# Pulse Electrodeposition of NiMoW Alloys

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NiMo and NiW alloys are of interest for their ability to catalyze hydrogen,[1,2] their robust corrosion resistance[3,4] and in the case of NiW for improved hardness.[5] The behavior of induced codeposition of W and Mo are still not well understood. Mo and W cannot be reduced alone by electrodeposition, but require iron elements, *e.g.*, Ni, codeposited with them, defined as induced codeposition.[6] Pulse deposition can affect the resulting deposit composition[7] and morphology[8] of deposits. Also, in NiMo and NiW systems pulse deposition can offer a better current efficiency than direct current.[7,9] The seminal work by Marlot *et al.*[7] showed that Mo wt % in the deposit was increase at high frequency and low duty cycle when compared to dc deposition. This was attributed to the increase in the limiting current density of Mo as a result of the pulsing.

In this work, the induced codeposition of Mo and W by Ni was examined from a citrate-boric acid electrolyte, without the typical ammonia addition, to fabricate ternary NiMoW alloy thin films. Different electrolytes were examined, including one with a lower amount of molybdate compared to nickel and tungstate ions, using rotating cylinder electrodes. The results of deposits fabricated under pulse vs dc deposition were compared by examining the deposit composition, partial current density and morphology.

## Experimental

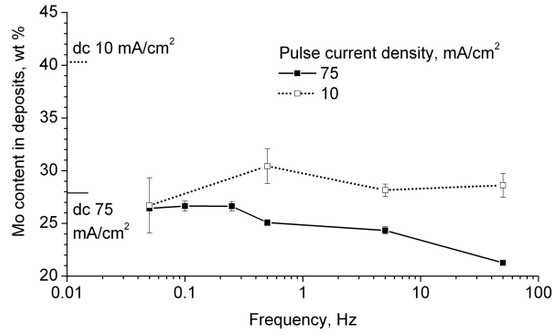
Galvanostatic and pulse electrodeposition were carried out using electrolytes containing sodium tungstate, 0.075 M; sodium molybdate, 0.005 to 0.075 M; nickel sulfate, 0.1 M; sodium citrate, 0.375 M; boric acid, 1 M and pH was adjusted by sodium hydroxide or sulfuric acid to 7. Applied current densities were varied from 10 to 500 mA/cm$^2$ and the rotation rate was constant at 517 rpm. Frequency, duty cycle and the pulse current density were varied. The rotating cylinder electrodes were copper with an area of 3.77 cm$^2$ and polished with SiC paper down to a grit size of 4000. Morphology was examined by FE-SEM and composition and thickness were analyzed by XRF.

## Results

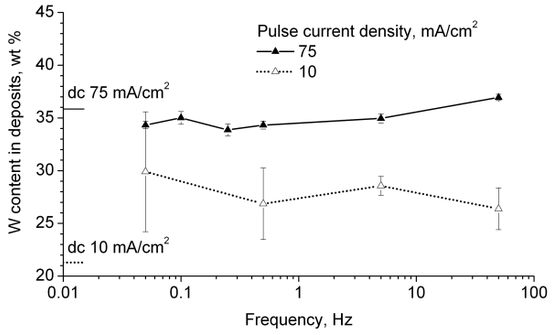
The composition observed during pulse deposition was sometimes altered when compared to the composition when deposition was not pulsed, *i.e.*, dc. An example is shown in Figure 1. At low current densities, *e.g.*, 10 mA/cm$^2$ pulse deposition lead to a significant decrease of more than 10 wt % of Mo content in the deposits compared to dc. The W content, however, increased during pulse deposition compared to dc. However, at larger current densities, such as 75 mA/cm$^2$ there was only a minor difference in the deposit composition when compared to dc. Changes of frequency in the range of 0.05 to 50 Hz did not affect the deposit composition significantly. Not shown, are the partial current densities and current efficiency that were influenced by the frequency.

## Conclusions

Compared to the composition of the deposits electrodeposited under dc, pulse electrodeposition significantly changed Mo and W content in the deposits. The partial current densities of all three elements were affected by varying frequency.




(a)




(b)

Figure 1. Mo (a) and W (b) content in the deposits pulse electrodeposited in the electrolyte of 0.005 M molybdate under pulse current densities of 75 and 10 mA/cm$^2$ and duty cycle of 0.5.

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