

Electrochemical aspects of the immersion treatment of aluminium

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The processes occurring during zinc immersion plating of aluminium have been studied in alkaline medium. The mechanism of immersion zinc deposition on aluminium has been elucidated by studying the kinetics of the partial electrode reactions involved in this complex process. The diffusion of zincate ions has been shown to play a decisive role on the cathodic reaction kinetics as well as on the global (cathodic and anodic) reaction rate.

1. Introduction

One of the steps preceding the electroplating of metal coatings on aluminium and its alloys is the process of immersion treatment. The application of this process allows considerable improvement of the adhesion of the metal coating to the substrate, as well as in promoting the corrosion resistance of aluminium articles. The basis of this method is an exchange reaction, leading to the dissolution of the electronegative metal phase (Al) and deposition of a more electropositive metal (e.g., Zn) during the so called 'immersion (zincate) treatment' of aluminium.

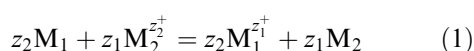
Studies devoted to elucidating the kinetics of the immersion treatment processes are scarce. A number of problems in connection with the theory of the process have not been investigated to a satisfactory extent [1–4]. Basic attention has been focused on the selection of solutions aimed at improvement of the surface properties (i.e., removal of the oxide layer) of aluminium and the formation of intermediate layers promoting the adhesion of metal coatings subsequently deposited on the substrate [5–8].

The aim of the present study was to investigate the kinetics of the formation of immersion zincate coatings on aluminium AD-1.

2. Theoretical background

Currentless metal deposition processes may be classified into two groups:

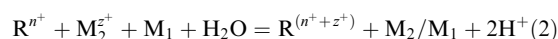
- (a) *Immersion metal plating*. In this case the entire exchange process may be represented by the following general equation:



where M_1 and M_2 are a pair of metals. The thermodynamic reversible potential of the system $M_1^{z_1^+} - [M_1]$ is more negative than the ther-

modynamic reversible potential of the system $M_2^{z_2^+} - [M_2]$.

- (b) *Electroless metal plating*. In this case the deposition of a metal on the surface of another metal (or on nonmetallic activated surface) is achieved by an oxidative reaction of the reducing reactant, present in the electrolyte, which supplies the necessary free electrons:



where R is the reducing agent undergoing oxidation in the process of electroless deposition of an M_2 coating on M_1 .

Paunovic described electroless metal plating as a system, characterized by a mixed potential [9, 10] and verified some of the basic concepts underlying the theory of Wagner and Troud [11]. Later Donahue [12] and Roldan *et al.* [13] established some restrictions on the application of the 'theory of mixed potentials' to the electroless plating of copper. They observed kinetic relationships which confirm the electrochemical nature of the process and proved the interconnection of the anodic and cathodic reactions occurring during this complex process.

Both methods for deposition of metal coatings, without applying electric current from an external source, may be represented, in the following way (Fig. 1) [14]: (a) immersion metal plating and (b) electroless metal plating.

There exists a specific feature which distinguishes immersion deposition from electroless deposition. The former involves anodic dissolution of the more electronegative metal, unlike the latter. This peculiarity allows us to represent the total exchange process of the immersion treatment as an electrochemical corrosion process. Under steady-state conditions there exists an equality between the sums of the electric currents of the anodic and cathodic reactions:

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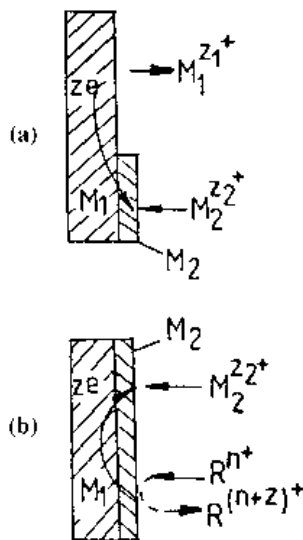


Fig. 1. Symbolic representation of currentless metal deposition: (a) immersion deposition; (b) electroless deposition.

$$\sum i_k = \sum i_a \quad (3)$$

It can be assumed that, at the initial moments of immersion treatment (when the immersion coating is still very thin), the aluminium dissolution is kinetically controlled and can be described by a Tafel-type equation:

$$E = E_{Al}^{\circ} - b_{Al} \ln i_{Al}^{\circ} + b_{Al} \ln i_{Al} \quad (4)$$

where the Tafel coefficient is given by the expression:

$$b_{Al} = \frac{RT}{(1-\alpha)nF} \quad (5)$$

in which α is the transfer coefficient, R the universal gas constant, T the absolute temperature, E the electrode potential, E_{Al}° the equilibrium electrode potential for the aluminium dissolution reaction, i_{Al}° the exchange current and i_{Al} the anodic partial reaction rate.

On the other hand the electroplating on zinc is known to proceed with diffusion limitation with respect to the cathodic reaction [15]. Assuming that the diffusion is the rate-determining step in immersion deposition of zinc, then the kinetic equation is

$$i_k = nF \frac{dj}{dt} = nFK c_{Zn} \quad (6)$$

where j is the number of mols deposited on a unit of surface per unit of time, F the Faraday number, K the mass transport coefficient and c_{Zn} the zinc ionic bulk concentration.

Under steady-state conditions it follows that $i_k = i_a$, so we can combine both equations obtaining the following expression for mixed potential:

$$E_c = E_{Al}^{\circ} - b_{Al} \ln i_{Al}^{\circ} + b_{Al} \ln nFK c_{Zn} \quad (7)$$

Equation 7 shows that the mixed potential is a linear function of the bulk concentration of zinc ions under the conditions of diffusion controlled partial reaction.

It is possible to represent the immersion process as a specific case of corrosion, determined by the reaction of Al anodic dissolution and the cathodic reaction of free electron acceptance, leading to the formation of the new metallic Zn phase. Such a physical concept enables us to express the rate of the immersion metal plating in the following way:

$$I = \frac{E_k^{\circ} - E_a^{\circ}}{R + P_k + P_a} \quad (8)$$

Where R , P_a and P_k are the resistivities of the partial stages, included in the total process in accordance with accepted concepts. It follows from Equation 8 that

$$E_k^{\circ} - E_a^{\circ} = I(R + P_k + P_a) = \Delta E_R + \Delta E_k + \Delta E_a \quad (9)$$

where ΔE_R is the ohmic drop at a definite value of current during the immersion process, ΔE_a is the anodic polarization and ΔE_k is the cathodic polarization.

This approach considers the anodic and cathodic processes as interconnected and therefore the rate of the total process is determined by the slower electrode process:

$$C_k = \frac{P_k}{R + P_k + P_a} = \frac{\Delta E_k}{\Delta E_R + \Delta E_a + \Delta E_k} \quad (10)$$

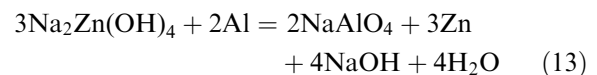
$$C_a = \frac{P_a}{R + P_k + P_a} = \frac{\Delta E_a}{\Delta E_k + \Delta E_a + \Delta E_R} \quad (11)$$

$$C_R = \frac{R}{R + P_a + P_k} = \frac{\Delta E_R}{\Delta E_k + \Delta E_a + \Delta E_R} \quad (12)$$

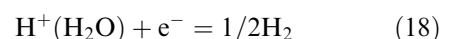
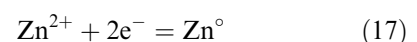
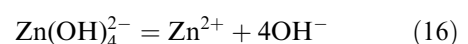
where C_k is the degree of cathodic control, C_a the degree of anodic control and C_R the degree of ohmic control.

In this sense the rate determining step of the total process is that with the highest resistance in comparison to the other steps. The correlation between ΔE_a , ΔE_k and ΔE_R illustrates the ratio between the resistances of the separate steps of the immersion process.

Considering a specific system the exchange process occurring during the zincate treatment of Al, can be represented by the following general equation.



The above equation summarizes the partial reactions, which are proceeding simultaneously on the anodic and cathodic regions of the Al surface:



3. Experimental details

The experiments were carried out in zincate electrolytes, varying the ZnO concentration from 5 to 80 g dm^{-3} and the NaOH concentration from 100 to 600 g dm^{-3} . The temperature of the operating solutions was kept constant at $25^\circ \pm 1^\circ\text{C}$.

The methods of potentiodynamic polarization curves and gravimetric measurements of the deposited zinc weight (g dm^{-2}) were applied [16]. The complicated reaction system was simplified by considering separately the conjugated anodic and cathodic processes (Equations 14–18). The anodic aluminium dissolution and cathodic hydrogen evolution were investigated in model solutions of the same ionic force as the zincate electrolyte but free of zinc metal ions. The process of cathodic zinc deposition was investigated in zincate electrolytes on pure zinc electrodes.

The polarization measurements were conducted in a standard three electrode cell, under potentiodynamic conditions (2 mV s^{-1}), with the help of a potentiostat p-5848 (Russia). A Pt electrode was used as counter electrode, while Cl^-/AgCl , Ag was used as reference electrode. The potential values were referred to the reversible hydrogen electrode. Al AD-1 and Zn electrodes with defined surfaces were used as working electrodes [17, 18].

The changes in the mixed potential of the Al electrode during the zincate immersion pretreatment of Al AD-1 were recorded by means of a two-channel storage oscilloscope C-813 (Russia) against a Zn reference electrode.

The Al surface structure, after the formation of immersion zinc coatings, was studied by electron microscopy (JXA-50A) (Japan).

4. Results and discussion

The model partial polarization curves of the conjugated reactions of zinc deposition on zinc (cathodic reaction) and aluminium dissolution (anodic reaction) are represented in Figs 2 and 3. Figure 2 illustrates the potential-current dependence in solutions of constant NaOH concentration, while the ZnO concentration varies: 5, 10, 40 and 80 g dm^{-3} . The same dependence, this time varying the NaOH concentration and keeping the ZnO concentration constant, is shown in Fig. 3. The crossing points of the partial polarization curves (Figs 2 and 3) determine the rate of the complex exchange process and the corresponding mixed potential (i_c and E_c).

Independently of these model studies the mixed potential was determined directly by means of recording the potential–time (E/τ) oscillograms of aluminium electrodes in the course of zincate pretreatment. These measurements were carried out with a zinc reference electrode. The results are given in Fig. 4(a) and (b) and show that during the initial 1–5 s the mixed potential is shifted in the positive direction, tending to a constant value.

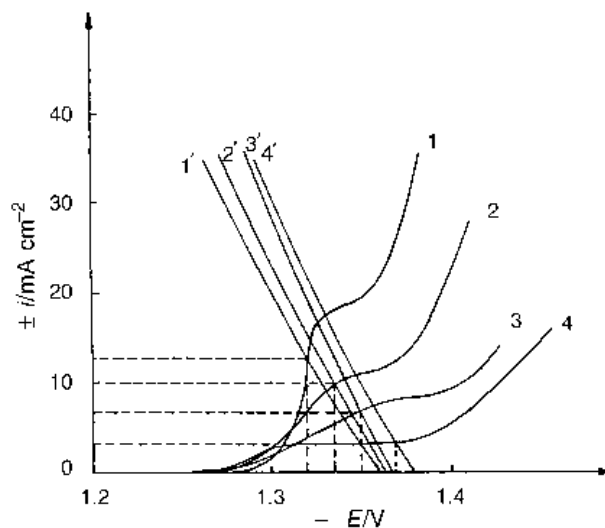


Fig. 2. Cathodic polarization curves of zinc deposition on Zn in the following solutions (in g dm^{-3}): (1) NaOH 400, ZnO 80; (2) NaOH 400, ZnO 40; (3) NaOH 400, ZnO 10; (4) NaOH 400, ZnO 5. Anodic polarization curves of Al dissolution in sodium hydroxide solutions (in g dm^{-3}): (1') 323.8; (2') 361.9; (3') 390.5; (4') 396.2.

The experimentally obtained potential difference varied from 50 to 150 mV, depending on the component concentration in the solution. These values of mixed potential under steady-state conditions show that during the zincate treatment the zinc layer changes the nature of the treated aluminium surface, whose potential approaches that of a compact zinc electrode after 5–10 s of immersion treatment.

Figure 5 represents the polarization curves for water reduction on the zinc surface – the second possible cathodic process. The juxtaposition of the partial curves (Fig. 5) during cathodic polarization of a zinc electrode in alkaline solution, free of zincate ions, with those of zinc coating deposition from a

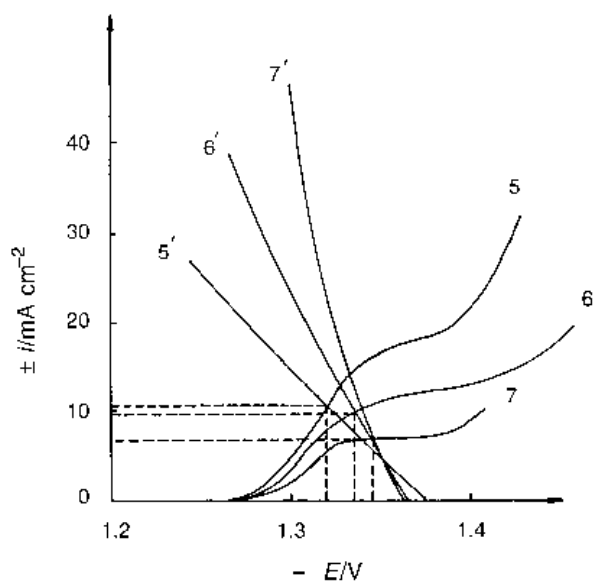


Fig. 3. Cathodic polarization curves of zinc deposition on Zn in the following solutions (in g dm^{-3}): (5) NaOH 100, ZnO 40; (6) NaOH 250, ZnO 40; (7) NaOH 600, ZnO 40. Anodic polarization curves of Al dissolution in sodium hydroxide solutions (in g dm^{-3}): (5') 61.6; (6') 211.9; (7') 561.9.

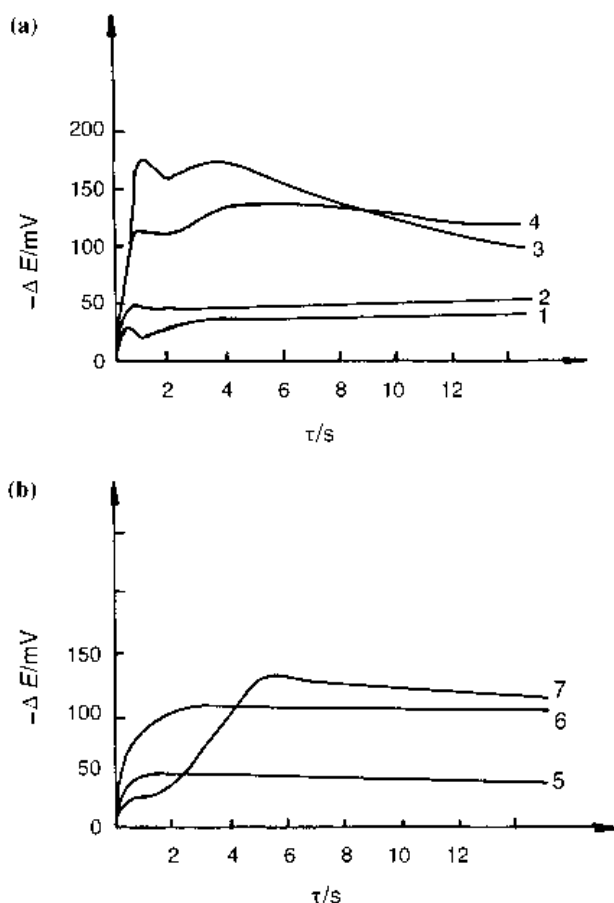


Fig. 4. Oscillograms of the potential change of the aluminium electrode ($-\Delta E$) from the moment of immersion into the zincate electrolyte of the following compositions (in g dm^{-3}): (a): (1) NaOH 400, ZnO 80; (2) NaOH 400, ZnO 40; (3) NaOH 400, ZnO 10, (4) NaOH 400; ZnO 5. (b): (5) NaOH 100, ZnO 40, (6) NaOH 250, ZnO 40, (7) NaOH 600, ZnO 40.

zincate electrolyte (Fig. 2, curves 1 and 3) shows that the zinc deposition proceeds at more positive potentials (70–90 mV) than those of hydrogen evolution. This difference suggests that the immersion process is defined by the conjugated reactions of cathodic deposition of zinc and anodic dissolution of aluminium, neglecting the reduction of H^+ (H_2O). It is probably the fast changing nature of the aluminium surface during the deposition of thin zinc films, that justifies this assumption. It is known that the overpotential of hydrogen evolution on zinc in alkaline medium is higher than that on aluminium by about 750 mV [19].

The rate of the exchange process (i_c), determined from the polarization curves, was juxtaposed with the

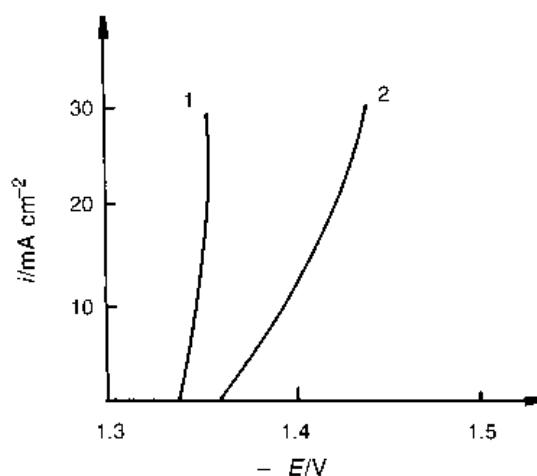


Fig. 5. Cathodic polarization curves of the hydrogen evolution process on Zn in sodium hydroxide solutions (in g dm^{-3}): (1) 328.8; (2) 390.5.

values from the gravimetric measurements (i_{Zn} , Table 1) in order to establish the average rate of zinc deposition. The results, obtained by these two independent methods, are summarized in Table 1. They coincide very well for all solutions. The corresponding potentials (E_c) are also compared to the steady-state values of the mixed potential (E_{Al}) of the aluminium electrode, determined from the oscillograms (Table 1). The comparison of the steady-state mixed potentials with the potentials obtained at the crossing points of the model polarization curves, confirm the adequacy of the approach, supposing complete conjugation of the occurring reactions.

The form of the cathodic polarization curves suggests that the metal ion reduction is diffusion controlled. The variation of the surface mixed potential in the course of the process leads to changes in the nature of the cathodic polarization.

As can be seen from Fig. 2, on decreasing the ZnO concentration from 80 to 5 g dm^{-3} the mixed potential is shifted in the negative direction and this results in changes in the reaction mode, the kinetic control (in solution 1) passes through mixed control (in solution 2 and 3) to diffusion control (in solution 4).

The same peculiarities were observed during variation of the NaOH concentration in the zincate electrolyte from 100 up to 600 g dm^{-3} , keeping the ZnO concentration at 40 g dm^{-3} . On shifting the mixed potential towards more negative values the kinetically controlled cathodic reaction also passed to

Table 1. Dependence of the immersion zinc plating rate on the electrolyte composition, determined graphically from the polarization curves (i_c) and from gravimetric analysis data (i_{Zn})

| | | | | | | | |
|------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| $C_{\text{NaOH}}/\text{g dm}^{-3}$ | 400 | 400 | 400 | 400 | 100 | 250 | 600 |
| $C_{\text{ZnO}}/\text{g dm}^{-3}$ | 80 | 40 | 10 | 5 | 40 | 40 | 40 |
| $i_c/\text{A dm}^{-2}$ | 1.3 | 1.00 | 0.65 | 0.30 | 1.05 | 0.95 | 0.65 |
| $i_{\text{Zn}}/\text{A dm}^{-2}$ | 1.5 | 0.94 | 0.65 | 0.39 | 0.97 | 0.79 | 0.59 |
| E_c/V^* | 1.320 | 1.335 | 1.365 | 1.365 | 1.320 | 1.335 | 1.350 |
| E_{Al}/V^* | 1.315 | 1.330 | 1.365 | 1.365 | 1.320 | 1.335 | 1.350 |

*The mixed potential values under steady-state conditions were determined graphically from the polarization curves (E_c), and measured oscillographically (E_{Al}).

Table 2. Degree of control of the partial electrode reactions C_a and C_k on the immersion zincate solution composition

| | | | | | | | |
|------------------------------------|-------|-------|-------|-------|-------|-------|-------|
| $C_{\text{NaOH}}/\text{g dm}^{-3}$ | 400 | 400 | 400 | 400 | 100 | 250 | 600 |
| $C_{\text{ZnO}}/\text{g dm}^{-3}$ | 80 | 40 | 10 | 5 | 40 | 40 | 40 |
| C_a | 0.39 | 0.38 | 0.14 | 0.09 | 0.48 | 0.28 | 0.16 |
| C_k | 0.61 | 0.58 | 0.85 | 0.91 | 0.52 | 0.78 | 0.84 |
| ΔE_a^* | 0.045 | 0.035 | 0.015 | 0.010 | 0.055 | 0.025 | 0.015 |
| ΔE_k^* | 0.070 | 0.055 | 0.090 | 0.105 | 0.060 | 0.090 | 0.080 |

* ΔE_a and ΔE_k were determined graphically under conditions of maximum current at $R = 0$, respectively, $IR = 0$; $\Delta E_a = E_a - E_a^0$; $\Delta E_k = E_k^0 - E_k$; where E_k and E_a are the effective values of anodic and cathodic potentials; E_a^0 and E_k^0 are the initial values of anodic and cathodic potentials.

diffusion control in this case. To specify the rate-controlling step of the process the cathodic and anodic polarization of the Al-Zn couple was determined from the partial polarization curves, considering the process as the operation of a galvanic corrosion element. The rate-controlling step of the total exchange process was determined, depending on the composition of the studied electrolyte, in accordance with Equations 10–12. The results obtained are given in Table 2.

These data show prevailing cathodic control in all the electrolytes. Although the rate limitations on the anodic and cathodic reactions in the highly concentrated ZnO solutions are commensurable, the degree of cathodic control increases with decrease in the ZnO concentration, due to diffusion difficulties for the zincate ions. Analogous changes in the exchange process type of control have also been observed during the variation of the NaOH concentration in the second series of experimental runs (Table 2).

Another argument to this effect is the linear dependence, obtained for the mixed potential E_c as a function of the metal ion concentration, represented in Fig. 6, corresponding to Equation 7.

An independent confirmation of the results is the electron microscopy study of samples covered by zinc

immersion coatings, formed under conditions of kinetic, mixed and diffusion control of the cathodic reaction (Fig. 7). It follows from Fig. 7 that the coatings obtained in solutions of low zincate ion

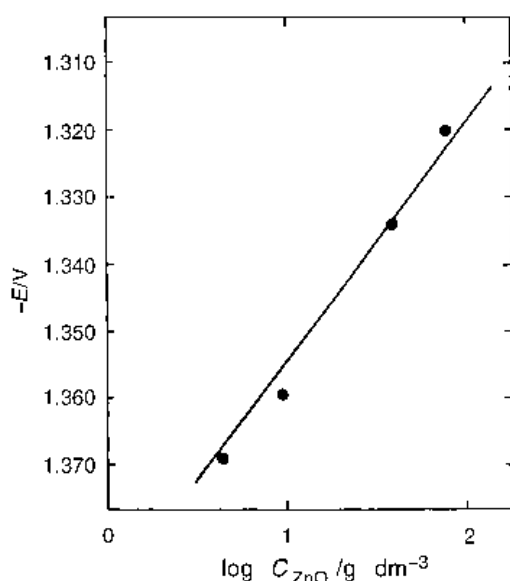


Fig. 6. The mixed potential of the plating solution plotted against the logarithm of the ZnO concentration.

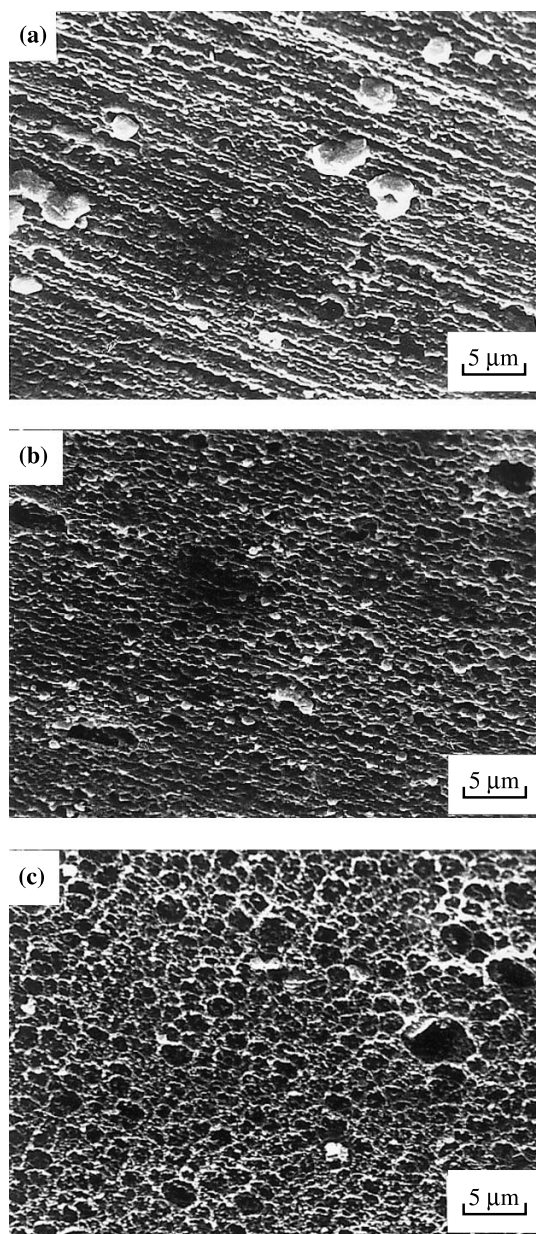


Fig. 7. SEM photographs of Al surface covered by an immersion Zn plating in the following solutions (in g dm^{-3}). (a): NaOH 100, ZnO 40; (b): NaOH 400, ZnO 40; (c): NaOH 400, ZnO 5.

concentration (for the case, when the limiting step is the diffusion of Zn^{2+} in accordance with Fig. 2, curves 4–4'), are of low quality with many defects (Fig. 7(c)). The coatings obtained under conditions of mixed control, determined by the mixed potential value (Fig. 2, curves 2–2') possess an improved structure (Fig. 7(b)). The mixed potential value in the highest ZnO concentration solution is within the region of kinetically controlled cathodic reaction (Fig. 3, curves 5–5'), and corresponds to the formation of zinc layers possessing finely dispersed structure, reproducing the structure of a polished Al substrate, (Fig. 7(a)). It is important to note that the increase in adhesion of the metal coatings subsequently electrodeposited over the zinc layers follows the same sequence [20].

5. Conclusions

The results from the studies on immersion zinc deposition, carried out in model and real systems, lead to the conclusion that the anodic and cathodic reactions, proceeding simultaneously, are interdependent. The cathodic partial reaction has been found to proceed under kinetic control at high zincate ion concentrations ($ZnO\ 80\ g\ dm^{-3}$) and at low NaOH concentration ($100\ g\ dm^{-3}$). Mixed control has been observed at intermediate zincate ion concentration ($ZnO\ 40\ g\ dm^{-3}$) and NaOH concentration ($250\ g\ dm^{-3}$), while diffusion control is to be expected at low zincate ion concentrations ($ZnO\ 5\ g\ dm^{-3}$) and high NaOH concentration ($600\ g\ dm^{-3}$). It has been shown that under diffusion control the zincate ion reduction rate determines the rate of the complex immersion process.

In conclusion it should be emphasized that the approach, adopted in the present study, is based both on mixed potential theory and the concepts which treat the immersion process as analogous to a galvanic corrosion element. The approach adequately

describes specific features of the immersion zincate treatment of aluminium.

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