# Pulse-Plated Nickel-Molybdenum Coatings

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**The current efficiency of pulse-plated bright nickel alloy deposits containing 15 to 35 percent by wt molybdenum was higher than that for dc plating when the average current density was 5 A/dm$^2$. The crack-free thickness of the deposits was also increased by pulse plating. The deposits showed a strong (111) crystal orientation. Their crystalline form depended mainly on pulse time.**

Wrought nickel-molybdenum alloys containing about 27 percent by wt Mo are reported to be highly corrosion resistant in non-oxygenated solutions, even in very aggressive environments such as those containing hydrochloric acid.[1,2] Electrodeposited Ni-Mo coatings could bean economical means of protecting ordinary materials. Although molybdenum cannot be deposited separately in aqueous solutions, it can be codeposited with other metals such as nickel or iron, which are assumed to induce deposition. The addition of certain completing agents is necessary.

Nickel-molybdenum deposited by direct current[3-5] is characterized by a limiting crack-free thickness (Ef) that depends on the experimental conditions.[6] At low current density, Me-rich layers with a low Ef are obtained, whereas at current densities greater than 5 A/dm$^2$, thick, crack-free deposits with less Mo are the result.

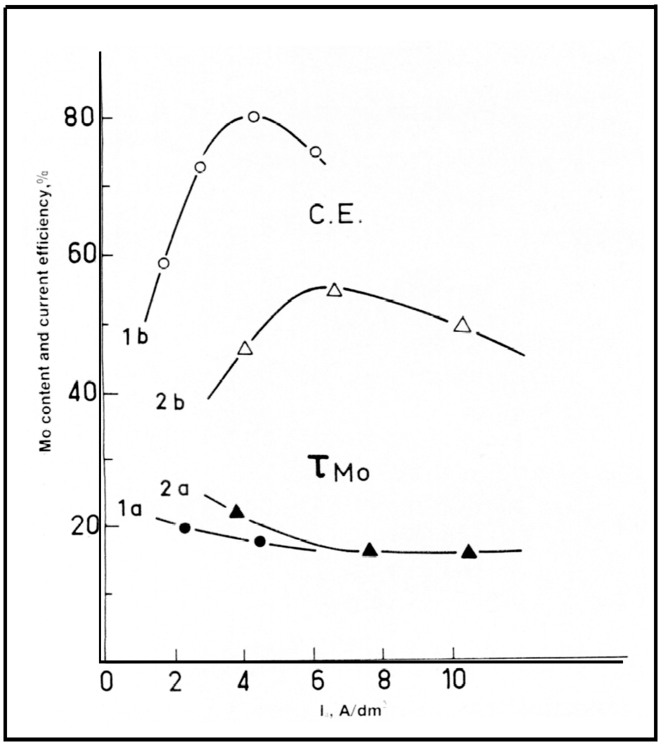

Fig. 1—Effect of average current density ($I_a$ on Mo content and current efficiency. (Curves 1a and b represent Bath 1,$I_p$ = 12 A/dm$^2$, f = 100 Hz curves 2a and b represent Bath 2, $I_p$= 18 A/dm$^2$, f = 100 Hz.)

The potential advantages of pulse plating were explored in the application of Ni-Mo alloys. The optimum electrolytic conditions were selected by investigating the effect of pulse parameters on the codeposition kinetics and coating properties.

## Experimental Procedure

Electrolytes commonly used for dc deposition were employed in this study of pulse plating. They were made UP of analytical-grade chemicals dissolved in distilled water and contained 0.2M nickel sulfate, various concentrations of sodium molybdate (0.015, 0.030 and 0.060M for Baths 1, 2 and 3, respectively), and 0.25M trisodium citrate as a completing agent. The pH was adjusted to 9.5 with ammonia and the temperature kept at 40° C. The anode was a nickel sheet with a large surface area. The cathodes were iron plates (4 to 10 cm$^2$) polished with Carborundum paper and then alumina powder. Electrolyte volumes ranged from 250 to 2000 mL. The coatings were deposited on a Pt sheet and the nickel content determined by complexometric analysis.’ The cathode current efficiency was calculated.

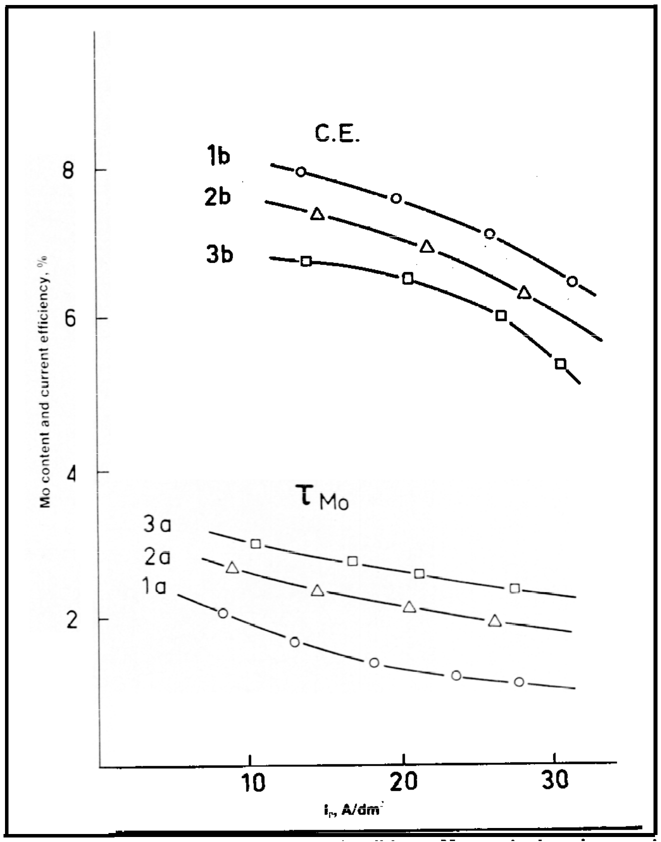

Fig. 2—Effect of peak current density ($I_p$) on Mo content and current efficiency (f = 100 Hz, L = 6 A/din’ for Baths 1,2, 3).

Rectangular pulses were generated by a wave function generator’ coupled to a fast-rise potentiostat.** An intensiostatic setup was used. Applied pulse frequencies ranged from 1 to 1000 Hz.

The crystalline structure of the layers was examined by X-ray diffraction and the roughness profiles were recorded. The Vickers microhardness under a 50- to 100-g load was measured for coatings 20 to 30 µm thick. Internal stress was determined by a dilatometric method.[8,9] The layers were deposited on both sides of a thin (50 µm), quenched carbon steel plate. One end of the plate was fixed and the other connected to a micrometric gage. The internal stress of the applied. coating resulted in contraction or dilation of the steel plate—a change that could be read on the gage.

The corrosion behavior of the coated plates in deaerated 3 percent NaCl solution was evaluated by the free corrosion potential ($E_{cor}$) and the corrosion current density ($I_{cor}$) obtained by Tafel extrapolation of the cathodic polarization curves. These tests provide quick, reliable data.

## Pulse Parameters

In the electrode position of alloys, the effects of pulse parameters can be predicted only in the case of simple codeposition mechanisms whereby either both metals are deposited under activation control or one is deposited under diffusion and the other under activation.[10] For the Ni-Mo alloy system, the reduction of molybdate is assumed to be induced by nickel reduction, but the mechanism of this codeposition system has not been fully elucidated.[11]

In pulse plating, four parameters are involved but only three are independent, according to the following:

$$1_a = 1_p \cdot T/(T+T') = 1_p \cdot T \cdot f = I_p \cdot \theta$$

where T is the pulse time; T’ the relaxation time; $I_a$ the average current density; $I_P$ the peak current density; f the pulse frequency; and O the duty cycle, T/(T+T').

When the pulse frequency was increased from 1 Hz to 1 kHz at a constant duty cycle (0.3) and constant average and peak current densities ($I_a$ = 6 and $I_p$, = 18 A/dm$^2$), the molybdenum content of deposits from Bath 2 increased only slightly (from 16 to 19 percent). With dc, the molybdenum content was higher (25 percent). The cathode current efficiency was about 70 percent, which was slightly lower than that for dc plating. In subsequent experiments, a frequency of about 100 Hz was chosen for optimum brightness.

When the average current density was increased to 5 A/din’ at a constant peak current density, the Mo content decreased and the current efficiency increased markedly (Fig. 1). A further increase in the average current density to 12 A/din’ had no marked effect on the Mo content of the deposit, but such an increase lowered the current efficiency by enhancing the reduction of protons.

When the peak current density was increased from 10 to 30 A/dm/$^2$ with a constant average current density of 6 A/dm$^2$, the Mo content decreased slightly; current efficiency also declined (Fig. 2). As with dc plating, current efficiency decreased with increasing molybdenum content.

When the pulse time was increased from 1 to 5 msec at a constant peak current density of 18 A/dm$^2$, the Mo content of the deposit decreased slightly and current efficiency increased (Fig. 3). With these conditions, the average current density increased from 1 to 5.5 A/dm$^2$. The effect of T is thus similar to that of the average current density (Fig. 1).

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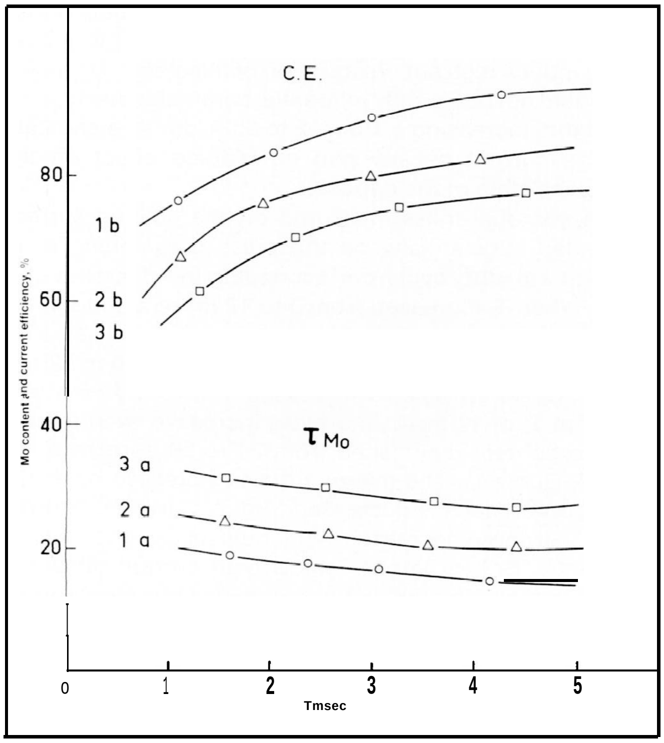

Fig. 3—Effect of pulse time (T) on Mo content and current efficiency ($I_p$ = 18 A/dm$^2$, T' = 12 msec).

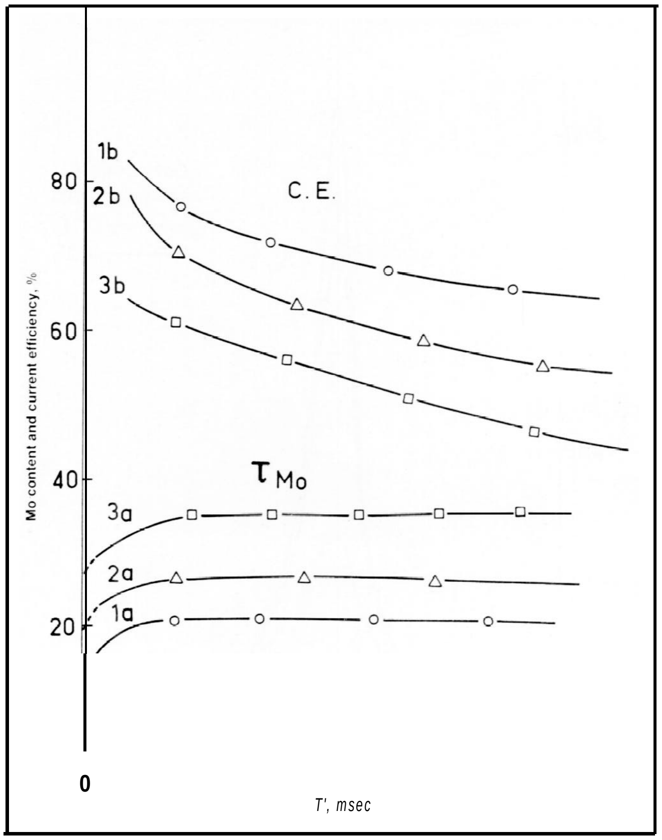

Fig. 4—Effect of relaxation time (T') on Mo content and cathode current efficiency ($I_P$ = 12 A/dm$^2$, T = 5 msec).

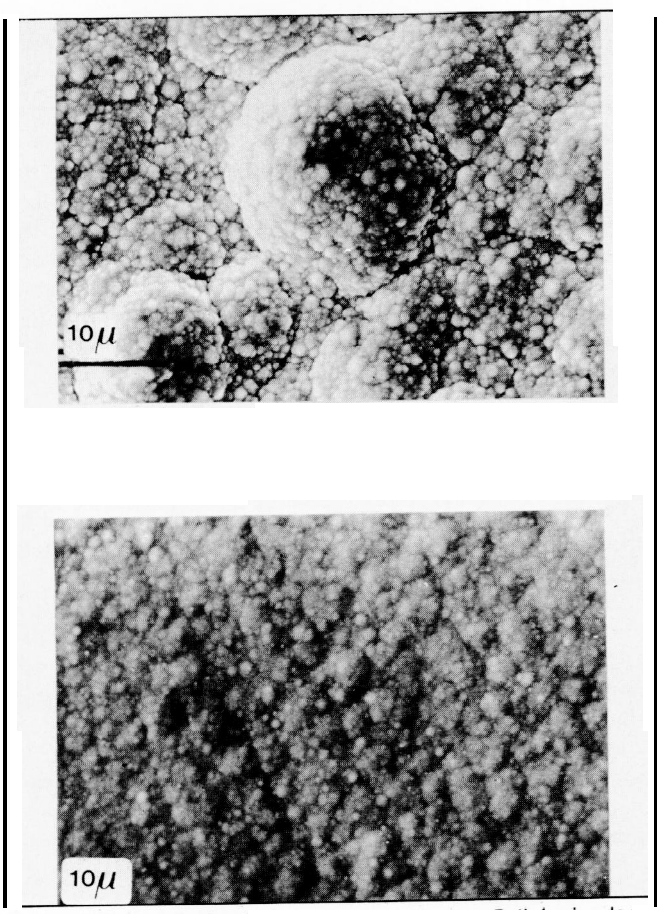

Fig. 5—SEM micrographs of Ni-Mo alloy deposited from Bath 1 using dc at 6 A/dm$^2$ (top) and pulse plating with $I_a$ = 6 A/dm$^2$, T = 5 msec, and T ' = 15 msec (bottom).

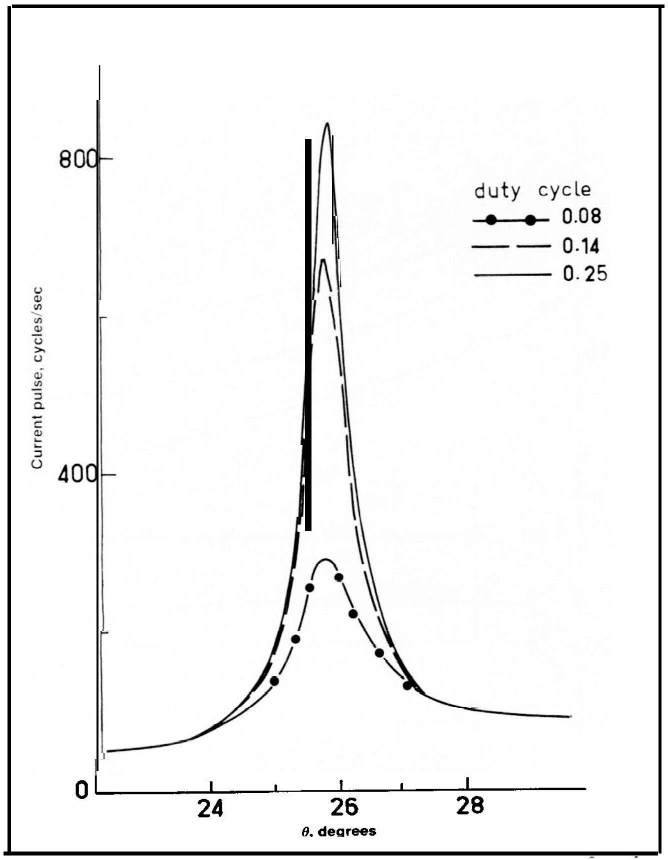

Fig. 6—X-ray diffraction patterns of Ni-Mo alloys plated in Bath 2 under different pulse conditions ($I_p$ = 20 A/dm$^2$).

Even short relaxation times have a marked effect on the deposit composition, but they are usually not employed (Fig. 4). As soon as T’ was long enough with respect to T, further increases in T’ did not alter deposit composition but decreased current efficiency. The current efficiency always increased with increasing duty cycles. In this case, $I_a$ was no longer the active parameter because the Mo content would increase with increasing T'. Current efficiency decreases would be expected when the electrodeposition kinetics involve the adsorption of hydrogen on the electrode surface area. The hydrogen tends to desorb during the off-time, and, at each new pulse, the adsorbed layer has to be rebuilt, leading to a decrease in current efficiency.[12]

## Deposit Characteristics

The effects of pulse time, relaxation time, and peak current density on the crystalline state, microhardness, and roughness were investigated for deposits obtained from Bath 2. The Ni-Mo exhibited a nodular morphology, which was rougher with dc than with pulse plating (Figs. 5a and b). Bright deposits were obtained for frequencies ranging from 10 to 100 Hz. For higher frequencies, cracks appeared at very low thicknesses.

The X-ray diffraction patterns of deposits exhibited the unique, broad (111 ) line of the Ni-Mo solid solution. This resulted from a strong preferred orientation, as observed in deposits obtained using de.’ Broadening of the diffraction lines may result from a very fine grain size, a high microstress level or non-uniform composition distribution. However, the electron diffraction molybdenum image was homogeneous over the entire surface. Therefore, a variation in composition is improbable.

The crystalline form of the deposits depends on the pulse parameters, especially duty cycle. The intensity of the (111) line increased markedly and the half-height width decreased when the duty cycle was increased from 0.08 to 0.25 percent, indicating the formation of larger grains for longer pulses, (Fig. 6). For higher duty cycles, the effect was less pronounced. These results agree with those of other investigators’ who mentioned an amorphous effect due to short duty cycles. The high overpotential of the pulses would induce high supersaturation of the alloy.[13] However, this would not be the only influential parameter because we found that increasing $I_p$ from 12 to 30 A/dm$^2$ at a constant average current density had no marked effect on the crystalline state of the deposit.

The microhardness measured on the coating surface depended substantially on the pulse parameters. It increased with duty cycle, corresponding to a decrease of T’ vs. T. When T' increased from 3 to 12 msec, although the molybdenum content in the deposit remained about 20 percent, the microhardness decreased from 850 to 725 Hv (Fig. 7, Curve 2). When T increased from 1 to 4 msec at a constant T' of 12 msec, hardness increased even though the Mo content diminished from 25 to 20 percent by wt (Fig. 7, Curve 1). The microhardness increased when the peak current density decreased (Fig. 7, Curve 3). Furthermore, hardness increased with duty cycle and current efficiency. Both a large O and a high current efficiency would be associated with low hydrogen resorption, resulting in more hydrogen inclusions and thus enhanced microhardness.

The roughness (R) expressed by the average depth between adjacent peaks also varied with duty cycle (Fig. 8). It decreased with increasing peak current density, possibly as a result of the enhanced nucleation rate.

The effect of average current density on internal stress was determined for a constant frequency (100 Hz) and a constant pulse current density of 12 A/dm$^2$(Table 1). As already observed in dc electrodeposition, the tensile stress first increased with thickness and then approached a nearly constant value for thicknesses of 8 to 15 µm. In pulse as in dc plating, the stress decreased markedly with increasing current density. For a low average current density (e.g., 3 A/dm$^2$), which corresponds to short pulses (T) and long off-times (T'), the deposit stress was much higher with pulse than with dc plating. For $I_a$= 9 A/dm$^2$(long pulses, short off-times), the stress was very low and even lower than with dc plating. For $I_a$= 6A/dm$^2$(T= T'), the stress was of the same order of magnitude. Hence, in the case of Ni-Mo deposits, the relaxation time does not seem to induce stress relaxation as would be generally expectedl$^{y}$

Steel coated with a 35- to 40-µm-thick layer of Ni containing 28 percent Mo is as corrosion resistant as cast Ni-Mo alloy of the same composition in deaerated 3 percent NaCl. When the deposit thickness increases from O to 80 µm, the corrosion current density decreases and the corrosion potential becomes less negative (Figs. 7 and 8). The improvement of these characteristics is associated with a decrease in coating microporosity with increasing thickness.

## Conclusion

Fairly thick, crack-free nickel alloy coatings containing 15 to 35 percent by wt molybdenum were obtained by pulse plating. The composition of the deposit depended mainly on average current density but also to a small degree on pulse frequency and peak current density. This could be related to the fact that Ni-Mo codeposition was less dependent on the transport process than a nickel-copper system.]'

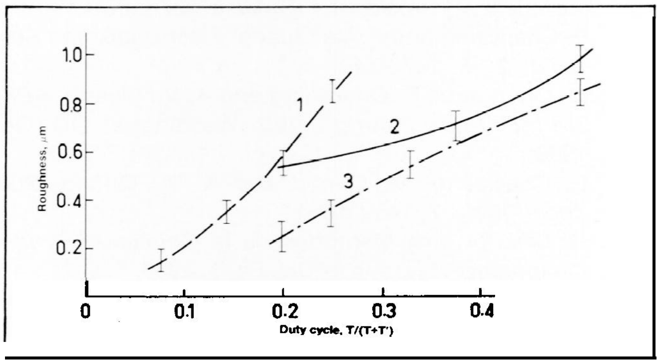

Fig. 8—Roughness of Ni-Mo deposits vs. duty cycle for same conditions as in Fig. 7.

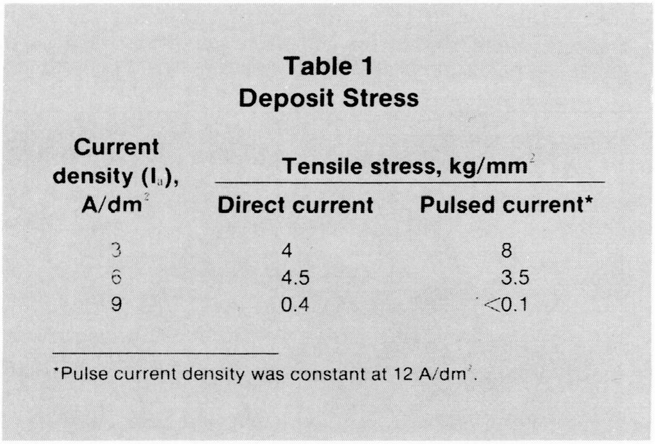

Table 1
Deposit Stress

| Current density ($I_a$), A/dm$^2$ | Tensile stress, kg/mm$^2$ | |
|---|---|---|
| | Direct current | Pulsed current* |
| 3 | 4 | 8 |
| 6 | 4.5 | 3.5 |
| 9 | 0.4 | <0.1 |

*Pulse current density was constant at 12 A/dm$^2$.

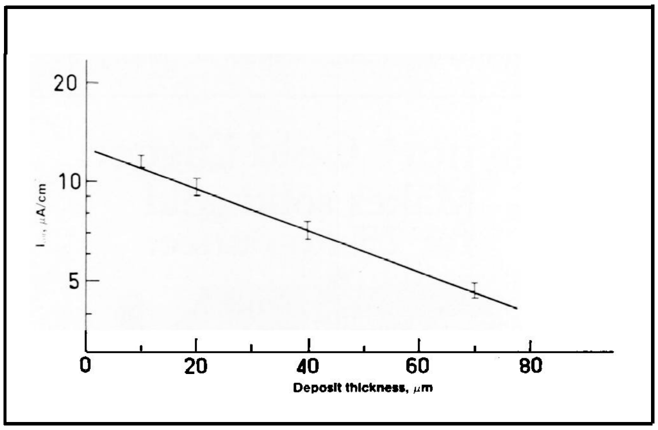

Fig. 9—Corrosion currant density ($I_{cor}$) vs. deposit thickness.

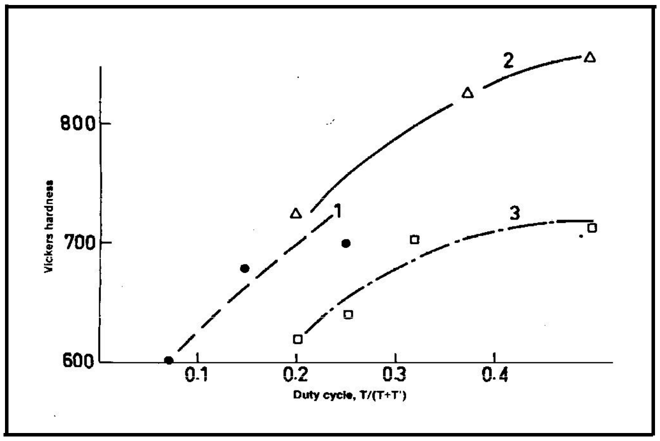

Fig. 7—Microhardness of Ni-Mo deposits vs. duty cycle. Curve 1 shows variation of pulse time (T); curve 2, variation of relaxation times (T'); and curve 3, variation of peak current density.

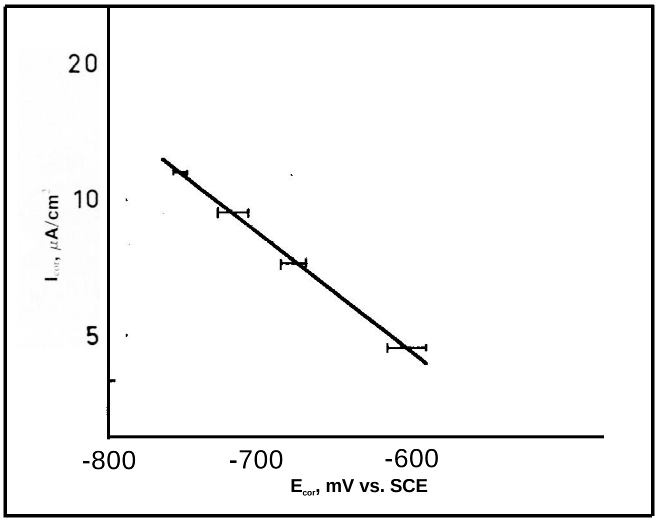

Fig. lo—corrosion currant density (L.) vs. free corrosion potential ($E_{cor}$).

Under appropriate conditions, the internal stress was reduced, roughness decreased, and brightness improved. Deposits showed a strong (111) preferred crystal orientation. The (111 ) line became broader and weaker for a short pulse time, indicating an alteration of the crystalline state.

## References

1. H.H. Uhlig, P. Bond and H. Feller, J. Electrochern. Sot., 110,650 (1963).
2. Publ. F-30, “Hastelloy Alloy B,” Stellite Div., Cabot Corp., p. 106E and 131 E (1970).
3. K. Vu Quang, E. Chassaing, F. Bourelier and J. Montuelle, *Corrosion T. P. F.,* 19,5,237 (1971).
4. E. Chassaing and K. Vu Quang, Electrodep. and Surf. *Treat.,* 2, 65 (1973-74).
5. M. Cherkaoui, E. Chassaing and K. Vu Quang, AESF *3rd Int’l. Pulse Plating Symp.,* Washington, DC (Oct. 1986).
6. E. Chassaing, M. Cornet and K. Vu Quang, *Surf. Technology, 7, 145* (1978).
7. G. Charlot, *Les Methodes de la Chimie Analytique Quantitative,* Masson et Cie, Paris, 1966; p. 807.
8. W.H. Cleghorn, K.S.A. Gnanasekaran and D.J. Hall, Met. *Fin.,* 92, (1972).
9. K. Sheppard and R. Weil, *Proc. Mat. Res. Soc. Symp., 47, 127 (1985).*
10. D. Landolt, *Oberflache-Surface, 1,6* (1984).
11. H. Fukushima, T. Akiyama, S. Akagi and K. Higashi, *Trans. Japan Inst. of Metals,* 20, 7 (1979).
12. *Theory and Practice of Pulse Plating,* J.C. Puippe and F. Lea-man (cd.), AESF, Orlando, FL, 1986; p. 358.
13. Y. Jyoko, I. Ohno and S. Haruyama, *Proc. Electrical Sot. Meeting,* p. 750 (1986).
14. K. Vu Quang, E. Chassaing and M. Cherkaoui, Proc. INCEF-86, Bangalore, India (1986).

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