Pulse Plating of Binary Alloys Exhibiting Induced Codeposition

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The influence of pulse plating variables such as pulse frequency, duty cycle and pulse current density on deposit composition are investigated for Ni-Mo alloys that exhibit induced codeposition behavior. The results are interpreted by considering non steady state mass transport processes. For Ni-Mo alloys, the pulse plating variables have relatively little effect on the alloy composition in electrolytes rich in Mo, but they have a strong effect in Ni rich electrolytes. The behavior is consistent with previously proposed mechanisms of induced codeposition. The effect of operating conditions on plated films morphology is also discussed. Molybdenum and its alloys are of interest for their wear and corrosion resistance properties along with their low hydrogen overpotentials. Many studies have reported their fabrication in the form of coatings using the electrodeposition technique.¹⁻⁵ The reduction of molybdenum oxyanions is highly irreversible and the element cannot be plated as a single metal from aqueous solutions. On the other hand, its deposition as an alloy can be induced by the iron-group metals Fe, Co and Ni.⁶ Several hypotheses have been put forward. One investigation recently conducted in our laboratory proposed the formation of a mixed oxide intermediate Mo^{IV}-M^{II} (M = Fe, Co or Ni) adsorbed at the electrode surface.⁷

Hydrogen evolution always accompanies the codeposition process and is responsible for the observed cracking of high molybdenum-content thin films. To minimize cracking, conditions must be found to minimize the side reaction while maximizing the Mo content of the alloy. In this study, the pulse plating technique is used and compared to the dc method to find optimum conditions to electroplate Ni-Mo alloys. The effects of pulse parameters on the alloy composition, their structure and the current efficiency are investigated. The present results are discussed by considering induced codeposition mechanisms.

Experimental procedure

Ni-Mo thin films were electrodeposited by using an inverted rotating disk electrode (IRDE) described elsewhere.⁸ Substrates were copper disks with an exposed surface area of 0.50 cm². Some experiments were conducted with a rotating cylinder electrode (RCE) system using silver cylinders (4cm²) as substrates. Both electrode systems permit the evacuation of the co-evolved gas during the electrodeposition process. A stationary stable anode and a mercurous sulfate electrode were used as counter and reference electrodes respectively. Deposits were prepared in galvanostatic conditions. The thickness of all plated films was approximately 1 μ m.

A labview program controlled a potentiostat/galvanostat equipment for pulsed electrodeposition. The current waveform is illustrated in Fig.1. Three independent pulse variables can be freely chosen. The duty cycle (γ) is defined as $t_p/(t_p+t_p')$, where t_p is the pulse on-time and t_p' , the relaxation time. It was varied between 0.2 and 0.6 in the present study. The pulse frequency $v = 1/(t_p+t_p')$ ranged between 0.02Hz and 1kHz and the peak current density i_p between 20 and 250 mA.cm⁻².)



Fig.1. Current waveform for pulsed electrodeposition.

Plating baths composition is given in Table 1. Trisodium citrate is used as a complexing agent for both Ni and Mo. Solutions were sparged with nitrogen for 1h before use.

| | Bath 1 | Bath 2 |
|----------------------------------|--------|--------|
| Chemicals (mol.L ⁻¹) | | |
| NiSO ₄ | 0.7 | 0.005 |
| Na ₂ MoO ₄ | 0.005 | 0.7 |
| Na ₃ Cit | 0.8 | 0.006 |
| NH ₃ | 0.28 | 0.28 |
| pH | 7.4 | 11.7 |
| Temperature | 25°C | 25°C |

Table 1. Plating baths composition.

Compositional analysis was performed by X-ray fluorescence (XRF). The current efficiency was determined by weighing the RCEs before and after the electrodeposition experiments, using the Faraday law. The surface morphology of plated films was observed by scanning electron microscopy (SEM).

Results and discussion

Effect of pulse variables

Figure 2 shows the films composition and the current efficiency (*CE*) as a function of pulse frequency. Both pulse on-time and relaxation time were varied. Deposits were plated at a current density of 50 mA.cm⁻² with a duty cycle of 0.4. The electrode rotation rate of IRDEs and RCEs was set to 1000 rpm and 2500 rpm respectively. The values were chosen to yield an equivalent diffusion layer thickness on both electrode systems.

With type-1 baths (Fig. 2a), the molybdenum content increases from 10 to 26% while the current efficiency remains almost constant ($55\pm3\%$) with increasing pulse frequency from 0.02 to 100Hz.



Fig.2. Molybdenum content and current efficiency as a function of pulse frequency for deposits prepared from type-1 (a) or type-2 (b) baths. $i_p = 50 \text{ mA.cm}^2$ and $\mathbf{g} = 0.4$. Dotted lines indicate dc values.

A very slight decrease of the molybdenum content is observed at higher pulse frequencies while the cathode efficiency increases up to 72%. Ni-Mo deposits are bright when deposited at pulse frequencies higher than 0.5 Hz. With dc plating at the same current density i_p , alloys are obtained with 10.0±0.5% of molybdenum and a cathode efficiency of 57%. Resulting deposits are dull.

The composition curve reveals an opposite variation when type-2 baths are used (Fig.2b). The Mo content is maximum (34%) at lower pulse frequency values and slightly decreases with pulse frequency. Cathode efficiency values are significantly lower than those obtained with a Nirich (type 1) bath. All deposits plated under conditions of Fig.2b are adherent and bright.

The results shown in Fig.2 indicate that the Mo content of the coating can be controlled by varying the duration of the pulses. For both electrolytes, the influence of the pc method on the codeposition process is not significant at pulse frequencies lower than 1Hz.

From Fig.2, it should also be noted that no systematic variation of the current efficiency is observed with respect to pulse frequency. For Ni-Mo alloys, it appears that *CE* is mostly dependent on the molybdenum content in deposits. This might be related to the electrocatalytic properties of Ni-Mo alloys for hydrogen evolution.⁹

Aimed at optimizing the plating process, another set of experiments was conducted by studying the effect of the pulsed current density. Results obtained for type-2 bath are shown in Fig.3.



Fig.3. Molybdenum content and current efficiency as a function of pulse current density for deposits prepared from type-2 bath. $\mathbf{n} = 250 \text{ Hz}$ and $\mathbf{g} = 0.4$.

When the current density i_p is increased from 20 to 250 mA.cm², the Mo content in deposits attains values up to 40%. Rich-Mo plated films are adherent, metallic and bright although the cathode efficiency becomes very low (< 10%) due to the enhancement of the side reaction at high i_p values.

Finally, other experiments have shown that the Mo content increases with decreasing duty cycle. For instance, deposits plated from a Ni-rich bath at a pulse current density of 50 mA.cm² and a pulse frequency of 83Hz contain 18.0 ± 0.4 , 25 ± 1 or 38 ± 2 at% of Mo when the duty cycle is set to 0.6, 0.4 or 0.2 respectively. Deposits were bright, except those containing more than 35% of molybdenum that were inhomogeneous and relatively thin, suggesting an optimum value of 0.4 for duty cycle.

Induced codeposition mechanisms

As shown in Fig.2, two different behaviors with respect to pulse frequency can be observed depending on the relative concentration of precursors in solution. Podlaha and Landolt studied in details the electrodeposition of Ni-Mo alloys by dc plating.³ The present data can be discussed on the basis of the codeposition mechanism they proposed.⁷ According to their model, the molybdate reduction is catalyzed by the Ni^{II}L species and involves the formation of an adsorbed intermediate species, where L is a ligand such as citrate:

$$MoO_4^{2-} + Ni^{II}L + 2H_2O + 2e = [Ni^{II}LMoO_2]_{ads} + 4OH^{-}$$
 [1]

$$[Ni^{II}LMoO_{2}]_{ads} + 2H_{2}O + 4e = Mo(s) + Ni^{II}L + 4OH$$
[2]

while the nickel deposition is independent of the other element :

$$Ni^{II}L + 2e = Ni(s) + L$$
[3]

In a plating bath containing a relatively small concentration of molybdate and an excess of nickel, they observed that the Mo content in deposits increases with increasing the electrode rotation rate because the molybdenum partial current is limited by mass transport while the nickel partial current is activation controlled. On the other hand, they have shown that the composition of alloys plated from a Mo-rich bath is insensitive to convection changes because

the partial deposition current of molybdenum in this case is coupled to that of nickel and both therefore are mass transport controlled.

Compared to dc, mass transport conditions at the electrode in pulse plating depend on pulse parameters in addition to hydrodynamic conditions.¹⁰ The limiting value of the instantaneous pulsed current for deposition can be considerably higher than that of dc plating. The value of the pulse limiting current density increases with decreasing duty cycle and increasing pulse frequency.¹¹ These effects would then explain the variation observed in Fig.2a. More detailed calculations will be published elsewhere.¹²

Finally, in comparison with Ni-rich baths, the Mo content slightly decreases with pulse frequency (Fig.2b) when electrolytes contain a relative excess of molybdate. The only slight variation confirms the induced codeposition model and certainly indicates mixed controlled deposition reactions.

Surface morphology

Fig.4 shows the changes in surface morphology by varying pulse frequency and duty cycle. Deposits were plated from type-1 baths at a pulse current density of 50 mA.cm^2 .



(a) Mo: 10% - *CE*: 57%



Fig.4. Effect of pulse frequency and duty cycle on surface morphology observed by SEM (x20000). Films were deposited from type-1 bath at $i_p = 50 \text{ mA.cm}^2$. (a) dc plating ; (b) $\nu = 83.3 \text{Hz} - \gamma = 0.2$; (c) $\nu = 0.1 \text{Hz} - \gamma = 0.2$; d $\nu = 83.3 \text{Hz} - \gamma = 0.6$; (e) $\nu = 0.1 \text{Hz} - \gamma = 0.6$.

Films prepared by dc plating show a nodular structure (Fig.4a). The use of a pulsed current can lead to fine-grained deposits as those obtained under conditions of Fig.4b. However, other pc plated deposits are very similar to dc plated films. A smoother and finer structure can be observed at v = 83Hz (Fig.4d) but the surface morphology is very similar to that obtained at

shorter pulse frequencies (Fig.4e) or by dc plating (Fig.4a). As seen from Fig.4c and 4e, duty cycle does not influence drastically deposit morphology. This was also observed at higher pulse frequencies (results not shown here).

Many investigations have studied the effect of pulse parameters on deposit morphology. The fact that Ni-Mo deposits are mostly nodular under the present conditions (Ni-rich bath, $i_p = 50$ mA.cm²) is consistent with data published by Chene and Landolt who showed that compact and non dendritic deposits can be obtained only when the applied current is well below the pulse limiting current density.¹³ Other authors have observed that alloy composition influences film morphology more than deposition parameters.¹⁴⁻¹⁵ Results shown in Fig.4 would support this assumption. Fig.5 shows the surface morphology of a Ni-Mo alloy plated from a Mo-rich bath.



Fig.5. Surface morphology of a Ni-Mo deposit plated from type-2 bath (Mo: 25.1% - CE: 21%). Conditions: $i_p = 50 \text{ mA.cm}^{-2}$, $\gamma = 0.4$ and $\nu = 83.3$ Hz.

Its composition is very close to that obtained under the same pulse conditions from a Ni-rich bath (Fig.2). However, the shown morphology is very different. The porous structure might be related to gas bubble effects resulting from the low *CE*. The results show that in addition to alloy composition the structure of Ni-Mo alloys is strongly affected by *CE*.

Conclusions

In summary, this study has stressed the importance of non steady state mass transport processes in pulse plating of Ni-Mo alloys. Because of higher instantaneous current densities, the molybdenum content in deposits plated from Ni-rich electrolytes containing only a low molybdate concentration can be increased by the pulsed current technique in comparison with dc plating. Deposits with a Mo content of 26 at% (37 wt%) were obtained with a *CE* of 60% from an electrolyte containing 5mM molybdate, using a pulse frequency of 100Hz and a duty cycle of 0.4. SEM observation of the surface of deposits produced under different pulse plating conditions indicates that their morphology is strongly influenced by current efficiency.

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