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SURFACE MODIFICATION OF STAINLESS STEEL INTRAMEDULLARY NAILS TO IMPROVE ADHESION OF POLYMERIC COATINGS

MODYFIKACJA POWIERZCHNI STALOWYCH GWOŹDZI ŚRÓDSZPIKOWYCH W CELU POPRAWY ADHEZJI POWŁOK POLIMEROWYCH

The aim of the study was to develop a method of surface modification of steel AISI 316L to improve polymeric coatings adhesion. Two methods were used: etching by solution of H_2SO_4 and H_2O_2 "piranha" and cathodic sputtering. The change of the surface topography and chemical composition were analyzed using optical profilometer and scanning electron microscope. The impedance electrochemical method and polarization method were used for corrosion resistance measurement. The scratch test was performed to assess adhesion of the polymer to the steel. The results show that after both modifications the surface roughness and polymer adhesion increase. However, significant decrease of steel corrosion resistance were observed after etching. In comparison the cathodic sputtering had a small influence on corrosion resistance of the steel.

Keywords: stainless steel, surface modification, corrosion resistance, polymeric coatings, adhesion

Celem pracy było opracowanie metody modyfikacji powierzchni stali AISI 316L w celu zwiększenia adhezji powłok polimerowych. Zastosowano dwie metody modyfikacji: trawienie roztworem H_2SO_4 i H_2O_2 tzw. „piranią” oraz proces rozpylania katodowego. Wpływ modyfikacji na topografię i skład chemiczny powierzchni oceniano przy użyciu profilometru optycznego oraz skaningowego mikroskopu elektronowego. Odporność korozyjną badano metodami impedancyjną i potencjodynamiczną. Do oceny przyczepności wykorzystano test zarysowania. Otrzymane wyniki wykazały, ze zastosowane modyfikacje powierzchni stali powodują wzrost jej chropowatości, i wynikający z tego wzrost przyczepności powłok polimerowych. Jednocześnie obserwowano zmiany w odporności korozyjnej stali. Trawienie spowodowało spadek odporności korozyjnej, natomiast rozpylanie katodowe tylko nieco zmieniło odporności korozyjną

1. Introduction

The common used method for stabilization of the long bones fractures is intramedullary nailing. This fixation method is often associated with complications, e.g. infections in treatment area [1-3]. Then pharmacologic treatment is necessary. The best results can be achieved by local drug release, directly to the healing zone. For this purpose an implant, which allows for simultaneous local drug release and good fixation is needed.

The idea of local drugs release is not new. In the literature, there are many papers describing novel polymeric drugs carriers and kinetics and mechanisms of local drugs release[4-5]. One of the metallic implant which is able to delivery drug locally is vascular stents coated with polymeric layer [6]. This polymeric layer plays a role of drug carrier. Similar idea could be applied to develop a novel drug-eluting intramedullary nail. For developing such a stent intramedullary nails, good adhesion of the polymeric coatings to the metal surface is required. If the coating doesn't adhere strong enough, then high risk of the coating failure during nail implantation exists. Improvement of polymeric coatings adhesion to the steel can be achieve by different methods, e.g. by roughness increase, plasma treatment, phosphatizing or using the adhesion promoters [7-8]. Of course these modification shouldn't decrease the corrosion resistance and biocompatibility of the implant.

The intramedullary nails mainly are fabricated from two types of metals: stainless steel 316L and titanium alloy Ti6Al4V[9]. Economical aspects cause that more often stainless steel nails are used. Therefore, in this paper, the stainless steel surface was modified to improve polymer adhesion. Two modification were performed:

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etching by "piranha" solution and cathodic sputtering. The electro-polished surface were used as a reference sample.

2. Materials and methods

2.1. Sample preparation

Widely applied in medicine stainless steel 316L was used in this study. The initial form of the material was rod with diameter of 20mm. The samples were prepared in the format small cylinder Ø20x2. They were grinded using the abrasive papers (with grit increases from 240 to 1000). Then electro-polishing was performed in electrolyte STRUERS A2 (solution of ethanol, 3-botoxyethanol, perchloric acid and water) at room temperature. The current density was 1A/cm2 and time of process of about 2 minutes.

2.2. Surfaces modification

Three groups of samples were prepared. The first group (I) consisted of non-modified samples (reference group). The second group of samples (II) was etched in "piranha" solution ($H_2SO_4:H_2O_2$ v/v 2:1) at 80°C during 25min. The last group (III) consisted of samples modified with cathodic sputtered in glow-discharge condition. In the working chamber mixture of argon and nitrogen (1:1) under 1mbar pressure was used.

2.3. Characterization of the surfaces

Roughness measurements, microscopic observation, chemical composition analysis and corrosion tests were performed to characterize the prepared samples. The surface roughness was measured using optical profilometer Wyko NT9300 (Veeco). Microscopic observations and chemical composition analysis were done by scanning electron microscopes Hitachi TM1000 and Hitachi 2600-N. The corrosion behavior was analyzed using electrochemical impedance spectroscopy (EIS) and DC polarization techniques. Both tests were done at temperature 37°C in 0.9%NaCl solution using AutoLab PG-STAT100 system. EIS was performed between 10^{-3} Hz and 10^5 Hz frequency range. All curves were normalized to 1 cm^2. DC polarization tests were made in potential range from -250 mV to 1500 mV at a scan rate of 0.1 mV/s (over 500 mV, it was 0.8 mV/s).

2.4. Polymer coating preparation

Polymer coatings on steel samples were prepared by dipping method. The biodegradable polymer poly(L-lactide) (PLLA Biomer®, molecular mass 200kDa) was used. 8% solution PLLA/chloroform was prepared by dissolving of PLLA granulate in chloroform in closed bottle at constant temperature of 45°C. Before coatings deposition metallic samples were cleaned in the ultrasonic washer in the water with addition of detergent for 5min and next in acetone for 10min. After cleaning and drying in air the samples were dipped for 10sek in the polymer solution, then slowly (about 1mm/sek) taken out. The coated samples were left for slow drying in air for one week.

2.5. Coatings adhesion measurement

Before adhesion tests the thickness of the coatings was measure with using optical profilometer. Polymer adhesion was estimated using scratch test, performed using CSEM REVETEST device.

3. Results and discussion

Surface modification was evaluated by two methods: roughness measurements and microscopic observations. During roughness measurement two parameters were measured: R_a and R_z (Tab.1). The results have shown that applied modifications increase the surface roughness. The highest values of roughness parameter (R_a=1.05-1.66 µm, R_z=6.01-10.93 µm) were obtained for samples etched by "piranha" (group III). Surface after cathodic sputtering (III) was characterized by few times lower roughness (R_a=106.2-164.6 nm, R_z=2.39-2.63 µm). The most smooth were electro-polished samples. These results were in agree with microscopic observation (Fig.1).

TABLE 1

Samples surfaces roughness

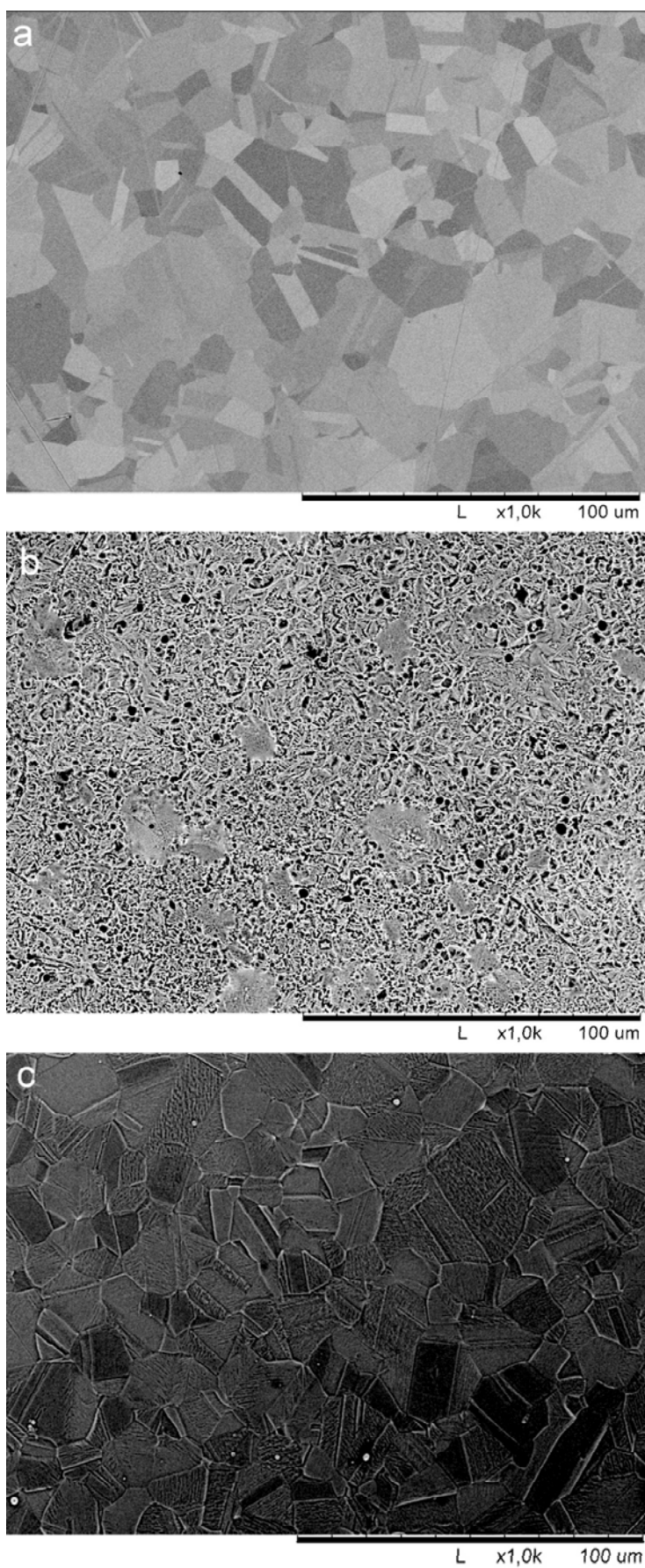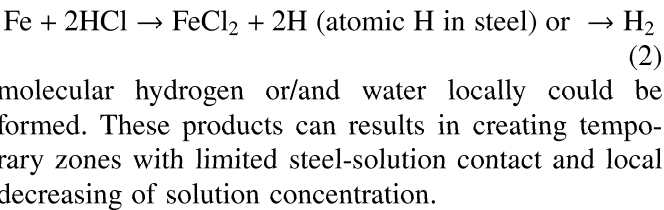| Samples group	R_a[nm]	R_z[µm]
I	4.9÷7.4	0.078÷0.085
II	1050÷1660	6.01÷10.93
III	106.2÷164.6	2.39÷2.63

Fig. 1. SEM images of the samples surfaces: a) non-modified, b) etched by"piranha", c) cathodic sputtered

SEM images of the polished samples have shown smooth surface with only few shallow scratches. The samples after modifications had totally different topography. After cathodic sputtering the samples had developed surfaces with etched grains boundaries. This is the effect of bombing of the surfaces by argon and nitrogen ions and diffusion process proceed on the defected surface layer. Surfaces after etching were irregular. There were deep etched areas (very porous), but also zones, where the etching wasn't so effective. This is the effect of the steel properties and process proceeding. During etching, as the results of chemical reaction, e.g.:

$$FeO + H_2SO_4 \rightarrow FeSO_4 + H_2O \qquad (1)$$

$$Fe + 2HCl \rightarrow FeCl_2 + 2H \text{ (atomic H in steel) or } \rightarrow H_2 \qquad (2)$$

molecular hydrogen or/and water locally could be formed. These products can results in creating temporary zones with limited steel-solution contact and local decreasing of solution concentration.

Influence of the applied surface modifications on the chemical composition of the surface layer was analyzed using SEM EDS Hitachi 2600-N. The results are shown in table 2.

TABLE 2

Samples chemical composition

Element	Group I (non-modified)	Group II (etched)	Group III (cathodic sputtered)
	Mass [%]	Mass [%]	Mass [%]
Fe	70.21	68.61	61.10
Cr	17.66	16.20	15.20
Ni	9.11	10.50	9.52
Mo	1.71	1.98	1.85
Mn	1.31	2.29	1.91
N	–	–	9.84

As it is shown, etching only in small degree changed the chemical composition. During the process surface was oxidized, but the oxygen contents was omitted in the table 2. The cathodic sputtered samples have high content of nitrogen. This is a result of diffusion processes during sputtering.

Corrosion resistance is very important issue for implants. Therefore the corrosion tests of the samples were performed. The EIS test (Fig.2) shows that for non-modified stainless steel 316L exists one time-constant. It means that one electrochemical process was observed at the surface (electron exchange through double layer). Durability of the passive layer on steel surfaces is high. The values of resistance (Rt=1.1 MΩcm^2) and capacity (0.4-0.5e-5 F/cm^2) proved that. The high resistance also indicates high corrosion resistance of stainless steel.
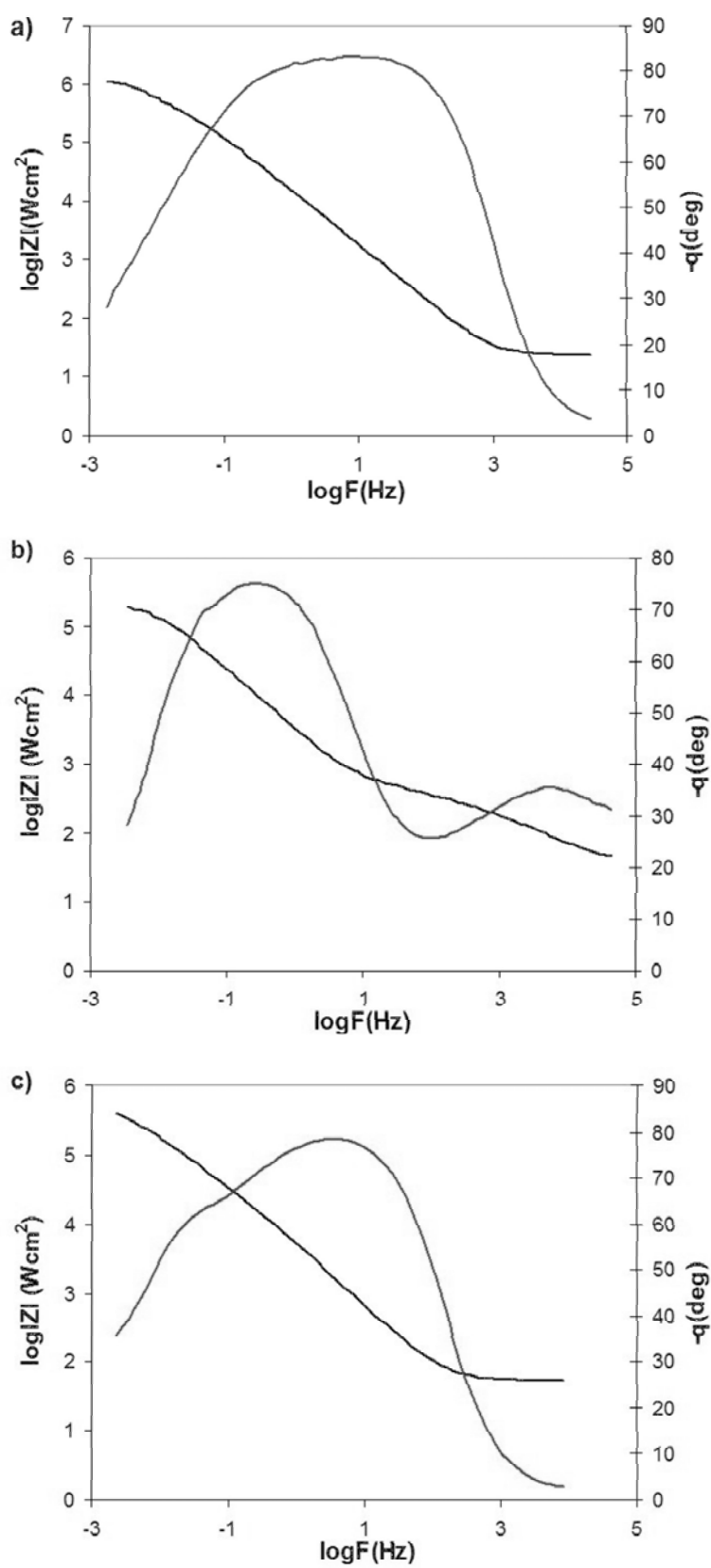
Fig. 2. Bode plots of sample immersed in 0.9%NaCl: a) non-modified, b) etched by "piranha", c) cathodic sputtered

Different EIS spectra were obtained for the modified samples. There was observed an additional peak. In the case of the samples etched by "piranha" the additional peak is connected with diffusion processes (α_{CPE}=0.5) which proceeded at surfaces, while for the samples after sputtering both processes occur in the metallic layer (α_{CPE} equal 0.88 and 0.92). First of them is connected with electrons exchange through double layer (iron oxidizing). Second one describes corrosion resistance of surface layer. The surface modifications decrease the corrosion resistance, two times (Rt=0.5 MΩcm^2) in the case of cathodic sputtering and four times (Rt=0.24 MΩcm^2) for etching.

DC polarization test also were performed (Fig. 3).

The stainless steel is in passive state. The sudden increase of current density, corresponded to potential 240 mV (breakdown potential), is a result of pitting corrosion initiation. This is typical for austenitic steel in chloride solution. In the rest cases uniform corrosion occurs and the process proceed faster than for non-modified samples. For the etched sample the corrosion potential is much lower (-100 mV) than for sputtered (30 mV) and non-modified samples. The corrosion current (corrosion rate) increases in the following order: electro-polished samples< cathodic sputtered samples <samples etched by "piranha" (0.04 μA/cm^2 <0.13 μA/cm^2 <0.81 μA/cm^2).
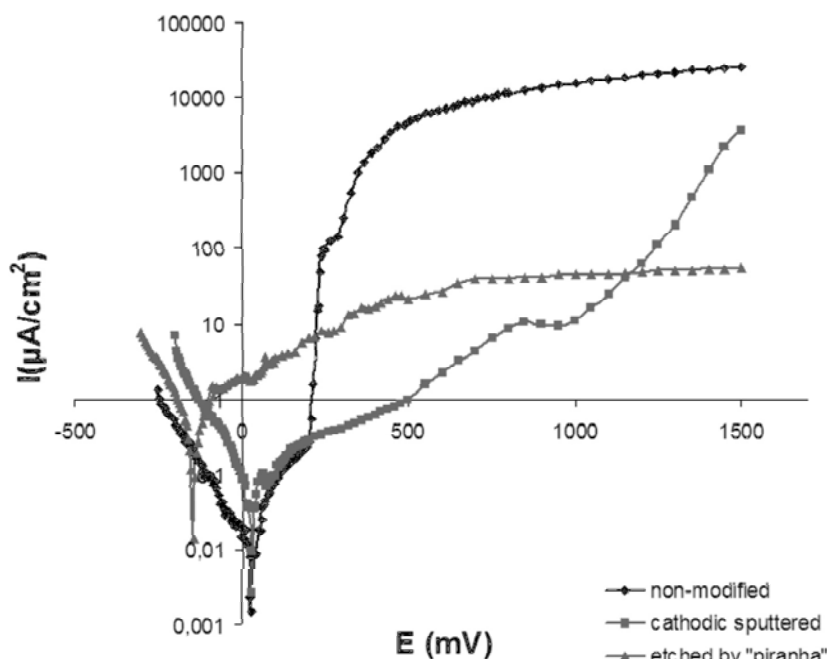

Fig. 3. Polarization curves of sample immersed in 0.9%NaCl: a) non-modified, b) etched by "piranha", c) cathodic sputtered

The polymeric coatings on the steel were performed by dipping of the samples in 8% solution PLLA/chloroform. The prepared coatings had smooth surface and were homogenous. The range all of coatings thickness was between 8 and 10 μm. The polymeric coatings adhesion measurements were used to evaluate the applied surface modifications methods. The adhesion was measured using scratch test (Fig.4). The scratch length was 10 mm, the load increased from 0 to 100 N during scratching.
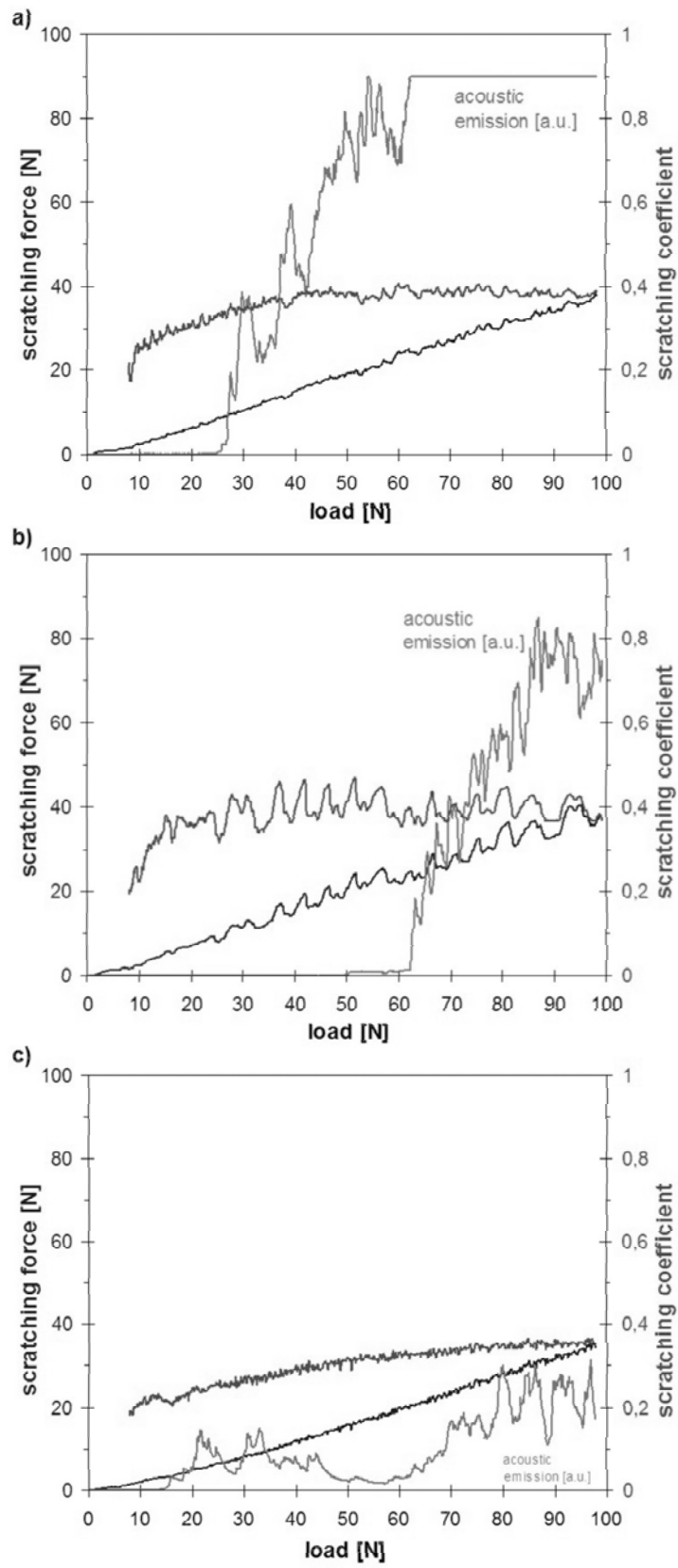
Fig. 4. Plots of scratching results and images of scratched samples : a) non-modified, b) etched by "piranha", c) cathodic sputtered

The plots of scratching force and scratching coefficient don't show the moment of coatings damage. Therefore, the adhesion evaluation was based on the acoustic emission curves and images of the scratches. The best adhesion was observe at etched sample – increase of the acoustic emission correspond with load 62 N, (for the electro-polished sample the load was only 27 N). For the cathodic sputtered sample two peaks of acoustic emission were registered, for loads 20 N and 67 N respectively. These results were ambiguous. Therefore, the analysis of scratch image was necessary. As it is shown at figure 4c, there were two stages of coatings damage. These stages correspond with peaks of acoustic emission. The comparison of all scratches images (areas free from coatings) have shown that the adhesion of the polymer coatings increase in the following order: samples etched by "piranha" > samples after cathodic sputtering > non-modified samples. These results are related to the roughness results. The increase of surface roughness results in increase of adhesion.

4. Conclusions

The paper described the methods of improving adhesion of polymeric coating to metallic nail. The two proposed surface modifications methods allow for obtaining developed surfaces. The surface roughness increased 20 times (Ra) after cathodic sputtering, and 200 times after etching in comparison to the non-modified samples. Ra increase resulted in better polymeric coatings adhesion. The adhesion is stronger if the surface development is bigger. However, significantly decrease of the corrosion resistance of the metallic samples were observed after etching. The cathodic sputtering decreases the corrosion resistance of the steel just a little. Therefore, the future study should be concentrated on optimization of this process in order to avoid its negative effect on corrosion resistance.

REFERENCES

[1] C-W. O h, B-C. P a r k, J-C. I h n, H-J. P a r k, Int Orthop **24**, 338 (2001).

[2] B. H. Z i r a n, M. D a r o w i s h, B. A. K l a t t, J. F. A g u d e l o, W. R. S m i t h, Int Orthop **28**, 235 (2004).

[3] K. Y o k o y a m a, M. U c h i n o, K. N a k a m u r a, H. O h t s u k a, T. S u z u k i, T. B o k u, M. I t o m a n, Injury, Int J Care Injured **37**, 554 (2006).

[4] A. L. L e w i s, T. A. V i c k, A. C. M. C o l l i a s, L. G. H u g e s, R. R. P a l m e r, S. W. L e p p a r d, J. D. F u r z e, A. S. T a y l o r, P. W. S t r a t f o r d, J. Mater Sci: Mater Med **12**, 865 (2001).

[5] J-P. X u, J. J i, W-D. C h e n, H-F. Z h a o, J-C. S h e n, J Mater Sci: Mater Med **15**, 137 (2004).

[6] S. E. B u r k e, R. E. K u n t z, L. B. S c h w a r t z, Adv Drug Deliv Rev **58**, 437 (2006).

[7] J. C o g n a r d, C. R. C h i m i e **9**, 13 (2006).

[8] P. K. S i n h a, R. F e s e r, Surf Coat Technol **161**, 158 (2002).

[9] J. M a r c i n i a k, W. C h r z a n o w s k i, A. K r a u z e, Intramedullary nailing in osteosynthesis, Monograph, WPŚl., Gliwice (2006).