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The effects of a SiO_2 coating on the corrosion parameters cpTi and Ti-6Al-7Nb alloy

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The aim of this paper was to evaluate the usefulness of the sol-gel method application, to modificate the surface of the Ti6Al7Nb alloy and the cpTi titanium (Grade 4) with SiO_2 oxide, applied on the vascular implants to improve their hemocompatibility. Mechanical treatment was followed by film deposition on surface of the titanium samples. An appropriate selection of the process parameters was verified in the studies of corrosion, using potentiodynamic and impedance method. A test was conducted in the solution simulating blood vessels environment, in simulated body fluid at t = 37.0 ± 1 °C and pH = 7.0 ± 0.2. Results showed varied electrochemical properties of the SiO_2 film, depending on its deposition parameters. Correlations between corrosion resistance and layer adhesion to the substrate were observed, depending on annealing temperature.

Introduction

Titanium and titanium alloys have been used as an implant material for blood contact. This type of biomaterials is used to produce mainly rings of prosthetic heart valves. Implants used in blood system should not undergo degradation or adsorb any blood components and should minimalize the occurrence of blood clot formation. Proper bond between an implant and a tissue environment is guaranteed by appropriately prepared surface of medical product. Combination of the advantages of implant metal constructions and biotolerance required for medical use is achieved by various methods of the implant surface treatment, i.e. electropolishing, chemical passivation, oxide films fabrication using sol-gel method. Modification based on the sol-gel technology is one of the most progressive methods of coating surface of different morphology and geometry with thin films, which gives surface desirable roughness and appropriate combination of mechanical properties. Siliceous films, depending on chemical composition of sols as well as parameters of the surface coating process, are characterized by i.e., good adhesion to the metal substrate, controlled macroscopic structure of gels, very high biotolerance and improved corrosion resistance comparing to non-coated material. Literature data indicate many undefined phenomenon accompanying oxide films fabrication involving silicon on surface of metal biomaterials. Selection of proper coatings production parameters, as well as complex studies presenting their behavior in conditions of implantation and long-lasting contact with tissue environment during use of an implant, are still an unsolved problem. Currently there are no reports on use of silicon-based coatings on metal implants used in blood vessels surgery. Few studies conducted in this field mostly do not comprise analysis of deformations that occur during implantation or use of this kind of implants. Authors of papers equally often omit issues connected to the influence of technological parameters of the sol-gel method on physicochemical and mechanical properties of siliceous coatings.[1-11] Therefore, in this paper authors attempted to analyze physicochemical and mechanical properties of the SiO_2 films deposited in defined technological conditions on titanium Grade 4 and Ti-6Al-7Nb alloy surface using sol-gel method

Results

Results of the pitting corrosion resistance tests of the Ti6Al7Nb alloy and titanium Grade 4 samples with differentiated surface preparation method, performed with potentiodynamic method, are presented in (**Table 1**; **Figs. 1 and 2**).

The obtained results showed that the average corrosion potential of the titanium Grade 4 samples in their initial state (grinding and mechanical polishing) was E_{cor} = -130 mV. Thereby determined anodic polarization curves indicated existence of the passive range to the potential value E = +4000 mV. In this case, no rapid increase in the anode current density in the analyzed measurement range, which would prove pitting corrosion initiation was observed. In addition, polarization resistance amounting R_p = 530 kΩcm² and corrosion current density amounting i_{kor} = 0.049 μA/cm² were determined using Stern method. Next,

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Table 1. Results of the potentiodynamic tests

The method of surface preparation of samples		E_{cor} [mV]	I_{cor} [μA/cm^2]	R_p [kΩcm^2]
cpTi Grade 4	Initial state	-130	0.049	530
	1	-185	0.014	1790
	2	-205	0.007	3370
	3	-187	0.011	2210
	4	-139	0.010	2590
Ti6Al7Nb alloy	Initial state	-275	0.10	237
	1	-108	0.010	2390
	2	-90	0.006	3970
	3	-136	0.022	1181
	4	-93	0.012	2030

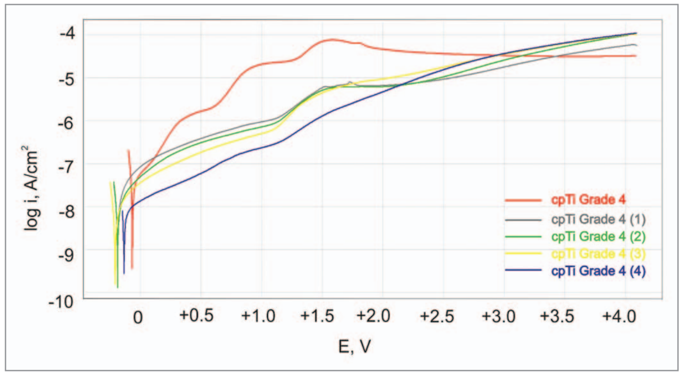

Figure 1. Polarization curves of the titanium Grade 4 samples after different stages of surface modification

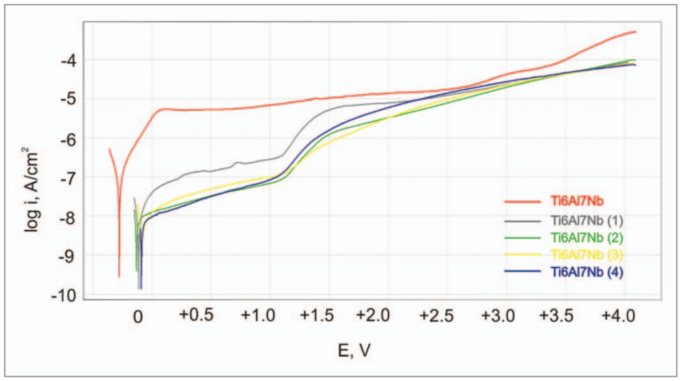

Figure 2. Polarization curves of the Ti6Al7Nb alloy samples after different stages of surface modification

samples coated with SiO_2 layer using sol-gel method, at different annealing temperatures were tested. The results showed that this process caused advantageous increase of polarization resistance R_p, compared with the initial state samples, regardless of applied variant. Passive range also occurred in all anodic range. Corrosion potential E_{cor} value in turn, slightly increased (**Table 1**; **Fig. 1**).

Next, Ti6Al7Nb alloy samples shaped by different surface modifications were analyzed. At the initial stage (grinding and mechanical polishing) corrosion potential amounted E_{cor} = -275 mV. As in case of titanium, analyzed alloy indicated existence of the passive range to the potential value E = +4000 mV. Also in this case no rapid increase in anode current was observed. Determined polarization resistance and corrosion current density amounted respectively Rp = 237 kΩcm^2, i_{kor} = 0.10 μA/cm^2. Subsequently, samples coated with SiO_2 using sol-gel method at different heating temperatures were tested. Based on the results it was ascertained that this process caused advantageous increase of corrosion potential value and polarization resistance compared with the initial state samples, regardless of applied variant. It is showed by the values of parameters characterizing their corrosion resistance (**Table 1**; **Fig. 2**).

Results of the films adhesion tests show diverse adherence of the SiO_2 layer to the Titanium Grade 4 and Ti-6Al-7Nb alloy substrates. It is showed by differentiated values of particular parameters determined on the basis of performed measurements (**Table 2**). On the basis of the results it was ascertained that samples coated with SiO_2 layer annealed at the temperature t = 430 °C (2) were characterized with the best adhesion. Critical load value, which caused inside and outside layer delamination for this type of layer amounted Lc = 6.5 N for Ti6Al7Nb alloy substrate and Lc = 9.6 N for titanium Grade 4 substrate (**Figs. 3 and 4**).

At the next stage of tests, electrochemical impedance spectroscopic measurements were conducted. Impedance spectrums recorded for titanium 4 and Ti-6Al-7Nb alloy samples with mechanically polished surface and coated with SiO_2 film. Nyquist diagrams determined for such prepared samples present fragments of large incomplete semi-circles, which are a typical impedance response of thin oxide films. Presented on the Bode diagrams, maximum values of the phase shift angles in the wide range of frequencies amount $\theta \approx 85°$. Slopes of log |Z| in the all range of frequencies are close to -1, which demonstrates the capacitive character of passive film (**Table 3**). High impedance values $|Z| > 10^6$ Ωcm^2 in turn, in the range of the lowest frequencies, indicate good dielectric and protective properties of the oxide film fabricated on the commercially pure titanium and Ti-6Al-7Nb alloy samples.

Electrode-oxide layer-solution phase boundaries impedance was characterized by approximation of the experimental data using equivalent electrical circuit model (**Fig. 5**). In the equivalent electrical circuit (**Table 3**) Resistor R_{ct} and constant phase element (CPE) represent respectively the ions transition resistance and the capacity of the passive oxide film fabricated on the biomaterial surface. In turn, R_s resistor represents the resistance of the simulated body fluid, in which the tests were performed.

Discussion

Processes of blood coagulation and restenosis are classified as factors limiting efficacy of using medical products in the cardiovascular diseases treatment. They are a result of not completely adjusted electrochemical properties of their surfaces

Table 2. Results of the SiO_2 films adhesion

Critical load Lc, N								
Surface modifcation	Ti-6Al-7Nb alloy				cpTi (Grade4)			
	Measurement 1	Measurement 2	Measurement 3	Average	Measurement 1	Measurement 2	Measurement 3	Average
1	2.7	3.2	1.2	2.3	8.63	6.6	3.3	6.1
2	6.7	5.53	7.5	6.5	10.54	11.65	6.79	9.6
3	11.38	3.94	4.03	6.4	5.43	5.36	6.72	5.8
4	7.04	6.54	4.04	5.8	4.02	2.23	14.6	6.9

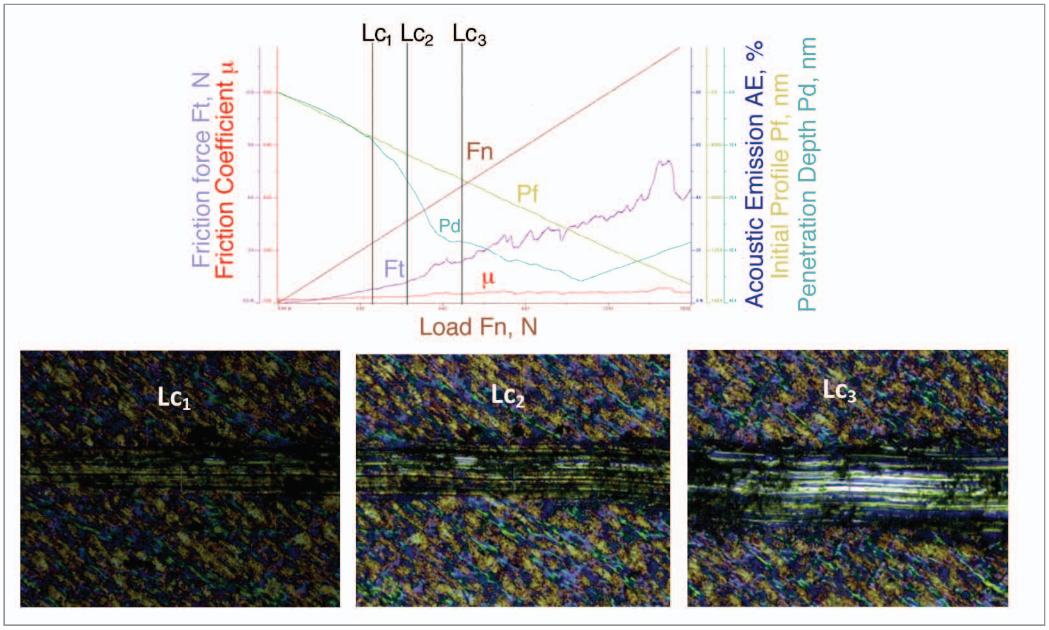

Figure 3. Exemplary test results of the SiO_2 film adhesion (variant 2) to the Ti6Al7Nb alloy substrate

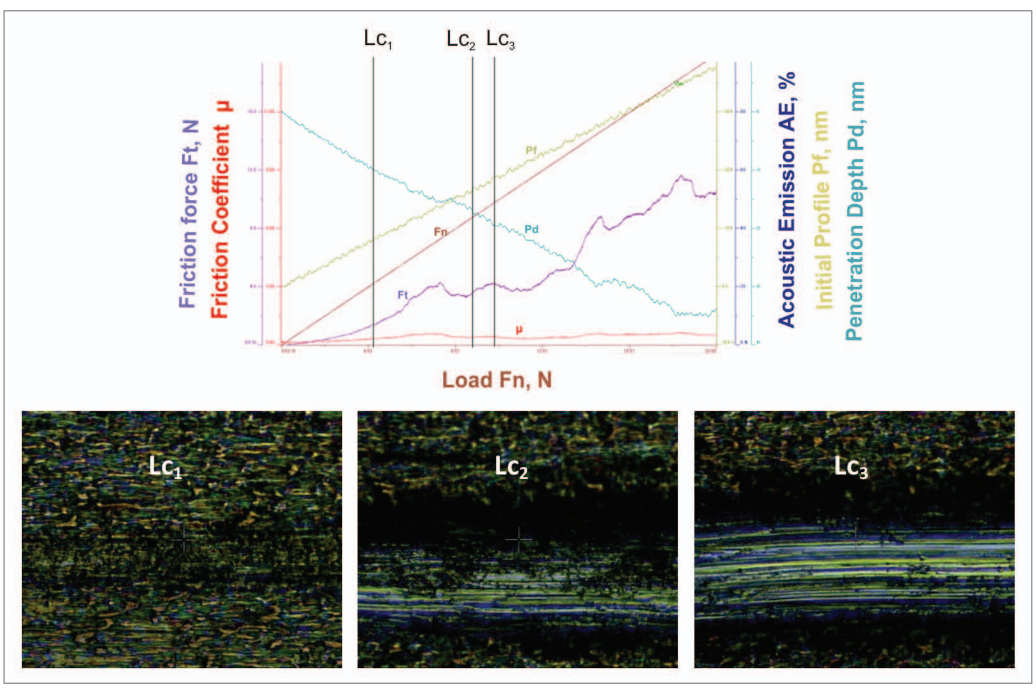

Figure 4. Exemplary test results of the SiO_2 film adhesion (variant 2) to the titanium Grade 4 substrate

Table 3. Results of the EIS test

Surface ---modification	R_s, Ω·cm²	R_{ct}, kΩ·cm²	CPE_{dl}	
			Y_{dl}, $Ω^{-1}cm^{-2}s^{-n}$	n_{dl}
cpTi				
1 (E_{cor} = -142 mV)	72	6940	0.4979E-5	0.92
2 (E_{cor} = -157 mV)	71	18790	0.6280E-5	0.92
3 (E_{cor} = -158 mV)	70	8570	0.6205E-5	0.91
4 (E_{cor} = -185 mV)	68	11980	0.5866E-5	0.93
Ti-6Al-7Nb				
1 (E_{cor} = -114 mV)	69	1920	0.5160E-5	0.91
2 (E_{cor} = -21 mV)	72	11840	0.4323E-5	0.92
3 (E_{cor} = -129 mV)	70	6470	0.4415E-5	0.93
4 (E_{cor} = -98mV)	71	8830	0.4447E-5	0.93

to the specificity of the vascular system. So far, mechanisms of generation and development of these adverse processes have not been discovered. An important issue, in view of the processes of generating and propagating action potentials of cardiac muscle cells, are the electrical and magnetic properties of the used metal biomaterials. Metal implant insertion in the blood vessels must not disturb these processes. Physical properties of the biomaterials have a special meaning due to the possibility of hemostasis process initiation as a result of implant insertion in the vascular system. Literature data indicate that the process of interaction between blood and implant materials has not been fully learned. Currently, different types of surface modifications, in order to improve hemocompatibility of the blood contact implants, become more common. Fundamental criterion of usefulness of a particular surface modification method, is obtaining a product with appropriate functional properties. These properties largely depend on the corrosion resistance in the environment of human blood. Hence, in the paper there was proposed a method of surface modification of the pure titanium Grade 4 and Ti-6Al-7Nb alloy with SiO_2 oxide in the controlled conditions, differentiating the annealing temperature in the range of 400 °C to 500 °C. Efficacy of the proposed technology of SiO_2 layer deposition was evaluated basing on voltammetric and impedance measurements. Supplementarily, in order to determine film adhesion the scratch-test was performed. Regardless of the type of metal substrate, beneficial influence of the surface modification with SiO_2 oxide was observed. Potentiodynamic and impedance tests showed differences in the electrochemical properties of the layers annealed in different temperatures. The most beneficial combination of electrochemical properties had SiO_2 film, annealed in the temperature of t = 430 °C (2). For this film the highest values of the polarization resistance R_p (in potentiodynamic tests) and ion transition resistance (in impedance tests) were obtained, which shows good properties of protecting biomaterials from corrosion environment such as blood. Film adhesion to the substrate is a relevant factor influencing its durability. Hence, critical load measurements were performed, which is a measure of the layer adhesion to the substrate. Also this test showed that the strongest adhesion, regardless of used metal substrate, was demonstrated by SiO_2 layer annealed in the temperature of t = 430 °C (2). For this variant, the force causing layer delamination was the highest and amounted f = 6.5 N for Ti-6Al-7Nb and for the cpTi (Grade 4) it amounted f = 9.6 N.

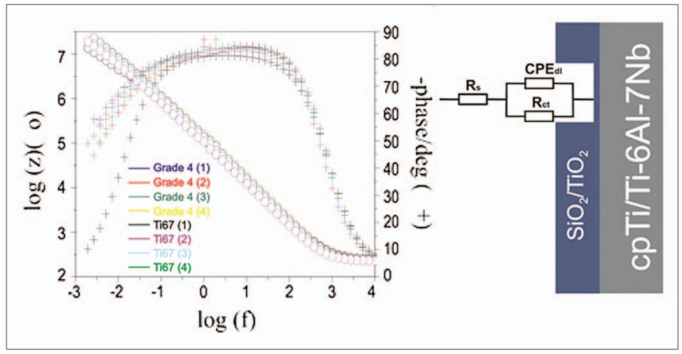

Figure 5. Impedance spectrums cpTi and Ti-6Al-7Nb alloy (Bode diagram)

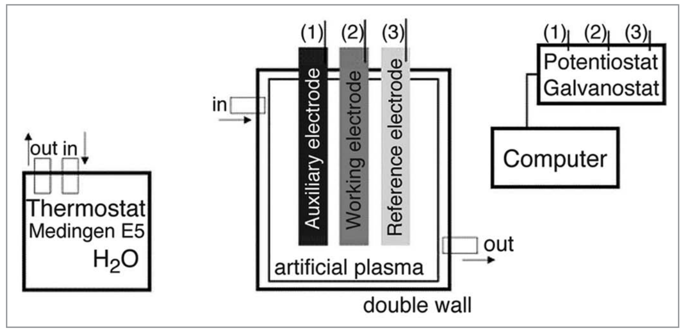

Figure 6. Scheme of the corrosion test

Suggesting appropriate variants of the surface treatment using sol-gel method is perspectively significant, and will contribute to the development of technological conditions with precise parameters of oxide coatings fabrication on the metal implants designed for blood contact, made of titanium alloys.

Materials and Methods

Material for the tests were Ti6Al7Nb alloy and titanium (Grade 4) discs, with diameter d = 14 mm and thickness g = 3 mm and chemical composition presented in **Table 4**.[12,13]

Samples were subjected to surface treatment including: grinding (Ra = 0.40 μm), mechanical polishing (Ra = 0.12 μm) prior to SiO_2 film deposition with sol-gel method (1 – v = 2.5 cm/min, t = 400 °C, t = 60 min, 2 – v = 2.5 cm/min, t = 430 °C, t = 60 min, 3 – v = 2.5 cm/min, t = 460 °C, t = 60 min, 4 – v = 2.5 cm/min, t = 490 °C, t = 60 min). Silicon precursors used in the tests was tetraethyl orthosilicate $Si(OC_2H_5)_4$ (TEOS), and tetramethoxysilane $Si(OCH_3)_4$ (TMOS). The rest of initial components included ethyl alcohol (EtOH) and water. Hydrochloric acid (HCl) was used as a catalyst. In the sol-gel method of film fabrication the following stages are distinguished:[9,11,14-16]

Table 4. Chemical composition of titanium Grade 4 and Ti-6Al-7Nb alloy

Type of material	C	N	O	Fe	H	Al	Nb	Ta	Ti
cpTi (Grade4)	0.05	0.03	0.4	0.4	0.005	-	-	-	rest
Ti-6Al-7Nb alloy	0.008	0.03	0.08	0.22	0.003	6.24	6.84	0.37	rest

1) Production of colloidal suspension (sol), in which used precursor is a dispersed phase and proper alcohol and water are a dispersing phase

2) Complete or partial hydrolysis, which depends on the amount of solvent and presence of catalyst:

$M(OR)_4 + H_2O \rightarrow HO - M(OR)_3 + ROH$ (1)

or

$M(OR)_4 + 4H_2O \rightarrow M(OR)_4 + 4ROH$ (2)

where M, metal atom; R, alkyl group; ROH, alcohol

3) Generation of manomer. Particles that were hydrolyzed earlier may now join together and form a manomer:

$(OR)_2M - OH + OH - M(OR)_2 \rightarrow (OR)_2M - O - M(OR)_2 + H_2O$ (3)

or

$(OR)_2M - OH + OH - M(OR)_2 \rightarrow (OH)_2M - O - M(OR)_2 + ROH$ (4)

4) Gel is formed as a result of manomer polymerization and growth of particles, which join together forming chains and then networks

5) Deposition of sol layer on a substrate

6) Drying and annealing of deposited layers

A condensation reaction begins before the end of hydrolysis. Proportions of initial elements used, type and amount of catalyst used as well as parameters characterizing particular stages of the process influence the properties of obtained films.[16]

One of the methods of verifying usefulness of this kind of surface modification are electrochemical tests. For this purpose, potentiodynamic and impedance test were performed to determine corrosion resistance (**Fig. 6**).[17–20]

Potentiodynamic tests were performed in accordance with PN-ISO 17475 recommendations. Polarization curves were recorded using Radiometer PGP-201 potentiostat. Saturated calomel electrode (SCE) type KP-113 was used as a reference electrode. Platinum electrode PtP-201 was an auxiliary electrode. At the beginning of the study, open-circuit voltage E_{OCP} under zero current conditions was measured. Then, anodic polarization curves were recorded. Measurements began when voltage came to $E_{POCZ} = E_{OCP} - 100$ mV, with voltage change in anode direction at a rate of 3 mV/s. When the anode current density reached i = 1 mA/cm^2, polarization direction was changed and return curve was recorded. To designate parameters characterizing corrosion resistance of tested materials, Stern method was also used.

In order to obtain additional information about physicochemical properties of analyzed samples' surfaces, tests using electrochemical impedance spectroscopy were conducted. Measurements were performed using Auto Lab PGSTAT 302N measurement system, equipped with FRA2 module (Frequency Response Analyzer). Used measurement system enabled to conduct studies in the frequency range $10^4 \div 10^{-3}$ Hz. In the studies, impedance spectrums of the circuit were determined and obtained measurement data was matched to the equivalent circuit. On this basis, numerical values of resistance R and capacity C of analyzed circuits were determined. Impedance spectrums of the studied circuit were presented in a form of Nyquista diagrams for different frequency values, and in a form of Bode diagrams. Obtained EIS spectrums were interpreted after matching, using least squares method, to the equivalent electrical circuit.

Table 5. Chemical composition of artificial plasma

Ingredients	Ingredients concentration. g/dm^3 distilled water
NaCl	6.800
$CaCl_2$	0.200
KCl	0.400
$MgSO_4$	0.100
$NaHCO_3$	2.200
Na_2HPO_4	0.126
NaH_2PO_4	0.026

All electrochemical tests were performed in simulated body fluid at the temperature of t = 37 ± 1 °C and pH = 7,0 ± 0.2 (**Table 5**).

Additionally, authors of the paper attempted to evaluate mechanical properties of films deposited with this method by testing adhesion to the titanium Grade 4 and Ti6Al7Nb alloy substrate. Adhesion tests of the deposited films were performed with a scratch test, using open platform equipped in CMS Micro-Combi-Tester in accordance with standard.[21] The test was based on generating a scratch using a penetrator—Rockwell diamond cone—with a gradual increase in the normal force loading the penetrator. Critical load, which is a measure of adhesion, is the lowest normal force which leads to the loss of the layer adhesion to the substrate. To evaluate a critical load Lc, record of acoustic emission signals changes were used, as well as friction force and friction factor and microscopic observations under an optical microscope, which is an integral part of the platform. Acoustic emission AE, also called stress-wave emission is defined as an elastic wave generated by release of an internally stored energy from the structure of material. AE detection can be recorded during scratch-test, only if the energy of the bond between layer and the substrate is high enough. As a result of damage generation and propagation during scratch-test, stress wave impact occurs, which leads to the spectrum signal emission, which amplitude corresponds to the damage generated in the interfacial layer-substrate area. Thus, the acoustic signal includes information about sizes and amount of damages. Tests were performed using increasing loading force at the range of 0.03 ÷ 30 N and following operation parameters—loading speed 100 N/min, speed of the table displacement 10 mm/min, length of the scratch ~3 mm.

Disclosure of Potential Conflicts of Interest

No potential conflicts of interest were disclosed.

Acknowledgments

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