

ABSTRACT AND REFERENCES

MATERIALS SCIENCE

DOI: 10.15587/1729-4061.2017.97550**EXAMINING THE FORMATION AND PROPERTIES OF TiO₂ OXIDE COATINGS WITH METALS OF IRON TRIAD (p. 4-10)****Mykola Sakhnenko**National Technical University
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We proposed a composition of citrate-pyrophosphate electrolytes with the addition of sulfates of iron triad metals for the formation of mixed oxide systems with the varied content of dopants. The introduction of an additional ligand contributes to an increase in the stability, operation period of working solutions and to the more uniform distribution of metals-dopants. The range of voltages for the single-stage plasma-electrolytic oxidizing of titanium alloys BT1-0 and OT4-1 is 120–160 V. As a result of oxidizing, we obtained metal-oxide systems TiO_xMO_y ($M=Fe, Co, Ni$), which, depending on the nature of a dopant, have different types of surface structures. The largest content of dopant and the minimum size of the grain are characteristic of the cobalt-containing coatings. A potential possibility of obtaining the mixed oxide systems $TiO_x(FeCoNi)O_y$ on the alloy OT4-1 is shown. We examined the dependences of spark voltage and the rate of change in the interelectrode voltage on the concentration of dopants in electrolyte. It was established that the formed mixed oxide coatings of titanium with the iron triad metals possess significant corrosion resistance; the highest value is inherent to the systems based on cobalt. It is shown that the incorporation of iron triad metals into the composition of oxide layers leads to an increase in the degree of surface development. This ensures an increase in the catalytic activity in the reactions of carbon monoxide oxidation. The obtained materials of varied thickness and morphology might be used in the technological systems of catalytic purification of natural and technogenic toxicants.

Keywords: catalyst, titanium oxides, oxide coatings, plasma-electrolytic oxidizing, catalytic activity.

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EXAMINING A MECHANISM OF GENERATING THE FRAGMENTS OF PROTECTIVE FILM IN THE TRYBOLOGICAL SYSTEM “EPOXYCOMPOSITE–STEEL” (p. 10-16)

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The influence of multifunctional fillers on wear resistance of epoxycomposites, operated under conditions of friction without lubrication at elevated slip velocity and loadings was explored. Introduction of these fillers in the optimum amount provides high cohesive strength and gives epoxycomposites tribotechnical properties. The developed composition of epoxycomposite materials allows the implementation of the effect of selective transfer during friction interaction.

Wear intensity of epoxycomposites under different loading and velocity modes was determined, which made it possible to establish favourable mode of formation of a protective film.

The analysis of structural elements of tribosurfaces of epoxycomposite materials and a counter body was carried out and chemical composition of fragments of the protective film on tribosurfaces was defined. It proved a hypothesis on the formation of a copper protective film at tribosurfaces as a result of selective transfer. The reasons for initiation of the process of generation of protective film fragments on surfaces of tribobodies was established and the sequence of stages of its formation in highly filled epoxycomposites was defined. The shape, dimensions and the area of fragments of a protective film, formed at tribosurfaces of the system “epoxycomposite – a steel counter body” system, were determined. The formed film in the form of fragments of elongated shape in direction of the friction process stabilizes the process of tribointeraction due to the capability of self-restoring.

Using the developed epoxycomposites, which operate under the mode of selective transfer, decreases friction coefficient and wear intensity due to the formation of laminar and porous structure of a film. Accordingly, it will allow controlling the process of friction, reducing material and economic costs in the process of maintenance and repair of equipment, which solves topical scientific and practical tasks of modern tribomaterials science.

Feasibility of using the protective copper films in tribonodes was established, which will make it possible to expand the area of using the epoxycomposite triboproducts in machine building, instrument engineering, chemical and light industries.

Keywords: epoxycomposite material, copper oxide powder, chemical analysis, selective transfer, tribosurface, counter body.

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**RESEARCH OF WEAR RESISTANCE OF BRONZE
BUSHINGS DURING PLASTIC VIBRATION
DEFORMATION (p. 16-21)**

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Optimum design parameters of the tool for vibration deformation of bronze bushings: the punch angle $\beta=9^\circ$; the height of the punch gauge part – 4–5 mm are obtained. For treatment of parts, the vibration amplitude of 1.0 mm, the machining allowance of 0.4 mm and the plastic deformation force of 217 N/m² should be used. The analysis of the microstructure improvement of the parts treated by vibration deformation is presented. Under deformation, more fine grains are formed and favorable conditions for dislocation generation are created, which promotes an increase in the radial deformation rate. The obtained process parameters of vibration deformation of bronze bushings allow reconditioning of worn-out surfaces. They can also be used for treatment of new parts, thus increasing the wear resistance of operating surfaces by 1.2 times. The research results can be useful in the development and improvement of the processes of reconditioning "bushing" type parts.

Keywords: vibration deformation, plasticity, bronze bushing, wear resistance, mechanical properties, reconditioning, hardening.

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**A STUDY OF INTERNAL FRICTION ANOMALIES
IN STAINLESS STEEL WITH NANOSTRUCTURED
PLASMA COATING (p. 21-27)**

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The study of the damping in the elastic vibration energy was conducted on the samples of steel Cr18Ni9Ti and 12Cr18Ni10Ti shaped as a solid rod and a capillary, respectively. Plasma coatings based on NiAl–SiO₂–Al₂O₃ were researched in broad temperature and deformation ranges. The research has proved an essential influence of plasma nanostructured coatings applied as

aerosols on the temperature and amplitude dependences of the internal friction in the sample composite materials. The research has revealed anomalies and peak effects in the coated samples in the temperature spectrum, both in the low-temperature and high-temperature areas. The study has revealed the effect of coating ($\text{NiA}_1\text{-SiO}_2\text{-Al}_2\text{O}_3$) on the peaks of various physical nature.

The presence of complex damping characteristics is due to the complex microstructure of the coating that contains internal interfaces and pores. Moreover, additional damping mechanisms are realized at the interfaces of individual grains, particles, and also at the interphase interaction boundary in the "coating-base" system.

The proposed damping criterion is based on understanding of the opposite influence of coatings on the display of various factors. Such factors include: an increase in the damping in the energy of elastic vibrations and, at the same time, fixation of dislocations and a decrease in the shear formation in the presence of nanocomponents in different coating zones.

Keywords: plasma coating, internal friction, damping, nano-components, anomalous properties, modulus of elasticity.

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THE ELECTROCHEMICAL CATHODIC TEMPLATE SYNTHESIS OF NICKEL HYDROXIDE THIN FILMS FOR ELECTROCHROMIC DEVICES: ROLE OF TEMPERATURE (p. 28-34)

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The influence of temperature on the synthesis of Ni(OH)_2 electrochromic films prepared using the cathodic template method has been investigated.

The influence of deposition temperature on the morphology of nickel hydroxide films has been determined. By means of scanning electron and atomic-force microscopy, it has been established that surface morphology depends on deposition temperature. The flattest film surface corresponded to a deposition temperature of 30 °C, which indicated high optical properties. The maximum profile shift of films deposited at different temperatures was 400 nM, while for the film deposited at 30 °C – 212 nM.

By means of X-ray diffraction, it has been established that all films have crystal lattice similar to $\alpha\text{-Ni(OH)}_2$, with a high number of defects. It also has been discovered that at a deposition temperature of 20–60 °C, a peak at 20–16° appears on the diffraction pattern, the highest intensity of which corresponds to the process temperature of 30–40 °C.

By means of cyclic voltamperometry and recording of transmittance changes, it has been demonstrated that nickel hydroxide film deposited at 30 °C has the best electrochemical and optical properties. A partial correlation between optical and electrochemical properties of films deposited at different temperatures has been noted.

Keywords: nickel hydroxide, Ni(OH)_2 , electrochromism, electrodeposition, cathodic template synthesis, polyvinyl alcohol.

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EFFECT OF OXIDATION AND NITRIDING ON THE PROPERTIES OF ZIRCONIUM ALLOYS (p. 34-42)

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In contrast to a large number of publications about the influence of interstitial elements (O, N) on the physical-mechanical properties of zirconium alloys, insufficient attention at present is paid to examining their influence on the characteristics of near-surface layers of the shells of heat generating element (HGE). Therefore, it is expedient to widen the knowledge about the influence of interstitial elements on the properties of zirconium HGE tubes. Authors experimentally established the influence of treatment in the controlled oxygen- and nitrogen-containing gas media on the mass increment and properties of the near-surface layer of samples-rings, cut out of the shells of heat generating elements. Differences in the saturation of internal and external surfaces of zirconium pipes were described. It was shown that roughness of the internal surface is less compared to that of the external surface. Results of examining the hardness of external and internal surfaces of the samples-rings after oxidizing and nitriding are presented here. For example, treatment of the samples-rings in the oxygen-containing medium ($T=650\text{ }^{\circ}\text{C}$, $t=20\text{ h}$) leads to the formation of hardness at the external surface $\text{HV}_{0.49}=1190\pm90$, and at the internal surface $\text{HV}_{0.49}=1190\pm90$. However, after treatment in the nitrogen-containing medium ($T=650\text{ }^{\circ}\text{C}$, $t=20\text{ h}$), the hardness on external surface is $\text{HV}_{0.49}=615\pm35$, while on the internal surface it is $\text{HV}_{0.49}=445\pm35$.

For example, after treatment in the oxygen-containing medium ($T=650\text{ }^{\circ}\text{C}$, $t=20\text{ h}$), depth of the strengthened layer at the external surface is $l=70\ldots75\text{ }\mu\text{m}$ and at the internal surface, it reaches $l=60\ldots65\text{ }\mu\text{m}$. Treatment in the nitrogen-containing medium ($T=650\text{ }^{\circ}\text{C}$, $t=20\text{ h}$) causes the formation of a strengthened layer on the external surface $l=60\ldots65\text{ }\mu\text{m}$ and on the internal surface – $l=55\ldots65\text{ }\mu\text{m}$.

The duration of isothermal holding in the oxygen mixture, which can lead to the crack initiation at the internal surface of zirconium HGE pipes, was experimentally discovered. Results of present work may be taken into account for the development of modes of treatment of zirconium alloys.

Keywords: zirconium alloys, interstitial elements, near-surface layer, hardness, mass increment, shell of a heat generating element.

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- INVESTIGATION OF ADSORPTION BEHAVIOR OF SMOOTHING ADDITIVES IN COPPER PLATING ELECTROLYTES (p. 43-49)**
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- Smoothing additives are the necessary component of copper plating electrolytes. Choice of the required additive is determined by the type of electrolyte and its pH values. Studies of adsorption behavior of such compounds in electrolytes with different acidities are of current interest. Adsorption activity of poly-N, N'-dimethylsafranine and poly-N, N'-diethylsafranine on the copper electrode in sulfate electrolytes was established in the present work. The dependencies of the differential capacitance of the double electric layer of the copper electrode on the potential which were obtained in acidic (pH 1.7) and neutral (pH 5.9) electrolytes indicate that acidity of the medium has a significant effect on the additive adsorption. The studied organic substances show high adsorption activity in an acidic solution. The likely cause of the established phenomenon in an acid medium is transition of these organic compounds to a protonated state with formation of positively charged amino groups. Cationic groups of the additives are responsible for an additional interaction with the cathode surface and provide stronger adsorption of poly-N, N'-dimethylsafranine and poly-N, N'-diethylsafranine on the copper electrode in comparison

with a neutral sulfate electrolyte. Poly-N, N'-diethylsafranine with its molecular weight higher than that of poly-N, N'-dimethylsafranine is characterized by higher adsorbability. Since the smoothing effect of additives in electrodeposition of copper coatings is determined by their adsorption properties, it should be expected that the most effective in this process will be the use of poly-N, N'-diethylsafranine at lower pH values of the copper plating electrolytes.

Keywords: electrodeposition, copper electrode, adsorption, double electric layer, smoothing additive.

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SIMULATION OF THE PHASE TRANSFORMATION FRONT ADVANCEMENT DURING THE SWELLING OF FIRE RETARDANT COATINGS (p. 50-55)

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Description of the intumescent coating behavior at the time of formation of the porous structure is a separate and challenging task, covering both stages of the thermal insulation process: swelling of the coating and subsequent heat transfer which is formed by the swelling. Therefore, there is a need to study the formation conditions of a barrier for heat conduction and reveal a mechanism of phase transition from the coating film to the coke layer. In this regard, the mathematical model of the phase transformation front advancement during the swelling of fire-proof coatings is developed. According to the dependencies, it is found that the front line of the phase transformations of the coating under high temperature passes instantly. It is found-experimentally that under the action of the heat flux on the samples for a short time at 190–200 °C, there is an intense swelling of the coating, the height of the

expanded foam coke layer increased to 22±38 mm. As a result of testing, it is revealed that the phase transformation front moves in the direction of high temperature to form foam coke. The foaming front boundary line in the form of a thin layer, which is slightly shifted towards the temperature, divides the coating into two parts. On the one side, there is a swollen coke layer, the outer part of which moves at a certain speed, on the other side – the layer of the source material, where the temperature is not sufficient to start the foaming process and the speed of transformations is zero.

Keywords: intumescence coatings, oven temperature, weight loss, surface treatment, phase transformation front.

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DEVELOPMENT OF A COMBINED TECHNOLOGY FOR HARDENING THE SURFACE LAYER OF STEEL 38Cr2MoAl (p. 56-62)

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Development of new combined strengthening technologies for treatment of steel surface layer is a topical issue. Influence of conditions of combined hardening treatment on variation of properties of the surface layer of 38Cr2MoAl steel was studied. Experimental data have shown that thickness of the hardened layer of 38Cr2MoAl steel, depending on the process conditions of combined treatment, varied in the range 0.18 to 0.69 mm with the surface hardness being 10.5–12.5 GPa. Mathematical models of the hardened layer thickness and surface hardness were obtained depending on variation of velocity of the laser beam travel and duration of nitriding of steel following the combined treatment. In their structure, the models are regression equations. These regularities have practical technological significance and ensure prediction of values of the hardened layer thickness and surface hardness. Nomograms of simultaneous influence of velocity of the laser beam travel and duration of nitriding on thickness of the hardened steel layer and surface hardness were constructed. Nomograms make it possible to determine concrete conditions of hardening processing, starting from specified thickness of the hardened layer or the surface hardness of 38Cr2MoAl steel, respectively and also to solve inverse problems. This method is suitable for hardening hard-to-reach part sections and local contact areas.

Keywords: structural steel, surface hardening, combined treatment, laser treatment, nitriding, layer thickness, hardness.

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