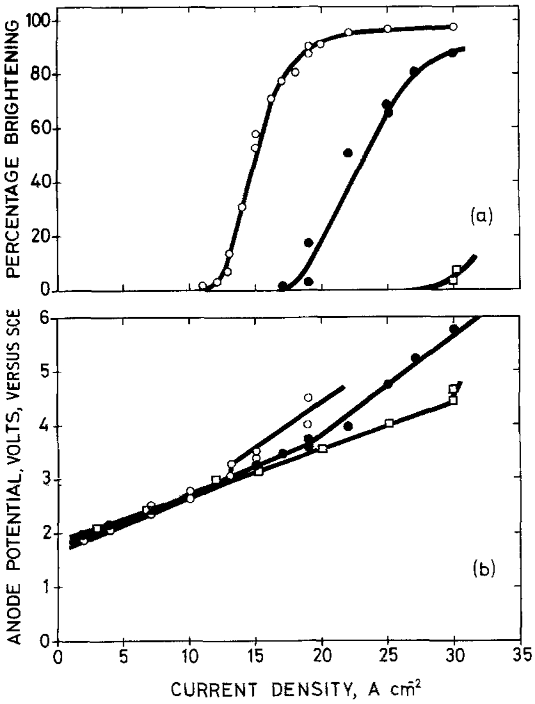

Fig. 1. Influence of electrolyte concentration on (a) surface brightening (b) overall anode potential, as a function of current density for nickel dissolution in 5 M $NaNO_3$ + 1 M HNO_3 (○), 3 M $NaNO_3$ + 1 M HNO_3 (●) and 1 M $NaNO_3$ + 1 M HNO_3 (□).

In Fig. 1, results obtained in acidified solutions of different nitrate ion concentrations, 5 M $NaNO_3$ + 1 M HNO_3, 3 M $NaNO_3$ + 1 M HNO_3, 1 M $NaNO_3$ + 1 M HNO_3, are given. It follows from the data that brightening sets in at a lower current density the higher the nitrate ion concentration in the bulk.

Fig. 2 illustrates the influence of temperature on surface brightening for a solution of 5 M $NaNO_3$ + 1 M HNO_3. The data obtained at 5, 25 and 40° C respectively, show that with increasing temperature higher current densities are required to obtain surface brightening. The effect of solution pH is illustrated by Fig. 3 which gives data obtained in 5 M $NaNO_3$ + 1 M HNO_3, 5·9 M $NaNO_3$ + 0·1 M HNO_3, and 6 M $NaNO_3$ + 0·1 M NaOH. Within the range studied, the acidity of the solution has no significant effect on surface brightening.

Current efficiency for nickel dissolution was measured by determining weight loss. A detailed discussion of the dependence of current efficiency on current density in relation to passive film

Table 1. Estimate of surface concentration corresponding to the onset of brightening

Solution	T (° C)	ν (cm^2 s^{-1})	(Re)	i_{ob} (A cm^{-2})	θ (%)	C_s (mol l^{-1})
5 M NaNO$_3$ + 1 M HNO$_3$	5	2·20 × 10^{-2}	4159	6·5	92·0	2·03
	25	1·45 × 10^{-2}	6310	13·0	97·0	2·25
	40	1·02 × 10^{-2}	8970	21·0	99·5	2·46
3 M NaNO$_3$ + 1 M HNO$_3$	25	1·25 × 10^{-2}	7320	19·0	97·0	3·00
1 M NaNO$_3$ + 1 M HNO$_3$	25	1·07 × 10^{-2}	8550	30·0	92·0	4·08

T = Electrolyte temperature; ν = Kinematic viscosity; (Re) = Reynolds number; i_{ob} = Current density at the onset of brightening; θ = Current efficiency for nickel dissolution at the onset of brightening; C_s = Surface concentration of nickel nitrate at the onset of brightening.

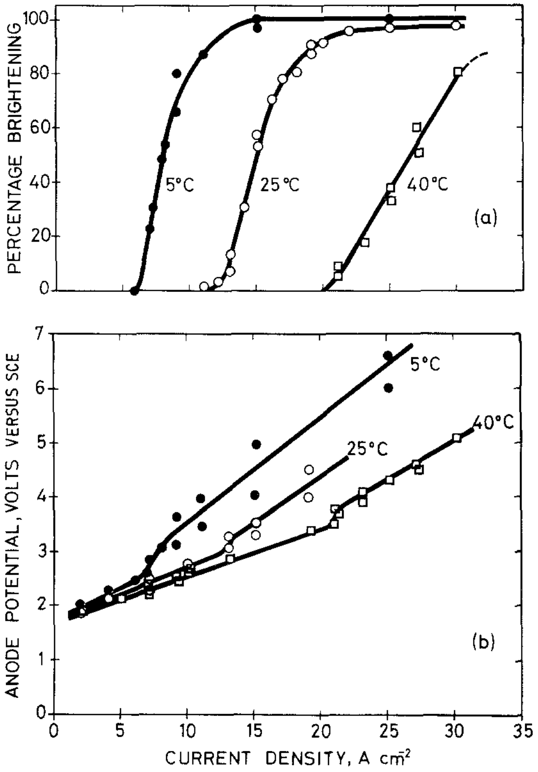

Fig. 2. Influence of electrolyte temperature on (a) surface brightening (b) overall anode potential as a function of current density for nickel dissolution in 5 M NaNO$_3$ + 1 M NaNO$_3$ at 5° C (●), 25° C (○), and 40° C (□).

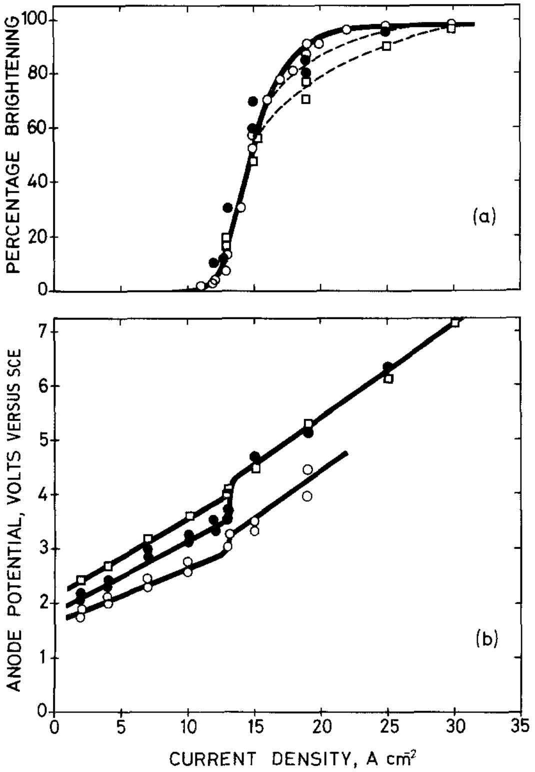

Fig. 3. Influence of electrolyte pH on (a) surface brightening (b) overall anode potential as a function of current density for nickel dissolution in 5 M NaNO$_3$ + 1 M NaNO$_3$ + 1 M HNO$_3$ (○), 5·9 M NaNO$_3$ + 0·1 M HNO$_3$ (●), 6 M NaNO$_3$ + 0·1 M NaOH (□).

break-down will be given elsewhere [5]. In the context of the present study, it is sufficient to note that current efficiency for nickel dissolution in sodium nitrate is an increasing function of current density. At the onset of surface brightening current efficiency for nickel dissolution (based on Ni^{2+} formation) is always close to 100% indicating that divalent nickel ion formation is the predominant reaction. Current efficiency values at the onset of brightening are summarized in Table 1.

4. Discussion

According to the previously developed salt

Table 2. Density of saturated solutions of nickel nitrate

System	*Temperature* (°C)	g/100 g *Sat. soln.* [6]		*Density* (g cc^{-1})
		$Ni(NO_3)_2$	HNO_3	
$Ni(NO_3)_2-HNO_3-H_2O$	25	43·5	7·6	1·579
		38·9	13·2	1·556
		34·3	19·1	1·532
		30·2	24·1	1·516
		24·7	32·1	1·494
		20·1	40·0	1·492
$Ni(NO_3)_2-H_2O$	0	44·2	–	1·530
	20	48·5	–	1·586
	25	50·0	–	1·610
	30	51·3	–	1·623
	40	54·3	–	1·668

precipitation model [3], surface brightening sets in when the local concentration of nickel nitrate at the anode exceeds the saturation concentration. The local concentration built up at the anode depends on applied current density and on mass transfer conditions, including flow rate, geometry, diffusion coefficient and viscosity. The saturation concentration depends on supporting electrolyte composition and on temperature. Complete solubility data for the system $Ni(NO_3)_2-NaNO_3-HNO_3-H_2O$ employed here are not available in the literature. However, the solubility of $Ni(NO_3)_2$ in HNO_3 as a function of concentration is known and also the solubility of $Ni(NO_3)_2$ in water as a function of temperature. Solubility data taken from the literature [6] and converted to the molarity scale by using appropriate density values measured in this laboratory (Table 2) are given in Fig. 4. They show that the solubility of nickel nitrate decreases with increasing bulk nitrate concentration and it increases with increasing temperature. Surface brightening at a given flow rate should therefore occur at higher current density the more dilute the sodium nitrate electrolyte, and the higher the temperature. This is qualitatively consistent with the data shown in Figs. 1 and 2.

For a more quantitative interpretation, one has to consider not only the variation of nickel nitrate solubility with supporting electrolyte concentration and temperature, but also possible variations of transport properties. An estimation of this effect is given in the following.

The current density at the onset of brightening, i_{ob} is given by Equation 1.

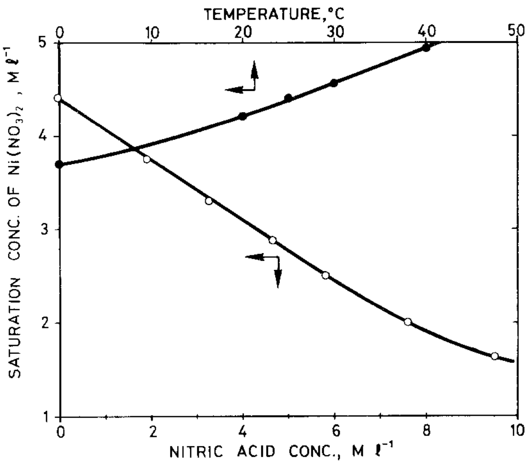

Fig. 4. (a) Saturation concentration of nickel nitrate in nitric acid solutions of different concentrations, (b) influence of temperature on saturation concentration of nickel nitrate in water.

$$i_{ob} = \frac{2FDC_s}{\theta\delta}. \tag{1}$$

Here D is the effective diffusion coefficient in cm^{2}s^{-1}; C_s is the surface concentration of nickel nitrate at the onset of brightening in mol cm^{-3}, and is equal to the saturation concentration. θ is the current efficiency for nickel dissolution at the onset of brightening, and δ is the thickness of the diffusion layer which can be evaluated from dimensionless relations describing mass transfer in flow channels [3]. For the present channel geometry and a constant flow rate of 1000 cm^{-1}s corresponding to turbulent flow, Equation 1 then becomes

$$i_{ob} = \frac{2{\cdot}41 \times 10^6 \nu^{-5/8} D^{3/4} C_s}{\theta}. \qquad (2)$$

Here ν is the kinematic viscosity in $cm^2 s^{-1}$. Table 1 contains measured values of i_{ob}, θ and ν for the experimental conditions of the data shown in Figs. 1 and 2. The current density at the onset of brightening was taken as corresponding to the situation when 5% of the surface was bright. The data given in Table 1 together with Equation 2 allow one to estimate the surface concentration, C_s, at the onset of brightening provided the effective diffusion coefficient D is known. For the present purposes, D was assumed to be given by $D = 9 \times 10^{-6} \{1 + 0{\cdot}02(T - 25)\}$, where T is the electrolyte temperature in ° C. The value $9 \times 10^{-6} cm^2 s^{-1}$ corresponds to the effective diffusion coefficient of nickel nitrate in 5 M $NaNO_3$ + 1 M HNO_3 at 25° C employed previously [3]. The given temperature coefficient of 0·02 per degree is a typical value for diffusion in aqueous electrolytes [7].

Values for the surface concentration C_s at the onset of brightening estimated in this manner are listed in the last column of Table 1. Their dependence on temperature and on bulk sodium nitrate concentration is qualitatively the same as that of the saturation concentrations listed in Fig. 4. Furthermore the order of magnitude of estimated C_s values is the same as one expects for the saturation concentration under the conditions of the experiments. The results obtained at different temperatures and different sodium nitrate concentrations are, therefore, consistent with a salt precipitation model for surface brightening.

In neutral and acidified solutions nickel nitrate solubility is independent of pH. In this pH range, the acidity of the solution should, therefore, have little effect on the onset of surface brightening. This is consistent with the experimental data for acidified solutions listed in Fig. 3. On the other hand, in the alkaline pH region one might expect that hydroxide precipitation would alter brightening conditions. The data of Fig. 3 show that such is not the case i.e. surface brightening in nitrate solution containing 0·1 M NaOH occurs at almost the same current density as in acidified nitrate solution. This behaviour surprising, at first sight, can be explained by postulating that during the experiment the local pH at the anode surface was different from that of the bulk. Indeed, small degrees of anodic oxygen evolution or hydrolysis of anodically generated nickel ions could produce sufficient H^+ ions near the anode to render the local pH neutral or acid. At the onset of brightening, salt precipitation then occurs just as in the previously studied acidified sodium nitrate solutions. The fact that when the bulk NaOH concentration was increased to 1 M, a different dissolution behaviour was observed [8], and no brightening was obtained within the current density range studied supports this explanation. Apparently the bulk hydroxyl ion concentration was sufficiently high in 1 M NaOH for the local pH at the anode to remain alkaline during the experiments [8].

5. Summary and conclusions

The influence of electrolyte concentration, temperature and pH on the onset of surface brightening during high rate nickel dissolution in sodium nitrate can be satisfactorily explained by postulating that the onset of surface brightening is mass transfer controlled and coincides with salt precipitation at the anode. The present data are therefore in good agreement with those reported previously on the influence of flow rate and of bulk nickel ion concentration on surface brightening [3]. Of particular interest is the observation that the onset of surface brightening is little affected by the pH of the bulk electrolyte. The proposed salt precipitation model originally developed for acidified electrolytes is therefore also applicable to the neutral sodium nitrate electrolytes commonly used in ECM practice.

Mass transfer controlled surface brightening and salt precipitation are frequently found in electropolishing and have been described by Hoar [9–12] and by others [13–15]. The role of mass transfer in ECM surface brightening has been recognized only recently, however. Landolt *et al.* [16, 17] found that surface brightening during high rate copper dissolution in nitrate and sulphate electrolytes is mass transfer controlled and appears to coincide with salt precipitation at the anode. Mao and Chin [18] although finding no influence of flow rate suggested that during the ECM of steel in $NaClO_3$, surface brightening is caused by salt precipitation. Mass transfer controlled salt precipitation also affects current–voltage behaviour and surface finish during high rate iron dissolution in concentrated chloride media [19]. The different literature data together with those of the present and the mentioned previous study [3] suggest that mass transport controlled salt precipitation at the anode governs the transition from etching to brightening in many ECM systems involving passivating as well as non-passivating electrolytes. Studies are now needed to investigate by which mechanisms salt precipitation affects the development of surface topography, and what factors govern the formation of hemispherical pits, flow streaks or 'orange peel' surface texture, all of which are undesirable phenomena frequently encountered during ECM under brightening conditions.

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