HEAT-RESISTANT ELECTROPLATINGS OF INDUSTRIAL FUNCTION

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The heat-resistant nickel- and nickel-molybdenum electroplatings of high quality were prepared on copper and aluminum bases using the method of galvanic electrolysis. The platings are uniform, non–porous and are characterized by high adhesion. The optimal parameters of the process (current density, electrolysis duration, ratio between anode currents of molybdenum and nickel) are determined. MicroX-ray and fluorescence analyses of the obtained samples are carried out. Molybdenum content in the plating is determined. The existence of fine-dispersed phases of $MoNi_3$ and $MoNi_4$ are established. Electrical and mechanical properties of above – mentioned platings are studied after the heat treatment for their operation at high temperatures.

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INTRODUCTION

Rapid development of the technique and creation of new technologies enhances the demand on new materials. Preparation of new corrosion- and heat-resistant and heatproof composite materials as well as the plating on the basis of rare and high-melting metals is necessary. The mentioned platings are used in a number of fields including agriculture, atomic and space industries etc. This clearly demonstrates a necessity for the study of the processes of preparation of mentioned platings.

As is well-known, chromium platings are characterized by good physical-mechanical properties, but toxicity and cancerogenity of chromium electrolytes and the reduction of hardness at high temperatures requires the search of alternative technologies for preparation of heatproof and corrosion-resistant platings.

Electrochemical deposition of nickel-based alloys with high-melting metals (Mo, W, Co and etc.) is one of the alternatives. By combining these metals the hard materials are obtained, characterized by high wear-resistance and strength at elevated temperatures together with a good heat- and electrical conduction. Alloys of nickel with Mo, W, Co and other high-melting metals are characterized by considerably higher corrosion resistance than nickel, cobalt, molybdenum and tungsten.[1,2] Ni-Mo alloys possess a high mechanical strength and are wear resistance (microhardness of nickel-molybdenum galvanic deposition comprises 550-600 kg-force mm^{-2} at 20 mass %). Above listed indexes determine its advantageous use in magnetically operated contacts (sealed switches), as barrier sub-layers for gold, ruthenium and gold alloys, which gives an economy of 60-90% depending on sealed switch type. By its physical characteristics and corrosion resistance the alloy Ni-Mo is close to ruthenium, but the technology of its coating is less labor-intensive than the technology of ruthenium coating. Therefore its use in nuclear reactors, operating on molten-saline fuel compositions, is of particular importance.[3,4]

EXPERIMENTAL

The goal of the present research is the preparation of nickel, nickel-molybdenum platings on copper and aluminum bases by electrochemical method, investigation of their metallographic, electrical and mechanical properties.

Nowadays the preparation of the mentioned platings by thermal method involves a number of technical difficulties. On the basis of the electrochemical properties the reduction of molybdenum from aqueous solution is impossible (it is obtained by fused electrolysis). Molybdenum is readily reduced from aqueous electrolytes as simultaneous co-deposit with nickel. The potentials of electrochemical reduction of Ni and Mo in aqueous solution are close to each other ($\varphi_{Ni/Ni}{}^{+2}$ = -0,257 V, $\varphi_{Mo/Mo}{}^{+6}$ = -0,200 V), which provides their combined electro-reduction in quasi-equilibrium condition and alloy formation at base surface.

Various compositions of the electrolytes for preparation of Ni-Mo platings are well-known.[5-7] We have selected a pyrophosphate electrolyte, characterized by high stability and scattering power. It does not require the plating on aluminum bases, and has a high negative value of reduction potential and tendency to pass into ionic state. The immersion of aluminum into nickel plating electrolyte allows aluminum dissolution and electrolyte correction over a long period of time and the preparation of a qualitative plating.

Electrochemical investigations were performed by galvanic static method by using the Cu and Al cathodes and simultaneous application of Mo and Ni as the anodes at various ratio of anode current. The preliminary treatment of the base (Cu, Al) surface was carried out before the electrolysis.

Table 1. Dependence of current efficiency and plating (Ni-Mo on Cu and Al bases) thickness on the ratio I_{Ni}/I_{Mo} and on electrolysis duration. [Electrolyte:pyrophosphate, current density: 0.05A/cm^2,T=313K, anode: (Ni, Mo)]

Base	Ratio I_{Ni}/I_{Mo}	Electrolysis duration, min.	Plating thickness, µm	Current efficiency, %
Cu	2	30	25	84
		60	44	69
	2,5	30	21	75
	3,0	30	21	75
		60	14	25
	3,5	30	21	75
		60	14	25
Al	2	30	18	57
	3	60	14	23
Al-Ni	2	30	15	50
	3	30	8	22
	4	30	11	34
Al-Cu	2	30	4	63
	3	30	8	25
	7	90	58	13

The complexity of aluminum plating on the surface is due to the presence of hard oxide film. Another reason is complicating technology of plating on aluminum bases, the high negative value of its reduction potential and its tendency to pass into ionic state. In immersing aluminum into nickel plating electrolyte, there is aluminum dissolution and contact deposition of loose nickel precipitate ($\varphi_{st.Al}$=-1.66 V, $\varphi_{st.Ni}$ =-0.25 V). This process inhibits an adhesion of plated metal with a base. Therefore, aluminum samples after pickling and washing are treated by zincate solution.

As a result of contact exchange reaction an oxide film at aluminum surface is dissolved and is plated by a thin layer of metallic zinc. This fact provides a high adhesion of nickel plating with aluminum base.

RESULTS AND DISCUSSION

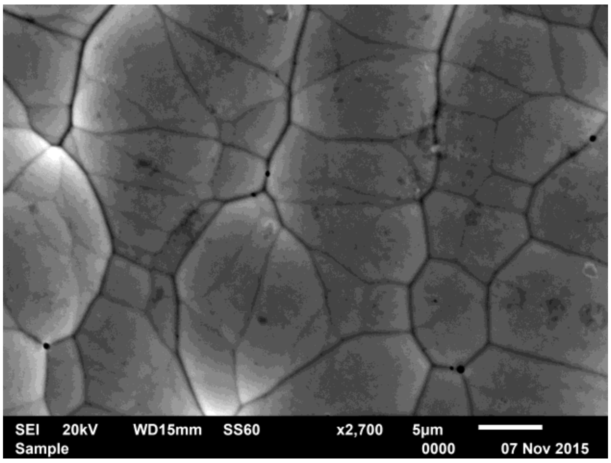
For preparation of Ni-Mo plating (on copper and aluminum bases) the galvanic static investigations are performed at various electrolysis parameters (current density, electrolysis duration, various ratio of I_{Ni}/I_{Mo}).

Results for Ni-Mo plating (on copper and aluminum bases), obtained from pyrophosphate electrolyte, are presented in Table 1.

Optimal parameters of the electrolysis are defined. The presence of the intermetallides, $MoNi_3$ and $MoNi_4$, as fine-dispersed phases is established. The platings are uniform, non-porous and are characterized by a high adhesion. The content of molybdenum in the alloy is determined which correlates well with the results of X-ray fluorescence analysis.

The Mo content on copper and aluminum bases is 31.95 mass% and 27.22mass% respectively. .

Comparison of the results obtained with the state diagram of binary metallic systems[8] have shown that $MoNi_4$ and $MoNi_3$ intermetallides –are obtained on aluminum and copper bases.



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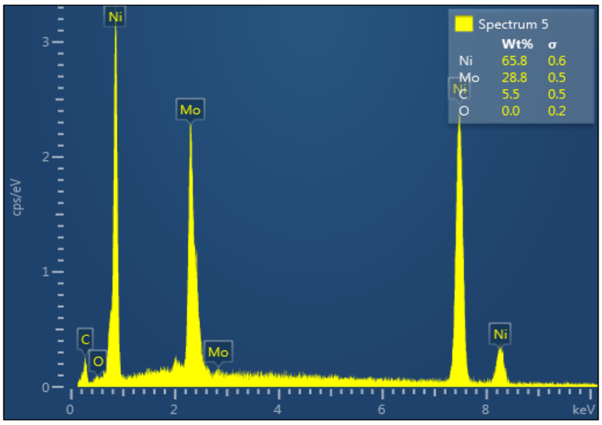

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Figure 1. Results of microscope research of Ni-Mo plating on aluminum: a) electronic image; b) micro X-ray spectrum;

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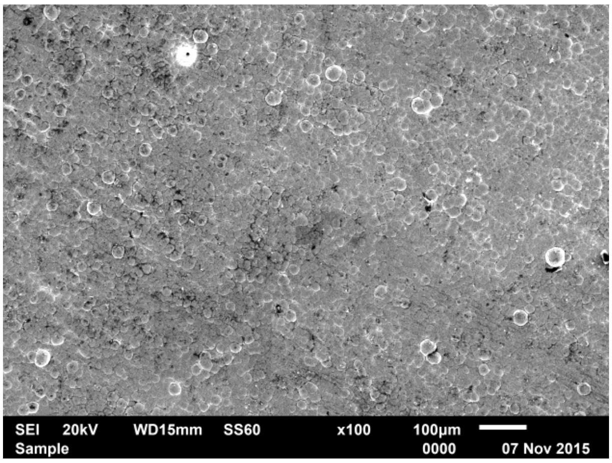

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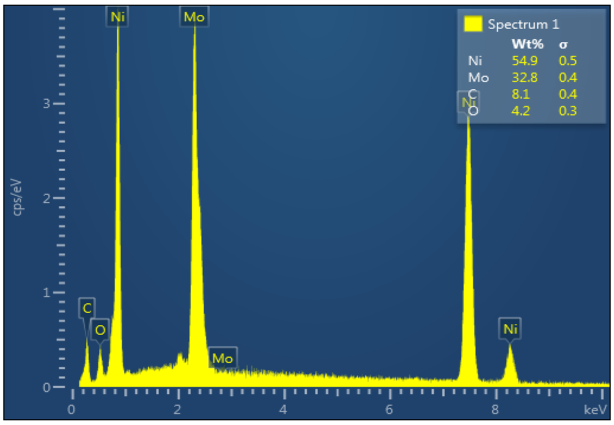

b

Figure 2. Results of microscope research of nickel-molybdenum plating on copper: a) electron image; b) microX-ray spectrum.

The analysis of obtained Ni-Mo platings was carried out at scanning electron microscope of JSM-65102V type.Electrical (specific resistance) and mechanical (Young modulus and internal friction) properties of nickel and nickel – molybdenum plating are studied by electron beam technology. The samples of required size are cut out at electro-spark discharge machine for particular exactness. The samples are annealed, before an experiment, in vacuum at 673K for one hour. Thereafter the specific resistance was measured for base material (copper and aluminum) as well as for the samples plated by nickel and nickel – molybdenum at various temperatures. Hereafter, the mentioned samples were placed in vacuum chamber and were subjected to short term heating at 873-1273 K for 30 seconds and their specific resistance was measured afresh. The standard four-point contact method was used for measuring the electric resistance, which is highly useful for control of composition structure.[9] The results obtained for nickel platings on copper and aluminum bases are presented in Fig. 3 and those for nickel-molybdenum platings are in Fig. 4.

Measurement of internal friction is one of the most sensitive methods to determine the structural defects, relaxation and diffusion providing the necessary information about the processes in the solids (metals and alloys) in the conditions of strong mechanical and heat effects of various type.[10]

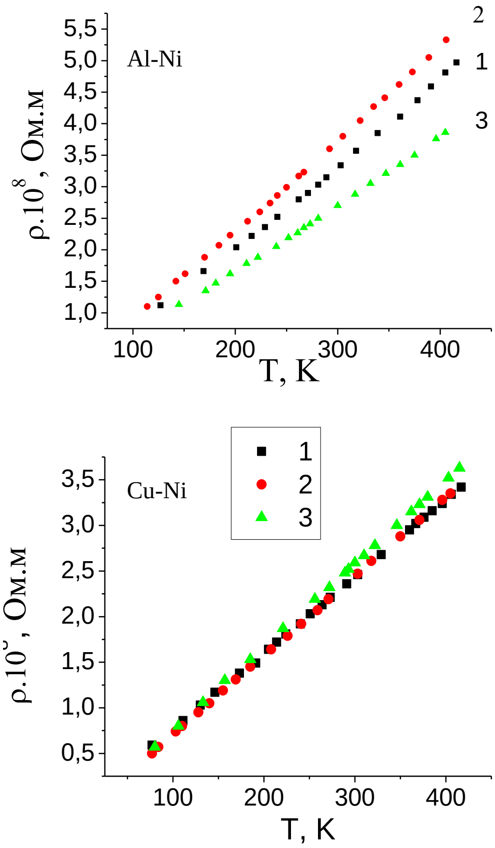

Figure 3. Temperature dependence of specific electrical resistance of nickel plated aluminum and copper, $\rho=f(T)$. 1-initial sample, 2-after annealing at 673K, 3- after annealing at 873K (for aluminum base) and at 1273K (for copper base)

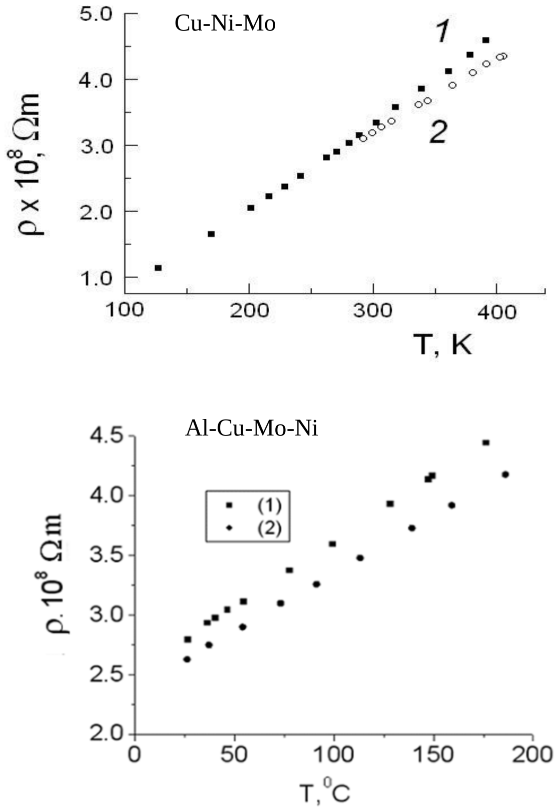

Figure 4. Temperature dependence of specific electrical resistance of nickel-molybdenum plated copper and Al-Cu, $\rho=f(T)$. 1-Initial sample, 2- after annealing at 873K (for aluminum base) and at 1273K (for copper base).

Young modulus and internal friction of aluminum and copper bases, plated with nickel (Fig. 5) and Ni-Mo (Fig. 6), were measured with acoustic spectrometer. $E(T)$ and $Q^{-1}(T)$ for initial samples were compared before and after thermal treatment with the shock heating (over one minute) of aluminum plated bases to 873K and copper bases to 1273K (in helium atmosphere). Thereafter these samples were kept in vacuum for 30 seconds and cooled to room temperature (Fig. 5)

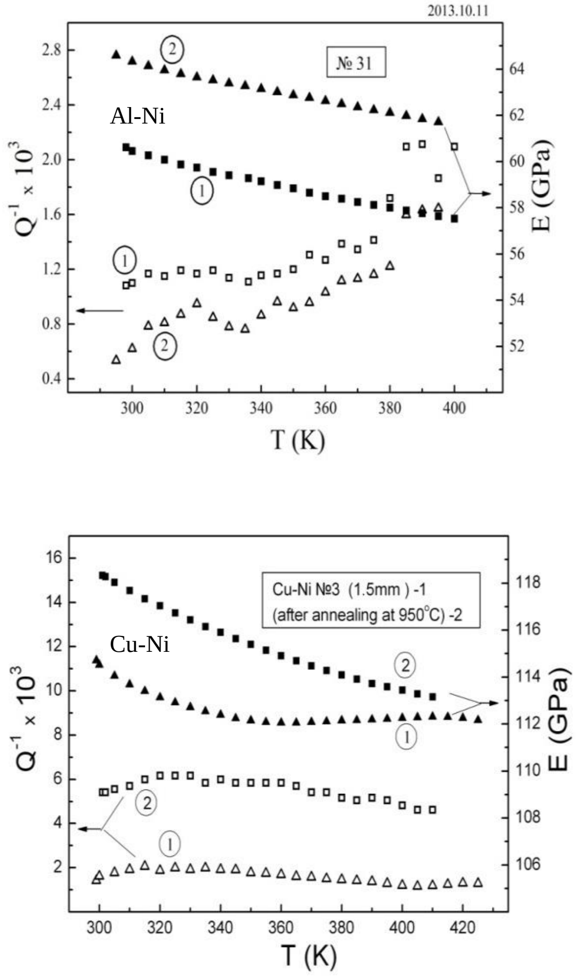

Figure 5. Temperature dependences of Young modulus (E) and of internal friction (Q^{-1}) for a nickel plated aluminum and copper, $\rho=f(T)$. 1-Initial sample, 2- after annealing at 873K (for aluminum base) and at 1273K (for copper base).

It is evident from Fig. 5 that the values of Young modulus for aluminum bases lie in the range of 40-65 GPa which are much the same as that for aluminum (70 GPa). Modulus variation in the range under measurement is ≈ 4 %.

The level of internal friction after thermal treatment decreases. The values of Young modulus for copper bases lie in the range of 112-118 GPa and are much the same as for copper (110 GPa). There are slight variations of Young modulus and the level of internal friction. At higher temperatures, Young modulus coincides with the Young modulus of copper.

It is evident from results in Fig.6 that the values of Young modulus lie in the range of 95-105 GPa which are much the same as that for pure copper (110 GPa). It varies by ≈ 2 % up to 393-423 K and increases slightly after heating to 1273 K. There is no significant variation of Q^{-1}, the internal friction, in the temperature range under measurement and increases slightly after heating at 1273K .

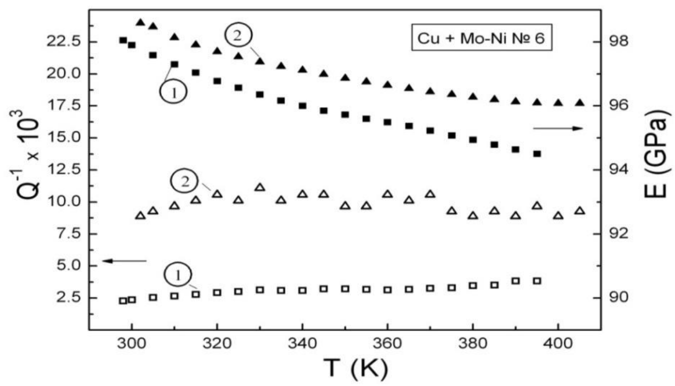

Figure 6. Temperature dependences of Young modulus (E) and of internal friction (Q^{-1}) for a nickel-molybdenum plated aluminum and copper, $\rho=f(T)$: 1- Initial sample, 2- after annealing at 873K (for aluminum base) and at 1273K (for copper base).

Electrical and mechanical properties of copper and aluminum bases, plated by nickel and nickel-molybdenum, were studied. On the basis of performed investigations it may be concluded that prepared corrosion- and heat resistant platings retain their electrical and mechanical properties after thermal treatment to 873K for aluminum bases and to 1273K for copper base.

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