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A kinetic and electrochemical study of the zincate immersion process for aluminium

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To plate aluminium, its surface is often first coated with a thin layer of zinc which is formed by immersion in an alkaline zincate solution. This paper describes a kinetic and electrochemical study of the zincate immersion reaction. Using an aluminium sample in the form of a rotating disc, the effects of varying the zinc concentration (0.01–0.5 M), disc rotation speed (66–1380 rpm), temperature (5–72 °C), and sodium hydroxide concentration (1.5–9.0 M) on the kinetics were investigated. It was found that the reaction was usually first order. When the zincate concentration was 0.1 M, the reaction was chemically controlled with an activation energy of 35 ± 7 kJ mol^{-1}. At high zincate concentrations, high disc rotation speeds and low sodium hydroxide concentrations, a thin film of zinc metal was formed on the aluminium surface, blocking the subsequent reaction. It was found that the most compact and adherent zinc films were formed at high zincate concentrations. This finding is consistent with industrial practice. These results are explained using mixed potential measurements and Evans' diagrams.

1. Introduction

It is difficult to plate other metals on aluminium since it is covered by a strongly adherent film of oxide which is highly resistive and which prevents an electrodeposit from sticking to the surface. This problem can be overcome by immersing the aluminium in a strong sodium hydroxide solution containing zincate ions. The aluminium oxide dissolves in the strong sodium hydroxide solution and zinc then deposits on the aluminium as a result of displacement from solution by the aluminium. The process is known as the zincate immersion process. Zincated surfaces may then be electroplated with a variety of metals including copper, nickel, silver and chromium [1, 2].

Although this method for coating aluminium has been widely used in industry for many years, the fundamentals of the process are still not understood. However, many of the factors which control the quality of the deposit are known. In 1950, Keller and Zelly [3] established that the weight of the zinc coating had a major influence on the corrosion resistance of the electrodeposit, the thinnest zinc films providing the best underlay. Furthermore, the zinc coating was strongly influenced by the rate of deposition. When the rate was high, the coatings tended to be heavier and less satisfactory. Subsequently, Zelly [4] showed that the weight of the zinc deposit increased appreciably as the zincate solution is diluted. Thus, although dilute zincate baths have the advantages of reducing drag-out and rinsing, concentrated baths are considered to be more reliable and are currently widely used by industry. A typical bath composition is 1.2 M zincate and 13 M sodium hydroxide [1]. A large proportion of the research carried out in the last decade or so has focussed on modifications to the zincate process such as double dipping, ferric chloride/tartrate additions and pretreatment sequences for the aluminium [5, 6].

In this paper, results from a kinetic and electrochemical study of the zincate immersion process without modifications are presented. The zincate immersion process is a cementation or metal displacement reaction and so can be studied by electrochemical methods [7]. In particular, Evans' diagrams have been shown to be useful in understanding the mechanism of cementation reactions and are used here for that purpose, together with mixed potential measurements. The zincate immersion process is a heterogeneous reaction and such reactions are best studied using samples in the form of rotating discs since the hydrodynamics at, and mass transfer to, a disc surface can be readily controlled [8]. Both the kinetic and electrochemical studies were carried out using rotating discs of aluminium and zinc.

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2. Experimental details

Reagents of analytical grade and deionized water obtained from a Millipore Milli-Q System were used in preparing the solutions. All electrodes were constructed from metals of 99.999% purity. The aluminium metal used in the kinetic measurements was supplied by Boyne Smelters Limited, while the zinc and aluminium metals used in construction of the rotating disc electrodes were from the Aldrich Chemical Company. The majority of zincate solutions were prepared from a concentrated stock solution of 1.0 M zincate and 15.0 M sodium hydroxide. The stock solutions were tightly sealed to minimize contamination by carbon dioxide. All solutions were deaerated with high purity nitrogen before the experiment commenced, and a nitrogen atmosphere was maintained for the duration of the experiment. A thermostated water bath was used to keep the experiments at the selected temperatures ± 1 °C.

In the kinetic experiments, 750 ml of test solution was used. This was placed in a vessel of 1 dm^3 capacity fitted with a water jacket through which water from a thermostated bath circulated. The 3.5 cm diameter aluminium disc was mounted in a teflon holder which was rotated by a laboratory stirrer. An optical tachometer was used to measure the rotation rate. The aluminium surface was pretreated by cleaning on various grades of silicon carbide paper and dipping in warm 1.2 M sodium hydroxide for 30 s. It was then rinsed with copious amounts of deionized water and immediately used in the experiment. At timed intervals, samples were withdrawn and analysed using atomic absorption spectrophotometry.

Errors in the rate constants correspond to the 95% confidence interval.

The rotating disc equipment and cell set up were as described previously [9]. A saturated calomel electrode (SCE) was used as the reference electrode and all potentials reported in this paper are expressed with respect to this. The rotating disc electrodes were pretreated by cleaning with silicon carbide paper and rinsing with deionized water. For the mixed potential measurements, it was necessary to dip the electrode in warm 1.2 M sodium hydroxide followed by rinsing with deionized water in order to obtain reproducible results. The polarization experiments were carried out using a PAR 273 Potentiostat. A scan rate of 1 $mV s^{-1}$ was employed.

3. Results and discussion

3.1. *Kinetic studies*

Metal displacement reactions usually obey a first order rate equation of the type [7]

$$\ln\left(\frac{C_0}{C}\right) = \frac{kAt}{V} \qquad (1)$$

where C_0 is the initial concentration of the precipitating metal (zinc), C is the concentration at time t, k is the rate constant for the reaction, A is the area of the precipitant metal and V is the volume of reactant solution. For each of the kinetic runs, the fit of Equation 1 to the experimental data, which was in the form of zincate concentrations at various reaction times, was tested. A typical plot is shown in Fig. 1(a). With the exception of certain kinetic runs which are discussed below, it was found that the plots were reasonable fits to straight lines passing close to the origin, correlation coefficients for these lines lying in the range 0.94–0.99, that is, the displacement of zinc from alkaline solution by aluminium is usually a first order process.

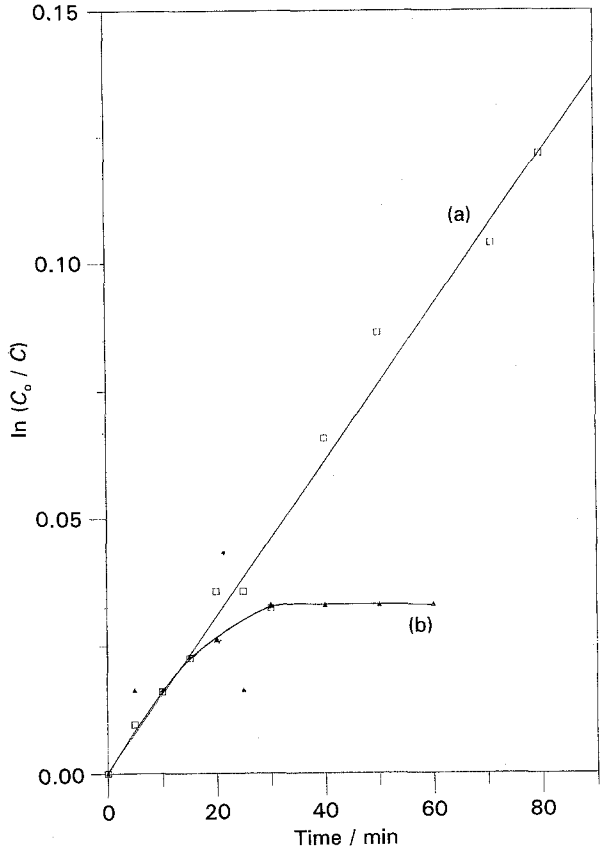

Fig. 1. First order plots for the cases of (a) a non-blocking reaction (zincate concentration, 0.1 M; sodium hydroxide concentration, 3.0 M; temperature; 21.8 °C and rotation speed, 66 rpm) and (b) a blocking reaction (zincate concentration, 0.1 M; sodium hydroxide concentration, 3.0 M; temperature, 21.8 °C and rotation speed, 1380 rpm).

However, the reaction is more complex than a simple first order process for which the rate constant is expected to be independent of the initial zincate concentration. As shown in Fig. 2, the first order rate constant decreases logarithmically with increasing zincate concentration over the range 0.01–0.1 M zincate. It seems that the area of aluminium available for reaction is reduced by the zinc deposit. If this reduction in area is not taken into account when calculating the rate constant, the rate constant will be apparently reduced. However, the reduction in reaction area is not a continuous process which takes place throughout the reaction. If it were a continuous process, the first order rate plots would be curved, which is not the case. It may be inferred, therefore,

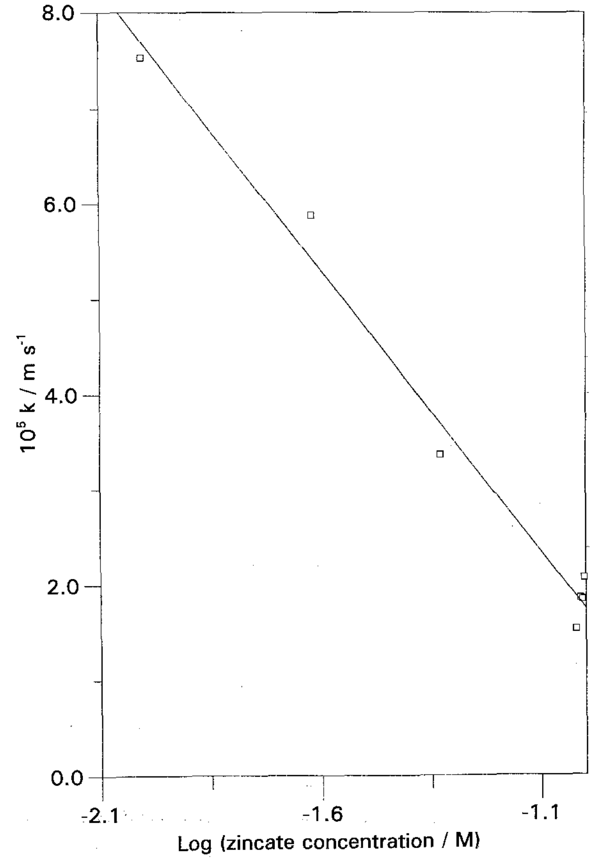

Fig. 2. Relationship between first order rate constant, k, and the zincate concentration (sodium hydroxide concentration, 3.0 M; temperature 21.8 °C and rotation speed, 262 rpm).

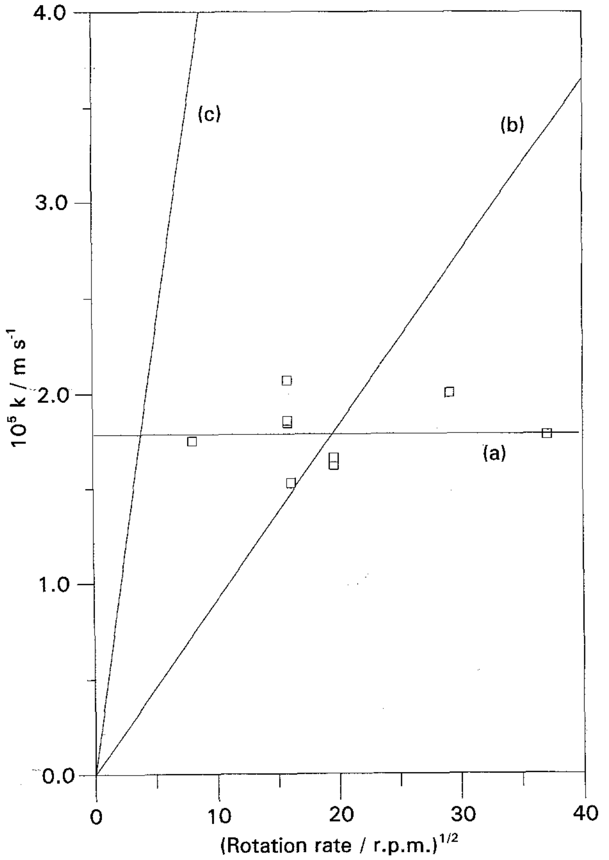

Fig. 3. Effect of rotation speed, ω, on first order rate constant, k. Line (a) is the average of the experimental points; line (b) is calculated assuming that laminar flow obtains and the Levich equation is applicable; line (c) is calculated assuming enhanced mass transfer occurs as a result of a rough deposit surface which causes turbulent flow (zincate concentration, 0.1 M; sodium hydroxide concentration, 3.0 M; temperature, 21.8 °C).

that the extent of the aluminium surface which is blocked is fixed in the first few minutes of the cementation reaction. Consistent with this hypothesis, it was found that at a sufficiently high concentration of zincate (approximately 0.5 M), the cementation reaction ceased shortly after the aluminium disc was exposed to the zincate-containing solution; the aluminium surface has been effectively blanketed by a film of zinc metal. Copper is similarly blocked by silver displaced from a cyanide solution [10]. Blocking of the aluminium surface was also found to occur at a sufficiently high disc rotation speed (1380 rpm). From Fig. 1(b), it can be seen that, after an initial period of reaction which approximately conforms to first order kinetics, the cementation process essentially ceases. It seems probable that the effect of high disc rotation speeds is similar to that of high zincate concentrations in that both sets of experimental conditions lead to a high flux of zincate ions to the aluminium surface. Zinc displacement from an alkaline solution by aluminium metal was also blocked when the concentration of sodium hydroxide was sufficiently low (1.5 M). As discussed later, it seems likely that this is again due to the formation of a film of zinc metal on the aluminium surface. However, it might be due to a layer of zinc oxide. Although data concerning the solubility of zinc oxide in sodium hydroxide solutions is limited and discrepancies exist, a critical evaluation of the literature by Dirkse [11] indicates that a solution containing 1.5 M sodium hydroxide and 0.1 M zincate is bordering on the solubility limit of zinc oxide.

As noted by Power and Ritchie [7], first order kinetics can be due to either a slow diffusion or a slow surface step. To distinguish between these two possibilities, a series of experiments was carried out in which the rate constant was determined as a function of the square root of the disc rotation speed. For a diffusion controlled reaction, a straight line plot passing through the origin is expected. For a chemically controlled reaction, the rate constant is independent of disc rotation speed. The results obtained are shown in Fig. 3. As can be seen, the reaction rate is essentially independent of disc rotation speed, implying that the rate of the reaction is governed by some slow chemical step. This conclusion was verified in two ways. In the first of these, a theoretical first order rate constant was calculated assuming that the reaction was diffusion controlled. For laminar flow to a rotating disc, the first order rate constant is given by Equation 2 [12]

$$k = 0.620 D^{2/3} \nu^{-1/6} \omega^{1/2} \quad (2)$$

where D is the diffusion coefficient of the zincate ions in the alkaline medium, ν is the kinematic viscosity of the solution and ω is the disc rotation speed. Thus, k can be calculated as a function of $\omega^{1/2}$ if the quantity

$D^{2/3}\nu^{-1/6}$ is known. This can be readily determined by measuring the limiting current density (i_L) as a function of disc rotation speed for the deposition of zinc onto a rotating zinc electrode from the same zincate solution. Using the Levich equation [8]

$$i_L = 0.62D^{2/3}\nu^{-1/6}\omega^{1/2}nFC \qquad (3)$$

where n is the number of electrons and F is the Faraday constant, $D^{2/3}\nu^{-1/6}$ was estimated to be $4.55 \times 10^{-6}\,\mathrm{m\,s^{-1/2}}$. Inserting the measured value for $D^{2/3}\nu^{-1/6}$ into Equation 2 gives line (b) in Fig. 3. This line and the horizontal line representing the average of the experimental points intersects at about $\omega^{1/2} \sim 20\,(\mathrm{rpm})^{1/2}$. Ideally, the reaction is expected to be diffusion controlled below this rotation speed and chemically controlled above it. As can be seen from Fig. 3, this is not the case. The reason for the discrepancy is that the zinc deposits are rough and coarse and so the Levich equation (Equation 3) which refers to laminar flow is inapplicable. Strickland and Lawson [13] have shown that for deposit masses of 0.3–5 mg cm^{-2}, the first order rate constant increases significantly with deposit mass. For the copper(II)/zinc system above a deposit mass of 5 mg cm^{-2} and up to at least 12 mg cm^{-2}, the first order rate constant is increased to some four to seven times the initial ('deposit free') value. The deposits obtained in this work were massive, and therefore the first order rate constant can be expected to have been enhanced by at least a factor of four to seven. Line (c) shown in Fig. 3 represents the enhanced rate constants calculated using an enhancement factor of five. Even though this value is probably conservative, it can be seen that it successfully accounts for the system being chemically controlled down to a rotation rate of $\omega^{1/2} = 8\,(\mathrm{rpm})^{1/2}$. Only at very low rotation rates is diffusion control likely to be observed for a zincate concentration of 0.1 M.

A second method of determining whether a cementation reaction is chemically controlled or not is to determine its activation energy under conditions of constant agitation. Under otherwise constant experimental conditions ($C_0 = 0.1$ M; $[\mathrm{OH^-}] = 3.0$ M; $\omega = 262$ rpm), first order kinetics were obeyed over the temperature range 5–72 °C. From an Arrhenius plot, constructed from a rate constant/temperature data set of eight points, an activation energy of 35 ± 7 kJ mol^{-1} was obtained with a correlation coefficient of 0.94. This activation energy is significantly higher than the usual range of, say, 15–25 kJ mol^{-1} [8] for a diffusion controlled reaction. This finding is consistent with the displacement of zinc from solution being controlled by some chemical step.

Because the zincate immersion process is chemically controlled, the dependence of the rate constant on sodium hydroxide concentration was investigated. With the other experimental conditions maintained at constant values ($C_0 = 0.1$ M; $\omega = 262$ rpm; $T = 21.8$ °C), the sodium hydroxide concentration was varied between 3.0 and 9.0 M. Within the limits of experimental error, there was no change in the rate constant over this range.

3.2. *Deposit structure*

Under nearly all of the experimental conditions investigated, the zinc coatings laid down had a dark grey, spongy appearance. They were somewhat crumbly in structure and adhered only poorly to the substrate metal. As the temperature was reduced, the deposits became progressively more compact and adherent, but even when formed at 5 °C, were still lacking in coherence and did not adhere well to the aluminium. Only under a very few experimental conditions were good adherent deposits obtained. High concentration (0.5 M) zincate solutions were found to produce the best results. The deposits formed in these circumstances were thin films of zinc which adhered very strongly to the aluminium surface. Given that these zinc films were essentially continuous, it is not surprising that they bring the cementation reaction to a halt, as noted in the previous section. The deposits formed at high rotation speeds were also thin and coherent, but adhesion to the aluminium was poor and the zinc film could be easily peeled from its surface. In solutions containing low concentrations of sodium hydroxide (1.5 M), thin, coherent zinc coatings were obtained. Unfortunately, the presence of blisters under the deposit limited its adhesion.

3.3. *Mixed potential measurements*

Mixed potentials often provide an insight into the mechanism of a corrosion reaction. In the particular case of the displacement of zinc from solution by aluminium, which is itself corroded during the course of the reaction, mixed potentials clearly show that blanketing of the aluminium surface by a film of zinc metal is the cause of the reaction ceasing at high zincate concentrations, high rotation speeds and low sodium hydroxide concentrations. An example of this is shown in Fig. 4 in which mixed potentials are recorded as a function of time for a series of displacement reactions in which the initial zincate concentration was varied, all other experimental variables being kept constant ($[\mathrm{OH^-}] = 3.0$ M; $\omega = 230$ rpm). Curve (a) shows that, at a high concentration of zincate ions (0.5 M), the mixed potential rises rapidly until a steady state potential of about −1.53 V vs SCE is reached. This steady state potential corresponds to that of zinc metal in the zincate solution. Thus, the aluminium surface behaves as if it had been completely, or almost completely, covered by a layer of zinc metal, as inferred from the kinetic measurements.

By contrast, in the absence of zincate (curve (e)) or at very low concentrations (0.01 M, curve (d)), the mixed potential starts and continues at a very negative potential which is characteristic of aluminium metal dissolving in a strong sodium hydroxide solution.

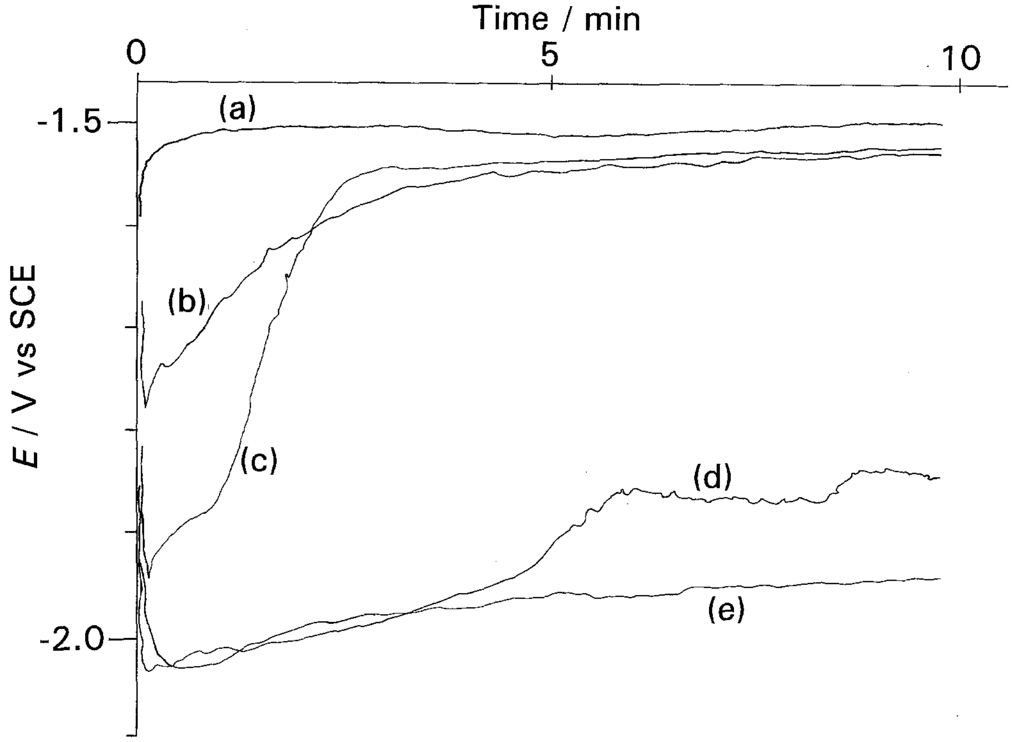

Fig. 4. Mixed potentials as a function of time for varying zincate concentrations (a), 0.5, (b) 0.1, (c) 0.05, (d) 0.01 and (e) 0 M (sodium hydroxide concentration, 3.0 M; temperature, 25 °C; rotation speed, 230 rpm).

At intermediate concentrations (0.05 M, curve (c) and 0.1 M, curve (b)), the initial potential is relatively negative, but then climbs rapidly in the first few minutes of the reaction towards the high steady state potential characteristic of zinc metal in the zincate solution. This is because the initial reaction is aluminium dissolution with hydrogen being evolved from the aluminium surface. As the surface becomes zinc coated, the dissolution reaction is progressively shut off, partly because the area available for aluminium corrosion is reduced by the zinc coating, and partly because the zinc coating tends to suppress the hydrogen evolution reaction since the overpotential for hydrogen evolution is much greater on zinc than on aluminium [14]. The net result is that the mixed potential increases. The change in mixed potential with the intermediate zincate concentrations also accounts for the observed decrease in the first order rate constant as the zincate concentration increases (Fig. 2). As can be seen from Fig. 4, the surface becomes coated with zinc in the first few minutes of the reaction, the coverage increasing with zincate concentration. Given the fact that the mixed potentials all tend progressively towards that of full zinc coverage, it is surprising that the first order rate constant does not decrease steadily during the course of the reaction. However, this was not observed.

Similar changes in mixed potential to those described above were observed when the disc rotation speed was increased and the sodium hydroxide concentration reduced. This confirms that the cessation of the cementation reaction at 1.5 M sodium hydroxide was due to blocking by a zinc film rather than a zinc oxide layer. It is interesting to note that in 1.5 M sodium hydroxide, after a steady potential had been reached at about 4.5 min, the mixed potential decreased. This corresponded to a loss of adhesion of the zinc deposit on the aluminium surface. If the zinc-coated aluminium is removed from the reactant solution before this and the deposit examined, the zinc film was found to have very good adhesion but the presence of very small blisters under the zinc deposit could be seen. Presumably at a time of approximately 6 min, these blisters have grown and cause the zinc layer to lose adhesion.

3.4. *Evans' diagram*

As discussed by Power and Ritchie [7], Evans' diagrams for cementation reactions usually consist of the superposition of the polarization curves (E against $\log|i|$) for the reduction of the more noble metal in solution and the oxidation of the less noble metal. In the case of the zincate/aluminium system, the system is more complex since aluminium reacts with water in strong alkaline solution. Thermodynamically, zinc should also dissolve in strong alkaline solution, but this is not an important consideration with pure zinc since the overpotential for hydrogen evolution on zinc metal is high [14]. We will therefore consider the polarization curves for zinc and aluminium in alkaline solution separately and then their superposition as a function of zincate concentration, rotation speed and temperature.

Lines (z_a) and (z_c) in Fig. 5 show the polarization curves for zinc in a solution containing 0.1 M zincate and 3.0 M sodium hydroxide. As can be seen, the anodic branch, z_a, goes from a Tafel region to a

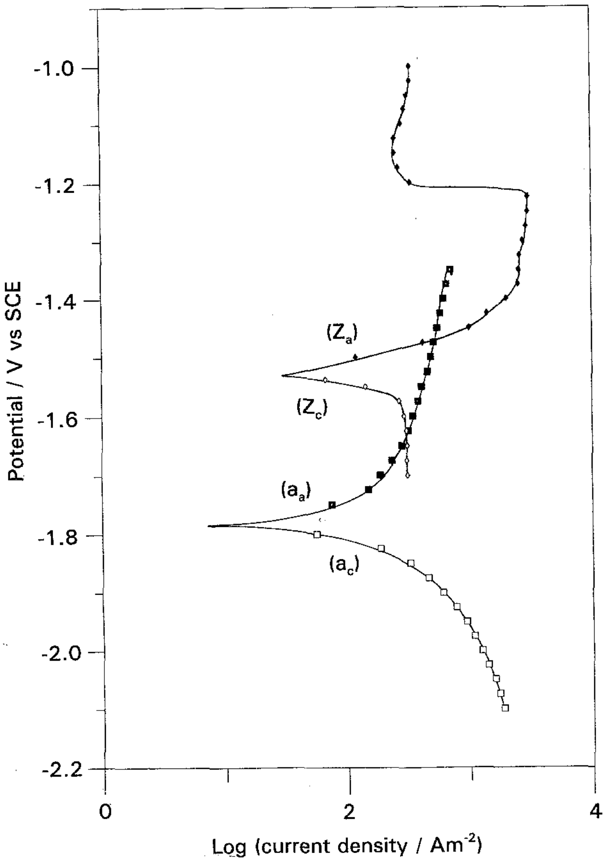

Fig. 5. Evans' diagram showing polarization curves for aluminium in a sodium hydroxide solution (a) and zinc in a zincate solution (z). (zincate concentration, 0.1 M; sodium hydroxide concentration, 3.0 M; temperature, 25.0 °C and rotation speed 270 rpm).

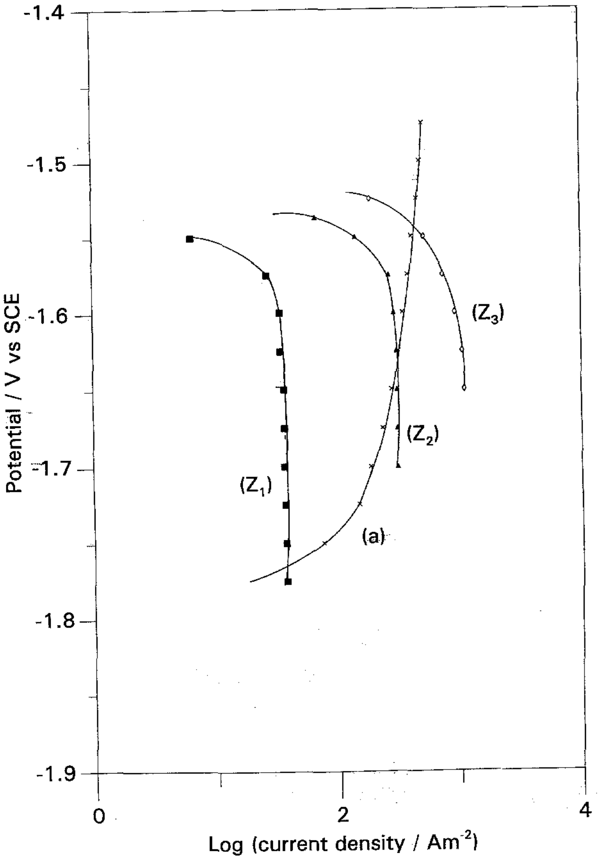

Fig. 6. Evans' diagram showing polarization curves for aluminium (a) and zinc (z) for different zincate concentrations: z_1, 0.01; z_2, 0.1 and z_3, 0.5 M (sodium hydroxide concentration, 3.0 M; temperature, 25.0 °C and rotation speed, 270 rpm).

plateau before the current drops sharply upon passivation [17]. On the cathodic side, z_c, which is of more interest to the present paper, the Tafel region is also followed by a plateau which in this case is due to the diffusion controlled reduction of zincate ions. Lines (a_a) and (a_c) show the anodic and cathodic polarization curves for the dissolution of aluminium in 3.0 M sodium hydroxide.

Superposition of the two diagrams, also shown in Fig. 5, suggests that the displacement of zinc from alkaline solution by aluminium metal should be a diffusion controlled reaction with a mixed potential of about −1.62 V vs SCE when the experimental conditions are zincate concentration 0.1 M, hydroxide concentration 3.0 M and rotation speed 270 rpm. Reference to Fig. 3 shows that under these experimental conditions, the reaction rate is in fact chemically controlled. Furthermore, according to Fig. 4, the mixed potential is about −1.53 V, i.e. much more positive than predicted. In seeking an explanation for these differences, it should be noted that Evans' diagrams are not an exact simulation of the reaction as a whole. The zinc deposition and aluminium dissolution lines shown in Fig. 5 are not recorded under the same conditions as those of the cementation reaction. In the Evans' diagram, zinc is deposited onto a flat zinc surface; in the cementation reaction, the deposit is a spongy mass. The effect of this rough surface will be to perturb the fluid flow which will not be laminar, but at least partially turbulent. As a result, the diffusion controlled plateau will be shifted to higher currents. Similarly, aluminium is not dissolved from a clean aluminium surface, as the Evans' diagram implies, but from a surface blocked by zinc. This will depress the aluminium line to lower currents. The net effect is for the system to operate under chemical control. Although Evans' diagrams similar to that shown in Fig. 5 are of limited value in accounting for the details of the cementation reaction, they are of considerable value in predicting its behaviour as the concentration, rotation speed and temperature are varied. In Fig. 6 for example, we see polarization curves for the reduction of various concentrations of zincate ranging from 0.01 to 0.5 M together with the polarization curve for the dissolution of aluminium in 3.0 M sodium hydroxide. From this diagram, it is clear that the cementation of zinc onto aluminium is most likely to be diffusion controlled at low zincate concentrations (z_1) and chemically controlled at high zincate concentrations (z_3), this latter observation being consistent with the experimental results presented in this paper. Kinetic measurements at low zincate concentrations confirmed that the reaction was diffusion controlled.

Finally, it should be noted that Fig. 6 also accounts for the variation of the mixed potential with time for the various zincate concentrations investigated (Fig. 4). At low zincate concentrations, the system as a

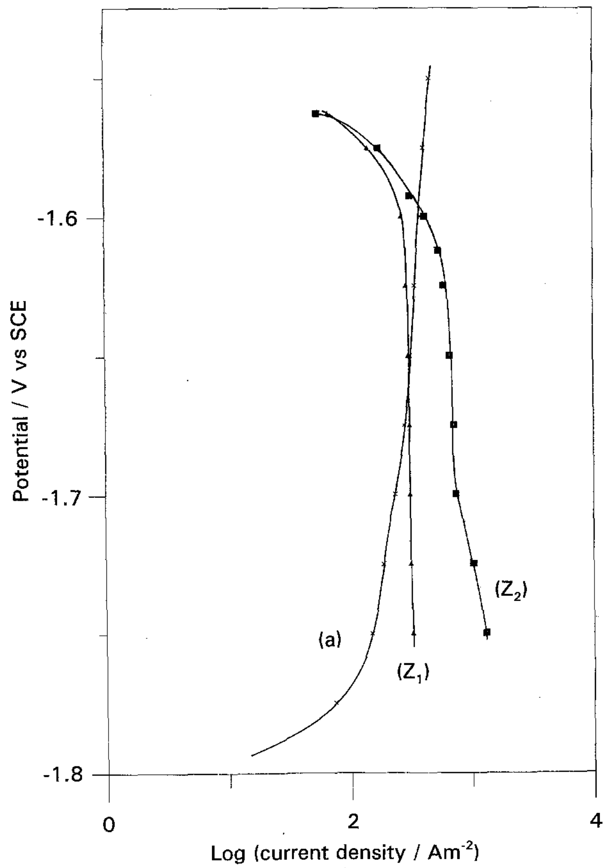

Fig. 7. Evans' diagram showing polarization curves for aluminium (a) and zinc (z) for different rotation speeds (z_1, 270 rpm and z_2, 1660 rpm) (zincate concentration, 0.1 M; sodium hydroxide concentration, 3.0 M and temperature, 25.0 °C).

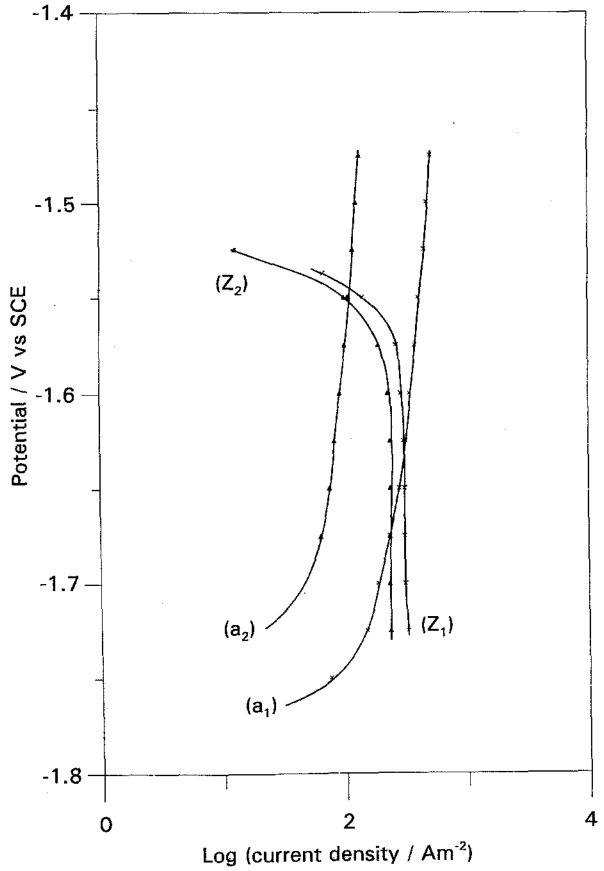

Fig. 8. Evans' diagram showing effect of temperature on the aluminium (a) and zinc (z) polarization curves: a_1, z_1, 25 °C; and a_2, z_2, 5 °C (zincate concentration, 0.1 M; sodium hydroxide concentration, 3.0 M, and rotation speed, 270 rpm).

whole is dominated by the aluminium dissolution reaction and the mixed potential is characteristic of that reaction rather than the displacement reaction. On the other hand, at high zincate concentrations, the aluminium dissolution reaction is far less important and the mixed potential tends towards that of the reduction of zincate on aluminium. Thus, hydrogen evolution is much greater at low zincate concentrations than at high, making it much more difficult to form adherent zinc films at low zincate concentrations than at high, as is found experimentally.

Figure 7 shows a series of Evans' diagrams in which the rotation speed of the aluminium disc is varied. As can be seen, the effect of increasing rotation speed is to push the cementation reaction more and more into the chemically controlled region. Naybour [16] has shown that, at a given current density, the morphology of the zinc deposited from a zincate solution depends on the flow rate of the electrolyte: the deposits laid down at higher flow rates tend to be smoother than those at low. It has also been reported [17] that when the reduction of zincate on zinc metal is carried out at low overpotentials with vigorous stirring, a smooth deposit is formed. On the other hand, dark grey porous deposits are formed in quiescent solutions. These observations are consistent with the results presented here. At low rotation speeds, the cementation product is rough and grey, but at the highest rotation speed investigated (1380 rpm), a smooth coherent zinc film is laid down, causing the reaction to cease (see Fig. 1, line (b)). A drop in temperature has a much greater effect on the oxidation of aluminium than on the reduction of zincate. This is illustrated in Fig. 8. The net result is to force the point of intersection of the aluminium oxidation curve and the zincate reduction curve from (a_1), (z_1), to (a_2), (z_2), i.e. into the chemically controlled region. It is therefore not surprising that, as the temperature is reduced, the deposits become progressively smoother.

Decreasing the concentration of sodium hydroxide causes both the oxidation of aluminium and the reduction of zincate ions to shift to more positive potentials. The net result of this is that the point of intersection of the aluminium oxidation curve and the zincate reduction curve moves progressively into the chemically controlled region where the overpotentials are low. This is consistent with the finding that the smooth, coherent and relatively adherent zinc film formed in 1.5 M sodium hydroxide is due to a change in the deposition kinetics rather than the formation of a zinc oxide layer.

4. Conclusions

The following remarks can now be made.

(i) Over most of the range of experimental variables investigated (zincate concentration: 0.01–0.1 M; disc rotation speed: 230–850 rpm; temperature: 5–72 °C;

sodium hydroxide concentration: 3.0–9.0 M), the zincate immersion reaction is first order with respect to zincate ion concentration and a spongy zinc deposit is laid down.

(ii) For the particular case of zincate concentration, 0.1 M; sodium hydroxide concentration 3.0 M; and disc rotation speed 262 rpm, the cementation of zinc onto aluminium is chemically controlled with an activation energy of about 35 kJ mol^{-1}.

(iii) At low zincate concentrations (<0.5 M) the dissolution of aluminium is an important side reaction.

(iv) At high zincate concentrations (approx 0.5 M), high rotation speeds (~ 1380 rpm) or low sodium hydroxide concentrations (<1.5 M), a thin, adherent film of zinc metal is deposited, which blocks further reaction. This is the probable explanation of why industry uses high zincate concentrations in the zincate immersion process.

(v) The above results can be explained using Evans' diagrams.

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