

Pulse Plating of Ni-Mo Alloys from a Citrate Bath
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Pulse-plating of metals and alloys is of practical interest because the composition and physical properties of deposits can be controlled by a suitable choice of parameters [1]. Despite the large number of studies devoted to pulse plating, very few concern Ni-Mo alloys [2-4]. These have principally focused on the effect of pulse parameters on composition, internal stress and protective properties of Ni-Mo deposits. Recently, models for the prediction of the composition of pulse-plated Cu-Ni alloys have been developed [5-6]. These take into account the influence of a displacement reaction occurring during the off-time when the less noble alloy component may corrode by reaction with the ions of the more noble component. Electrodeposition of Ni-Mo alloys from a citrate was studied with the aim to investigate whether such a displacement reaction takes place during the off-time. The results are then compared with models in the literature.

Figure 1 shows a schematic of the alloy composition behavior with off-time length, in the presence and absence of displacement reaction. The duty cycle ϕ , defined as the ratio of the on-time on the pulse period, is constant. At very short off-times, the rate of the displacement reaction is controlled by the rate of mass transport of the ions of the more noble component which deposits at its limiting current i_{lim} during both the on- and off-time. During the pulse on-time, the alloy deposits with an overall current efficiency γ . At longer times, the growth of a M_1 -rich layer on the alloy surface suppresses further dissolution of the less noble metal and the composition of pulse-plated deposits is equal to that of direct current-plated layers.

Figure 2 shows experimental variations of the composition of Ni-Mo alloys as a function of pulse off-time length for different duty cycles. Deposits were plated using an electrolyte with 0.7M NiSO₄, 5mM Na₂MoO₄, 0.8M sodium citrate and 0.28M NH₃ (pH 7.4) at 25°C. An inverted rotating disk electrode at 1000 rpm was used for deposition on bulk Cu substrates. The on-time and off-time current densities were -50 and 0 mA cm⁻² respectively. Curves follow the trend indicated in Fig.1. The Mo content decreases with off-time length, approaching a limiting value close to that measured for direct current plating (10.0 ± 0.5). At shorter times, the upper limit depends on the duty cycle. AES depth profiles showed no oxide formation in the deposit. The data suggest that a displacement reaction occurs during the pulse plating of Ni-Mo alloys.

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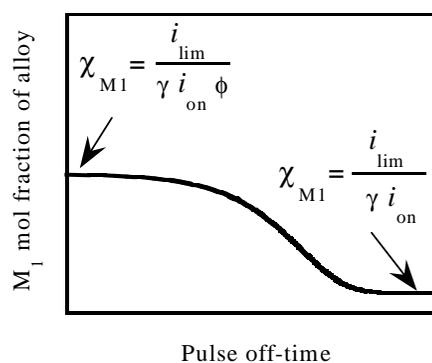


Figure 1. Schematic of alloy composition vs. off-time for a displacement reaction $M_1^{n+} + M_2 \rightarrow M_1 + M_2^{n+}$.

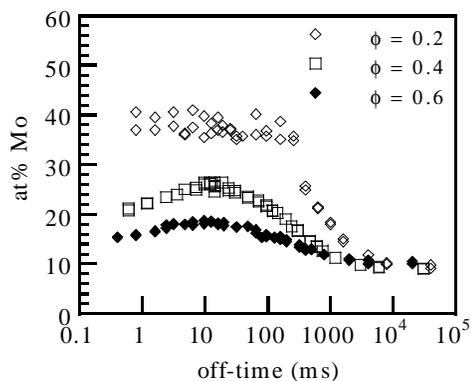


Figure 2. Effect of pulse off-time on alloy composition.