Electrodeposition and characterisation of Ni-based anticorrosive coatings

Agnieszka Bigos

1. Introduction

Hard chromium coatings, characterized by enhanced functional properties, are widely used in many industrial applications. However, according to the European Union legal restriction (Directive: 2000/53/EC), they should be eliminated from the manufacturing process due to toxicity of electrolytes (containing carcinogenic hexavalent chromium) used to their preparation [1]. Ni-based alloys with refractory metals are proposed as a promising substitute of chromium coatings, characterized by good anticorrosion properties in many aggressive environments and catalytic activities for hydrogen evolution [2, 3]. Moreover, the addition of molybdenum or tungsten to nickel deposit should improve significantly their hardness, wear and friction resistance.

Among the methods for obtaining Ni-based coatings, electroplating is a relatively simple and low cost technique, which enables uniform covering of substrates with defined shapes. In addition, it eliminates the problem of the conventional thermal processes, associated with the large differences in melting points of metals (e.g., Ni-1455°C, Mo-2620°C) and their limited mutual solubility [4].

The electrodeposition of binary alloys (e.g. Ni-Mo or Ni-W) is generally affected by the type of galvanic bath [5, 6]. Non-toxic citrate acid and its salts belong to the most promising complexing compounds use to produce that kind of coatings. Moreover, citrate aqueous solutions are characterized by buffering, leveling and brightening properties, which allow to obtain good quality coatings.

The mechanism of electrodeposition process is still not clearly understood, despite of a few hypotheses presented in literature [7, 8]. It is known that, pure Mo can not be electrodeposited in metallic state from aqueous solution of its salts. The process is hindered by the formation of a molybdenum oxide layer of lower valences on the cathode surface. Only co-deposition of alloy with iron-groups metals (Fe, Co, Ni) is possible. According to Brenner that phenomena is called as induced co-deposition [9].

As an example of Ni-based protective coatings Ni-Mo alloys were chosen. Thus, the aim of the present study was to determine the correlation of Ni-Mo electrodeposition parameters, from an aqueous citrate solution, with coating characteristics, such as chemical and phase compositions, crystallite dimension, microhardness as well as friction and wear resistance.

2. Experimental details

Micrometre-thick Ni-Mo alloys were electrochemically deposited from the citrate bath solution, containing $Na_3C_6H_5O_7$, $NiSO_4$, Na_2MoO_4 of pH 8.5 (adjusted by an addition of ammonia). No detergents, wetting agent or brightener were used. The cathode was a low carbon steel disc of 0.028 dm^2, rotating at 11 and 68 rad/s, whereas 0.05 dm^2 Pt spiral was used as an anode. The cathode potential was referred to the saturated calomel electrode (SCE). Electrolysis was carried out in 0.75 dm^3 cell in a model system with a rotating disc electrode (figure 1). Current density was controlled by a PAR 273A potentiostat/galvanostat with correction of ohmic drop by the current interrupt method. Ni-Mo alloys were deposited under galvanostatic conditions in the range of current density from 0.5 to 5 A/dm^2, at room temperature.

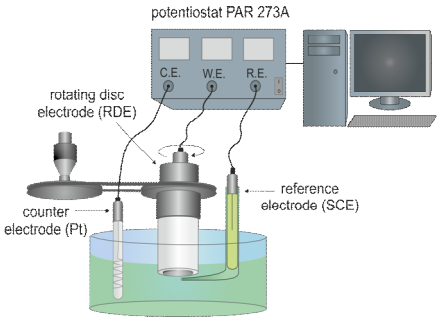

Figure 1. Experimental system with a Rotating Disc Electrode (RDE)

The microstructure of the deposits were characterized by scanning and transmission microscopy techniques (FEI E-SEM XL30, TECNAI G^2). Samples for TEM investigation were prepared by FIB Dual Beam by FEI with an ion gun based on scanning microscope. Concentrations of elements were determined by energy-dispersive X-ray spectroscopy (EDS) in a FEI E-SEM XL30 equipped with spectrometer X EDAX GEMINI 4000. A phase composition and crystallite size measurements were carried out by X-ray diffraction, using CoK_α line (diffractometer Philips PW 1710 with X'Pert system). The measurements of surface roughness were conducted by using TOPO 01P profilometer. The friction and wear tests were performed at room temperature on a ball-on-disc type tribometer with a constant rotation speed of 60 rpm, a constant radius of 4 mm and loads 1 N. Al_2O_3 ceramic balls of 1 mm diameter were used as the counter body. Wear tests were performed for 2000 to 20 000 cycles. Number of cycles was dependent on the wear resistance, to ensure low depth of the wear scar in comparison with coating thickness. Coefficient of friction was calculated from friction force recorded during the test. The corrosion resistance measurements were carried out in a 0,5M KOH solution, in the potential range ± 15 mV from stationary potential OCP with the scan rate of 1 mV/s.

2. Results and discussion

Process of electrochemical deposition is determined mainly by cathodic current density. That crucial operating parameter controls the chemical composition and microstructure as well as the rate of the electrodeposition process and current efficiency.

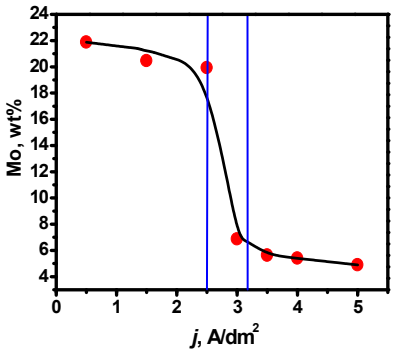

Figure 2. Mo content (wt.%) in function of current density

Figure 2 shows dependence of chemical composition of the coatings (determined by the EDS technique) on applied current density. As can be seen, an increase of current density is strictly correlated with decrease in Mo content (from about 22 to 5 wt.%).

The SEM cross-section examination revealed that all deposits (regardless of the current density at which they were deposited) were crack free, homogenous and well adherent to the steel substrate what is presented on figure 3.

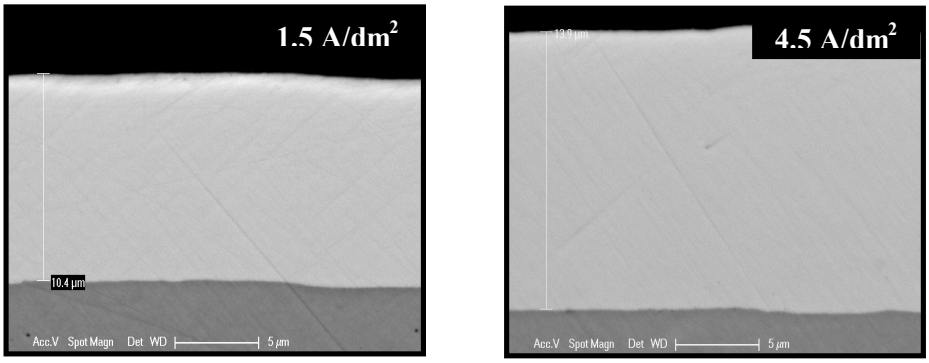

Figure 3. SEM image of cross-section of metallic Ni-Mo coatings electrodeposited at 1.5 and 4.5 A/dm^2, at RDE speed of 640 rpm

However, a scanning electron microscopy observations of the Ni-Mo surface show marked influence of current density on the microstructure of coatings (figure 4).

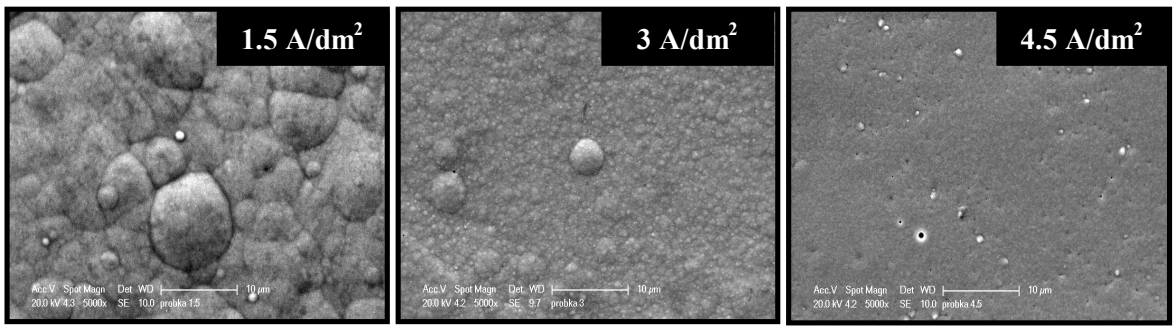

Figure 4. SEM (BSE) images of surface morphology of Ni-Mo coatings electrodeposited at 1.5, 3 and 4.5 A/dm^2, at RDE speed of 640 rpm

In the first range of low current densities (0.5–2.5 A/dm^2) the Mo content is relatively high (about 20–22 wt.%) and coatings are characterized by nodular morphology.

When the density range increase to 2.5-3.5 A/dm^2 size of nodules are considerably reduced, what is correlated with diminish of Mo content from about 19 to 6 wt.%. At the current density above 3.5 A/dm^2 coatings have smooth and compact morphology with relatively low content of Mo (about 5 wt.%).

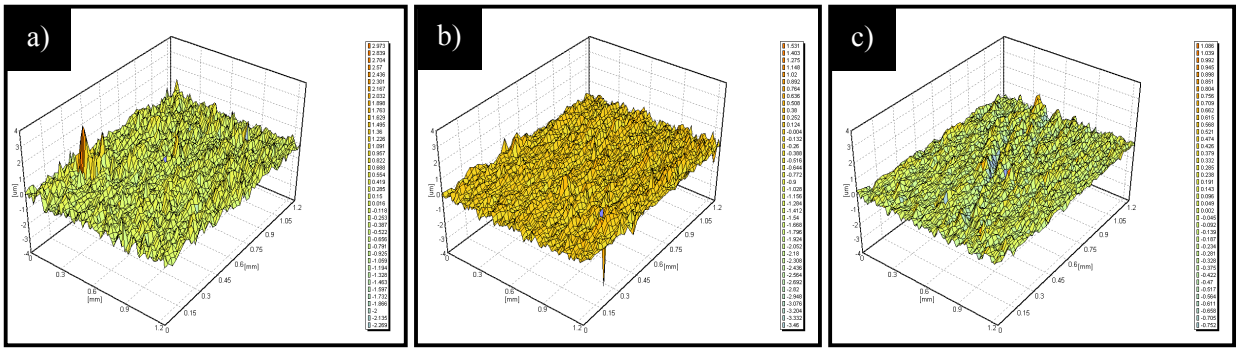

Figure 5. 3D surface profile of Ni-Mo coatings deposited at a) 1.5 A/dm^2, b) 3 A/dm^2 and c) 5 A/dm^2 current density

Moreover, deposit morphology change is correlated with decrease of roughness coefficient R_a from the value of 0.27 to 0.15 µm up to 3 A/dm^2 (figure 5).

The decrease of the Mo content promotes a shift of the corrosion potential (in 0.5 M KOH) towards more positive values from -0.458 V for deposit of 19 wt% Mo (*j* deposition - 0.5 A/dm^2) to -0.416 V for 3 wt% Mo (*j* deposition - 4 A/dm^2). The corrosion rate decreases from $1.46 \cdot 10^{-6}$ A/cm^2 to $0.87 \cdot 10^{-6}$ A/cm^2 for the range of deposition current from 0.5 A/dm^2 to 2.5 A/dm^2 and then it increases again to $1.27 \cdot 10^{-6}$ A/cm^2 for 4 A/dm^2.

TEM analysis reveals that the Ni-Mo layers exhibit the face-centred-cubic solid solution of molybdenum in nickel and they are characterized by an equiaxial nanocrystalline microstructure with a grain size below 20 nm (for coatings deposited at 5 A/dm^2) (figure 6).

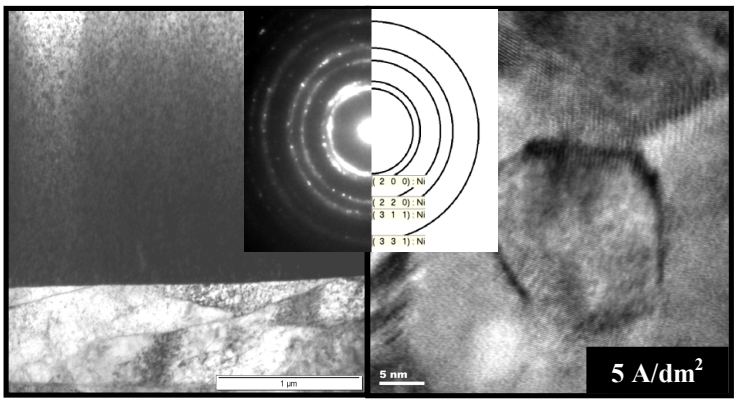

Figure 6. TEM images of an example of Ni-Mo coatings obtained at current density of 5 A/dm^2

XRD shows that with increasing molybdenum content in the electrodeposits, the lines of the XRD patterns increasingly broadened, their intensities decreased and the (111) preferred orientation becomes less pronounced (figure 7). The grain size (the size of the coherent domains) was calculated from the line broadening, using Scherrer's equation. They decrease slightly (from 10 to 4 nm) when the molybdenum content increases from about 5 to 22 wt.%.

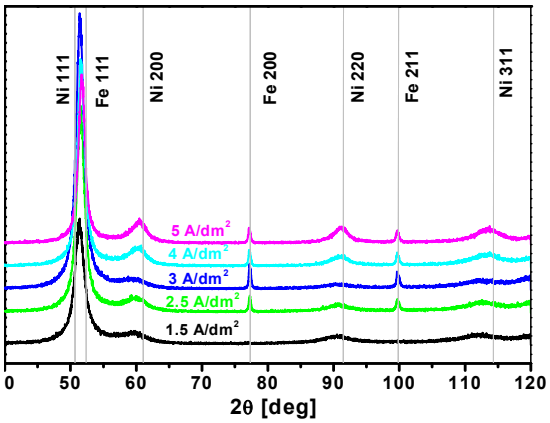

Figure 7. XRD patterns of Ni-Mo coatings deposited at different current densities (1.5-5A/dm^2)

Microstructure and chemical composition of electrodeposited Ni-Mo alloys are closely related to their mechanical properties [10].

Microhardness and elastic modulus value, analysed by microindentation test, rise from 6.6 to 7.8 GPa with increase of current density up to 3 A/dm^2. Further rise of this operating parameter leads to stabilisation its value till 4 A/dm^2 and slightly drop above 5 A/dm^2. Deformation mechanism and adhesion to the steel substrate were investigated by scratch test (figure 8). For coating deposited

under low current density any form of cracks and delimitations were observed up to maximal load. For stiffer coatings, prepared at 3.5 A/dm^2, first cohesive cracks appeared when load excided 18N, what is correlated with increase value of elastic modulus. At the higher current densities again plastic character of deformation was observed.

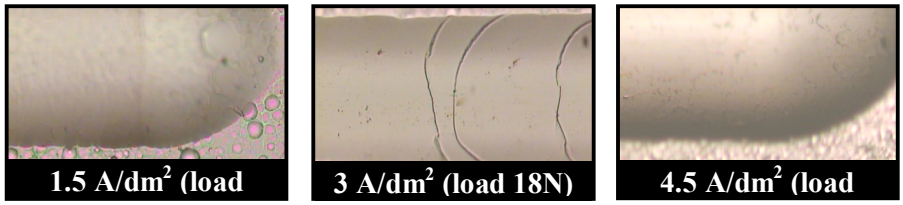

Figure 8. LM images of scratch track of Ni-Mo coating obtained at 1.5, 3 and 4.5 A/dm^2

Results of tribological test indicated that significant rise of wear resistance was found for electrodeposits prepared under densities higher than 3 A/dm^2. Moreover, friction coefficient is the lowest for the Ni-Mo alloys obtained in high current densities.

3. Conclusion

- Electrodeposition of alloys from the designed citrate bath solution containing considerable excess of Ni(II) relative to Mo(VI) content results in obtaining a good quality Ni-Mo coatings: crack free, compact and well adherent to the steel substrate.
- Cathodic current density is an operating parameter which controls the efficiency of the electrodeposition process as well as the chemical composition and microstructure of alloys.
- The nanocrystalline Ni-Mo coatings of smooth surface microstructure and relatively low molybdenum content, obtained at the highest examined current densities, are characterized by the best micromechanical and tribological properties. Thus, the Ni-Mo alloys obtained under these conditions, are promising materials from the point of view their potential application as an alternative to hard chromium coatings.

Acknowledgments

The results presented in this paper have been obtained within the project "KomCerMet" (contract no. POIG.01.03.01-14-013/08-00 with the Polish Ministry of Science and Higher Education) in the framework of the Operational Programme Innovative Economy 2007-2013. All researches were carried out in the team of Ewa Bełtowska-Lehman.

References

[1] Brooman E.W.: *Corrosion Performance of Environmentally Acceptable Alternatives to Cadmium and Chromium Coatings: Chromium* – Part I, Metal Finishing , July (2000) 38 – 43.
[2] Ghahin G.E.: *Alloys are Promising as Chromium or Cadmium Substitut*es, Plating and. Surface Finishing 8 (1998) 8-14.
[3] Hille R.: *Molybdenum and tungsten in biology*, Trends in Biochemical. Science 7 (2002) 360-367.
[4] Massalski T.B.: *Binary alloy phase diagrams*, ASM INTERNATIONAL, The Materials Information Society, The United States of America 1990.
[5] Donten M., Cesiulis H., Stojek Z.: *Electrodeposition of Amorphous/ Nanocrystalline and Polycrystalline Ni-Mo Alloys from Pyrophosphate Baths*, Electrochimica Acta 50 (2005) 1405 – 1412.
[6] Fukushima H., Akiyama T., Akagi S., Higashi K.: *Role of Iron-group Metals in the Induced Codeposition of Molybdenum from Aqueous Solution*, Transaction of the Japan Institute of Metals 20 (1979) 358 – 364.
[7] Chassaing E., Yu Quang K., Wiart R.: *Mechanism of Nickel-Molybdenu Alloy Electrodeposition in Citrate,* Electrolytes, Journal of Applied Electrochemistry 19 (1989) 839 – 844.
[8] Podlaha E.J., Landolt D.: *Induced Codeposition: II. A Mathematical Model Describing the Electrodeposition of Ni-Mo Alloys*, Journal of the Electrochemical Society 143 (1996) 893 – 899.
[9] Brenner A.: *Electrodeposition of Alloys*, Academic Press, New York, London, 1963.
[10] Kot M., Beltowska-Lehman E., Bigos A., Indyka P., Morgiel J, Rakowski W.: *Mechanical and tribological properties of electrodeposited Ni-Mo coatings*, Material Enginering 3 (2010) 373-376.