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Vasyl Stefanyk Precarpathian National University

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O.M. Hertsyk[1], T.H. Hula[1], M.O. Kovbuz[1], N.L. Pandiak[2], O.A. Ezers'ka[3]

Adsorption of organic peroxides on the surface of amourphous alloys for the drugs immobilization

[1]Department of Physical and Colloidal Chemistry at Ivan Franko National University of Lviv, Kyryla and Mefodiya Str. 6, 79005 Lviv, Ukraine, djunjer1@gmail.com
[2]Ukrainian National Forestry University, Gen. Chuprynka Str. 103, 79057 Lviv, Ukraine, pandyakn@ukr.net
[3]Fraunhofer Institut Fertigungstechnik Materialforschung, Wiener Straße 12, 28359 Bremen, Germany

It was investigated wetting of surfaces of the amorphous metallic alloys (AMA) based on iron and cobalt with aqueous-ammonium solutions of oligoperoxides based on vinyl acetate, 2-tert-butylperoxy-2-methyl-5-hexen-3-yne and maleic anhydride (OP-1) and based on vinyl acetate, 3-tert-butylperoxy-3-phenylbutylmethacrylate and maleic anhydride (OP-2). The surface tension of thin films of oligoperoxide's aqueous-ammonia solutions was determined and were calculated values of the macromolecules adsorption. A higher surface activity of OP-2 was observed in comparison with OP-1. The values of the adhesion work between contact and external metallic surfaces and solutions of oligomers were calculated.

Keywords: amorphous metallic alloys, surface activity, adsorption of oligoperoxides, thin films.

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Introduction

Intensive development of nanotechnology is associated with the modification of polymeric and metallic surfaces in order to provide them the specific physico-chemical properties. An alternative activation method is formation of a grafted polymeric thin layer from macromolecules of heterofunctional oligoperoxide (HFO). Such oligoperoxides can produce radicals at low temperatures, so they can be used for modification of the amorphous metallic alloys' (AMA) surface.

The affinity of HFO macromolecules to solid surfaces leads to the localization of peroxide groups in the interphase. Surface activity of heterofunctional oligoperoxides can be used in medicine, where surface phenomena occur at the tissue's interphase. By formation of interphase layers with a predestinate structure and nature it is possible to receive polymeric layers with the required properties [1-3].

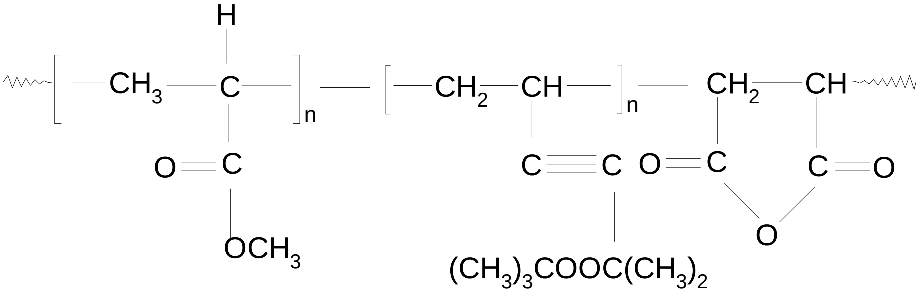
Since more and more AMAs based on ferrum and cobalt are used as special purpose materials [4, 5], investigation of their surface modification is very important. Modification of metallic surfaces by polymers can be used to form protective thin coatings, as well as for immobilization various monomers and medical drugs.

However, the efficiency of the metallic surfaces' modification depends on the surface properties of heterofunctional oligoperoxides and amorphous metallic alloys. The adsorption interaction at the interphase determines the adhesion of the polymers to the solid surface and depends on the nature of the interaction of the polymer's functional groups with the surface and the shape of the macromolecules.

I. Experiment

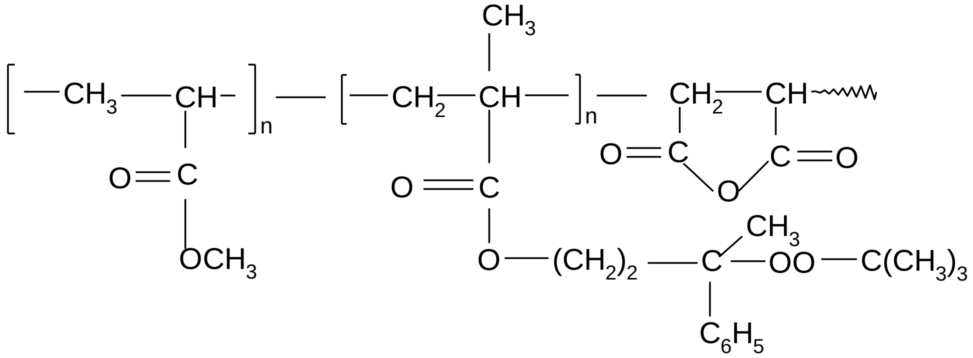
To study the adsorption capacity of the AMA methods of measuring wetting angle and electrochemical impedance spectroscopy were used.

For the chemical modification of the surface, we used $(0.5\div5.0)\cdot10^{-3}$ M aqueous-ammonia solutions of a heterofunctional oligoperoxides based on vinyl acetate (VA), 2-tert-butylperoxy-2-methyl-5-hexen-3-yne (VEP) and maleic anhydride (MA) taken in the following ratio: VA:VEP:MA = 1:1:1



(OP-1)

and based on VA, 3-tert-butylperoxy-3-phenylbutylmethacrylate (TBPPM) and MA taken in the following ratio VA:TBPPM:MA = 1:1:1



(OP-2)

in which amorphous samples were held for 600 s. The film-forming peroxide oligomers were synthesized by the researchers of the Organic Chemistry Faculty at the Lviv Polytechnic National University [6].

As solid surfaces AMAs were used in the form of tapes with $4 \cdot 10^{-5}$ m thickness and $2 \cdot 10^{-2}$ m widthess, obtained by ultrafast cooling on a copper drum (G.V. Kurdyumov Institute for Metal Physics of the N.A.S. of Ukraine): $Fe_{80}Si_6B_{14}$, $Fe_{78.5}Ni_{1.0}Mo_{0.5}Si_{6.0}B_{14.0}$, $Fe_{51,7}Ni_{21,7}Cr_{6,2}Mo_{0,6}V_{1,5}Si_{5,2}B_{13,1}$ та $Co_{75.5}Fe_{4.6}Si_6B_{16.7}$, $Co_{73.2}Fe_{4.3}Mo_{0.5}Si_{5.3}B_{16.7}$, $Co_{73}(Fe,Ni,Mo,Mn)_{5.7}(Si_{0.2}B_{0.8})_{21.3}$. Evaluated surface activity of the contact (c) and external (e) surfaces of the tape [7].

The Rebinder method was used for measuring the surface tension $(0,5 \div 5,0) \cdot 10^{-3}$ M of aqueous-ammonia solutions of OP-1 and OP-2. The wetting of the metallic surface by solutions of oligoperoxides was researched by measuring the edge angle at the three-phase line and calculated by formula $\cos\theta = ((d/2)^2 - h^2) / ((d/2)^2 + h^2)$, where d – diameter of the drop, h – the drop’s height. Measurement of the edge angle was carried out at the three-phase line: solid-liquid-gas, which depends on the molecular properties of phases. The effect of wetting is estimated by the adhesion work: $W_a = \sigma_{1,2}(1 + \cos\theta)$, where $\sigma_{1,2}$ – the surface tension of the solution. It was measured the wetting angle of $(0,5 \div 5,0) \cdot 10^{-3}$ M aqueous-ammonia solutions of OP-1 and OP-2 on the tape amorphous alloys.

The electrochemical impedance spectroscopy (EIS) was realized with the help of an Autolab®/PGSTAT-20 device equipped with a frequency analyzer and a differential electrometric amplifier (Eco Chemie BV, the Netherlands). The accumulated results were processed by using the Autolab-4.9 software. The impedance components were computed for a circuit containing two resistors and a capacitor ($R_1(Q_{dl}R_2)$), where R_1 is the resistance of electrolyte, 0,5 M NaCl aqueous solution, R_2 is the charge-transfer resistance, and Q_{dl} is an element of constant phase characterizing the capacitance of the double layer [8].

II. Results and discussions

To evaluate the surface activity of oligoperoxides it was investigated the influence of the solution’s concentration on the surface tension. The molecules of OP-1 and OP-2 have a large molecular weight (≈ 2000 g/mol), which slows down their movement in aqueous solutions. Therefore, the changes of surface tension in time were analyzed (Fig. 1).

With increasing concentrations of both oligoperoxides, the surface tension decreases. However, the form of these dependencies is different (Fig. 2). The ability to form the thin films in aqueous-ammonia solutions is influenced by the nature of heterophunctional oligoperoxide. At lower concentrations, the OP-2 molecule is poorly solvated with solvent molecules and has a higher film formation ability at the solution-air boundary.

Based on the surface tension values, the adsorption (A) was calculated (Table 1). The irregular decrease of adsorption values of the OP solutions at different

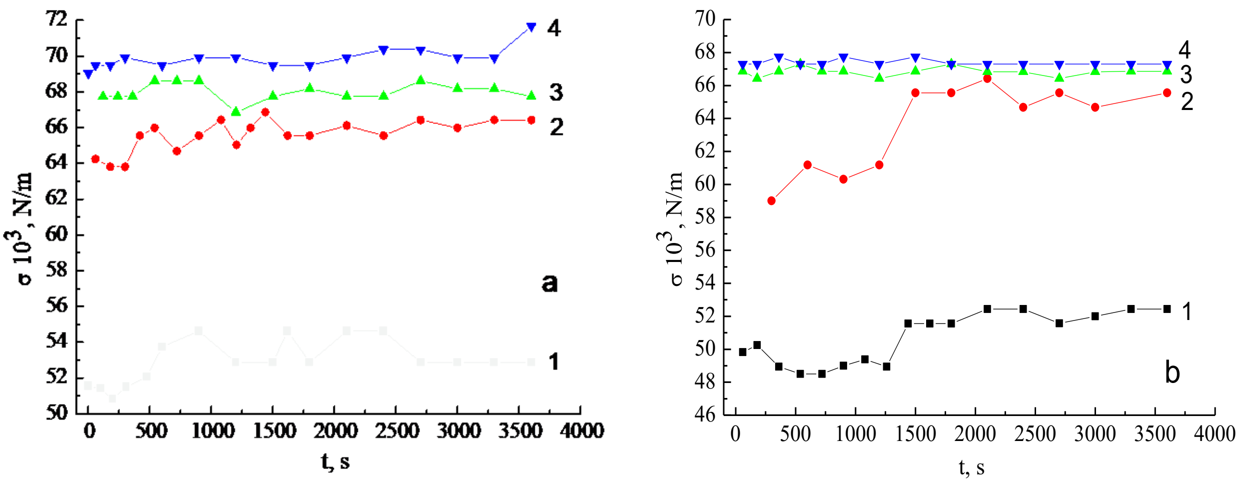


Fig. 1. The time dependence of the surface tension of OP-1 (a) and OP-2 (b) solutions at different concentration: 1 – $5 \cdot 10^{-3}$ M; 2 – $2{,}5 \cdot 10^{-3}$ M, 3 – $1{,}25 \cdot 10^{-3}$ M, 4 – $0{,}5 \cdot 10^{-3}$ M.

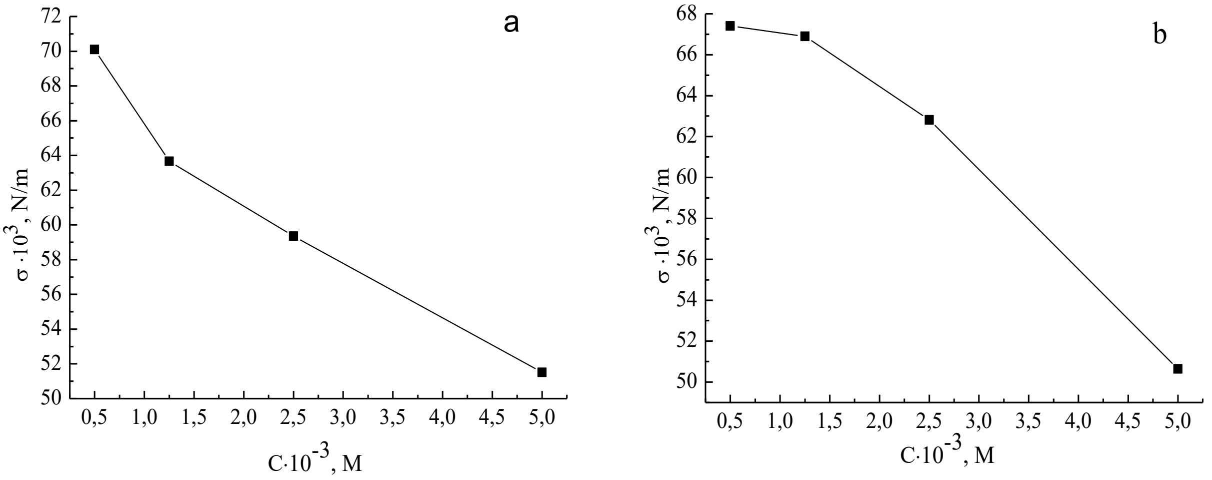


Fig. 2. The dependence of the surface tension of OP-1 (a) and OP-2 (b) solutions on the concentration (T = (293 ± 2) K).

concentrations is associated with different structure of the surface layers of oligoperoxide presented in the solution.

Table 1

The adsorption of oligoperoxides from aqueous-ammonia solutions at different concentrations.

$C \cdot 10^{-3}$, M	OP-1	OP-2
	$A \cdot 10^{-7}$, mol/m^2	$A \cdot 10^{-7}$, mol/m^2
5.0	114.44	100.67
2.5	21.05	33.74
1.25	15.18	6.48
0.5	4.68	15.83

Oligomeric peroxide surface layers have partially protective properties from external influences, but are mainly used for implantation of various monomers and creation of polymeric coatings. Wetting is the first stage in the formation of a surface thin film.

For the creation dense oligoperoxide films with high degree of adhesion on the surface of AMA it was investigated wetting by aqueous-ammonium solutions of HFOs at different concentrations the surfaces of amorphous alloys based on iron and cobalt.

By the way of manufacturing a tape of amorphous alloys we distinguish the contact (c) surface, which directly contacts with the cooling element and external (e) surface. They differ in elemental composition and structure [5]. These two factors influence the affinity of oligomeric molecules to the surfaces (Table 2). Multicomponent alloy $Fe_{51,7}Ni_{21,7}Cr_{6,2}Mo_{0,6}V_{1,5}Si_{5,2}B_{13,1}$ shows in most cases the highest affinity for OP solutions. Sufficiently high adhesion is also observed for $Fe_{75.5}Ni_{3,5}Mo_{3,0}Si_{2,0}B_{16.0}$ alloy. Obviously, Mo and Cr additions form surface oxides, which adsorb organic molecules better [9, 10].

Based on the calculated values of the adhesion (Fig. 3), which is a direct characteristic of sticking oligoperoxidic layers to the surface, it was determined that the external surface of the $Fe_{80}Si_6B_{14}$ alloy has a slightly higher affinity than contact. With the increasing number of alloy’s components, especially in the presence of molybdenum and chromium, the contact surface of the tape has better adhesive ability.

For cobalt tapes, it was also observed better wetting of the surfaces of Mo-containing alloys (Table 3).

The affinity of the AMA surfaces to the OP solutions more depends on the elemental composition of the alloy than the nature of the macromolecular film-forming agent (Fig. 4, Table 4).

Table 2

Wetting (cos θ) of the contact (c) and external (e) surfaces of the AMA based on Fe by aqueous-ammonium OP solutions at different concentrations.

Alloy	Surface	$5.0 \cdot 10^{-3}$ M		$2.5 \cdot 10^{-3}$ M		$1.25 \cdot 10^{-3}$ M		$0.5 \cdot 10^{-3}$ M	
		OP-1	OP-2	OP-1	OP-2	OP-1	OP-2	OP-1	OP-2
$Fe_{80}Si_6B_{14}$	c	0.62	0.72	0.55	0.52	0.48	0.58	0.56	0.43
	e	0.58	0.55	0.68	0.64	0.65	0.58	0.63	0.74
$Fe_{78.5}Ni_{1.0}Mo_{0.5}Si_{6.0}B_{14.0}$	c	0.68	0.73	0.71	0.63	0.54	0.47	0.49	0.33
	e	0.72	0.63	0.75	0.65	0.67	0.73	0.61	0.44
$Fe_{51.7}Ni_{21.7}Cr_{6.2}Mo_{0.6}V_{1.5}Si_{5.2}B_{13.1}$	c	0.71	0.82	0.86	0.77	0.77	0.72	0.72	0.71
	e	0.85	0.80	0.59	0.66	0.71	0.40	0.69	0.35

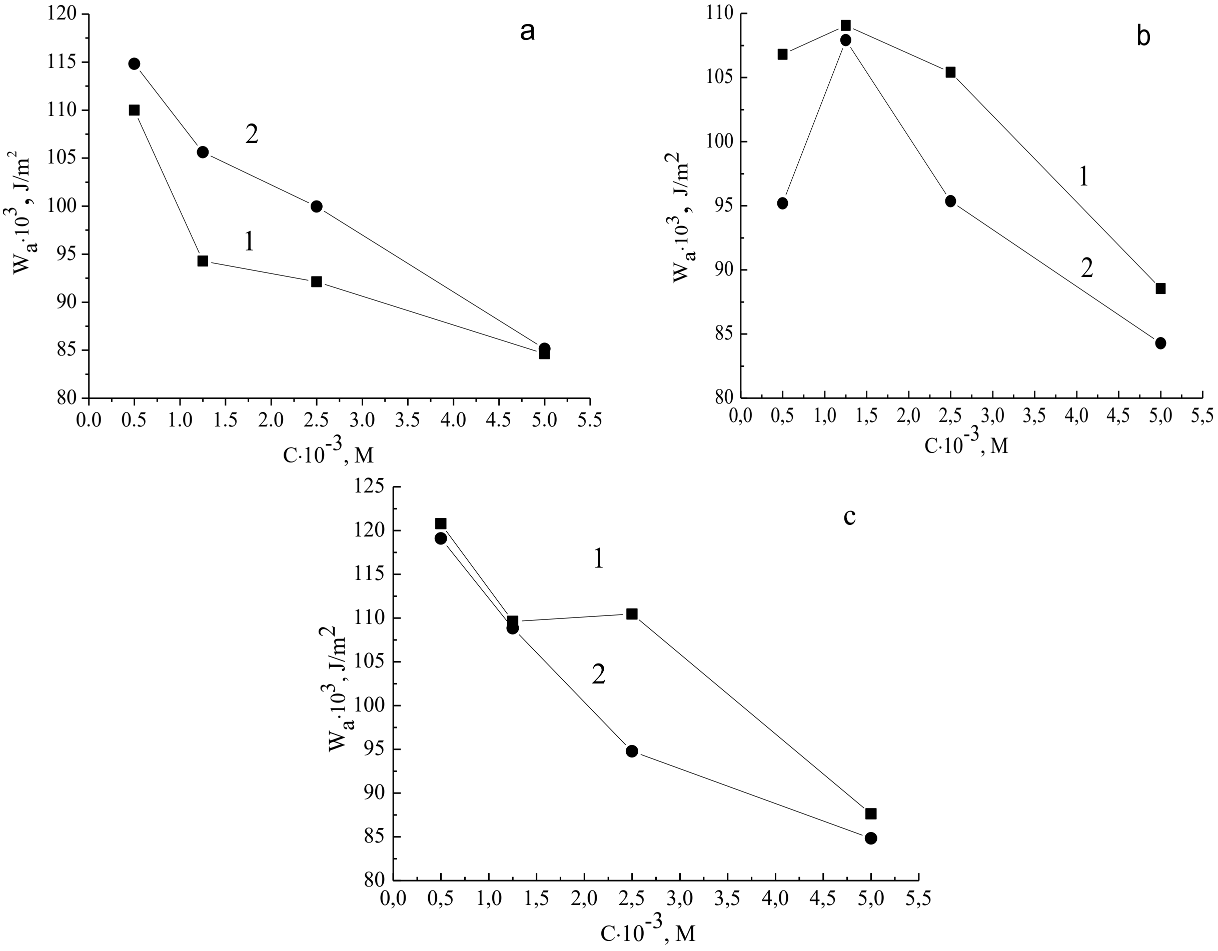


Fig. 3. Dependence of the adhesion of OP-1 solution from the concentration on the amorphous metallic surface: $Fe_{80}Si_6B_{14}$ (a); $Fe_{75.5}Ni_{3.5}Mo_{3.0}Si_{2.0}B_{16..0}$ (b); $Fe_{51.7}Ni_{21.7}Cr_{6.2}Mo_{0.6}V_{1.5}Si_{5.2}B_{13.1}$ (c).

Table 3

Wetting (cos θ) of the contact (c) and external (e) surfaces of the AMA based on Co by aqueous-ammonium OP solutions at different concentrations.

Alloy	Surface	$5.0 \cdot 10^{-3}$ M		$2.5 \cdot 10^{-3}$ M		$0.5 \cdot 10^{-3}$ M	
		OP-1	OP-2	OP-1	OP-2	OP-1	OP-2
$Co_{75.5}Fe_{4.6}Si_6B_{16.7}$	c	0.56	0.49	0.49	0.42	0.34	0.52
	e	0.65	0.47	0.63	0.51	0.49	0.40
$Co_{73.6}Fe_{3.2}Mn_{3.2}Si_{5.8}B_{15}$	c	0.53	0.62	0.41	0.71	0.43	0.29
	e	0.61	0.51	0.52	0.44	0.34	0.24
$Co_{73}(Fe,Ni,Mo,Mn)_{5.7}(Si_{0.2}B_{0.8})_{21.3}$	c	0.62	0.56	0.58	0.47	0.35	0.38
	e	0.61	0.54	0.40	0.33	0.56	0.32

Table 4

The values of the adhesion of $5 \cdot 10^{-3}$ M oligoperoxide from aqueous-ammonia solutions on the surface of the AMA.

Alloy	Surface	$W_a \cdot 10^3$, J/m^2	
		OP-1	OP-2
$Fe_{80}Si_6B_{14}$	c	84.62	80.67
	e	85.13	82.54
$Fe_{78.5}Ni_{1.0}Mo_{0.5}Si_{6.0}B_{14.0}$	c	91.48	87.76
	e	88.57	82.85
$Fe_{51,7}Ni_{21,7}Cr_{6,2}Mo_{0,6}V_{1,5}Si_{5,2}B_{13,1}$	c	87.71	91.96
	e	84.83	91.05
$Co_{75.5}Fe_{4.6}Si_6B_{16.7}$	c	78.08	76.77
	e	86.53	85.08
$Co_{73.2}Fe_{4.3}Mo_{0.5}Si_{5.3}B_{16.7}$	c	86.58	85.13
	e	82.15	80.77
$Co_{73}(Fe,Ni,Mo,Mn)_{5.7}(Si_{0.2}B_{0.8})_{21.3}$	c	80.81	79.45
	e	80.05	78.24

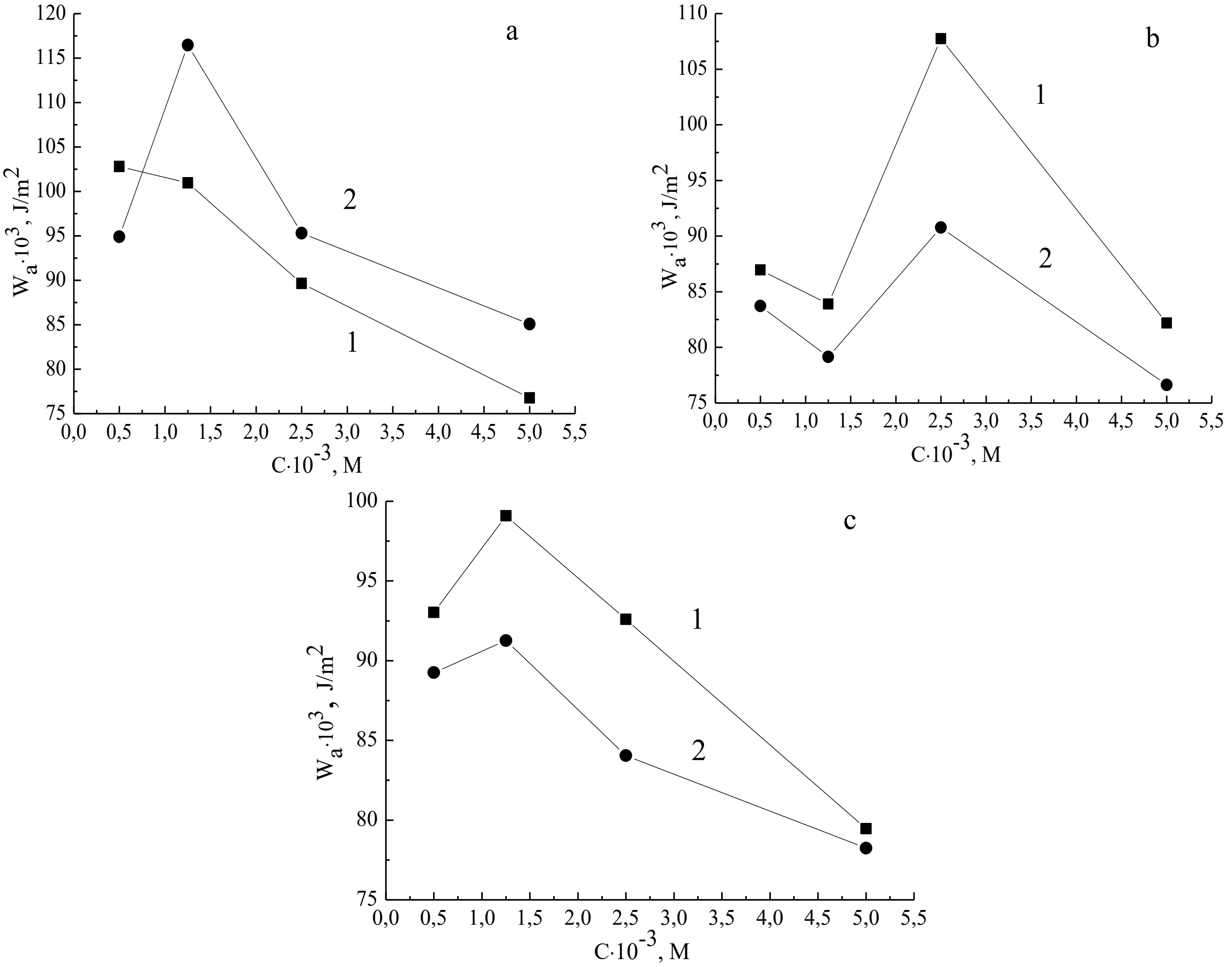


Fig. 4. Dependence of the adhesion of OP-1solution from the concentration on the amorphous metallic surface: $Co_{75.5}Fe_{4.6}Si_6B_{16.7}$ (a); $Co_{73.6}Fe_{3.2}Mn_{3.2}Si_{5.8}B_{15}$ (b); $Co_{73}(Fe,Ni,Mo,Mn)_{5.7}(Si_{0.2}B_{0.8})_{21.3}$ (c).

Table 5

Electrochemical parameters of AMA in 0,5 M NaCl aqueous solution based on electrochemical impedance spectroscopy.

Alloy	Surface	Modification	R_1, $\Omega\cdot cm^2$	R_2, $\Omega\cdot cm^2$	$Q_{dl}\cdot 10^5$, $F\cdot cm^{-2}$	α
$Fe_{80}Si_6B_{14}$	c	-	49.2	1432	3.45	0.83
		OP-1	53.1	1765	4.56	0.81
		OP-2	55.4	1876	5.67	0.80
	e	-	49.4	2987	3.21	0.85
		OP-1	51.3	3214	3.05	0.84
		OP-2	54.6	3456	2.93	0.86
$Fe_{78.5}Ni_{1.0}Mo_{0.5}Si_{6.0}B_{14.0}$	c	-	48.9	2338	5.07	0.87
		OP-1	52.2	5623	9.73	0.82
		OP-2	53.5	2661	6.22	0.85
	e	-	49.7	10470	2.38	0.80
		OP-1	50.8	10877	2.08	0.85
		OP-2	54.8	11614	1.81	0.86
$Co_{75.5}Fe_{4.6}Si_6B_{16.7}$	c	-	49.5	767	10.8	0.79
		OP-1	51.6	2229	3.28	0.75
		OP-2	55.0	2506	12.1	0.72
	e	-	50.1	748	9.93	0.74
		OP-1	53.2	3762	2.10	0.82
		OP-2	55.1	2524	2.41	0.76
$Co_{73.2}Fe_{4.3}Mo_{0.5}Si_{5.3}B_{16.7}$	c	-	48.9	1018	6.32	0.75
		OP-1	51.8	2207	0.93	0.79
		OP-2	54.2	2636	0.95	0.78
	e	-	49.6	697	0.51	0.83
		OP-1	51.9	3068	0.24	0.76
		OP-2	54.7	5134	0.48	0.81

The higher values of the adhesion (Table 4) can be traced for AMA based on Fe and Co containing Mo.

The quality of the applied oligoperoxidic coatings on metallic surfaces was investigated by electrochemical impedance spectroscopy in 0,5 M NaCl aqueous solution (Table 5). For tapes previously modified with oligoperoxidic layers, higher values of resistance R_2 can be traced. The reason is formation of dense surface coatings. We obtained more dense coatings for the external surfaces of Fe-based amorphous alloys. The higher affinity of oligoperoxidic layers to alloys with Mo addition was confirmed.

Conclusions

Higher surface activity in aqueous-ammonia solutions shows OP-2 in comparison with OP-1. Wetting by aqueous-ammonia solutions of oligoperoxides based on vinyl acetate, 2-tert-butylperoxy-2-methyl-5-hexen-3-yne and maleic anhydride (OP-1) and 3-tert-butylperoxy-3-phenylbutylmethacrylate (OP-2) surfaces of amorphous metallic alloys based on iron and cobalt depends on the elemental composition of the alloy. The higher affinity of oligoperoxidic layers to alloys with Mo additions was confirmed.

O.M. Hertsyk – candidate of chemical sciences, associate professor, associate professor of physical and colloid chemistry department

T.H. Hula – candidate of chemical sciences, junior research fellow of physical and colloid chemistry department

M.O. Kovbuz – candidate of chemical sciences, associate professor, senior research fellow of physical and colloid chemistry department

N.L. Pandiak – candidate of chemical sciences, associate professor, associate professor of chemistry department

O.A. Ezers'ka – candidate of technical sciences, research fellow

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О.М. Герцик[1], Т.Г. Гула[1], М.О. Ковбуз[1], Н.Л. Пандяк[2], О.А. Єзерська[3]

Адсорбція органічних пероксидів на поверхні аморфних сплавів для іммобілізації лікарських препаратів

[1]Львівський національний університет ім. І. Франка, Львів, Україна, вул. Кирила і Мефодія 6, 79005 Львів, Україна,
djunjer1@gmail.com
[2]Національний лісотехнічний університет України, вул. Генерала Чупринки 103, 79057 Львів, Україна, pandyakn@ukr.net
[3]Інститут технології виробництва та передових матеріалів Фраунгофера, 28359 Bremen, Germany

Досліджено змочування водно-аміачними розчинами олігопероксидів на основі вінілацетату 2-трет-бутилперокси-2-метил-5-гексен-3-їну і малеїнового ангідриду (ОП-1) та на основі вінілацетату 3-трет-бутилперокси-3-фенілбутилметакрилату та малеїнового ангідриду (ОП-2) поверхонь аморфних металевих сплавів (АМС) на основі заліза та кобальту. Визначено поверхневий натяг (0,5-5,0)·10^{-3}М водноаміачних розчинів олігопероксидів та обчислені величини адсорбції макромолекул. Встановлено дещо вищу поверхневу активність ОП-2 у порівнянні з ОП-1. Обчислені значення роботи адгезії між контактною і зовнішньою металевими поверхнями та розчинами олігомерів.

Ключові слова: аморфні металеві сплави, поверхнева активність, адсорбція олігопероксидів, тонкі плівки.