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Kinetic correlations in codeposition of coatings of molybdenum–iron group metal alloys

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Electrodeposition of Ni–Mo and Fe–Mo alloy coatings from acid citrate electrolyte was investigated over a wide range of cathode potentials and under various hydrodynamic conditions. Such alloys had been found to be deposited with substantial depolarization against iron group metals. With the same electrodeposition conditions, the molybdenum percentage in Fe–Mo coatings is much higher than in Ni–Mo. The molybdenum presence results in a lower overvoltage of hydrogen evolution, so that these alloys are deposited with a current efficiency much lower than that in the separate reduction of iron group metals. For a Ni–Mo system, the Mo percentage in the coating is increased together with increase of the transport rate of ions towards the cathode and with decrease of the cathode potential value being reduced; while for Fe–Mo alloy an inverse relation is observed. When passing from the Ni–Mo to the Fe–Mo system, the control of the molybdenum reduction reaction is changed. In codeposition with nickel it shows a diffusion control, while in discharging with iron its control is of the activation type. The Ni–Mo coatings obtained contained from 1.5–6% molybdenum whereas Fe–Mo deposits contained from 12–40% depending on electrolysis conditions. The quality of the coatings containing more than 20% Mo deteriorated and in these deposits some nonmetallic inclusions were present.

1. Introduction

The electrodeposition of alloys of molybdenum with iron group metals has been gaining in importance in recent years owing to their interesting properties, in particular the high hardness, thermal and corrosion resistance, as well as special magnetic properties.

The theory on metal ion codischarge provides no means of prescribing the conditions for simultaneous reduction of molybdenum with other metals, and the cathodic behaviour of individual cations is highly irregular, which reflects the complex mechanism of the alloy deposition.

Attempts at clarifying the mechanism of the induced molybdenum codeposition with iron group metals have been made by a number of investigators. However, no universal theory is available as yet which explains all the effects accompanying the process [1–5]. A knowledge of the induced discharge process is indispensible to correlate the properties of coatings to the conditions of their deposition and to a proper control of the galvanic process.

The present work aimed to examine the kinetic correlations in passing from a separate nickel and iron discharge to Ni–Mo and Fe–Mo coreduction and, consequently, to obtain new experimental data on the deposition of such coatings from acid citrate electrolytes.

2. Experimental details

Citrate electrolytes, ensuring a stable pH value of the electrolyte, were used for the purpose of our studies, the deposit from such electrolytes being more compact. Based on the initial experimental results, as shown in [6], an electrolyte containing the following compounds (in $g\,l^{-1}$) was selected for further experiments: $NiSO_4 \cdot 7H_2O$–212; $FeSO_4 \cdot 7H_2O$–15; $Na_2MoO_4 \cdot 2H_2O$–2; $Na_3C_6H_5O_7 \cdot 2H_2O$–66; NaCl–1.1; saccharine–0.4, wherein the nickel and iron levels were the same as in the bath used to obtain permalloy coatings [7]. Any electrolytes subsequently used to study the Ni–Mo and Fe–Mo binary systems and the separate reduction of each metal were derived from this primary bath.

Our experiments show that for the above electrolyte composition, the molybdenum percentage in the alloy reaches a maximum with pH = 4.2 and, for this reason, this pH value was chosen.

This effect is related to a strong influence of the pH on the type of complexes formed and on their equilibrium in the electrolyte. Spectrophotometric tests of the molybdenum citrate complexes [8] show that with pH 4.2, for which maximum Mo percentage in the coating is achieved, a single complex is produced, corresponding to $MoO_4^{-2} : H_x\text{cit} = 1 : 1$ with formation constant $K = 2.58 \times 10^5$.

In order to define the effect of hydrodynamic conditions on Ni–Mo and Fe–Mo deposition kinetics, the Baymakow-Brenner method was used to determine the total and the partial polarization curves. To ensure constant and controlled hydrodynamic conditions, a system with a potentiostatically power supplied rotating disc electrode (RDE) was used [7]. The cathodes were copper discs 19 mm diameter,

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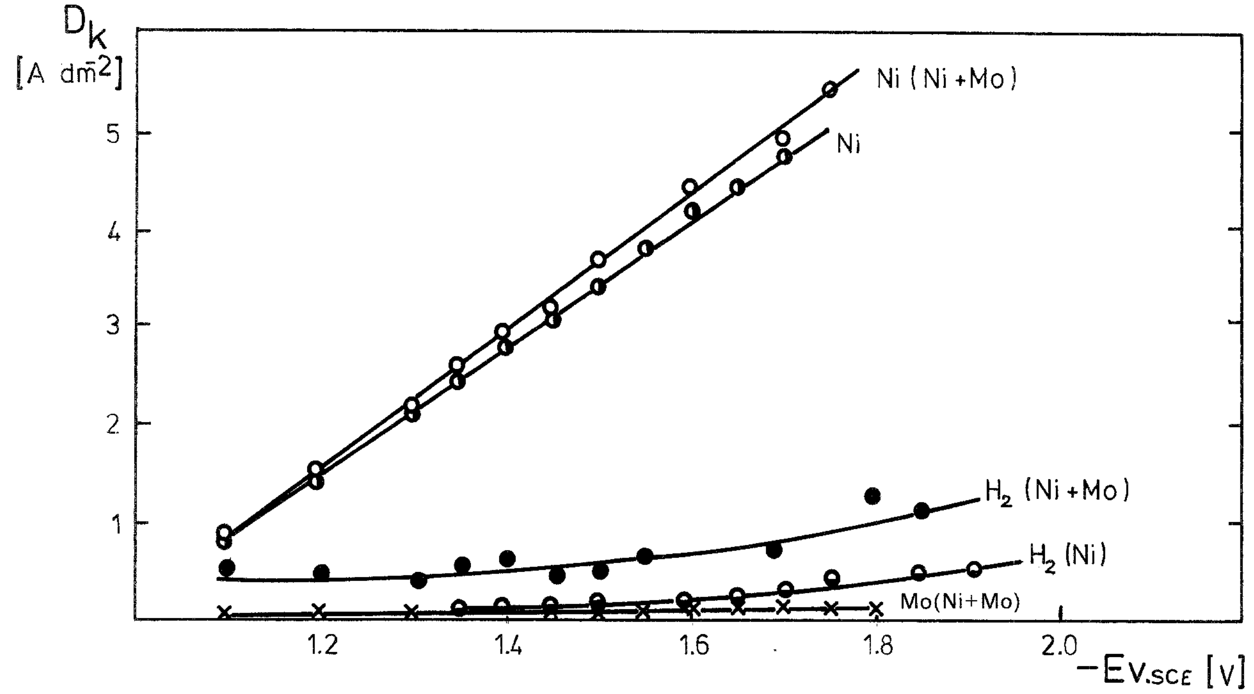

Fig. 1. Partial cathodic polarization curves of nickel, molybdenum and hydrogen for their coreduction. Disc rotation speed 1.7 rps.

chemically polished prior to measurement. The disc electrode rotation speed varied between 1.7 and 13.7 rps. The anode was a platinum sheet. The cathode potential was measured against a SCE. The anodic and cathodic spaces were separated by sintered glass. The measuring temperature was 25° C.

The electric charge used for H^+ reduction was calculated from the difference between the charge passing, recorded by means of an electronic coulometer, and the charge used to deposit the metallic alloy components.

Chemical analyses of the metal and alloy specimens were conducted by atomic absorption spectrophotometry, using a UNICAM SP-90 spectrophotometer. In order to check the quality of the coatings obtained, their surface morphology was examined by means of a scanning electron microscope (JXA50). For chemical analyses of the resulting alloy coating microareas, an X-ray energy spectrophotometer (Kevex) was used.

3. Results and discussion

3.1. *Molybdenum/nickel codeposition*

Figure 1 shows sample partial polarization curves for nickel, molybdenum and hydrogen reduction with

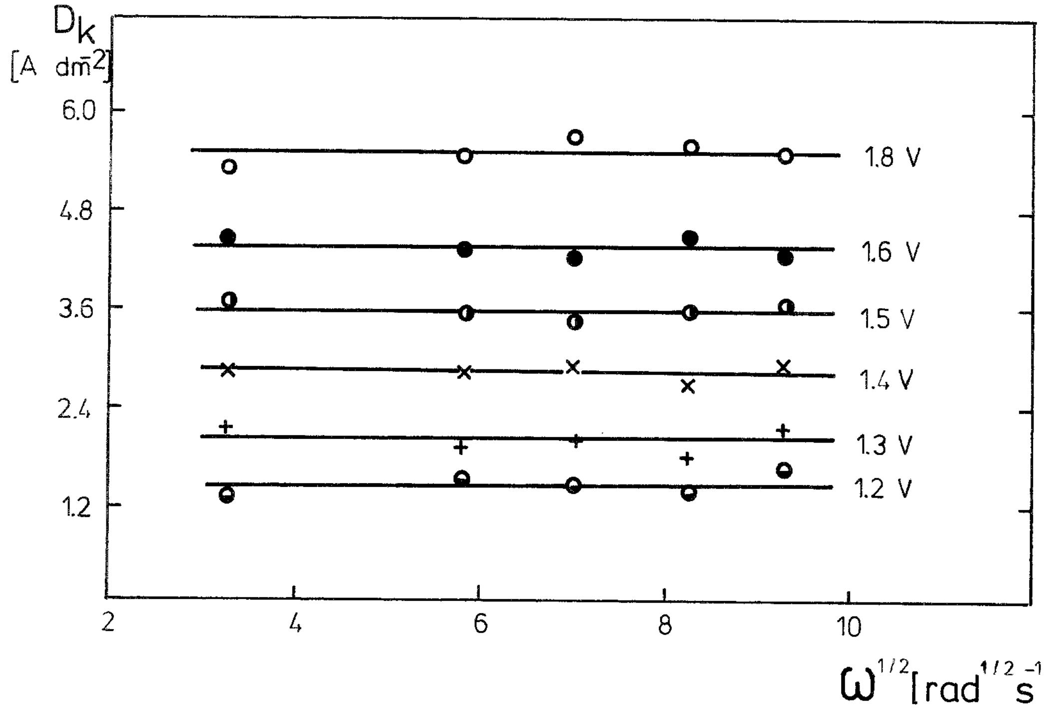

Fig. 2. Dependence of partial current density of nickel reduction in codeposition with molybdenum on square root of electrode angular speed.

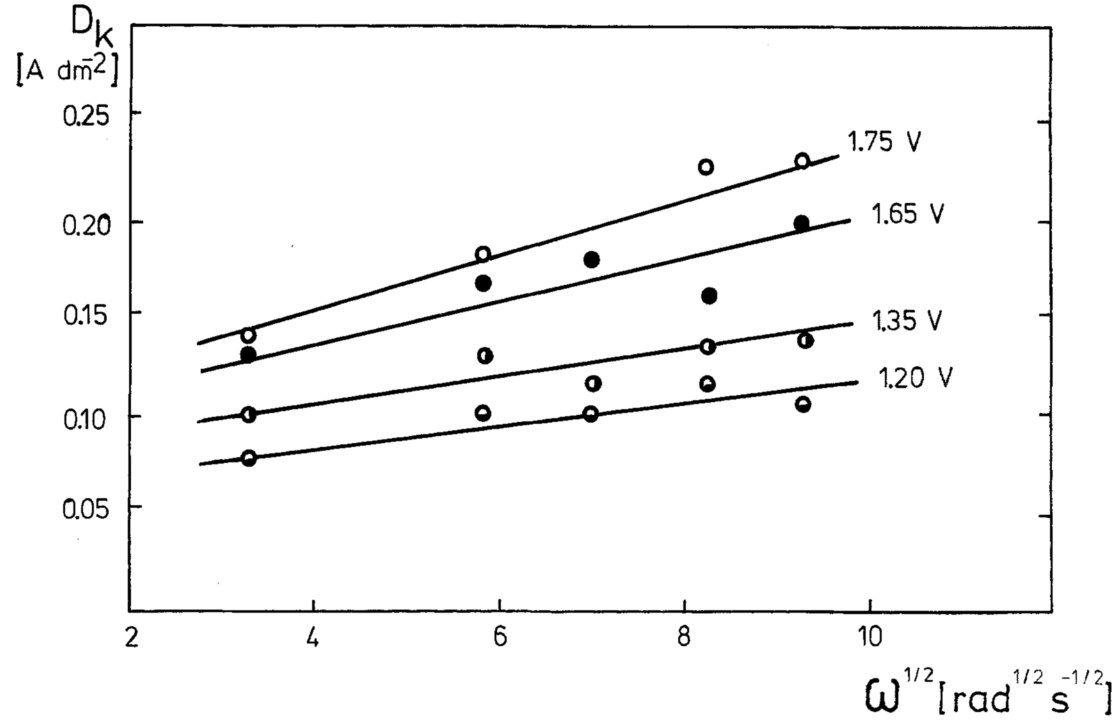

Fig. 3. Correlation of partial current density of molybdenum reduction in codeposition with nickel to the square root of the disc electrode angular speed.

Ni–Mo coating deposition for a disc electrode speed of 1.7 rps. For reference, the data for separate nickel reduction in the same conditions are plotted. The data indicate that the Ni–Mo alloys are deposited together with hydrogen evolution, while nickel is discharged separately up to considerable current densities without substantial hydrogen evolution. In the case of nickel and molybdenum being codeposited from ammonia/citrate bath [9], the increase in the hydrogen evolution rate was much more rapid than in coreduction with nickel alone. Also, the reduction rate of Ni^{2+} in codeposition with Mo was much lower than in separate reduction. For the acid citrate bath under consideration, the total process of Ni–Mo alloy deposition is accompanied by strong depolarization, which is probably related to electrolyte changes consisting of partial molybdenum (6+) reduction to transient compounds. This assumption is confirmed by the measurements of nickel polarization from a bath with lower-valency molybdenum compounds added. The depolarization effect in depositing such alloys was also found in [10]. However, when the partial nickel reduction is compared, it can be seen that in codeposition with molybdenum the partial nickel reduction curve is only slightly shifted towards more positive potentials.

The nickel and hydrogen discharge reactions, in their coreduction with Mo, showed activation control (Fig. 2). On the other hand, due to the low concentration of molybdate ions in the electrolyte, Mo reduction takes place at limiting current, under diffusion control, the current density being dependent on the square root of disc angular velocity (Fig. 3).

Table 1 shows kinetic parameters b_k, for nickel and molybdenum in codeposition, as well as for separate nickel reduction, as defined from the straight linear sections of the logarithm of the partial cathode current density correlation against the cathode potential for various disc electrode speeds.

With transition from separate reduction to codeposition with Mo, the nickel reaction control remains unchanged, while the kinetic parameter, b_k, is

Table 1. Kinetic parameters b_k, for nickel reduction and for nickel and molybdenum in codeposition

		Disc electrode rotation speed (rps)				
		1.7	5.4	7.8	10.8	13.7
Ni	b_k (V)	0.26	0.19	0.25	0.26	0.26
(Ni + Mo)	αz	0.10	0.14	0.10	0.10	0.10
Mo	b_k (V)	0.76	0.73	0.70	0.66	0.60
(Mo + Ni)	αz	0.03	0.04	0.04	0.04	0.04
Ni	b_k (V)	0.19	0.21	0.21	0.21	0.22
	αz	0.14	0.12	0.12	0.12	0.11

$b_k = RT/\alpha zF$; R – gas constant = 8.31 J mol^{-1} K^{-1}; T – 298° K; F – Faraday constant, C mol^{-1}; z – number of electrons; α – Transfer coefficient.

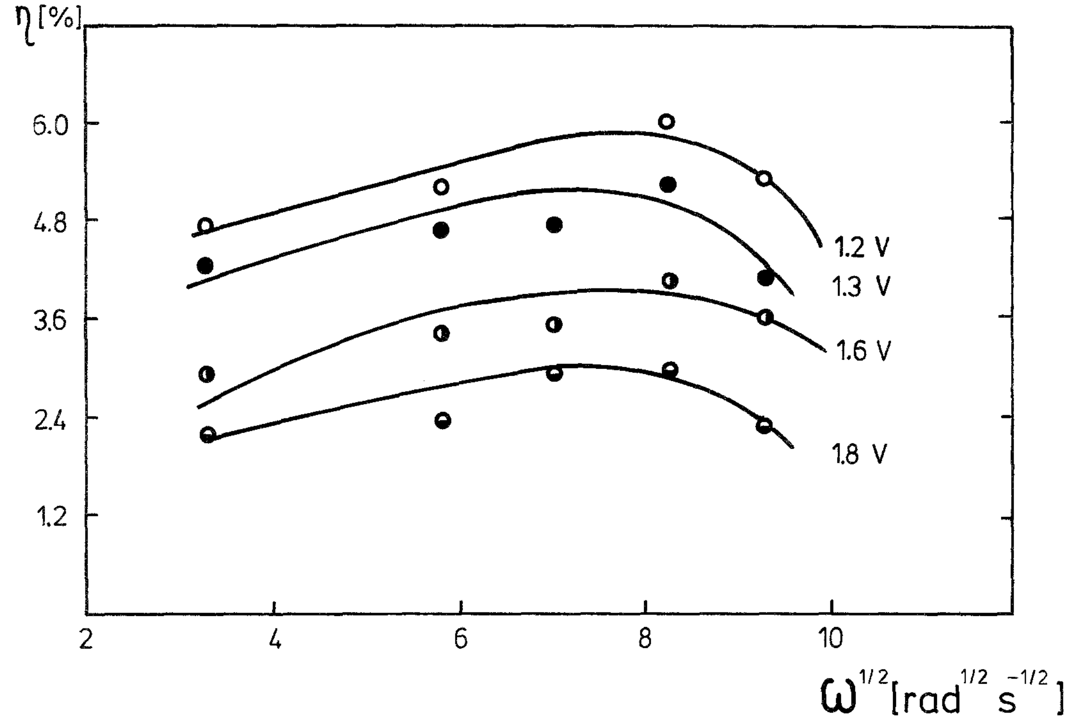

Fig. 4. Correlation of the cathode current efficiency of molybdenum in codeposition with nickel to the square root of the disc electrode rotation speed.

somewhat increased, demonstrating the influence of the molybdate ion reduction.

The cathodic current efficiency of molybdenum coreduction with nickel increases with the transfer rate toward the cathode up to approximately 10.8 rps, when it reaches its maximum value and subsequently decreases. On the other hand, an increase in cathode polarization results in this value becoming lower (Fig. 4). The molybdenum content of Ni–Mo alloys thus obtained is about 6% maximum, this being confirmed by Kevex chemical analyses of such coating microareas. Good quality coatings were achieved. Figure 5 shows the surface topography of a typical Ni–Mo coating.

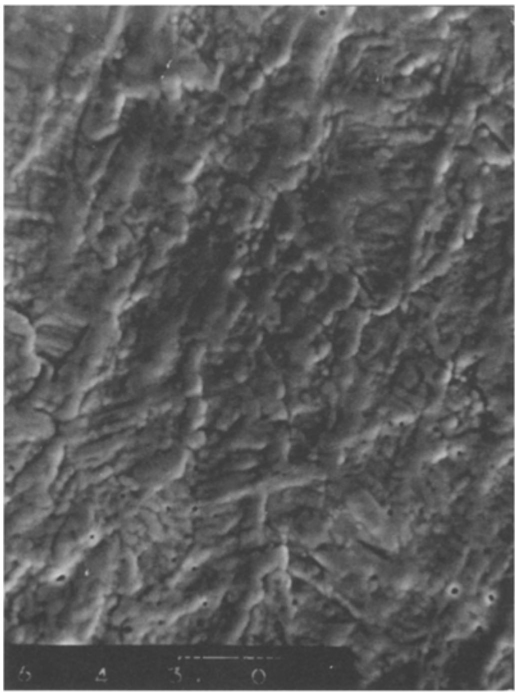

Fig. 5. Surface topography (SEI) of Ni–Mo coating (× 1000).

3.2. *Molybdenum/iron coreduction*

Evaluation of the partial polarization curves for iron, molybdenum and hydrogen during coreduction from the acid citrate bath indicates that the Fe–Mo alloy is deposited with large depolarization. Figure 6 shows such sample curves obtained for a disc electrode speed of 5.4 rps. For reference, the curves for separate Fe reduction and the curve for molybdenum codeposited with nickel are also plotted in the same chart. In this case, the depolarization effect may be partially due to Fe/Mo atomic interactions resulting from the formed alloy favouring molybdenum reduction.

Evaluation of the spectrophotometric characteristics of the combined Mo (6+) and Fe (2+) water solutions confirmed the ability of Fe^{2+} ions to interact with the molybdenum ions chemically [11]. Taking into account the complexity of the phase diagram of Fe–Mo alloys and the solid solution area being very restricted, the possibility of a chemical compound being formed cannot be excluded.

It is also shown by the cathode current density versus cathode potential dependence that, with more negative potentials ($>$ 1.6 V vs SCE), the Fe^{2+} reduction rate in codeposition with molybdenum is higher than in separate reduction by a factor of 16 to 44. Below this potential value, the Fe^{2+} discharge rate in separate deposition is higher, the effect disappearing as disc electrode speed is increased.

The kinetic correlations also indicate that in codeposition of Fe–Mo coatings hydrogen evolution

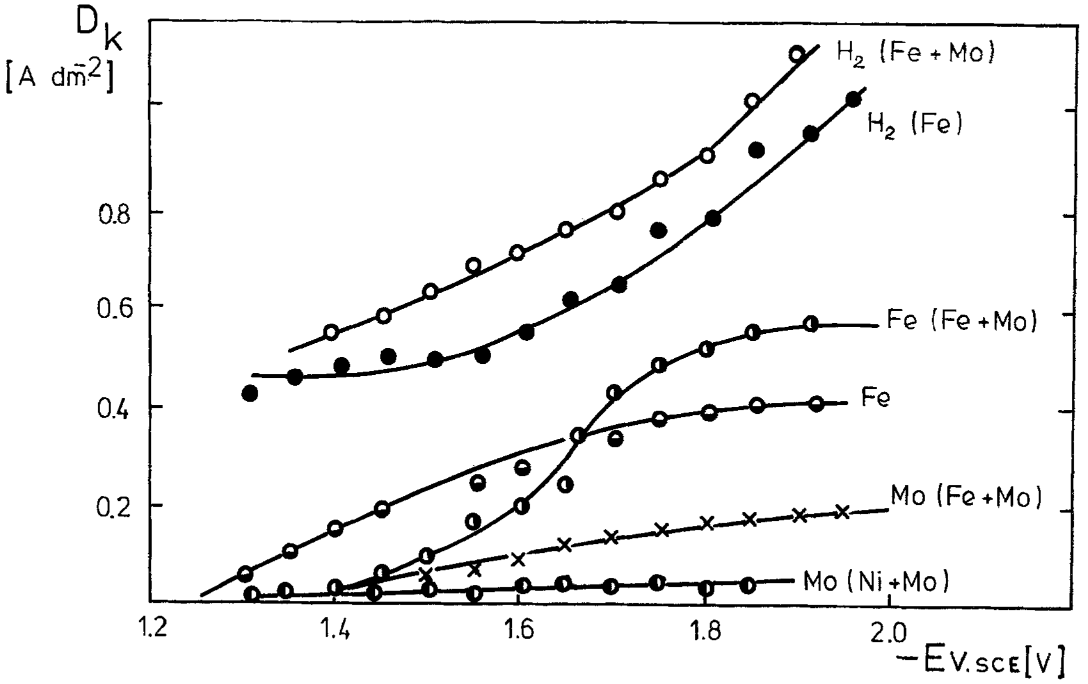

Fig. 6. Partial cathodic polarization curves of iron, molybdenum and hydrogen reduction in codischarge. Electrode speed 5.4 rps.

is favoured by molybdenum addition. It has also been found that in coreduction with iron, the cathodic current efficiency of molybdenum falls with increase of transfer rate toward the cathode and with the cathode potential drop (Fig. 7). It may be presumed that in these conditions, as the disc rotation speed is increased, the concentration of molybdate ions within the cathodic layer is also increased, formation of lower-valency molybdenum compounds thus being easier. The latter compounds block the cathode surface and, consequently, the percentage Mo in the coating is decreased. A black bloom arising on the cathode surface in such conditions supports this mechanism. A similar effect is observed with increased Na_2MoO_4 concentration in the electrolyte.

For Fe–Mo alloys, the kinetic parameters, b_k, for various hydrodynamic conditions were also determined (Table 2).

From the correlations of partial current densities for iron, molybdenum and hydrogen in coreduction with the square root of the disc electrode angular velocity, the reaction control mechanisms for these components of Fe–Mo alloys were determined. The reaction of molybdenum reduction was found to be

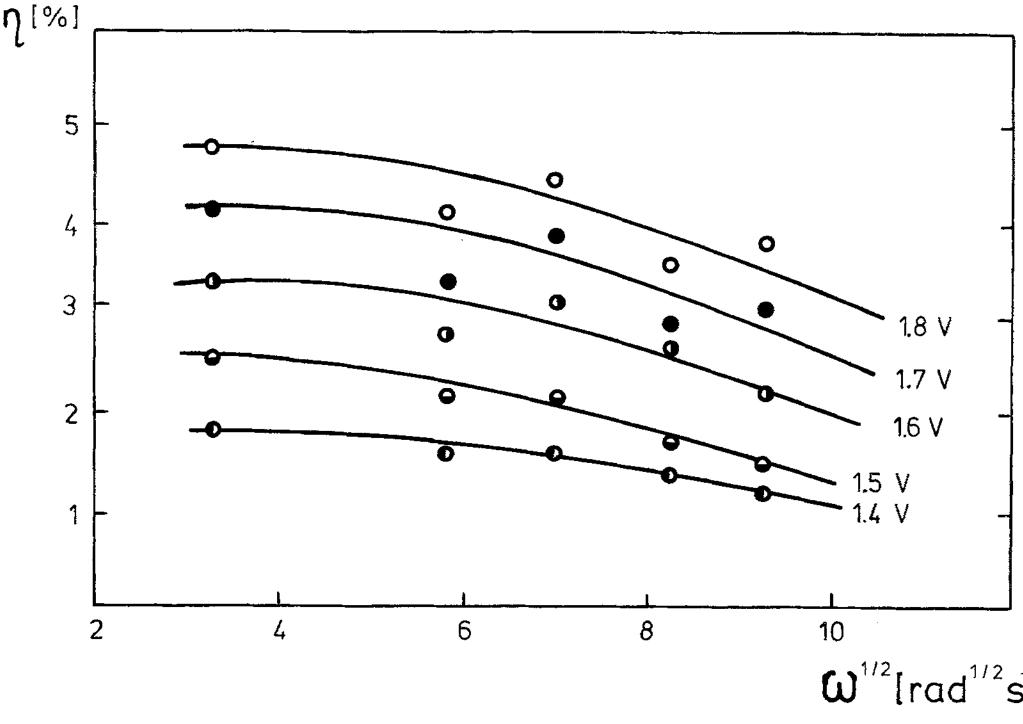

Fig. 7. Correlation of the cathodic current efficiency of molybdenum in codeposition with iron, to the square root of the disc electrode rotation speed.

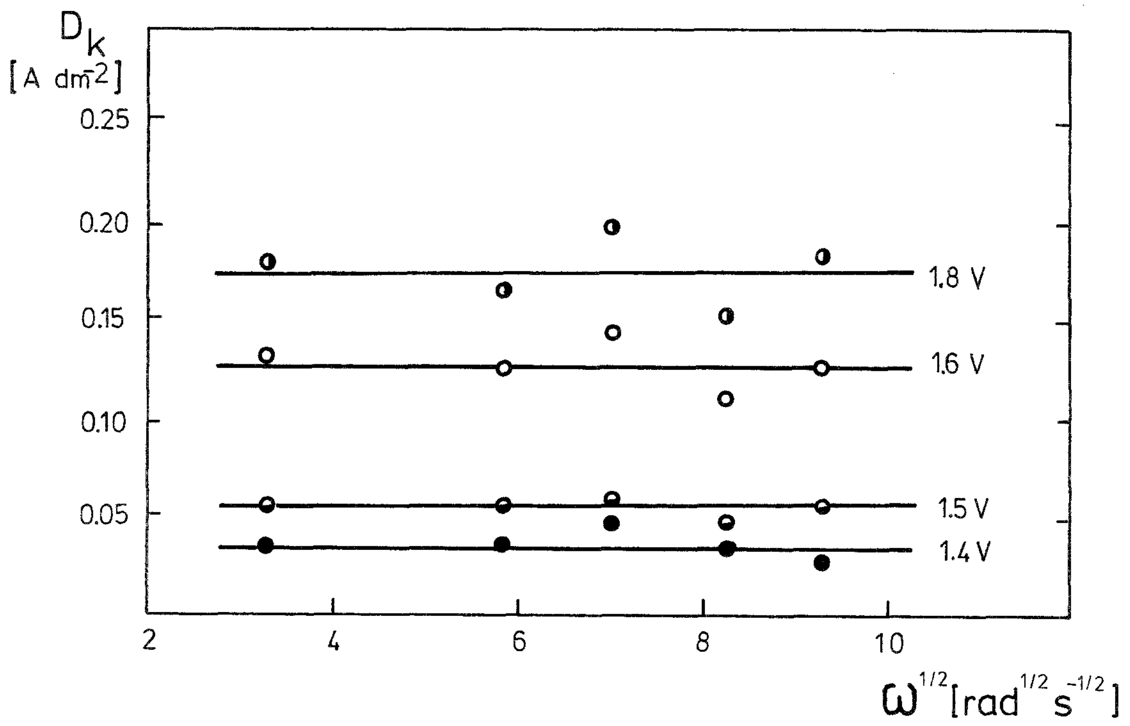

Fig. 8. Correlation of the partial current density of molybdenum reduction in codeposition with iron to the square root of the disc electrode angular speed.

activation-controlled (Fig. 8), and hydrogen discharge to be diffusion-controlled. However, for Fe^{2+} reduction within this system, an abnormal correlation is observed, i.e. the process rate is higher with low speeds and vice versa. The effect may be related to an intermediate active product being formed during the process and taking part in indirect reactions on the electrode (cathode surface blockage by lower-valency compounds and by iron hydroxides).

In separate iron reduction, no such form of correlation is observed, and the Fe^{+2} discharge reaction shows clear diffusion control.

The molybdenum content in the Fe–Mo alloys thus produced a range of 11–38% which is much higher than the values obtained for the Ni–Mo system. The same is indicated by chemical analyses of microareas in such coatings. Figure 9 shows a surface topography which is specific to Fe–Mo alloy coatings.

4. Conclusions

Nickel and iron alloys with molybdenum are electrodeposited with considerable depolarization against iron group metals, which is probably related to the electrolyte changes involving partial reduction of molybdenum (6+) to transient compounds. In the case of the Fe–Mo alloy this effect may also be due to iron/molybdenum chemical interaction.

Under similar galvanostatic conditions, the molybdenum percentage in Fe–Mo coatings is much higher (about 38% max.) than in Ni–Mo coatings (6% max.). Molybdenum present in iron group metal alloys favours hydrogen evolution leading to the fall in current efficiency. This may be due to the decrease in hydrogen evolution overvoltage as the deposits become more molybdenum-rich. Iron and nickel alloys with molybdenum are deposited with a current efficiency about 10 per cent lower than in separate reduction of those metals.

For a Ni–Mo system, the molybdenum percentage in the coating increases with increased ion transfer toward the cathode and with potential drop. For the Fe–Mo alloy, an inverse correlation is observed. This difference may be explained by various mechanisms of deposition by the effect of ions being discharged and by the reaction kinetic variations. When passing from

Table 2. Kinetic parameters b_k, for Fe–Mo alloys

		Disc electrode rotation speed (rps)				
		1.7	5.4	7.8	10.8	13.7
Fe	b_k (V)	0.11	0.13	0.15	0.14	0.13
(Fe + Mo)	αz	0.23	0.20	0.17	0.18	0.19
Mo	b_k (V)	0.20	0.24	0.26	0.26	0.17
(Fe + Mo)	αz	0.13	0.11	0.10	0.10	0.14
Fe	b_k (V)	0.13	0.12	0.12	0.16	0.12
	αz	0.20	0.21	0.22	0.15	0.22

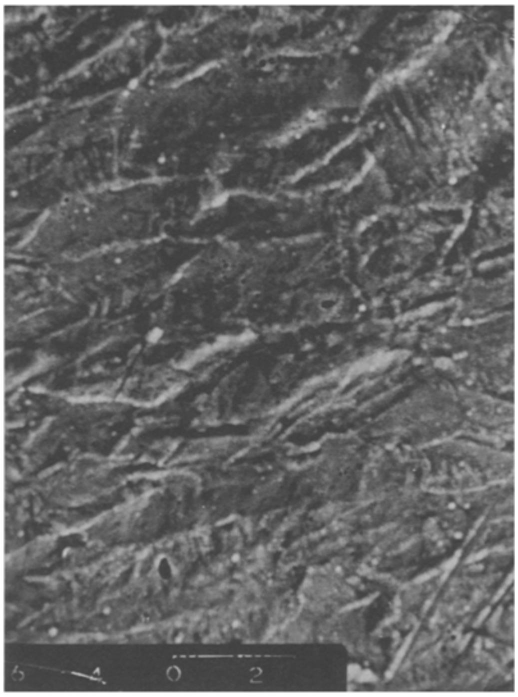

Fig. 9. Surface topography (SEI) of Fe–Mo coating (× 1000).

the Ni–Mo to the Fe–Mo system the control of the reaction of molybdenum reduction changes. In codeposition with nickel it shows diffusion control and with iron activation control.

In general the coatings obtained were bright and compact. The quality of the coatings containing more than 20% Mo deteriorated.

Acknowledgement

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