SYNTHESIS AND CORROSION CHARACTERIZATION OF ELECTRODEPOSITED Ni-Mo ALLOYS OBTAINED FROM AQUEOUS SOLUTIONS

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Printre procesele electrochimice cu impact considerabil asupra dezvoltării tehnologice, electrodepunerea aliajelor de Ni-Mo joaca un rol important datorită caracteristicilor superioare mecanice, anticorozive şi a stabilităţii termice a acestor aliaje. Acest proces reprezintă şi o alternativă ecologică pentru acoperirile cu crom, fiind un exemplu de "codepunere indusă", în care un anumit metal (de exemplu: Mo, W) se poate codepune ca aliaj, dar nu se poate depune în stare pură. Astfel, lucrarea prezintă o serie de rezultate experimentale referitoare la electrodepunerea şi caracterizarea fizico-chimică a unor aliaje Ni-Mo, utilizând electroliţi apoşi de tip citrat amoniacal. Sunt prezentate de asemenea investigaţii ale rezistenţei la coroziune a acestor aliaje prin curbe de polarizare în regim potenţiodinamic şi spectroscopie de impedanţă electrochimică în 0,5M NaCl pentru diferite durate de imersie continuă.

Among electrochemical processes having a considerable impact on technical development, the electrodeposition of Ni-Mo alloys plays an important role, due to better mechanical, anticorrosive and thermal stability characteristics of these alloys. This process is an ecological alternative to chromium plating, belonging to so-called 'induced co-deposition' systems, when nickel's reaction rate enhances the codeposition. With this in view, the paper presents some experimental results regarding the electrodeposition and physical-chemical characterization of Ni-Mo alloys involving ammonium-citrate aqueous electrolyte. Some investigations dealing with their corrosion resistance, involving potentiodynamic polarization curves and electrochemical impedance spectroscopy spectra in 0.5M NaCl, for various immersion periods, are also presented.

Keywords: Ni-Mo alloys; electrodeposition; corrosion resistance

1. Introduction

Among electrochemical processes having a considerable impact on technical development, the electrodeposition of Ni-Mo alloys plays an important role, due to better mechanical, anticorrosive and thermal stability characteristics

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of these alloys. They may be used as cathodic materials during water electrolysis to produce hydrogen, offering superior performances as compared with pure nickel [1] or as catalysts for hydro processing of aromatic oils and gas phase hydrogenation of benzene [2]. Moreover, Ni-Mo alloys coatings are considered as ecological alternatives to chromium plating due to their good corrosion protection characteristics [3, 4].

From a theoretical point of view, electrodeposition of Ni-Mo alloys is an example of the induced co-deposition mechanism [5], when nickel's reduction reaction rate enhances the codeposition of molybdenum. An investigation of the induced discharge process is essential to correlate the coating properties with the conditions of electrodeposition. Several hypotheses have been proposed and many investigations describe the possible multi-step reduction of some Mo species. Thus, Chassaing et al.[6,7] have proposed a codeposition mechanism based on a gradually (step by step) molybdate reduction involving formation of an intermediary MoO_2 that further is reduced to Mo^0 by the Ni metallic atoms. Additionally, three main polarization domains have been identified during Ni-Mo co-deposition, assigned to the following processes: (i) the molybdate reduction to a Mo(IV) oxide due to Ni(II) species, thus forming a nickel molybdenum mixed oxide with MoO_2Ni_4 formula which facilitates hydrogen discharge generated by citrate reduction, in the case of low values of the applied polarization; (ii) the nickel molybdenum mixed oxide reduction for higher polarization values, that leads to the formation of a hydrogen reaction inhibiting surface compound – slow reaction and (iii) the mixed oxide reduction up to the alloy formation, facilitated by the previous step. As a consequence of polarization behaviour, the Mo content within the deposit firstly remains almost constant and then it decreases as the applied current density is higher. Up to 150 mA/cm^2 applied current density Mo is preferentially deposited, so that its content is higher in the deposit than in the electrolyte. For higher polarization values, Mo discharge becomes more and more controlled by the Mo (VI) species diffusion towards the cathode.

Podlaha and Landolt [8, 9] have proposed a model based on adsorption and catalytic reduction of molybdate species starting from the use of a citrate type electrolyte. According to their results, the reduction of Ni complex compound is a mass transport controlled process; the species arriving electrode surface through diffusion are subjected to a two-step reduction process, taking into account the presence of an intermediate which is adsorbed. Thus, species as $[Ni(II)HCit]^-$ may catalyze molybdate reduction forming a surface-adsorbed intermediate, $[Ni(II)HCit\text{-}MoO_2]_{ads}$. This model considers that Mo deposition may be only possible if Ni(II) ions are present, while nickel ions reduction follows an independent path. Podlaha and Landolt's mechanism has been proved to be valid both in the case of both Ni-Mo and Ni-W alloys.

Generally, the alloy composition is closely dependent on the applied operation conditions. Thus, a higher Ni(II) concentration in a citrate type electrolyte as compared with that of molybdate species determines an increase of Mo content within the alloy, when an intense hydrodynamic regime is applied. On the other hand, when molybdate rich solutions are used, the hydrodynamic regime doesn't affect the alloy composition. The electrolyte temperature associated with various current densities domains influence the Mo content within the deposit, too [8]. When the alloy contains 50-70% Mo the deposit presents strong internal stresses and cracks, so that it is not usable for practical applications. If Mo content is kept at lower values, of about 10-15%, the obtained electrodeposited layer is characterized by a cracks free, granular structure [8].

In this respect, the paper presents some experimental results regarding the electrodeposition and physical-chemical characterization of Ni-Mo alloys involving ammonium-citrate aqueous electrolyte.

Some investigations dealing with their corrosion resistance, involving potentiodynamic polarization curves and electrochemical impedance spectroscopy spectra in 0.5M NaCl, for various immersion periods, are also presented.

2. Experimental

The electrochemical measurements have been performed in a conventional three-electrode cell involving Zahner IM 6e electrochemical equipment. There have been recorded cathodic polarization curves in a potentiodynamic regime, with a scan rate of 10mV/s. A glassy carbon rotating disk electrode (Bioanalytical System Model RDE 1 – SUA) with a constant geometrical surface of 0.07 cm^2 has been used as working electrode. All potentials are referred to the Ag/AgCl reference electrode. The counterelectrode was a large surface of Pt strip. All involved electrolytes have been prepared using chemical reagents of analytical grade and deionized water. Various hydrodynamic conditions have been applied, evaluated by rotation speeds in the range of 0-5000 rpm. The electrolytes composition and the applied experimental conditions are presented in Table 1.

To investigate the influence of operation conditions on the alloy composition, morphology and structure, bulk electrolysis in stationary conditions has been involved. It has been used a two-electrode cell configuration with copper sheets of 0.2 mm thickness and 99.9% purity as metallic substrate (cathode), of 70x35 mm sizes and a Ni anode. To evaluate the electrodeposition rate and consequently the layer thickness as well as cathodic efficiency, the electrodeposition has been performed using stainless steel or Ti working electrodes that allow further the detaching of the deposit as a thin metallic foil. Before electrodeposition, the surface was subjected to a chemical pickling in 1:1 HNO_3:H_2O solution at 25^{o}C for 20-30 s, followed by rinsing with running water and distilled water. Current densities between 0.5-15 A/dm^2 have been applied, with electrolyte temperatures in the range of 25-60^{o}C and electrodeposition durations between 10-60 minutes

Table 1

Electrolytes composition and the applied experimental conditions for electrodeposition of Ni-Mo alloys

Electrolyte	$NiSO_4 \times 7H_2O$ mol/L	Na_3Citrate mol/L	$Na_2MoO_4 \times 2H_2O$ mol/L	pH (NH_3)	t,^{0}C
NiMo1	0.2	0.95	0.05	10 (NH_3)	30-60
NiMo 2	0.018	0.14	0.1	9	30-60
NiMo 3	0.036	0.14	0.1	9	30-60
NiMo 4	0.16	0.14	0.1	7	30-60
NiMo 5	0.16	0.25	0.1	7	25-60
NiMo 6	0.35	0.2	0.03	6 and 9	40-60

The obtained electrodeposits have been characterized from as function of appearance, adherence and layer thickness (deposition rate). XRD investigation has been also done to get information on the composition and structure of the alloy deposit, involving Bruker AXS ADVANCE equipment, with a Cu Kα radiation. Morphological investigations have been performed by optical microscopy (NU2 Carl Zeiss – Jena metallographic optical microscope) and AFM microscopy (Quesant Scope 350 equipment). The chemical composition of Ni-Mo alloys coatings has been determined by atomic absorption spectroscopy (AAS) involving a NOVAA 300 equipment (Analytik Jena, Germany).

To evaluate corrosion behaviour, several accelerated corrosion tests have been performed, respectively: (i) continuous immersion in 0.5M NaCl for 96 hours with intermediary visual examinations and recording of corrosion potential for at least three coated specimens (70x35mm) with a coating thickness of 10±3 μm; (ii) potentiodynamic polarization curves in aerated 0.5M NaCl against a Ag/AgCl reference electrode and Pt mesh counterelectrode, with a sweeping rate of 5 mV/s, for Ni-Mo alloys electrodeposited on copper as working electrode; (iii) electrochemical impedance spectra in 0.5M NaCl at open circuit potential in the same three-electrode cell. For both electrochemical investigations the geometrical surface of working electrode was 0.636 cm^2..

3. Results and discussion

3.1. Ni-Mo alloy electroformation – the influence of operating parameters

There have been recorded cathodic polarization curves for various citrate type electrolytes (compositions as shown in Table 1), at various rotation rates and operating temperatures between 30-60°C, an example being presented in Figure 1 for NiMo-1 electrolyte at 40°C.

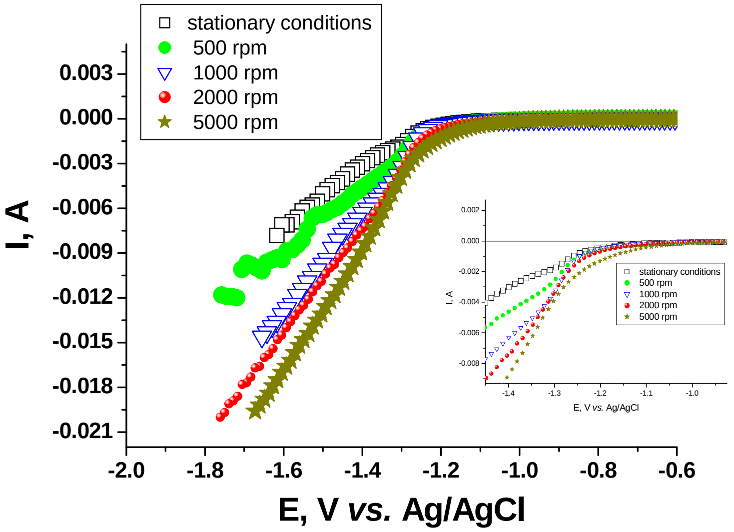

Fig. 1. Cathodic polarisation curves for Ni-Mo deposition from NiMo-1 electrolyte at various rotation rates, 40°C, 10 mV/s (WE – glassy carbon, S=0.07 cm^2)

Generally, the cathodic current increases directly proportional with rotation speed, that facilitates mass transfer, more pronounced above 1000 rpm. Deposition potential is situated in the range of -1 ÷ -1.3 V/Ag/AgCl, as a function of electrolyte composition and hydrodynamic regime. The increase of operating temperature from 25°C towards 40°C did not produce a substantial increase of the current.

Higher current densities, of more than 100 mA/cm^2 have been found to be required when the electrolyte temperature increased up to 60-80°C to facilitate the deposit formation.

Usually the formation of a coherent Ni-Mo deposit with a metallic appearance is favored by relatively high current densities (min.5 A/dm^2). However, these values enhance the internal stresses and reduce the cathodic efficiency, due to hydrogen reaction intensification, which is a characteristic phenomenon for Ni and its alloys electrodeposition.[7,10,11]. Higher Mo contents within the alloy, of about 40-45% are facilitated by low values of the applied current density, in the range of 0.5 – 2 A/dm^2 and low Ni(II) cations concentrations in the electrolyte. However, in what concerns the appearance, higher Mo contents lead to thin blue up to dark brown deposits that suggest the formation of various Mo oxides with lower valences incorporated in the coating. The use of current densities of around 5-12.5 A/dm^2 facilitates the obtaining of adherent, uniform, light grey Ni-Mo alloys coatings with about 15-30% Mo onto the Cu substrate. An increase of citrate concentration from 0.2M to 0.95M determined a slight increase of Mo content in the alloy and led to an improvement of deposit quality from appearance point of view. The appearance and quality of the obtained alloys coatings for the investigated electrolytes compositions are synthetically presented in Table 2.

Table 2

Ni-Mo alloys coatings visual characterisation as a function of electrolyte composition

Electrolyte type	***Visual characterisation as a function of operating conditions***
NiMo1	Uniform, thin, dull grey deposit, about 35-45% Mo (wt.%)
NiMo2	Blue-blackish layer (probably mostly as molybdenum oxides) for applied current densities between 2-25 A/dm^2, t=25-40^{o}C
NiMo3	Dull blue-grey layer for applied current densities between 2-25 A/dm^2, t=25-40^{o}C
NiMo4	Bright uniform blue layer with metallic aspect on the specimen's edges
NiMo5	Thin, uniform, metallic layer for applied current densities between 6-10 A/dm^2, about 25-28% Mo (wt.%)
NiMo6	Thin, uniform, metallic layer for applied current densities between 6-10 A/dm^2, about 15-30% Mo (wt.%), with high internal stress

The Mo content within the alloy has been found to decrease as the applied current density increased, as exemplified in Figure 2, for a NiMo6 type electrolyte containing various molybdate concentrations, for a working temperature of 53±5^{o}C and deposition duration of 20 minutes. The Mo content in the electrolyte slightly influences the alloy composition.

The obtained Ni-Mo alloy deposits have been characterized by a very good adherence to the Cu substrate, are uniform and with a bright-grey metallic appearance.

From morphological point of view, both optical and AFM microscopies revealed a coherent deposit, with a granular structure, as exemplified in Figures 3a and 3b for an alloy containing about 25%Mo.

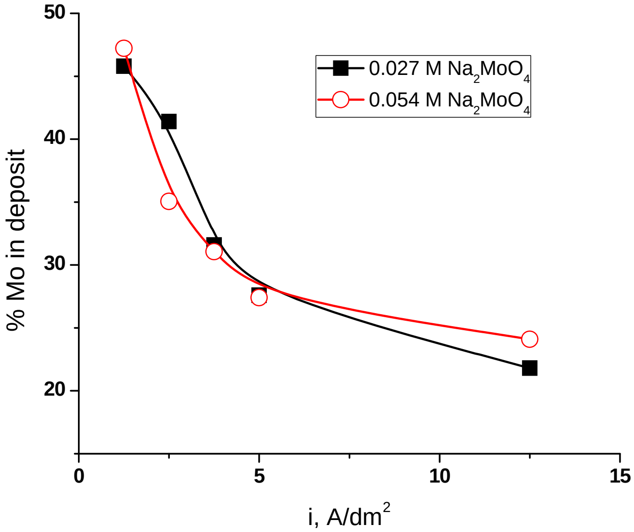

Fig. 2. The influence of applied current density on the Mo content within the alloy deposit (NiMo6 type electrolyte, 53±5°C, 20 min., stationary conditions)

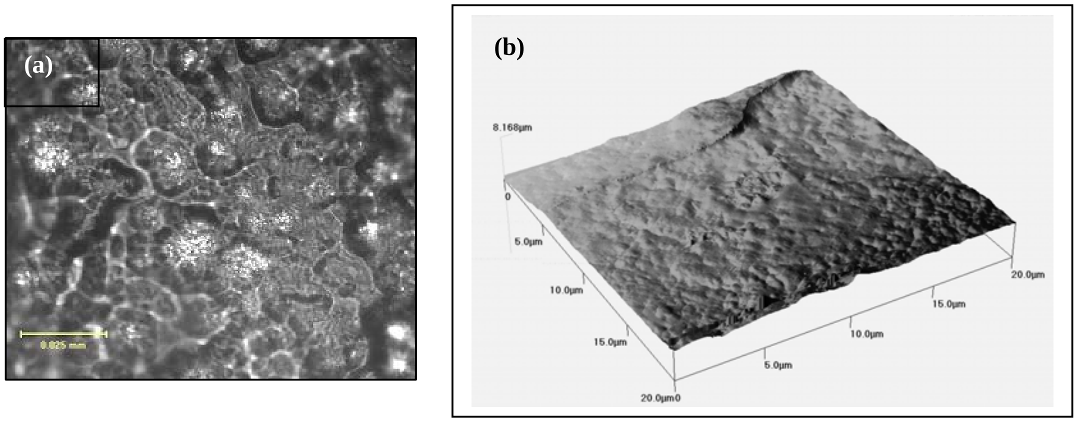

Fig. 3 – Optical micrography (a) and AFM image (b) for a Ni-Mo alloy deposit on Cu substrate (6 A/dm^2, NiMo6 electrolyte, 50°C)

By means of XRD analysis, some information of the electroformed alloys structure were obtained. Generally, the Ni characteristic peaks (at $2\theta = 44^o$, 51^o and 76^o) have been evidenced and no peaks corresponding to any Mo containing intermetallic compound were identified, as shown in Fig. 4.

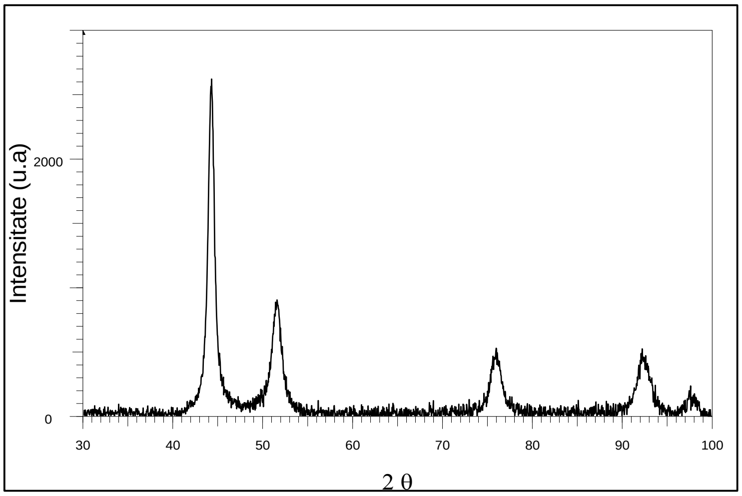

Fig. 4 - X-ray diffractogram for Ni-Mo alloy (17%Mo) electrodeposited from NiMo6 electrolyte , pH 6 (6.85 A/dm^2, 60^{o}C)

As compared with the reference X-ray diffraction pattern of standard nickel powder, a very slight reduction in Bragg's angle can be found for most of Ni-Mo nanocrystals. This can be attributed to the expansion of Ni lattice by the introduction of Mo into the Ni lattice. From XRD analysis, the average sizes of crystallites have found to be around 9-18 nm. Moreover, the obtained results have shown a quasi-linear increase of crystallites sizes as a function of the applied current density, as presented in Table 3.

Table 3

The dependence of average crystallites sizes on the applied current density in the case of Ni-Mo alloy electrodeposition (NiMo6 type electrolyte, pH=6, 53±5^{o}C)

i, A/dm^2	Mo content in the alloy, wt%	Grain size, nm
1.9	35.6	9
2.7	35.6	12.5
4.9	27.5	15.7
7.3	17.2	18.1

If the pH value of NiMo6 electrolyte was changed to 9, XRD evidenced the presence of monoclinic NiMoO4 phase, as shown in Figure 5, with average crystallites sizes between 9.4-15.4 nm.

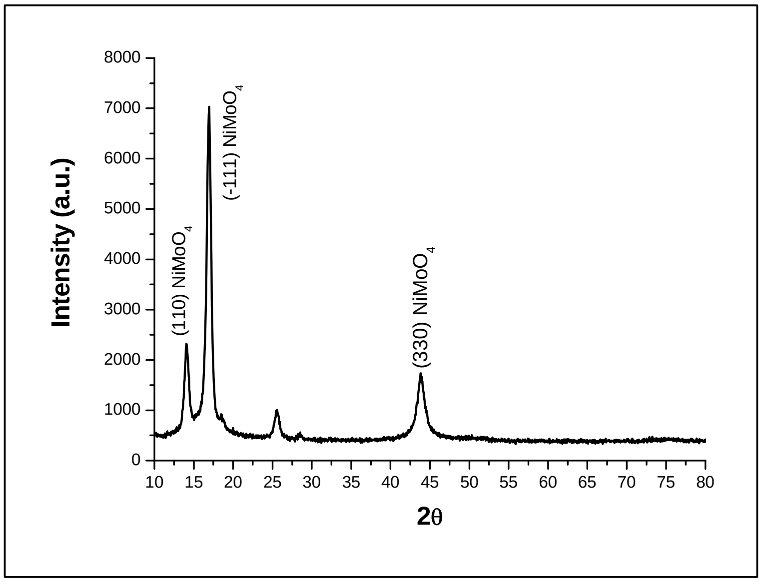

Fig. 5. X-ray diffractogram for Ni-Mo alloy (17.26 %Mo) electrodeposited from NiMo6 electrolyte , pH 9 (5 A/dm^2, 60^{o}C)

3.2. Corrosion behaviour of NiMo alloys obtained from aqueous electrolytes

To characterize Ni-Mo alloys from the point of view of corrosion protection, potentiodynamic polarization curves in 0.5M NaCl as well as electrochemical impedance spectra in 0.5M NaCl at open circuit potential have been recorded for various continuous immersion periods up to 96 hours. Two Ni-Mo alloy compositions have been subjected to the electrochemical tests, containing 27-30% Mo and 13-15% Mo, respectively.

Figures 6 and 7 show examples of polarization curves for various immersion periods in 0.5M NaCl in the case of a Ni-Mo alloy coatings having various compositions, electrodeposited on Cu metallic supports from electrolyte NiMo6 (according with Table 1).

At the beginning of conditioning, corrosion potential around -0.014V *vs.* Ag/AgCl was evaluated in the case of 27-30 % Mo containing alloy. For a Mo content lower than 13-15% it was of about -0.749 V *vs.* Ag/AgCl. As the immersion period increased, the corrosion potential moved towards more electronegative values, down to about -0.930 V *vs.* Ag/AgCl, regardless the alloy composition.

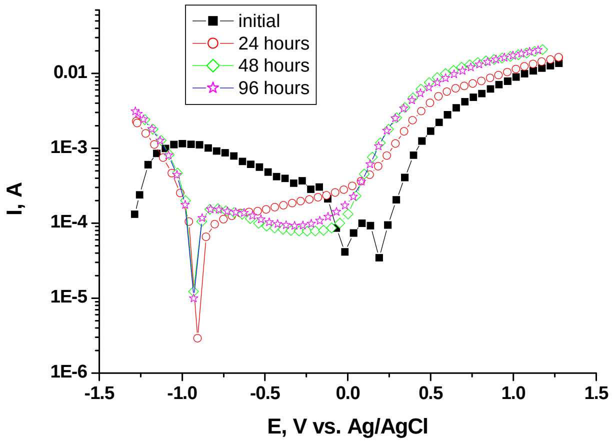

Fig. 6. Polarization curves in semilogarithmic coordinates for Ni-Mo alloy (27-30%Mo) deposit in 0.5 M NaCl for various periods of continuous immersion (25^{o}C, 5 mV/s; geometrical surface of WE-0.63585 cm^2)

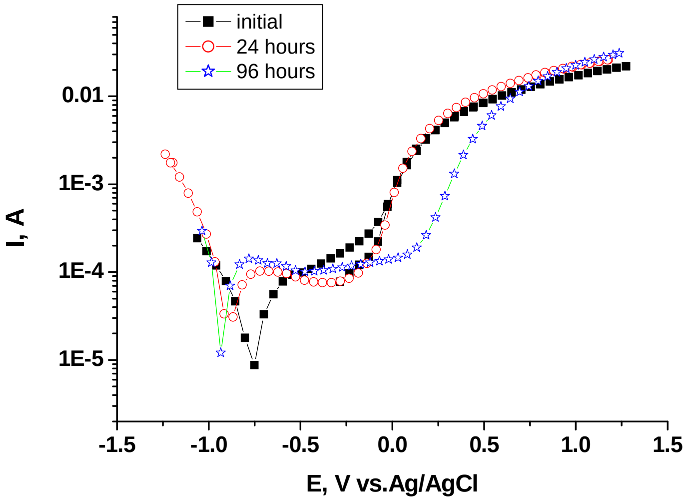

Fig. 7. Polarization curves in semilogarithmic coordinates for Ni-Mo alloy (13-15%Mo) deposit in 0.5 M NaCl for various periods of continuous immersion (25^{o}C, 5 mV/s; geometrical surface of WE-0.63585 cm^2)

Corrosion currents of tens of microamperes per square centimeter have been determined, slightly lower for longer immersion periods, as it can be seen in

Table 4, which summarizes the characteristic values resulted from polarization curves in 0.5M NaCl solution, in the case of the two investigated alloys coatings.

Table 4

Characteristic values resulted from polarization curves in 0.5M NaCl for different Ni-Mo alloys during continuous immersion

Immersion period, hours	NiMo (27-30% Mo)			NiMo (13-15% Mo)		
	E_{cor}, V *vs.* Ag/AgCl	E_{pit}, V *vs.* Ag/AgCl	I_{corr}, $\mu A/cm^2$	E_{cor}, V *vs.* Ag/AgCl	E_{pit}, V *vs.* Ag/AgCl	I_{corr}, $\mu A/cm^2$
0	-0.014	0.19	59	-0.749	-0.471	14
24	-0.934	0.073	40.22	-0.882	-0.263	36.8
48	-0.929	-0.083	20.3	-	-	-
96	-0.929	-0.21	15.5	-0.919	0.077	20.13

This behaviour may suggest the formation of a protective passive film on the surface probably due to the presence of Mo within the alloy which was also sustained by the appearance of the specimens that did not suffer any aspect modifications even after 120 hours of conditioning. The presence of a passive film which improves the corrosion performance of Ni alloys coatings is usually taken into account when the immersion test is performed in aerated solutions, especially when the alloying element is Mo, W or V [12-16].

For the same Ni-Mo alloys, electrochemical impedance spectra have been recorded in 0.5M NaCl solution at the same immersion periods, at open circuit potential, in a frequency range between $1.10^4 – 5.10^{-2}$ Hz.

Figure 8 presents an example of the recorded impedance spectra for a Ni-Mo (27-30%Mo) alloy deposit in 0.5M NaCl during immersion as Bode plot.

To fit experimental data, a simple equivalent circuit model has been used (as shown in the right side of Figure 8), comprising the solution resistance (R_{Sol}), in series with a combination between a constant phase element corresponding to the double layer capacitance (CPE_{dl}) in parallel with coating resistance (R_{coat}). To take into account the diffusion process that occurs through the metallic layer, a Warburg element has been added. This model was proposed by other authors as well to evaluate corrosion behaviour of Ni and Ni alloys coatings [12, 13].

The CPE behaviour may suggest a variation of the layer composition along its thickness [17], phenomenon that can be taken into account, due to the presence of various phases as also XRD revealed during electrodeposition process. Also, the use of CPE takes into account the coating possible inhomogeneities and better simulates corrosion processes [18, 19]. The fitting parameters are presented in Table 5.

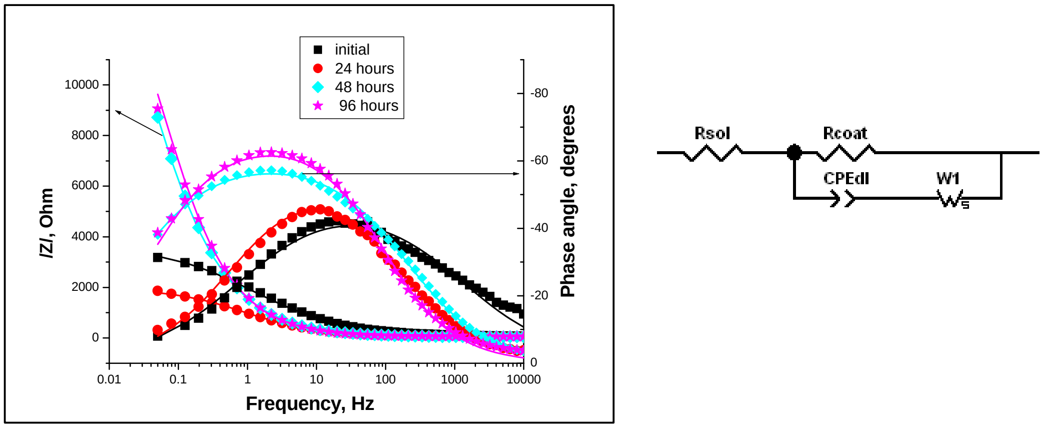

Fig. 8 – Nyquist plot in 0.5 M NaCl at open circuit potential for NiMo alloy (27-30%Mo) initially and after various periods of continuous immersion, representing both experimental and fitted points. On the right side: the proposed equivalent circuit

Table 5

Fitting parameters of Ni-Mo alloys deposition in 0.5 M NaCl for various immersion periods using the proposed equivalent circuit from Fig. 8

Conditioning period, hours	NiMo (27-30% Mo)					NiMo (13-15% Mo)				
	R_{sol} Ω	R_{coat}, Ω	CPE_{dl}		R_W, Ω	R_{sol} Ω	R_{coatt}, Ω	CPE_{dl}		R_W, Ω
			$C, .10^{-6}$ $\Omega^{-1}.s^n$	n				$C, .10^{-6}$ $\Omega^{-1}.s^n$	n	
0	45.03	3315	83.3	0.71	840	50.25	3500	37.13	0.98	6000
24	52.81	1939	225.8	0.7	232	43.63	10000	249.5	0.73	2538
48	43.83	19484	187.6	0.71	540	46.79	5237	101.5	0.78	4000
96	52.91	16000	158.39	0.8	394	5	3752	148	0.75	40

The coating resistance is quite low in the beginning of immersion, of about 3-3.5 kΩ, regardless the alloy composition. A 45° phase angle may be evidenced on Bode plot for the first 24 hours, which is characteristic to mass transport controlled migration of the aggressive anion. As the conditioning period increased, the R_{coat} value becomes higher, around 16-19 kΩ in the case of Ni-Mo alloy having a relatively high Mo content (27-30%Mo). For a lower content of Mo within the alloy, the increase of polarization resistance has been more evidenced after the first 24 hours of conditioning, followed by a slight decrease. This behaviour suggests again the possible formation of a passive film on metallic alloy surface that may enhance protective characteristics, materialized also by the lack of major aspect modifications at the end of conditioning period.

4. Conclusions

Ni-Mo alloys having Mo contents between 5-40% Mo may be deposited from aqueous citrate-ammonium type electrolytes with relatively low molybdate concentrations (0.03M – 0.1M). The essential role of the complexing agent (alkaline citrate) has been evidenced, associated with NH_3 addition, facilitating the diminishing of hydrogen evolution reaction.

From XRD analysis, the phases of $NiMoO_4$ have been identified if the applied electrolyte pH is in an alkaline domain (pH=9). For quasi-neutral solutions, no Mo characteristic peaks have been identified suggesting that Ni and Mo co-deposit as a single-phase solid solution. All the electrodeposited Ni-Mo alloys have shown a nanocrystalline structure, with average sizes of crystallites being around 9-18 nm.

From the corrosion protection point of view, the obtained NiMo alloys coatings showed promising protective characteristics evidenced by polarization resistance values of about 3.5-17 kΩ . Further studies are to be done for a more detailed and quantitative information regarding NiMo electrodeposition and corrosion protection properties.

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