

# Electrodeposition of Ni-Cu-Mo ternary alloys from citrate electrolytes

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Conditions for the electrodeposition of Ni-Cu-Mo alloys from citrate electrolytes have been developed. The composition variations of the deposits with electrolyte pH and concentration have been investigated. A maximum molybdenum and nickel content is obtained for a pH of 7 and for low copper and large citrate concentrations. Molybdenum and copper are preferentially discharged at low current density whereas at high current density nickel becomes predominant. The deposits have a nodular morphology similar to that of the binary Ni-Mo layers

## 1. Introduction

With the aim of preparing protective coatings, the electrodeposition of ternary Ni-Cu-Mo alloys was investigated. Nickel-based alloys containing molybdenum or copper such as Hastelloy B or Monel 400 commercial alloys, are known to exhibit a high corrosion resistance in certain aggressive media [1]. Several studies have been devoted to the electrodeposition of Ni-Mo [2-8] and Ni-Cu alloys [9-16], mainly from pyrophosphate and citrate complexing electrolytes. In earlier work we examined the electrocrystallization mechanism and the properties of Ni-Mo and Ni-Cu deposits from citrate solutions [17-22]. The electrodeposition of ternary alloy systems has been the subject of fewer investigations, some concerned with Ni-Mo-Fe alloys [23-24], but none were related to the electrodeposition of Ni-Mo-Cu alloys. This ternary system combines one induced codeposition system (Ni-Mo) and a regular one (Ni-Cu, mainly controlled by the mass transfer of the cupric species towards the electrode). Because of interactions between the elements during the codischarge it is necessary to investigate the effect of the various electrolysis parameters (composition and pH of the solutions, current density, etc.) on the deposit composition and properties.

## 2. Experimental procedure

Citrate and citrate/ammonia complexing agents, which provide good pH stability, were used (less than pH 0.1 variation during a run). The initial composition was derived from the electrolytes developed for Fe-Ni-Mo [24] and Ni-Cu [28]. It contained 0.75 M NiSO<sub>4</sub>, 7H<sub>2</sub>O, 0.125 M CuSO<sub>4</sub>, 5H<sub>2</sub>O, 0.01 M Na<sub>2</sub>MoO<sub>4</sub>, 2H<sub>2</sub>O, 0.22 M Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, 2H<sub>2</sub>O. Sodium chloride (1.1 g dm<sup>-3</sup>) and saccharine (0.4 g dm<sup>-3</sup>) were

added to decrease the internal stresses. The solution pH was varied between 2 and 10.

The electrolysis was carried out in a 750 ml cell at 25°C. The cathode was a low-carbon steel disc (surface area 2.8 cm<sup>2</sup>) rotating at 5 rev s<sup>-1</sup>. It was chemically etched in solutions of oxalic acid and hydrogen peroxide prior to electrolysis. The anode was made of platinum plate; it was separated, from cathodic compartment by sintered glass. The current density was varied between 0.25 and 7 A dm<sup>-2</sup>.

Deposit composition was determined by means of atomic absorption spectroscopy.

The concentrations of uncomplexed species were calculated from the dissociation constant data [25-28]. All calculations are based on stability constants for 87 various ionic forms of nickel, copper and molybdenum with citrate, sulphate, ammonium chloride and hydroxyl ions, mixed complexes and precipitates of Ni<sub>4</sub>(OH)<sub>6</sub>SO<sub>4</sub>, Cu<sub>4</sub>(OH)<sub>6</sub>SO<sub>4</sub>, Ni(OH)<sub>2</sub> and Cu(OH)<sub>2</sub>.

## 3. Results

### 3.1. Effect of electrolyte pH

In a previous study a strong pH dependence of the deposit composition was noticed [29]. As exemplified in Fig. 1, the Mo content in the deposit,  $\tau_{\text{Mo}}$ , exhibits a maximum for a critical current density,  $I_c$ , which depends on electrolyte pH. At low pH's, the Mo content is very low.  $\tau_{\text{Mo}}$  increases with increasing pH up to 7.0 and decreases again at higher pH's. As shown in Fig. 2 the critical current density for maximum  $\tau_{\text{Mo}}$  depends markedly on pH; it is minimum at pH 7.

For the nickel content two types of variations,  $\tau_{\text{Ni}} = f(i)$ , are observed depending on electrolyte pH. The highest Ni content (70-80 wt %) is obtained for pH's ranging between 6.5 and 8.5 (Fig. 3). At low pH's the Ni content exhibits a non monotonic variation

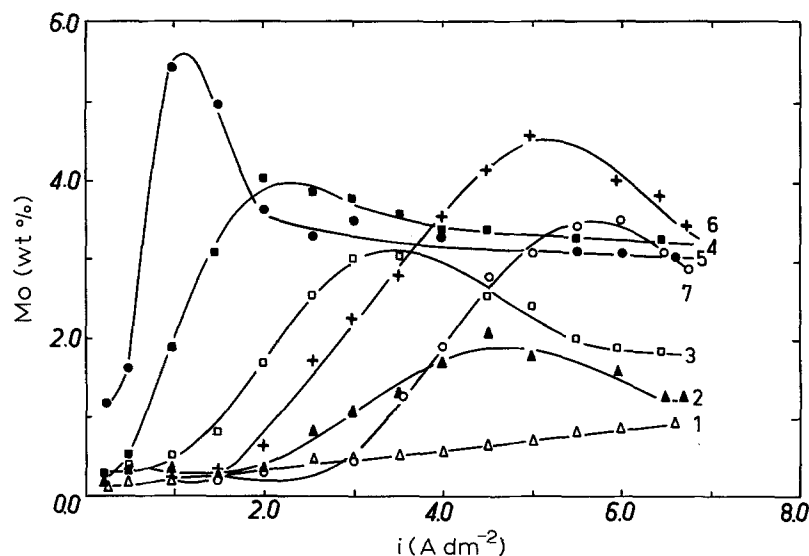


Fig. 1. Current density dependence of the molybdenum content in the deposits from electrolytes of various pH's: (1) pH 3.4, (2) 4.2, (3) 5.4, (4) 6.1, (5) 7.0, (6) 9.2 and (7) 10.1.

whereas as pH's higher than 4.2 it continuously increases. At high current densities the nickel discharge becomes predominant due to its high bulk concentration. A similar pH dependence was observed by Ernst *et al.* for Ni-Mo deposits [3].

It is noted that the nature of the complexed Mo(VI) species depends on the electrolyte pH [27]. Mixed complexes with citrate ions can be formed. In addition, calculations from the equilibrium constant data showed that, with increasing pH, the concentration of uncomplexed  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  species decreased. The concentration ratio  $\text{Cu}^{2+}/\text{Ni}^{2+}$  exhibits a minimum for a pH value between 7.5 and 8.5; this critical pH value increases with citrate concentration (Fig. 4). These pH dependencies of the nature and concentration of the complexed species probably explain the

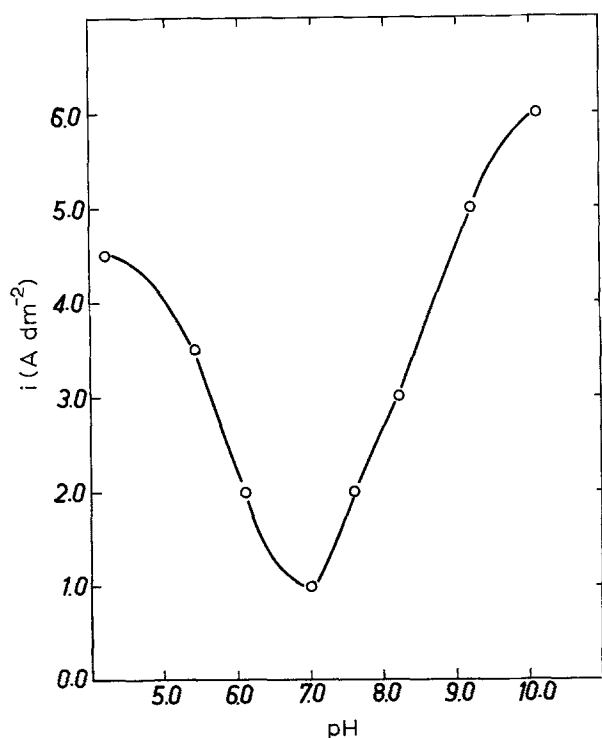


Fig. 2. pH dependence of the critical current density corresponding to maximum molybdenum content in the deposits.

effect of pH on the electrocrystallization process and, as a result, on the deposit composition.

In the subsequent experiments the pH was maintained at 7 which was considered to be the optimum value for obtaining the highest Mo and Ni contents.

### 3.2. Effect of sodium citrate concentration

Because of the large difference in the discharge potentials of the considered metals, complexing agents are necessary to achieve the codeposition. Sodium citrate appears to be the most suitable. It is very efficient in inhibiting the discharge of copper and thus promoting its codischarge with nickel [17]. In the case of Ni-Mo it allows hydrogen evolution, thus enabling further reduction of molybdate species [18]. The sodium citrate concentration was varied in the range 0.22–0.45 M which corresponds to the maximum solubility. As shown in Fig. 5 for  $5 \text{ A dm}^{-2}$ , the molybdenum content increases with citrate concentration from  $\sim 3 \text{ wt } \%$  for 0.22 M  $\text{Na}_3\text{Cit}$  to 6 wt % for 0.45 M  $\text{Na}_3\text{Cit}$ . The critical current density for which  $\tau_{\text{Mo}}$  is maximum also increases with sodium citrate concentration as well as  $\tau_{\text{Ni}}$ . Indeed it was shown that in the case of the Ni-Cu system, citrate inhibits the copper discharge but does not markedly affect the nickel deposition [11, 17].

### 3.3. Effect of molybdate concentration

The molybdate concentration was varied between 0.016 and 0.083 M, the citrate concentration being 0.45 M. As shown in Fig. 6 the maximum Mo content increases up to 16 wt %. At the same time the nickel content is drastically reduced; for example when the molybdate concentration is increased from 0.016 to 0.032 M, the Ni content decreases from 70 to 10 wt % for  $4 \text{ A dm}^{-2}$  (Fig. 7). In addition the cathodic current efficiency decreases markedly from  $\sim 85$  to 45%.

The molybdenum proportion in the deposit is larger than that in the electrolyte except at very low current density ( $0.5 \text{ A dm}^{-2}$ ) as often observed for induced

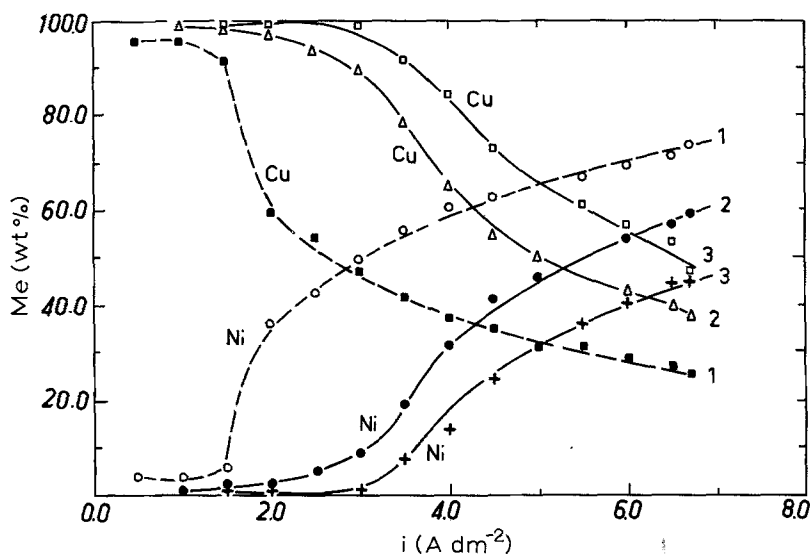


Fig. 3. Current density dependence of the nickel and copper content in the deposits from electrolytes for pH 8.2 (1), 9.2 (2) and 10.1 (3).

codeposition systems (Fig. 8) [2-4]. The molybdenum discharge is generally enhanced by the codeposition of nickel. However this effect becomes less pronounced when the current density is increased; this is due to the low molybdate bulk concentration as compared to those at the nickel and copper sulphate; the molybdenum discharge becomes then increasingly controlled by diffusion and the nickel deposition becomes predominant. For comparison the dashed line represents the variation for binary Ni-Mo alloy electrodeposition.

#### 3.4. Effect of copper sulphate concentration

A copper sulphate concentration increases from 0.015

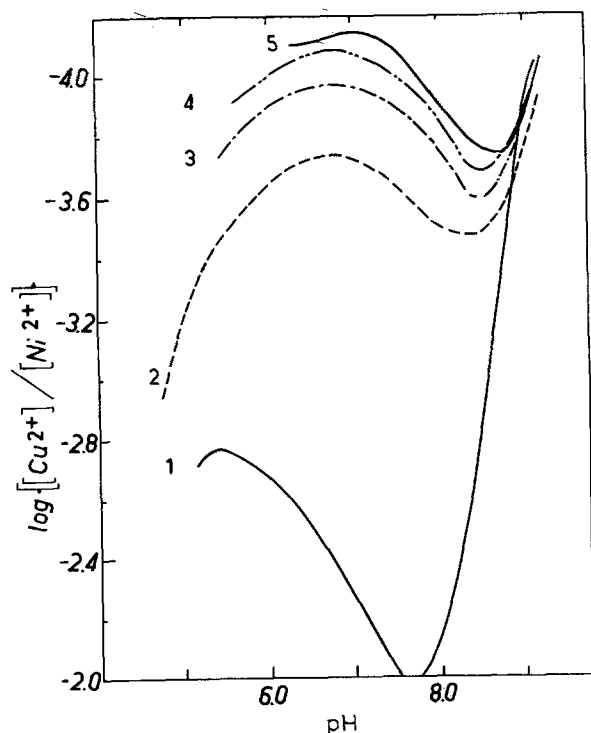


Fig. 4. Logarithm of the ratio of uncomplexed cupric over nickelous ions as a function of electrolyte pH for various sodium citrate concentrations: 0.1, 0.22, 0.4, 0.6 and 1.0 M for curves 1 to 5, respectively.

to 0.12 M leads, in electrolytes containing 0.083 M sodium molybdate, to a decrease in Mo content (Fig. 9). For example, at a current density of 4 A dm<sup>-2</sup>,  $\tau_{\text{Mo}}$  is reduced from 30 wt % to 12 wt %. Simultaneously the nickel content increases considerably from 14 to 50 wt %.

#### 3.5. Effect of experimental conditions, multilinear regressions

A multilinear regression was carried out from fifty six experiments to determine the effects of molybdate, copper sulphate concentrations and current density on deposit composition and cathodic current efficiency. The molybdenum content was shown to decrease markedly when the copper sulphate bulk concentration was increased and was slightly reduced, though the analysis shows some scatter, when the current density was raised.

$$\log \tau_{\text{Mo}} = 1.385 + 0.399 \log C_{\text{Mo}} - 0.275 \log C_{\text{Cu}} - 0.035 \log i_{\text{K}}$$

(correlation coefficient  $\chi^2 = 0.80$ )

Though the nickel sulphate concentration was kept constant in these experiments, the nickel content decreased strongly with increasing copper sulphate bulk concentration; it increased with current density. The current efficiency (C.E.) increased markedly with copper sulphate concentration; it decreased strongly with molybdate concentration and only slightly with current density.

$$\text{C.E.} = 12.13 - 152C_{\text{Mo}} + 578C_{\text{Cu}} - 2.5i_{\text{K}}$$

$\chi^2 = 0.82$

A triangular diagram, commonly used for ternary alloy representation, is helpful in explaining the effect of electrolyte composition on the alloy deposit composition (Fig. 10). The line A-B corresponds to solutions containing 0.75 M NiSO<sub>4</sub>, 0.12 M CuSO<sub>4</sub> and increasing molybdate concentrations from 0.008 M

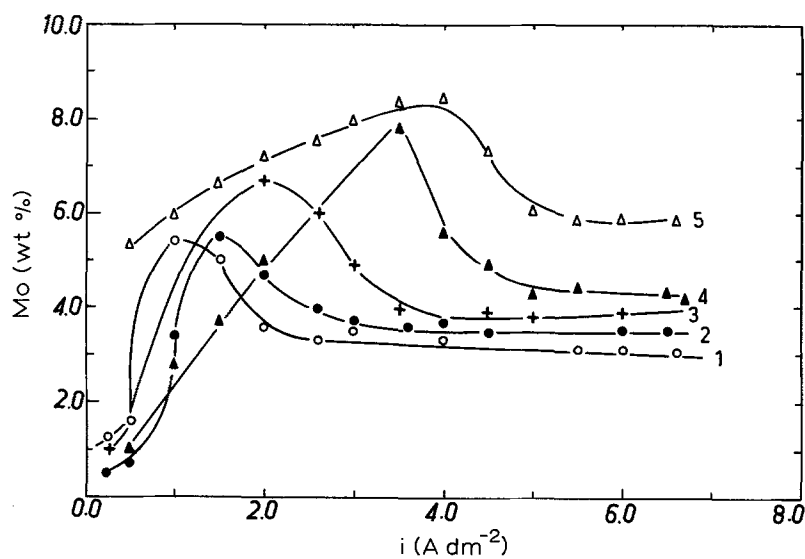


Fig. 5. Current density dependence of the molybdenum content in the deposits for various sodium citrate concentrations: 0.22, 0.3, 0.35, 0.4 and 0.45 M for curves 1 to 5, respectively.

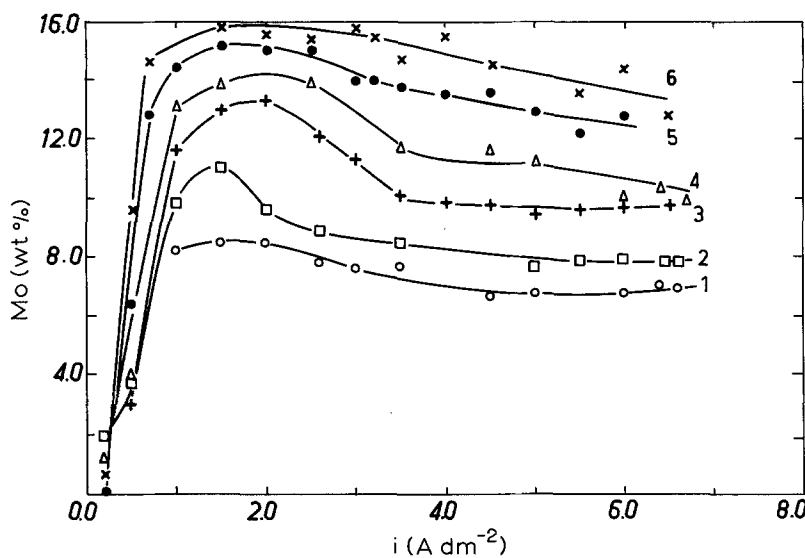


Fig. 6. Current density dependence of the molybdenum content in the deposits for various molybdate concentrations: 0.016, 0.020, 0.041, 0.049, 0.062 and 0.083 M for curves 1 to 6, respectively.

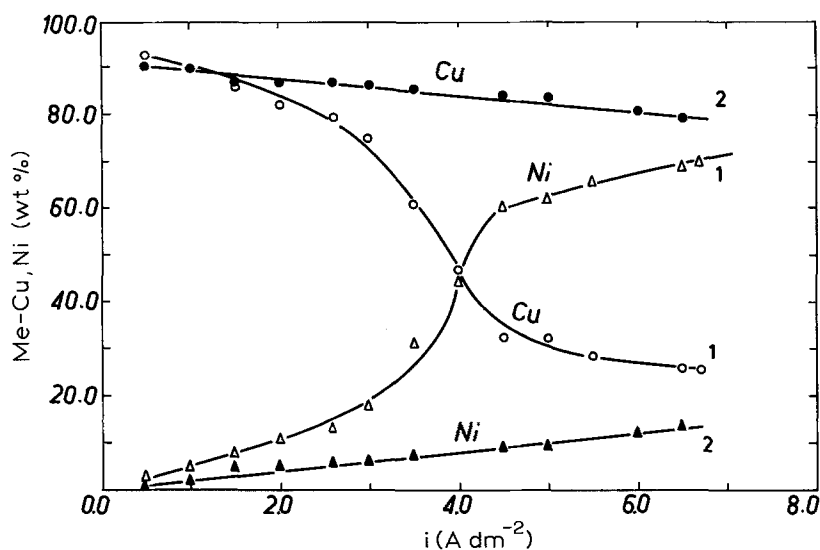


Fig. 7. Current density dependence of the nickel and copper content in the deposits from electrolytes containing 0.008 M (1) and 0.016 M (2) sodium molybdate.

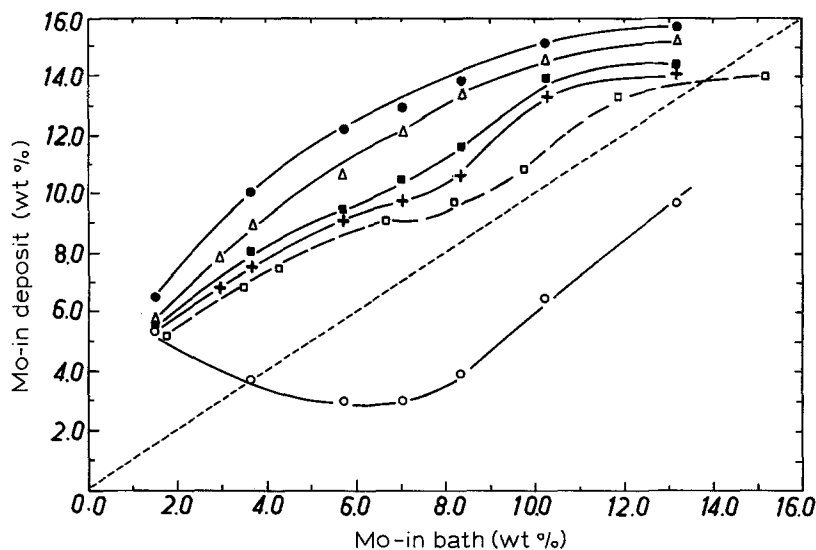


Fig. 8. Molybdenum proportion in the deposits as a function of Mo percentage in the electrolyte. Dashed line: electrolyte without copper sulphate. At current densities: (●) 1.5, (Δ) 2.5, (■) 4.5, (+) 6.0, (□) 6.0 and (○) 0.5 A dm<sup>-2</sup>.

to 0.083 M. The composition of the alloys deposited at 1.5, 3 and 6.5 A dm<sup>-2</sup> are plotted respectively on curves 1, 2 and 3. The line C-D corresponds to solutions containing 0.083 M Na<sub>2</sub>MoO<sub>4</sub>, 0.75 M NiSO<sub>4</sub>, and various copper sulphate concentrations between 0.0075 M and 0.06 M. The composition of the alloys deposited at 1.5, 3 and 6.5 A dm<sup>-2</sup> are plotted respectively on curves 4, 5 and 6. This diagram shows that the nickel discharge is strongly inhibited (much lower content in the deposit than in the bath). On the contrary molybdenum, and especially copper, deposition are promoted: the contents of these elements are higher in the deposit than in the bath.

#### 4. Morphology, structure and internal stress

The Ni-Cu-Mo alloy deposits exhibit a rough nodular morphology as shown by scanning electron micrographs, similar to that of the binary alloy layers (Fig. 11). The layers obtained at low current density are well crystallized by contrast with Ni-Mo layers, which are amorphous at low polarization [29, 17]. They exhibit the f.c.c. structure characteristic of the Ni-Cu-Mo solid solution. They show a marked

preferred growth in the <110> direction and a less pronounced one in the <411> direction. Deposits obtained at high current densities (7 A dm<sup>-2</sup>) are poorly crystallized and exhibit a high microdeformation level.

The internal stresses were measured by the method of the flexible cathode [30] and by dilatometry [31]. The Ni-Cu-Mo alloy layers present tensile stresses of rather high level up to 100 kg mm<sup>-2</sup>. The stress level decreases slightly when saccharine is added to the electrolyte: for 3 μm thick layers deposited at 4 A dm<sup>-2</sup> (from an electrolyte containing 0.75 M NiSO<sub>4</sub> · 7H<sub>2</sub>O, 0.06 M CuSO<sub>4</sub>, 5H<sub>2</sub>O, 0.016 M Na<sub>2</sub>MoO<sub>4</sub> · 2H<sub>2</sub>O, 0.45 M Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, 2H<sub>2</sub>O) the stress level decreases respectively from 21 to 12 and 10 kg mm<sup>-2</sup> for saccharine concentrations of 0, 0.4 and 1 g dm<sup>-3</sup>.

#### 5. Conclusions

Ternary Ni-Cu-Mo alloys of various compositions can be electrodeposited in citrate electrolytes. Their composition strongly depends on the electrolysis conditions. The molybdenum content is maximum for a pH of 7. It increases when the copper discharge is inhibited, i.e. when citrate concentration is increased

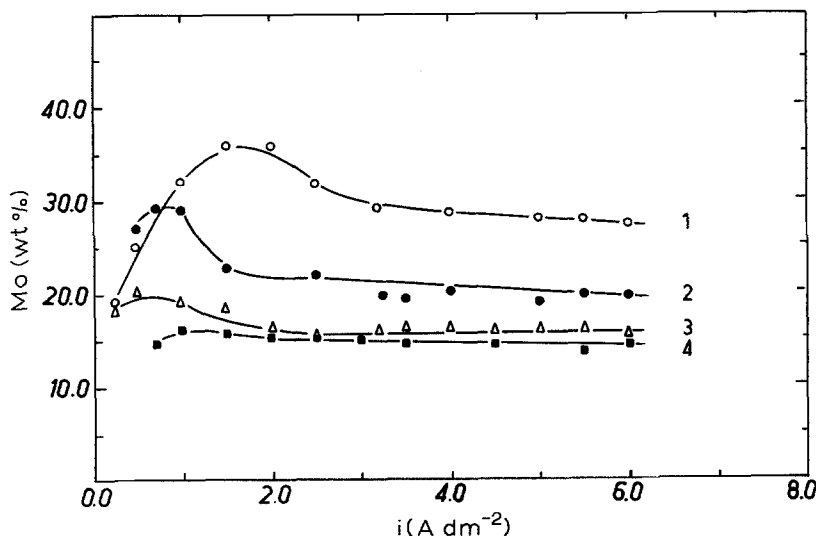


Fig. 9. Current density dependence of the molybdenum content in the deposits from electrolytes containing various copper sulphate concentrations: 0.015, 0.03, 0.06 and 0.12 M for curves 1 to 4, respectively.

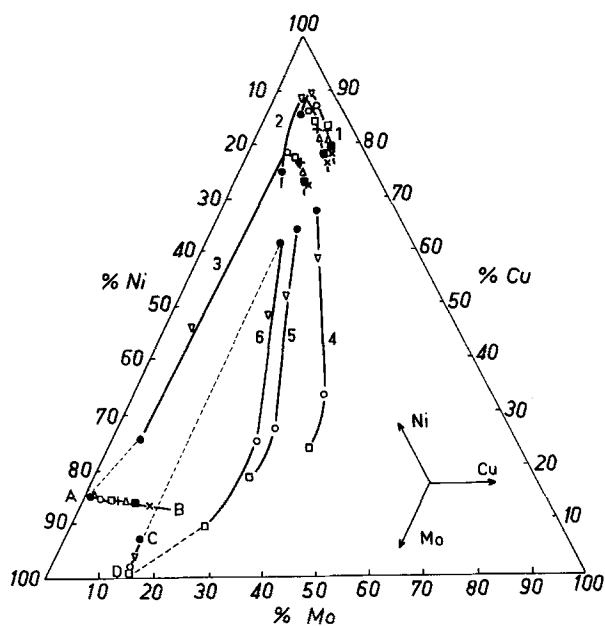


Fig. 10. Ternary diagram for Ni-Cu-Mo layers deposited under various conditions. Electrolyte compositions: lines A-B and C-D. Deposit compositions: (1) 1.5, (2) 3 and (3) 6.5 A dm<sup>-2</sup>, from electrolytes A-B; and (4) 1.5, (5) 3 and (6) 6.5 A dm<sup>-2</sup>, from electrolytes C-D.

or when the copper sulphate concentration is reduced. When the current density is increased, the Mo content exhibits a maximum value which depends on electrolyte pH and composition. At high current density the nickel discharge is predominant whereas at low current density molybdenum and especially copper are preferentially deposited.

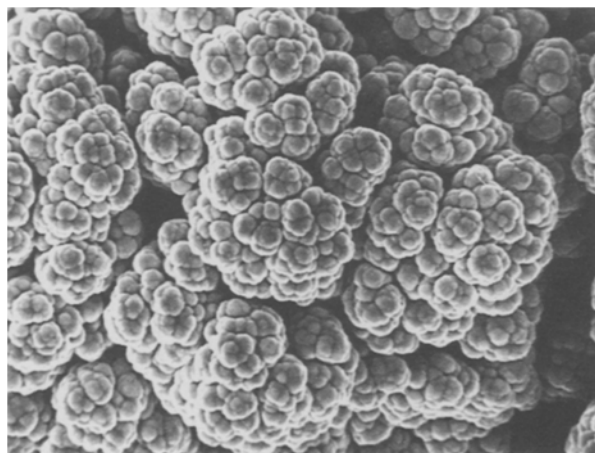


Fig. 11. Surface morphology of the Ni-Cu-Mo alloy layers. (Magnification  $\times 1000$ )

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