

ELECTROCHEMICAL PRODUCTION OF NANOCRYSTALLINE LAYERS CONTAINING MOLYBDENUM

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ELEKTROCHEMICKÁ PRÍPRAVA NANOKRYŠTALICKÝCH VRSTIEV OBSAHUJÚCICH MOLYBDÉN

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Abstrakt

Elektrodepozíciou z citrátového roztoku boli pripravené Ni-P vrstvy obsahujúce molybdén. Elektrochemický proces bol realizovaný v galvanostatických podmienkach. Štúdium štruktúry pripravených vrstiev sa realizoval rtg. difrakčnou fázovou analýzou. Bolo zistené, že elektrodepozíciou získané Ni-Mo-P zliatiny boli amorfné, Ni-Mo zliatiny boli v nanokryštalickom stave a Ni+Mo kompozitné vrstvy mali kryštalickú štruktúru. Chemické zloženie vrstiev sa určovalo fluorescenčnou spektroskópiou. Z analýz vyplynulo, že Ni-Mo-P zliatiny obsahovali 75% Ni, 10% Mo a 15% P, Ni-Mo zliatiny obsahovali 90% Ni a 10% Mo a Ni+Mo kompozitné vrstvy obsahovali 90%Ni a 10% Mo. Pripravené vrstvy boli charakterizované elektrochemickými metódami ($j=f(E)$) voltametrou a Sternovou metódou odolnosti voči korózií). Z korózných testov vyplynulo, že z pripravených vrstiev má najlepšiu odolnosť voči korózií nanokryštalická Ni-10%Mo zliatina.

Abstract

The electrochemical layers with molybdenum were obtained by electrodeposition from citrate bath. The process was carried out under galvanostatic conditions. Structural investigations were conducted by X-ray diffraction method. It was ascertained that electrodeposited Ni-Mo-P alloys were characterized by amorphous structure, Ni-Mo alloys were characterized by nanocrystalline structure whereas Ni+Mo composite layers had a crystalline structure. The chemical composition was determined using X-ray fluorescence spectroscopy method. It was stated that Ni-Mo-P alloys contained 75%Ni, 10%Mo and 15%P, the Ni-Mo alloys contained 90%Ni and 10%Mo, Ni+Mo composite layers contained 90%Ni and 10%Mo. These layers were characterized by electrochemical methods ($j=f(E)$ voltammetry and corrosion resistance by Stern method). The results of corrosion tests show that from among obtained layers the highest corrosion resistance exhibit nanocrystalline Ni-10%Mo alloys.

Key word: nanocrystalline Ni-Mo alloys, amorphous Ni-Mo-P alloys, electrolytic layers, electrodeposition, corrosion resistance.

1. Introduction

Good corrosion and heat resistance and electrochemical activity towards cathodic hydrogen evolution and anodic oxygen evolution characterize electrolytic nickel and nickel-

molybdenum alloys. They are also used as protection covers for elements working in aggressive environments [1-6]. Apart from metallurgical way of alloy production, which is very expensive because of high Mo melting temperature other methods of their obtaining like mechanical alloying, sputtering or electrolytical deposition are known [7-10]. The main problem of these methods is low stability of obtained alloys' structure which causes that these alloys changed their characteristics during prolonged exploitation. Taking into account economic factors electrolytical deposition from water baths seems to be the most convenient method of alloys production, as it doesn't require any expensive instruments.

Such layers exhibit good adhesion to the substrate, stability of its structure and good protective properties. These features could be modified by means of proper choice of their deposition parameters like: composition of the galvanic bath, temperature, pH, current density, etc. [1, 2].

The purpose of this work was electrolytical deposition of nanocrystalline and amorphous nickel-molybdenum alloys and making comparison of their properties with the properties of Ni+Mo composite layers. The investigations of phase and chemical composition, surface morphology and investigation of the influence of bath composition on the layers structure were conducted. The corrosion resistance of Ni-Mo, Ni-Mo-P and Ni+Mo layers in alkaline environment was determined by Stern method.

2. Materials and experimental methods

Electrolytical layers with molybdenum were deposited from galvanic bath having diversified chemical composition. The nanocrystalline Ni-Mo layers were deposited from the solution of composition ($\text{mol}\cdot\text{dm}^{-3}$): Na_2MoO_4 0,035; NiSO_4 0,75; $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ 0,45 and Ni-Mo-P alloy were obtained from the same bath containing additionally sodium hypophosphite ($\text{mol}\cdot\text{dm}^{-3}$). Ni+Mo composite layers were electrodeposited from nickel bath containing molybdenum powder suspension ($10\text{ g}\cdot\text{dm}^{-3}$): (100 mesh, 99,9%Mo, *Aldrich*). Reagents of analytical purity (POCH Gliwice) and distilled water were used for the solution. All components of Ni-Mo bath were solubilized separately in small volume of distilled water.

The layers were electrodeposited under galvanostatic conditions ($j_{\text{dep}}=150\text{ mA}\cdot\text{cm}^{-2}$, $t=0,5\text{ h}$). The layers were plated on St3S steel substrate (4 cm^2), which was prepared by mechanical polishing and chemical etching in 1:1 HCl solution for 5 min. The other side of the plates was covered with non-conductive resin. The mass increment and the chemical composition were the basis to determine the thickness of the layers.

Chemical composition of layers was determined by X-ray fluorescence spectroscopy using a special attachment to the X-ray generator TUR-M61. Structural investigations were conducted by X-ray diffraction method using a Philips diffractometer and $\text{Cu}_{K\alpha}$ radiation ($U = 40\text{ kV}$, $J = 20\text{ mA}$). The diffraction patterns were recorded in the 2θ range of 20-100°. Qualitative phase analysis was carried out basing on ICDD card standards (2000).

The surface morphology, microscopic cross-section and plane section studies of the coatings were carried out using a scanning microscope (Hitachi S-4200) provided with a digital system of the image recording (Voyager 3500).

Electrochemical studies were conducted in a three-electrode thermostatic, electrolytical vessel with VOLTAMASTER PG 201 (potentiostat-galvanostat) from RADIOMETER. Tests were carried out in the $5\text{ mol}\cdot\text{dm}^{-3}$ KOH solution. The materials were characterized by electrochemical method: $j=f(E)$ voltammetry and corrosion resistance tests by Stern method.

3. Results and discussion

The Ni-Mo-P, Ni-Mo and Ni+Mo layers show good adhesion to the substrate and no delamination is observed. The surface of Ni-10%Mo and Ni-10%Mo-P alloys was compact, smooth, mat and grey (Fig. 1a, b). The analysis of Ni-10%Mo-P surface indicates the presence of phosphorus solid solution in molybdenum and nickel (Fig. 1a). On the surface of this layer several microcracks are observed. The surface of Ni-10%Mo alloy is characterized by island structure (Fig. 1b). The surface of Ni+10%Mo composite layers was porous, mat and light-grey. On the surface of a nickel grains the smaller molybdenum grains are clearly visible (Fig. 1c). The metal particles in the obtained layers are uniformly embedded into the nickel crystalline matrix with tendency to agglomeration (Fig. 1c). The thickness of the Ni-Mo-P and Ni-Mo alloys is about 60-80 μm . The thickness of the Ni+Mo composite layers is about 100-130 μm .

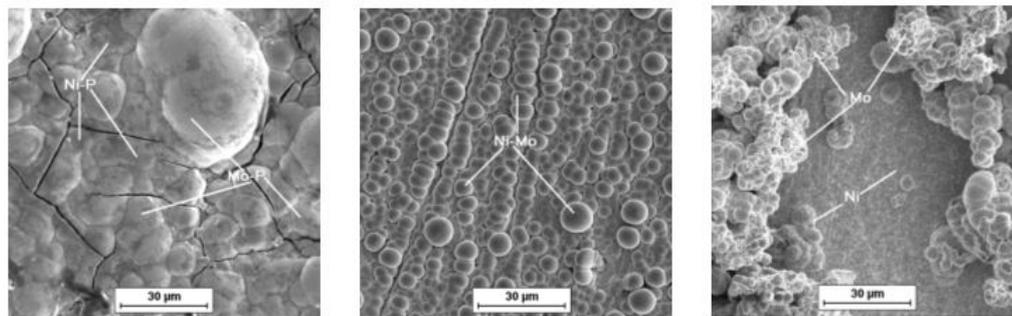


Fig.1 Surface morphology of amorphous Ni-10%Mo-P alloy (a), nanocrystalline Ni-10%Mo alloy (b), and Ni+10%Mo composite layer (c).

The chemical composition was determined using X-ray fluorescence spectroscopy method. It was stated that the Ni-Mo-P amorphous layers contains about 75% of nickel, about 15% phosphorus and about 10% of molybdenum. The Ni-Mo alloys contain about 90% of nickel and about 10% of molybdenum. The Ni+Mo composite layers contain also about 90% of nickel and about 10% of molybdenum.

The phase composition of the electrodeposited layers depends on the composition of galvanic bath. It was stated that Ni-Mo-P alloys are amorphous, and on their surface the presence of nickel and molybdenum phosphides was stated (Fig. 2a). Ni-Mo alloys obtained by induced codeposition from nickel-molybdenum bath are Mo/Ni solid solution characterized by nanocrystalline structure (Fig. 2b). Ni+Mo composite layers obtained from the bath containing dispersed molybdenum powder have a crystalline structure (Fig. 2c).

All layers were subjected to electrochemical investigations included chronovoltammetric studies and corrosion resistance tests by Stern method in alkaline environment. Basing on j - E chronovoltamperometric curves recorded in 5 mol $\cdot\text{dm}^{-3}$ KOH we can state that there is a difference between electrochemical activity of tested materials. From all investigated layers no distinct oxidation/reduction peaks within the range $-1,00 < E < +0,40$ V were observed, which could cause passivation in this potential range. For higher potential values we can observe the peaks coming from nickel oxidation and reduction processes. These peaks differ in j values, which depend on the kind of layer, its phase composition and surface morphology. The lowest peaks current values were observed for nanocrystalline Ni-10%Mo layers. For

amorphous Ni-10%Mo-P alloys these values were higher. The highest peak current values were characteristic for Ni+10%Mo composite layer. Probably because of high roughness of electrode surface resulting from the presence of molybdenum grains built-in into crystalline nickel matrix. The lower peak current values for Ni-10%Mo-P amorphous alloys could be explained by the presence of Ni and o phosphides on their surface, which partially blocked the layer's surface and limited the possibility of nickel oxidation/reduction processes. The similar situation is observed for Ni-10%Mo, where the microscopic tests stated the presence of Mo/Ni solid solution. Because of the slight difference between Mo and Ni atom radius the atoms of Mo could be built in Ni crystalline lattice and limit the process of Ni oxidation.

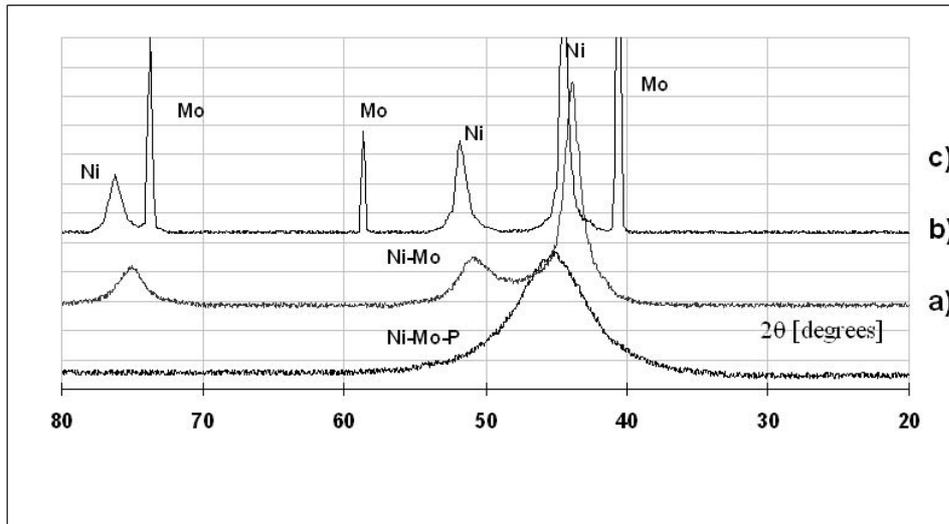


Fig.2 X-ray diffraction pattern of amorphous Ni-Mo-P alloy (a), nanocrystalline Ni-Mo alloy (b), and Ni+Mo composite layer (c).

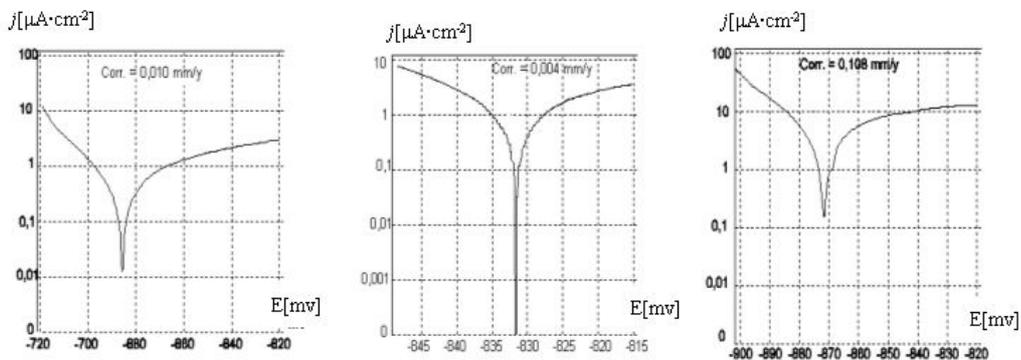


Fig.3 Corrosion resistance parameters for Ni-10%Mo-P alloys (a), Ni-10%Mo alloys (b) and Ni+10%Mo composite layer (c) determined by Stern method.

The results of voltammetric tests were confirmed by corrosion resistance investigation of obtained layers. The results of corrosion tests show that the lowest corrosion rate (0,004

mm·y⁻¹) exhibit nanocrystalline Ni-10%Mo alloy. The corrosion current density for this layer is equal 0,3474 μA·cm⁻² (Fig. 3), so this layer could be recommended as protection cover. The lower corrosion resistance exhibit Ni-10%Mo-P amorphous alloy ($j_{cor}=0,9214 \mu\text{A}\cdot\text{cm}^{-2}$, $v_{cor}=0,010 \text{ mm}\cdot\text{y}^{-1}$), which could come from the presence of microcracks. The highest corrosion rate (0,108 mm·y⁻¹) is characteristic for Ni+10%Mo composite layer. It is caused by the developed, rough surface of the electrode and its high electrochemical activity. So, these layers could be recommended as electrode materials catalysing electrochemical reaction in less aggressive environments.

4. Conclusion

It was found that composition of galvanic bath had an influence on the phase composition of electrodeposited materials. Using baths of diversified composition it was possible to obtain amorphous Ni-Mo-P alloys, nanocrystalline Ni-Mo alloys and Ni+Mo composite layers.

Surface morphology of obtained materials depends on parameters of electrodeposition process. The most homogenous surface had amorphous Ni-Mo-P layers, however on SEM images several microcracks were observed. The structure of Ni-Mo alloy's surface is regular and characterized by the presence of grains of Ni-Mo solid solution. The surface of Ni+Mo composite layers is porous and irregular with clearly visible Mo grains built into nickel matrix.

The results of corrosion tests show that from among obtained layers the highest corrosion resistance exhibit nanocrystalline Ni-10%Mo alloys. Amorphous Ni-10%Mo-15%P layers have a lower corrosion resistance probably because of the presence of microcracks. The lowest corrosion resistance is characteristic of Ni+Mo composite layers.

Acknowledgements

This research was financed by the Polish Committee for Scientific Research(Project 3T08C 028 26).

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