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Influence of Permanent Perpendicular Magnetic Field on the Electrodeposition of Nickel

MEHDI EBADI*, WAN JEFFREY BASIRUN and YATIMAH ALIAS
Department of Chemistry, Faculty of Science,
University of Malaya, 50603 Kuala Lumpur, Malaysia
Tel: 60172097738; E-mail: mehdi_2222002@yahoo.com

This work focuses on the electrodeposition of nickel from a Ni Watt's solution in presence and absence of a permanent perpendicular magnetic field (PPMF) to the cathode surface. It was found that the difference between the mass deposition were enhanced in the presence of PPMF (B = 4.4 T) and in absence of PPMF (B = 0) with increasing of current density (Δm = 0.413 to 4.173 mg cm^{-2} in 6 min). The thickness of deposited layers with PPMF was smaller than without PPMF. Therefore, the dense deposited layers were carried out from magneto-electrode position. The Ni Watt's solution contains thiourea as a brightener. The grain size of deposited nickel crystals decreased with PPMF compare to without PPMF. The deposited layers characterized by scanning electron microscopy, X-ray diffraction and atomic force microscopy.

Key Words: Nickel, Magneto-electrodeposition, Morphology, Mass deposition.

INTRODUCTION

Electrodeposition is one of the convenient techniques to control the surface morphology for the decorative and industrial propose. In electrochemical process four forces can play roles as the ion driving force which are diffusion, migration and convection (natural and forced)[1]. It was established that the perpendicular permanent perpendicular magnetic field (PPMF) to electric current, effects on the electrochemical process through changes on the quantity (mass deposition rate) and quality (morphology) on the electrode surface[2].

The permanent perpendicular magnetic field (PPMF) affect on the dynamics of electrochemical system, could be explained as magnetic 'body forces' *i.e.*, paramagnetic force ($\vec{F}_P$), field gradient force ($\vec{F}_B$), Lorentz force ($\vec{F}_L$), electrokinetic force ($\vec{F}_E$) and magnetic damping force ($\vec{F}_M$)[3].

Lorentz force ($\vec{F}_L$) and electrokinetic force ($\vec{F}_E$) carried out from the interaction of PPMF with electric force[4]. When the stationary magnetic field placed as perpendicular to electric current, Lorentz force ($\vec{F}_L$) drastically make role to the transition of ions toward the cathode surface. The magneto hydrodynamic (MHD) is maximal, that is carried out from Lorentz force ($\vec{F}_L$), if the magnetic field lines cross the electric field lines.

$$\vec{F}_L = \vec{j} \times \vec{B} \quad (1)$$

where $\vec{j}$ is the current density and $\vec{B}$ is the magnetic flux density.

It is known that the MHD increases the limiting current j_l, because the thickness of Nernst layer is reduced by means of the magnetically convection. Several authors have investigated[5,6] on the correlation of j_l and magnetic field that they were found empirical relations in the form of eqn. 2:

$$j_l = j_{l,0} + m\ p^b \quad (2)$$

where j_l and $j_{l,0}$ are the limiting current density in the presence and in absence of magnetic field, respectively.

Leventis *et al.*[7], Aogaki *et al.*[8] and Aboubi *et al.*[9] on the magneto-electrodeposition showed that the limiting current (j_l) was proportional to the viscosity of solution (ν), the bulk concentration of electroactive species (C), the strong of magnetic field (B), the diffusion constant (D), the electrode surface area (A) and the number of electron per molecule (n).

$$j_l \propto n^{3/2} A^{3/4} D \nu^{-1/4} C^{4/3} B^{1/3} \quad (3)$$

$$j_l = (4.3 \times 10^3) n^{3/2} A^{3/4} D \nu^{-1/4} C^{4/3} B^{1/3} \quad (4)$$

The correlation between magnetic flux density (B) and diffusion layer thickness (δ) was proposed by Fahidy[6] as shown the following equation:

$$\delta_{D,B} = \delta_{D,0} - \alpha B^m \quad (5)$$

where $\delta_{D,0}$ is the hydrodynamic boundary layer thickness without applied magnetic field and α and m are the empirical constant. Oleg *et al.*[10,11] has formulated the relation between the limiting current (j_l) and diffusion layer thickness (δ_D) in the magneto-electrodeposition process that could be written as:

$$j_l = ADnFC / \delta_D \quad (6)$$

where F is the faraday constant. Oleg *et al.*[10,11] also showed that the diffusion layer thickness δ_D was decreased with magnetic flux and due to the limiting current (j_l) was enhanced. Eventually the mass transport increased in this route. Other interest point is the magnetic field affected on the quality (morphology) of electrodeposition layer within electrochemical process. Ebadi *et al.*[12] suggested that the magnetic field crossing line to the current density generated the uniformity on substrate. The smoothness and the reducing dendrites were carried out of the current density uniformly.

The present paper reports the influence of the permanent perpendicular magnetic field (PPMF) on the deposition rate and morphology of nickel on copper plates during the galvanostate deposition.

EXPERIMENTAL

The deposition of nickel films on copper plate (0.001 cm × 1 cm × 2 cm) was performed using a conventional nickel Watt's solution ($NiSO_4.6H_2O$ 260 g L^{-1}, $NiCl_2.6H_2O$ 60 g L^{-1}, H_3BO_3 g L^{-1}, thiourea 0.2 g L^{-1}). The pH was adjusted to 4 ± 0.1 by adding sulphuric acid. The electrofabrication was operated with different

current density (10, 25, 50, 75, 100 mA cm^{-2}) with two electrode system and the temperature was set between 50-55 ºC. The cell made from Teflon (10, 6, 3 cm) was used for electrodeposition of Ni in presence and absence of PPMF. The distance between the cathode and nickel anode was 4.5 cm. The stationary magnetic supply was placed perpendicular to the electric direction. Fig. 1 shows magneto-electrodeposition set up. The nitrogen bubbles were used to the stirring and the agitation of electrolyte. Before electroplating copper plates were activated and chemical polished by immersion into mixed acids (HCl + H_2SO_4 + CrO_3 + HNO_3) for a few seconds and then rinse with distilled water. The topography of the deposited layers was investigated *via* atomic force microscopic (AFM PS 3000-NS3a). The nickel electrodeposited is analyzed from X-ray diffraction (D_8-Advanced XRD) set using a CuK_α radiation with wavelength 1.540 Å. The mass was determined with difference weight of bar and coated Cu plates. The scanning electron microscopy (SEM-FEI Quanta 200F) was used to survey of surface morphology of electrofabricated samples and it was included EDX (electron dispersive system INCA energy 400).

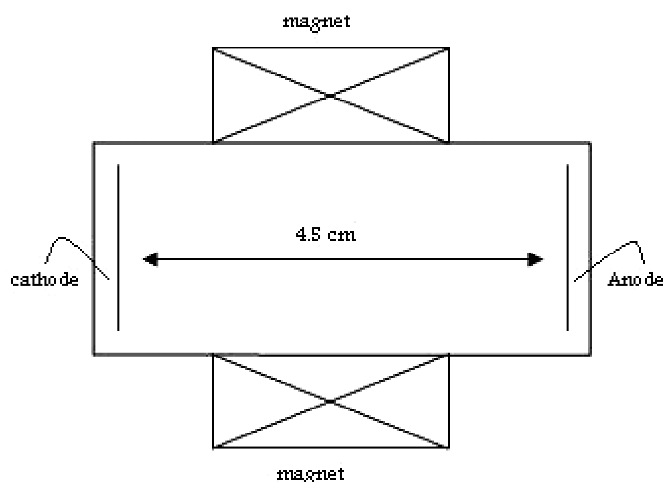


Fig. 1. Schematic diagram of experimental set up. A Teflon cell (10 cm × 6 cm × 3 cm), cathode plate is copper (2 cm × 1 cm) which held by 4.5 cm from Ni anode. The copper plate faced to PPMF (4.4 T)

RESULTS AND DISCUSSION

Mass deposition: The mass deposition was increased with increasing the current density. Ispas *et al.*[13] were emphasized the number of grains deposited in PPMF much higher comparison to the absence of magnetic flux. This phenomenon can be explained by the increasing of the more mass transport of Ni ions within magneto-electrodeposition. The massograph (Fig. 2) shows the empirical effect of the PPMF to enhance the mass deposition in variety current density. The equation 4 could be predicted the influence of PPMF on the increasing of limiting current (I_L) and hence

the mass elevation. The average slop of the mass deposition of Ni with PPMF to without magnetic field was 1.26 for 6 min electrodepositing with variety current. The mass of deposited layers were determined by the difference of bar and coated of Cu plates.

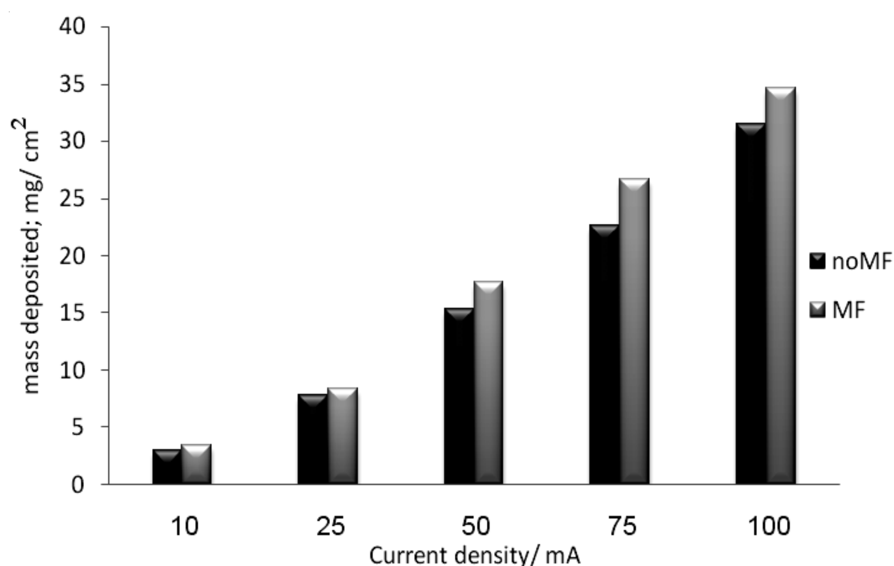


Fig. 2. Mass deposition of Ni on electrodeposited in the presence PPMF (4.4 T) and absence of PPMF at different current density in Ni Watt's bath

Atomic force microscopy (AFM): The influence of additives to the surface morphology of electrodeposited layer has been focused[14]. The adsorption of additives on cathode plate may hinder the surface diffusion of atoms to introduce a smoother surface. The numeral simulation predicts a slower surface diffusion rate to result in smoother parameter of a roughness (α)[15].

The AFM 3D-image of Fig. 3 permits to identify the morphology of the nickel film evolved on variety of current density in the absence and in presence of magnetic field (4.4 T).

It appears that uniformity was enhanced with the increasing of current density while thiourea was existed as an additive in the electrodeposition solution. On the other hand, the PPMF was another factor to the enlargement of smoothness. As already mentioned that the magnetic flux (B) reduces the Nernest layer (δ_D). The emphasize point is the perpendicular magnetic field was able to brushing and arraying of the adsorption atoms. Matsushima *et al.*[16] have investigated the influence of magnetic field on the atoms arraying in the electrodeposition process.

X-Ray diffraction (XRD) studies: The nickel coated layers investigated by X-ray diffraction (XRD). Six electrocoated samples were chosen for the XRD analysis, which are shown in Fig. 4a. Three XRD peaks 4a(C,E,G) belongs to Ni coated

samples with PPMF and three other peaks 4a(B,D,F) were arisen without PPMF. The intensity of peaks (220) was shrinked with the increasing of current density, whereas the intensity of peaks (111 and 200) was enlarged with increasing of current density in electrodeposition process.

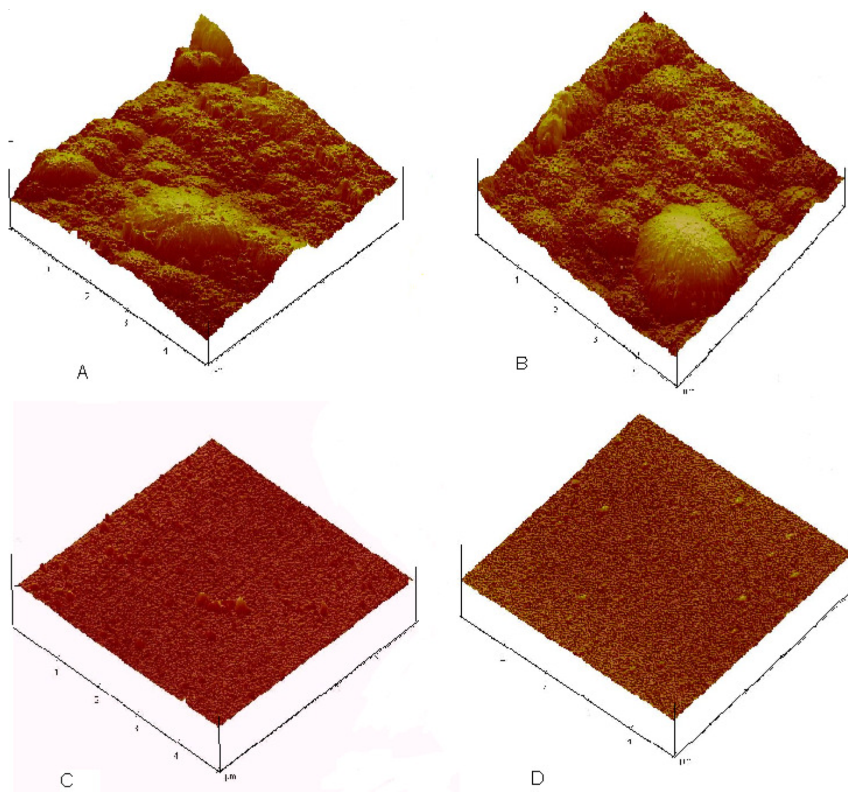


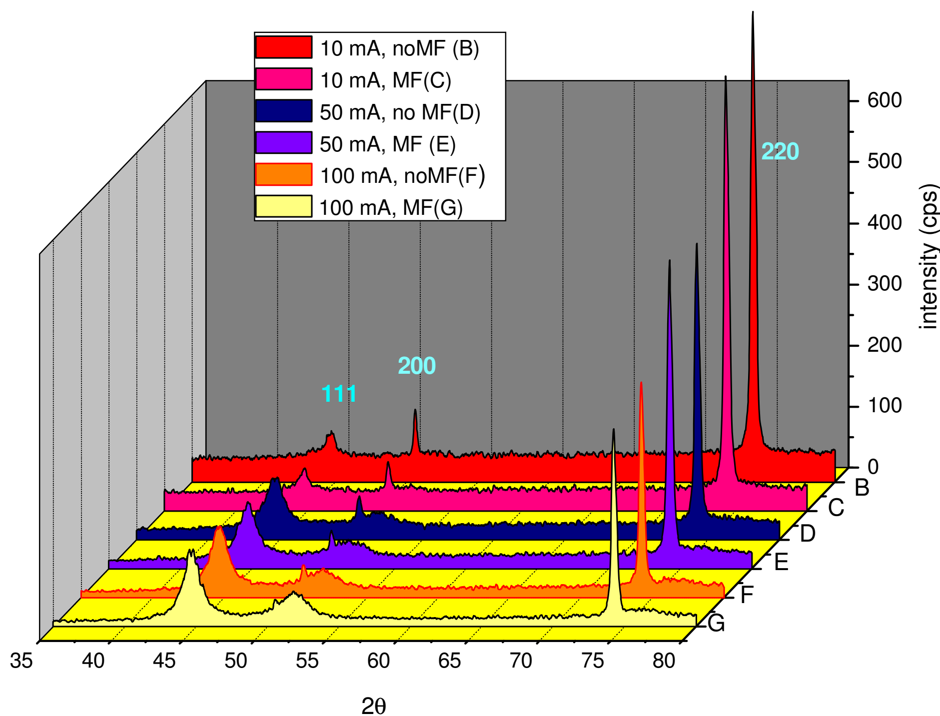
Fig. 3. AFM images of the Ni films electrodeposited in absence of PPMF; A) 10 mA cm^{-2}, B) 50 mA cm^{-2} and in presence of PPMF; C) 10 mA cm^{-2}, D) 50 mA cm^{-2}

The grain size changing of Ni deposited layers were calculated from XRD data through the Debye-Scherrer equation[17]:

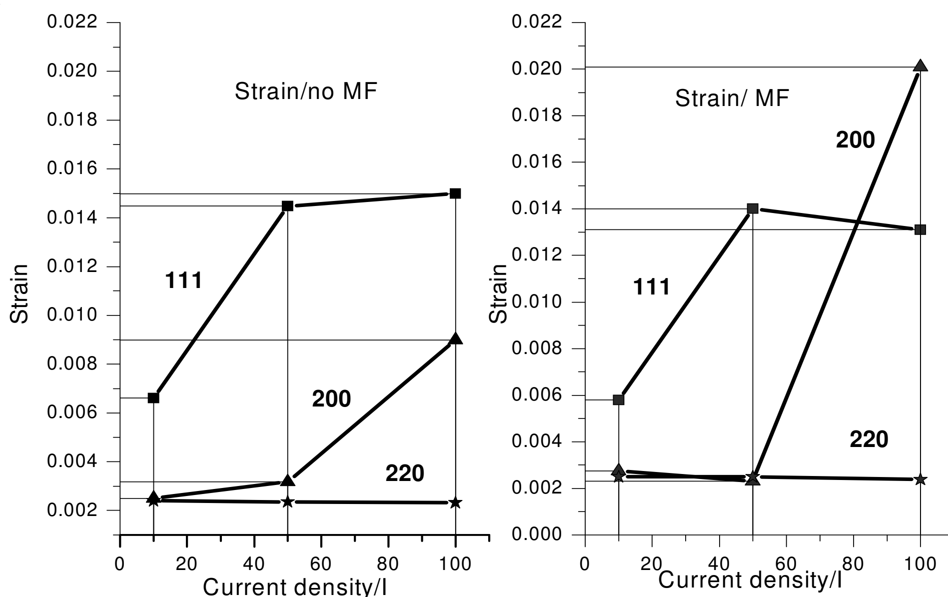
$$l = \frac{0.9\lambda}{\text{FWHM}\cos\theta}$$

where λ = 1.540 Å is the wavelength, FWHM is full width at half maximum, 'l' is the grain size/nm and θ is the angle satisfying Bragg's law.

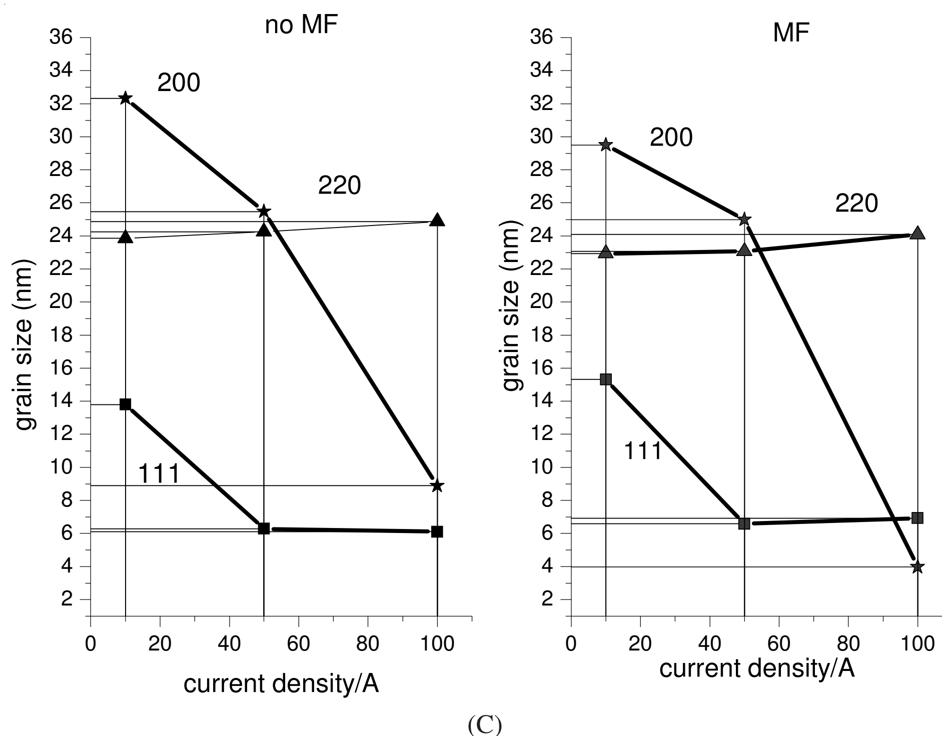
Fig. 4b detected the strain of Ni deposited layers with and without PPMF at different current density. The nickel layers deposited through 220 has no changing with Lorentz force of PPMF at different current density. On other hand, 111 and 200 were changed with increasing of current density. The strain on 220 was more increased with PPMF.



(A)



(B)



(C)

Fig. 4. A) XRD spectra with and without PPMF (4.4 T) at different current density. B) The effect of PPMF on strain of Ni deposited layers. C) the effect of PPMF on the grain size of deposited Ni crystals

Fig. 4c shows the grain size of peaks (200) was decreased with increasing of the current density. The major influence of PPMF was on peaks (200) hence the finer grain size on (200) was carried out with PPMF. The grain size of coated layers on (111) was decreased with increasing on current density from 10 to 50 mA cm^{-2}. The PPMF affect was not more sensible on grain size of (111) and (220). The difference of grain size peaks (200) between Ni obtained layers with and without PPMF was calculated about ($\Delta S = 0.011$) while the layers deposited with 100 mA cm^{-2}.

SEM analysis and characterization of Ni: Deposited Ni layers were also investigated using SEM. Fig. 5 shows the SEM images of nickel surfaces were electrodeposited at 10 and 50 mA cm^{-2} for 20 min using Ni Watt's solution in pH = 4.2 ± 0.1. Fig. 5(A,B,C) and 5(D,E,F) are SEM images of Ni surface deposited in absence and in presence of PPMF, respectively. The SEM 5A and 5D Ni layer images were obtained by electrodeposition at 10 mA cm^{-2}, in case the 5B and 5E are images of Ni layers coated by electrodeposition at 50 mA cm^{-2}. The SEM cross section of deposited layers were presented in Fig. 5C and 5F without and with an applied PPMF, respectively. It was found that the thickness of layer which electro-

deposited with PPMF is smaller than the deposited layer without PPMF at the same current density. It was mentioned on the mass deposition section that the mass electrodeposition was increased with an applied PPMF. Consequently, the deposition layer which obtained with PPMF was denser comparing to nickel deposited layers without PPMF.

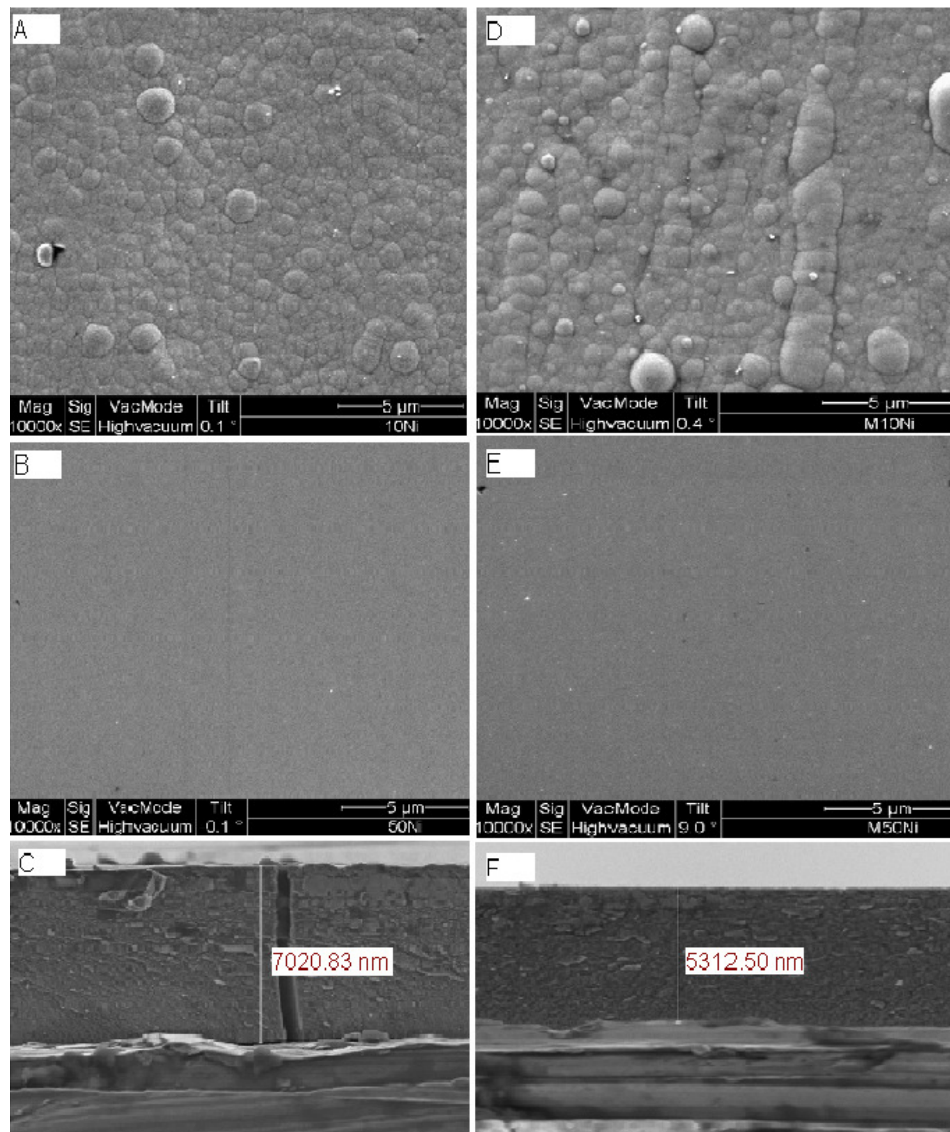


Fig. 5. SEM micrograph of Ni deposited; without PPMF A) 10 mA cm^{-2}, B) 50 mA cm^{-2}, C) the crass section of Ni deposited layer at 50 mA cm^{-2}, with PPMF D) 10 mA cm^{-2}, E) 50 mA cm^{-2}, F) the crass section of Ni deposited layer at 50 mA cm^{-2}

Conclusion

Electrodeposition of Ni was studied in absence and in presence of PPMF at various current densities. The difference of mass depositing on the presence and absence of PPMF was enhanced with increasing of current density. Important point on XRD data carried out with the finer grain size and higher strain on 200 with using a PPMF. The peaks (220) were not changed either with or without PPMF as well as not change at various current density.

It was mentioned on the mass deposition section that the mass deposition was increasing with applied a PPMF. In spite of high mass deposition by PPMF, the thickness was smaller than the layer fabricated without PPMF (L_{PPMF} = 5312.50 nm, L_{noPPMF} = 7020.83 nm for 6 min electrodeposition). It was rationalized that the layers fabricated with PPMF were denser compare to without PPMF. The dendrites on surface layers were shrinked using a PPMF.

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