

EFFECT OF APPLIED CURRENT DENSITIES ON ELECTRODEPOSITED NI-MO COMPOSITE COATINGS

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ABSTRACT

Ni-Mo composite coatings were obtained on pretreated copper substrates by electrolytic deposition in which molybdenum powders were held in suspension. The electrodeposition process was carried out at a current density range of 100-300 mA/cm² and a temperature of 303 K during 90 minutes. The surface morphology of the coatings was examined by scanning microscopy (SEM). X-ray diffraction method was used to determine the phase composition of the layers. The coatings deposited were uniform and adherent to the substrates. It was revealed that composite coatings are characterized by a fissured and porous surface in comparison with pure nickel coating deposited. X-ray examination of the Ni-Mo layers indicated that they have a three phases (MoNi₄, Mo_{1.24}Ni_{0.76} and Ni₃Mo) of crystallites of nickel and molybdenum.

KEY WORDS: Nickel; molybdenum; electrodeposition process; Ni-Mo layers.

1 INTRODUCTION

It is acknowledged [1,2] that broad application of nickel and nickel-based composite coatings in electrochemistry results from special properties of nickel such as good corrosive resistance in aggressive environments and high catalytic activity in many electrochemical processes [3]. Incorporating a metal powder into a metallic matrix as a composite component and its embedding into the matrix structure allows us to obtain a new kind of composite material [4]. Among electrolytic composite layers the materials particular importance are those containing metals like Ti, Mo, and W, which could not be directly codeposited in cationic form from aqueous solutions. However, it is possible to introduce these metals in a form of powders and electrolytic embedding their particles into a metal matrix [5]. Molybdenum as a component of composite coatings seems to be particularly interesting on account of its electrochemical properties. The rate of particle entrapment depends on many factors related either to particles (size, density, composition, zeta potential, conductivity) or to the electrolytic solution (composition, pH, temperature, the presence of additives) [6].

The current density is probably the most studied parameter. Approximately two different effects of the current density can be distinguished [7]:

- Some authors have found little or no influence of current density on the number of occluded particles;
- Others report a significant effect with the presence of one or more maxima of the incorporation of particles depending on the current density applied. Regardless of whether the current density influences

the co-deposition or not, the current density itself is affected by the presence of particles [7].

This work aims to investigate the influence of deposition current density on Ni and Mo percentage in the Ni - Mo layers, their surface morphology, grain size and structure.

2 EXPERIMENTAL

The substrate material used in this study was a cylindrical copper sheet (99.99%) on which Mo-Ni coatings were electrodeposited. Specimens of 2 cm of length and 0.019 cm as a diameter were used as cathode, whereas electrolytic Ni sheets of 99.99% purity and dimensions of 2×1×0.2 cm were employed as anode. The substrates were degreased in alkaline solution and treated in HCl (10% by volume), prior to deposition. Electrodeposition was carried out at 303 K temperature from a solution containing NiCl₂·6H₂O-21.375g/l, NH₄Cl-21.4g/l, NaCl-5.85g/l, H₃BO₃-18.6g/l and molybdenum powders -12.35g/l. The pH of the solution was between 5.5-6. The current density ranged from 100 to 300 mA/cm² and the time of electrodeposition was fixed at 90 min. The solution pH was adjusted by addition of the aqueous HCl or NaOH solution. During electrodeposition, the bath was stirred by a magnetic stirrer with the same value of agitation rate in all experiments.

The morphology and the microstructure of the coatings were investigated using a JSM-6390 Lv scanning electron microscopy (SEM). The compositions of Ni-Mo coatings were determined with energy dispersive x-ray spectroscopy (EDS) analysis tool attached to SEM. Structural investigations and phase composition of the coatings were conducted by XRD method using a Bruker diffractometer

(D8 Advance model) with Cu K α -radiation (1.5406 Å).

3 RESULTS AND DISCUSSION

3.1 Adherence

Thermal shock tests show that electrodeposited composite coatings have an excellent adherence to the substrates.

3.2 Morphology

The surface morphology of Ni-Mo coatings at different current density was shown in (Fig. 1a-e) respectively. In general, the presence of the embedded Mo particles in nickel matrix distinctly enlarges the real surface of the layers. The whole area of composite coatings observed at higher current density is rough and reveals deep narrow pores (Fig. 1.e), which is in good agreement with literature[8]. (Figure. 1.a-d) display a fissured surface of Ni-Mo deposit coatings.

3.3 Chemical Composition

Chemical composition of Mo-Ni alloy depends on the current density (Fig. 2). An increase of the Mo content in the deposit was achieved by an increase of the current density. In the current density range of 100-200 mA/cm², obtained coatings contain from 13 to 20.wt% of Mo, this behavior is due to the rise in the movement of the Mo powder suspension towards the cathode [4]. The increase of current density more than 200 mA/cm² causes a decrease of Mo content in the deposit, this decrease could be explained by a partial trained of Mo powders by nickel ions as result of particles resulting from the strong effect of electric field produced by the increase in current density [9].

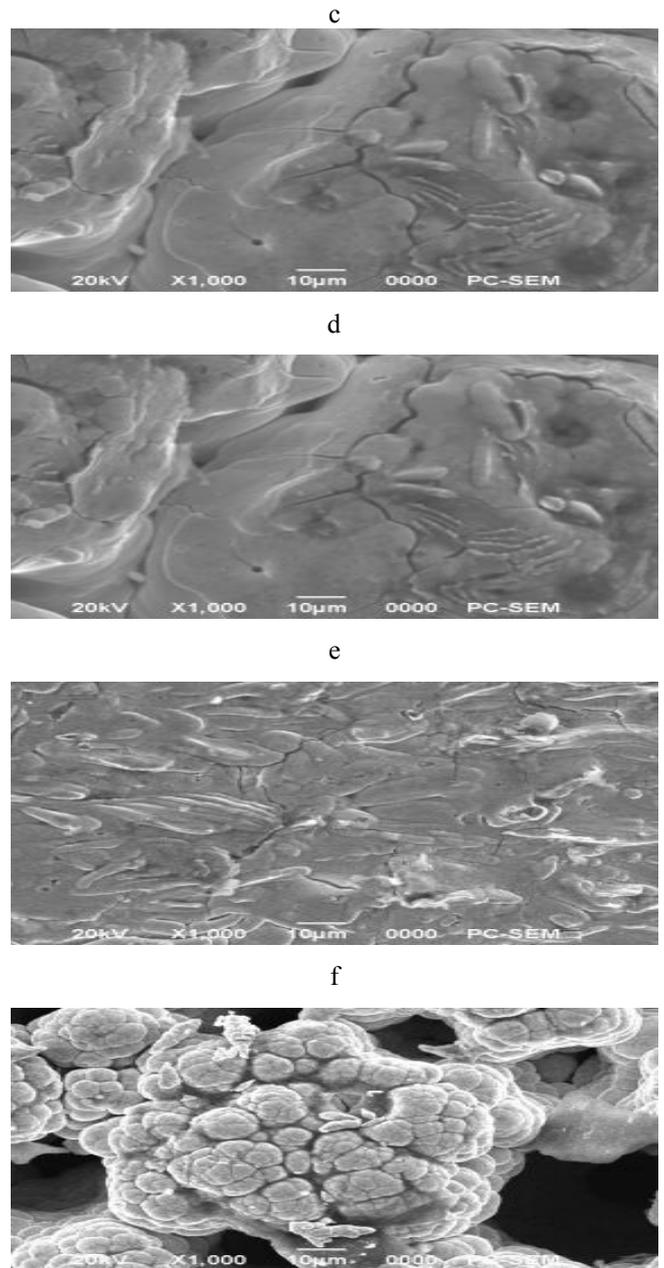
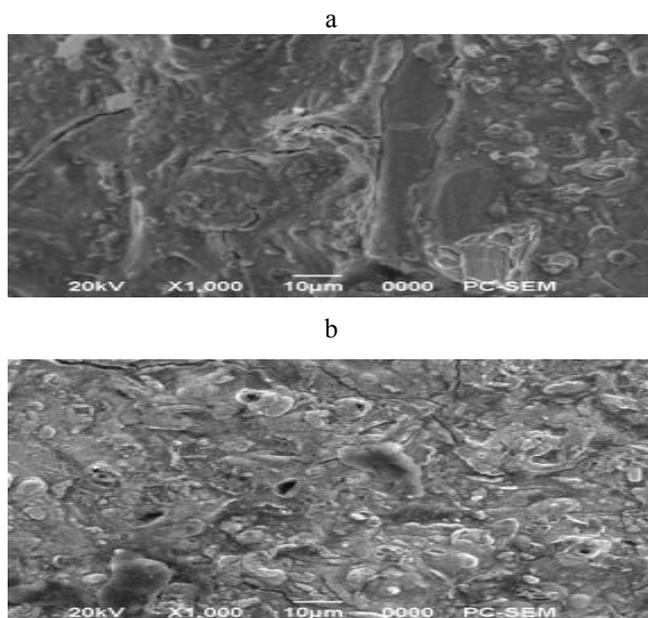


Figure 1: SEM morphologies of Ni-Mo alloy deposits as a function of the current density (a) 100 mA/cm², (b) 150 mA/cm², (c) 200 mA/cm², (d) 250 mA/cm², (e) 300 mA/cm².

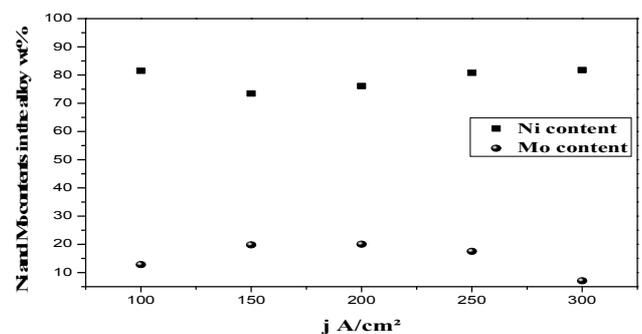


Figure 2: Influence of the current density on the composition of Mo and Ni in Mo-Ni alloys.

3.4 Grain Size

As reported [10], the current density has an effect on the grain size of the coatings deposits. Grain size of deposit under different conditions was determined indirectly from the XRD data using the methods for the termination of the grain size [10, 11]. The dependence of the grain size of Mo-Ni alloys deposits on current density is shown in (Fig. 3). An increase of the current density applied in the bath causes the rise in grain size of the deposits due to the increase of molybdenum composition in the alloy as shown in (Fig. 2). A decrease of the grain size in the deposit was achieved by an increase of the current density to more than $j_{dep} = 250$ mA/cm². This behavior is attributed to the faster transport of metallic ions to the cathode by diffusion than particle transport by mechanical agitation, as current density increases [9].

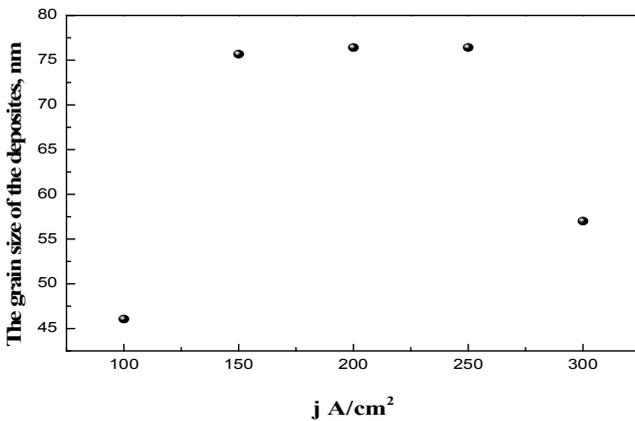


Figure 3: Influence of the current density on the grain size of the deposits

3.5 Phase Analysis by Means of XRD

X-ray analysis of the deposits showed the phase change progressively with the current density of the bath (Fig. 4). The intensity of the peak is related to the MoNi₄ with a preferred orientation (200), (Figure. 4. e) is higher than that measured of the coating obtained using a current density of $j_{dep} = 100$ mA/cm² with preferred orientation (113) (420), which indicate a high incorporation of particles. We can also see Ni₃Mo phase with an important (101) peak intensity has been observed in the coating (Fig. 4. b). Mo_{1.24}Ni_{0.76} peaks were revealed with a preferred orientation of (313) and (121) using a current density of $j_{dep} = 100$ and 200 mA/cm² progressively. But as can be seen no presence of pure Ni or Mo peaks, which leads us to think that at varied current density a strongly bound of MoNi₄, Ni₃Mo, Mo_{1.24}Ni_{0.76} phases were formed in comparison with crystallites phases of Ni or Mo, which in good agreement with literature[12].

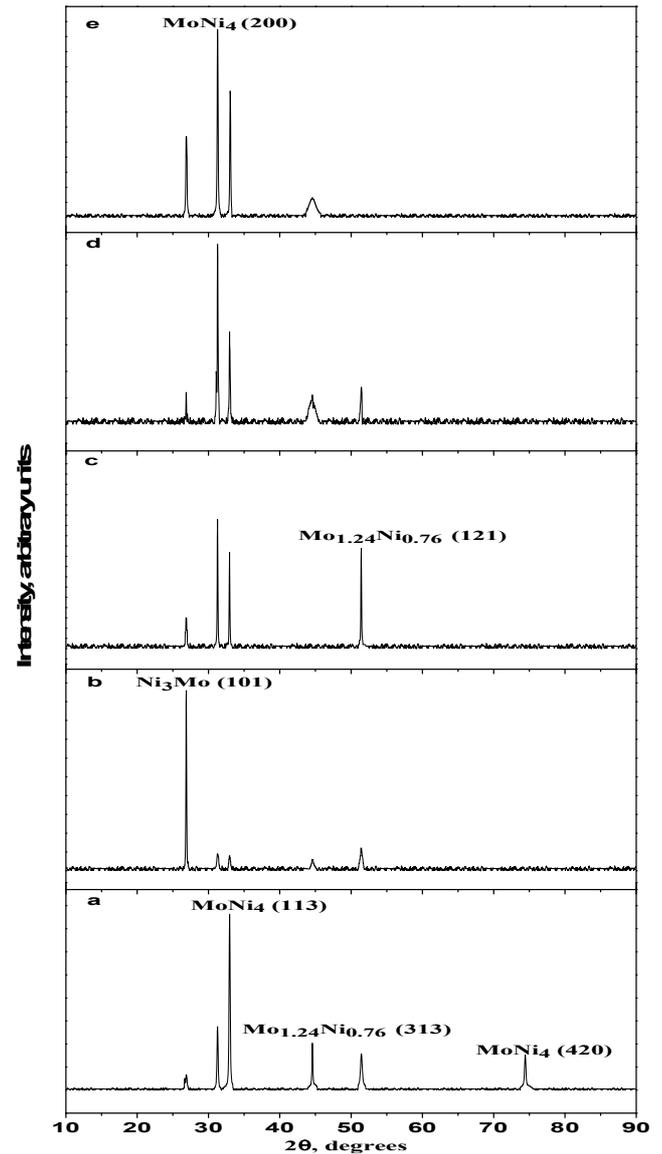


Figure 4: XRD patterns of Ni-Mo alloys deposits as a function of current density (a) 100 A/cm², (b) 150 A/cm², (c) 200 A/cm², (d) 250 A/cm², (e) 300 A/cm².

4 CONCLUSION

The investigations presented show that Mo particles can be embedded into the Ni matrix during the electrodeposition. The thermal shock test reveals that coatings deposited present a good adherence to substrates. The morphology of different coatings shows that the deposited coatings are fissured and porous. The deposition current density influences both the coatings chemical composition and the grain size of the deposits. The XRD indicates a good crystalline structure with (101), (121), and (200) preferred growth orientation.

REFERENCES

- [1] B. R. Tian, Y. F. Cheng, *electrochim. Acta.* 53 (2007) 511.
- [2] R. J. Llewelyn, S.K. Yick, K.F. Dolman, *Wear.* 256 (2004) 592.
- [3] J. Kubisztal, A. Bundniok, *Int. J. Hydrogen Energy.* 33 (2008) 4488.
- [4] I. Naploszek-Bilnik, A. Budniok, E. Lagiewka, *Alloys.Comp.* 382 (2004) 54-57.
- [5] J. Kubisztal, A. Bundniok, *Appl. Surface.* 252 (2006) 8605.
- [6] Hachemi Ben Temam, Larbi Zeroual, Abdelouahad Chala, Saad Rahmane, Corinne Nouveau, *Plasma Process. Polym.* (2007)S618.
- [7] P. Beçot, *Dépôts composites par électrolyse. Paramètres et Applications. Techniques de L'ingénieur.*M1623, p. 3.
- [8] J. Kubisztal, A. Bundniok, A. Lasia, *Int. J. Hydrogen Energy.*32 (2007) 1212.
- [9] R. Q. Faratari, A. Robin, *Surf. Coat. Technol.* 200 (2006)4086.
- [10] G. Qiao, T. Jing, N. Wang, Y. Gao, X. Zhao, J.
- [11] Zhou, W. Wang, *Electrochim. Acta.* 51 (2005) 89. [11] Stephan Armyamov, *Electrochim. Acta.* 45 (2000) 3323.
- [12] N. V. Krstajić, Lj. Gajić-Krstajić, U. Lačnjevac, B. M. Jović, S. Mora, V. D. Jović, *Int. J. Hydrogen Energy.* 36 (2011) 6446.