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Effect of silica precursors-type on mechanical properties of sol-gel coatings

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Reversion to narrowing, called restenosis, still remains an important problem of coronary angioplasty. Analysis of the problem revealed that the application of surface layers aimed at creating on the stent surface a neutral barrier between its metallic framework and tissues of the blood-vascular system is decidedly best to impede the restenosis. They also play the role of medicine carriers. This article presents a new sol-gel technology, to be applied in coronary stent coatings. Currently, this is one of the most progressive methods allowing the modification of surface layers of metallic biomaterials. The results presented prove that due to a proper selection of silica precursors it is possible to obtain continuous, smooth, plastic deformation-resistant sol-gel coatings, which additionally are characterised by very close adherence to the base material, nanometer thickness and low degree of surface development.

Key words: coronary stents, sol-gel technology, silica precursor

1. Introduction

The diseases of the vascular-heart system come to the fore in the statistics of diseases and deceases of the present century. In Poland, the heart ischemic disease afflicts almost one million inhabitants and results in ca. 90 thousands deaths a year. The currently applied method of coronary angioplasty does not assure a 100-per cent effectiveness of treatment, since it is associated with the reversion into narrowing, called restenosis, which affects 15 to 30% of the patients subject to this treatment [1], [2]. The analysis of the problem proved that the application of surface layers aimed at creating on the stent surface a neutral barrier between its metallic framework and tissues of the blood-vascular system is decidedly best to impede the restenosis. They also play the role of medicine carriers [3], [4].

Over recent years, a growing interest in applying non-metallic materials for the implants used in operative cardiology can be observed. Nowadays, the most popular are synthetic non-biodegradable polymers (polyurethane, silicone, polyethylene terephtalate) and biodegradable polymers (among others, lactic polyacids and polyglycolide) [3], [5]. Recently, extensive research is also conducted on the application of amorphous silicon carbide and DLC-type layers [6], [7]. A great progress in the treatment of an early and late thrombosis as well as of the secondary narrowing of coronary vessels was achieved by using stents which release medicines. Athrombogeneous and antiphlogistic substances can be introduced to polymeric coatings of the stents to be released to the blood vessels after implantation. The results of clinical trials indicate that this is one of the most important achievements in operative cardiology since the introduction of implants to restore patency [8], [9].

This work presents a new sol-gel technology to be applied in coronary stent coatings. The technology is based on a chemical synthesis of inorganic and non-metallic materials (ceramic materials). It consists in

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preparing colloidal solutions (sols) by electrolysis and condensation of the precursors applied. An advanced condensation process combined with solvent evaporation allows gels to be obtained. The metallic implants are covered with sol-gels which after burning become ceramic coatings [10], [11], see figure 1.

Fig. 1. Sol-gel method

The sol-gel method permits some surfaces of various, even very complicated shapes, to be coated with thin sol-gel layers. Based on an available information on this technology it may be inferred that the coatings can be modified in different ways in order to obtain their expected roughness and porosity. Making use of proper precursors it is possible to modify the microhardness and mechanical properties of coatings [12]. The sol-gels can be also doped with compounds which change the coating parameters, e.g., biocompatibility or athrombogeneity. Moreover, this method reveals many valuable features, e.g., full microstructure control, low temperature of the process and the possibility of applying the coatings as both one- and multicomponent or one- and multilayer [12], [14].

The sol-gel technology is currently widely applied in the manufacture of optical, electronic, porous and protective coatings [10], [12], [15]. The interest in this technology has also grown in the field of preparing surface layers designed for implants, e.g., dental, orthopaedic and traumatologic implants [16]–[18].

The researchers from various scientific centres try to solve the problems they still encounter during the sol-gel synthesis of coatings for osseous implants. Considering dynamic development of this technology and the results of currently conducted research on osseous implants, it can be inferred that the coatings synthesised by this method can be applied in the manufacture of surface layers designed for coronary stents and, in addition, the coating obtained by this technology can make a matrix releasing medicines to the coronary circulatory system.

2. The purpose and methodology of the research

The research was aimed at determining the quality of silica layers obtained by the sol-gel method, their resistance to plastic deformation, adhesion to the base and thickness, as well as at assessing the influence of the layers on surface roughness of steel specimens.

Microscopic examination of steel specimens covered with the sol-gel coatings was carried out using a scanning electron microscope JEOL 5800LV at magnifications from 500× to 5000×. The specimens were subjected to microscopic examination before and after plastic deformation being the result of static tensile test with a testing machine MTS 810.

The adherence of the coatings to the base was evaluated by the cross-cutting method according to EN ISO 2409. The examination procedure consisted in making cuts in two perpendicular directions and next in performing the pull-off test using a special adhesive tape. A six-blade cutter was used in this test. After the test, the adherence of the layers was evaluated by macro- and microscopic examinations. Thickness measurements of the silica coatings were carried out by multi- and two-beam interference methods, at magnification of 500×. To avoid edge non-homogeneities, the analysis was performed in the area between 1/3s and 2/3s, where s is the plate width.

The examination of surface topography of the sol-gel layers obtained was conducted by contactless laser method using a profilometer UBM. The measurements were carried out three times for a clean sample and for the samples whose 5-mm segments were coated with the sol-gel layer. The specimens were subjected to examination before plastic deformation.

3. Object of examination

To prepare the silica sol-gel coatings, three types of precursors were used: tetraethyl orthosilicate (TEOS), diethoxydimethylsilane (DEMS) and vinylotrieth-oxysilane (VTES). Sols were obtained by mixing, at various molar ratios, two precursors together with ethyl alcohol and hydrochloric acid, see table 1. Specimens were prepared of AISI 316L steel in the form of plates (70 mm × 9 mm × 1 mm). Before applying the surface layers, the outside surfaces were mechanically ground

and polished in order to remove the pickled layer remaining after previous operations.

Table 1. Molar compositions of initial solutions – sols

Sample	TEOS [ml]	VTES [ml]	DEMS [ml]	EtOH [ml]	HCl [ml]
1	7	3	–	20	0.05
2	5	5	–	20	0.05
3	3	7	–	20	0.05
4	–	3	7	20	0.05
5	–	5	5	20	0.05
6	–	7	3	20	0.05

The coatings were obtained by dip coating method of the steel specimens in the sol at a constant speed of 30 mm/min. Next, the specimens were dried for 48 hours in quiet air and burnt for 1 hour at 500 °C. The burning temperature was so selected that no precipitation of $M_{23}C_6$ carbides occurred in steel (precipitation range from 600 to 900 °C) but, at the same time, hydroxyl and organic groups were removed from the coating material [19], [20]. In the case of coatings for medical implants, all the organic "residues" could start toxic, mutagenic or immunologic reactions which lead to the implant rejection [11], [21].

4. Results of experiments

Microscopic examination of the specimen surfaces revealed no negative influence of plastic deformation on the quality of the silica coatings synthesized. After plastic deformation simulating working conditions of real coronary stents, all the sol-gel layers analysed were still continuous (figures 2–5). Even slip lines and bands appearing during tension caused neither the coating cracking nor spalling. At the same time, microscopic examination showed in all silica layers some defects in the form of numerous, uniformly distributed pores with the diameters ranging from 0.6 to 0.8 μm.

The results of mechanical testing of the adhesive joint revealed the close adherence of the silica sol-gel layers to the steel base. The edges of the cuts were completely smooth both in the macro- and micro-scale. Neither cracks nor spalls were observed in any area, but only uniform wear of the coating (figures 6–9).

The averaged results of the thickness measurements performed ten times revealed nanometric layers on the steel bases. The thickness of all the silica coatings under examination was similar and approached 60 nm. The results are given in table 2.

The topography of the steel specimens coated with silica layers is presented in the form of two-dimensional profilograms. The curves obtained according to DIN 4776 are characterised by small development degree with respect to the results obtained for the uncoated steel specimens (see figures 10 and 11). In the profilograms analysed, the pores, observed previously in microscopic examination, and fine scratches left after grinding and polishing operations are clearly visible.

Additionally, in order to describe quantitatively the results of roughness measurements, the averaged values of selected geometrical parameters are shown in table 3. The parameters are determined according

Table 2. Results of thickness measurements of silica sol-gel layers

Series	Sample					
	1	2	3	4	5	6
1	72.4 nm	28.2 nm	67.0 nm	61.1 nm	44.5 nm	64.4 nm
2	59.3 nm	47.8 nm	72.8 nm	41.6 nm	39.0 nm	65.1 nm
3	46.6 nm	51.5 nm	39.0 nm	36.7 nm	43.4 nm	72.8 nm
4	74.5 nm	69.3 nm	43.4 nm	53.7 nm	63.9 nm	94.5 nm
5	49.0 nm	78.0 nm	63.9 nm	47.6 nm	57.4 nm	51.9 nm
6	43.4 nm	73.8 nm	67.0 nm	81.4 nm	88.6 nm	88.6 nm
7	63.9 nm	49.6 nm	72.8 nm	71.8 nm	53.6 nm	53.6 nm
8	53.2 nm	51.7 nm	57.4 nm	67.0 nm	67.0 nm	54.2 nm
9	63.3 nm	45.5 nm	88.6 nm	72.8 nm	72.8 nm	43.8 nm
10	60.7 nm	64.3 nm	53.6 nm	57.4 nm	53.6 nm	47.2 nm
d	58.6 nm	55.9 nm	62.6 nm	59.1 nm	58.4 nm	63.6 nm

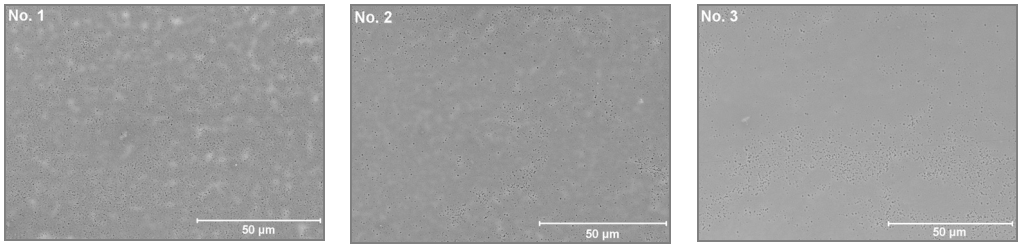


Fig. 2. Surface of AISI 316L steel specimens coated with sol-gel layers No. 1 to 3 before deformation. The defects in the form of numerous uniformly distributed pores are visible. SEM

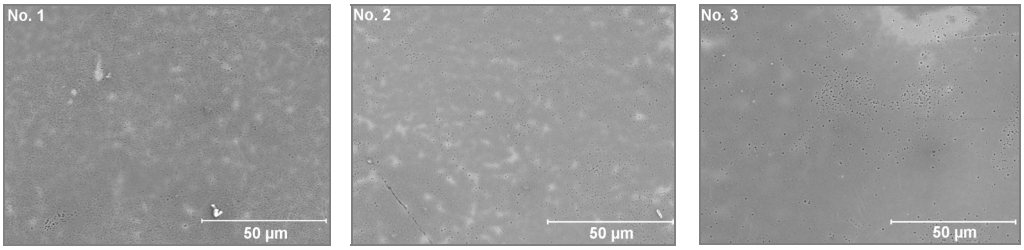


Fig. 3. Surface of AISI 316L steel specimens coated with sol-gel layers No. 1 to 3 after deformation. The slip lines and bands created during tension are visible under the coatings. SEM

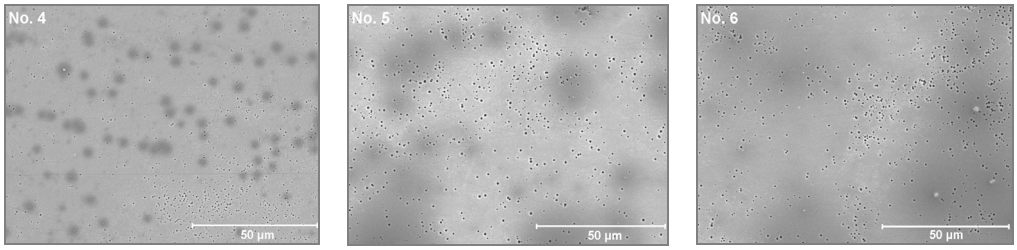


Fig. 4. Surface of AISI 316L steel specimens coated with sol-gel layers No. 4 to 6 before deformation. The defects in the form of numerous uniformly distributed pores are visible. SEM

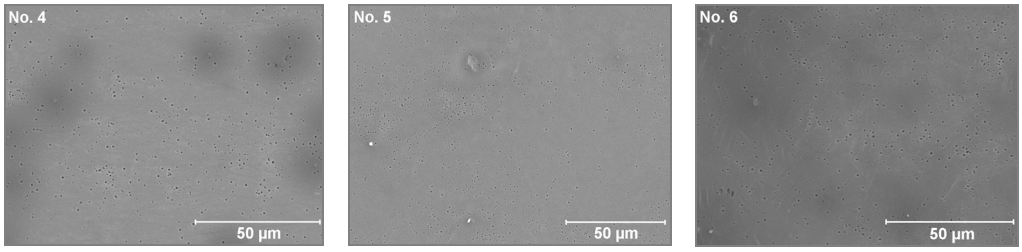


Fig. 5. Surface of AISI 316L steel specimens coated with sol-gel layers No. 4 to 6 after deformation. Slip lines and bands created during tension are visible under the coatings. SEM

Table 3. Some selected geometrical parameters of the surface layers obtained

Samples	R_a [µm]	R_q [µm]	R_z [µm]
pure steel	0.040	0.057	0.530
1	0.093	0.120	0.736
2	0.087	0.097	0.663
3	0.043	0.057	0.423
4	0.050	0.077	0.607
5	0.067	0.083	0.577
6	0.060	0.087	0.593

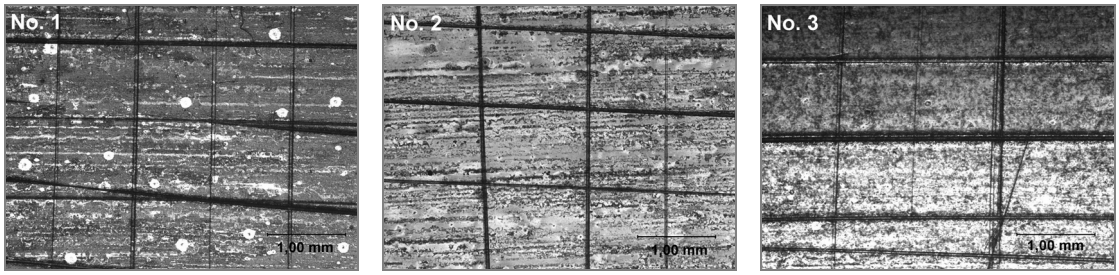


Fig. 6. Macroscopic view of AISI 316L specimens coated with sol-gel layers No. 1 to 3 after adherence testing

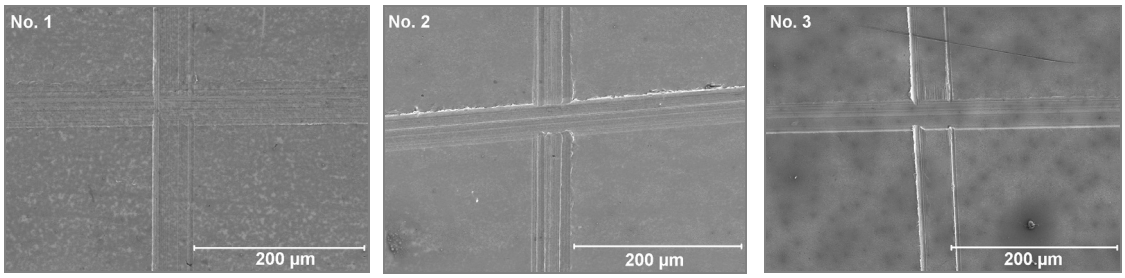


Fig. 7. Surface of AISI 316L specimens coated with sol-gel layers No. 1 to 3 after adherence testing. No sign of cracking proves good adherence to the base. SEM

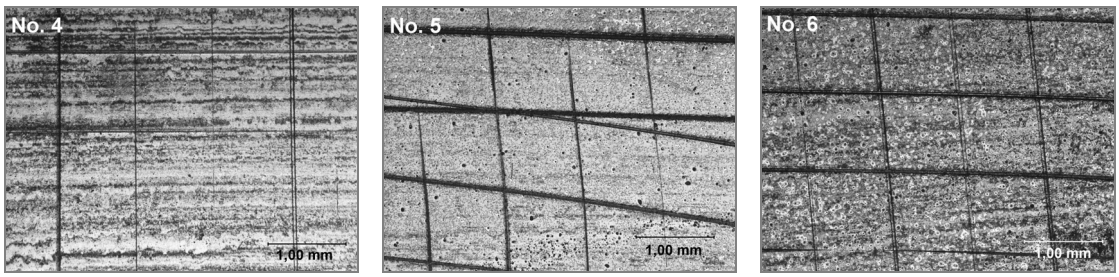


Fig. 8. Macroscopic view of AISI 316L specimens coated with sol-gel layers No. 4 to 6 after adherence testing

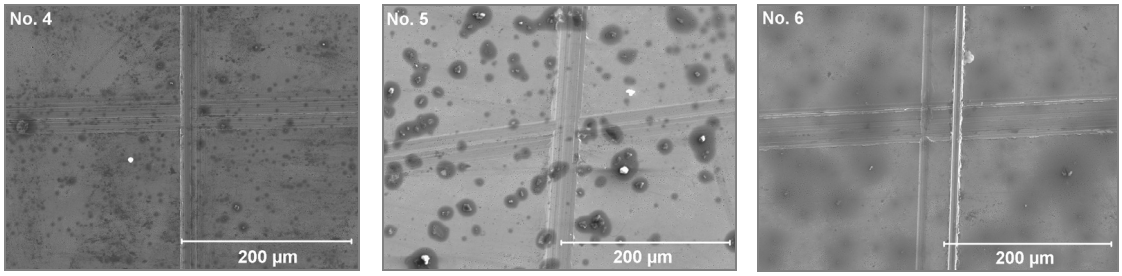
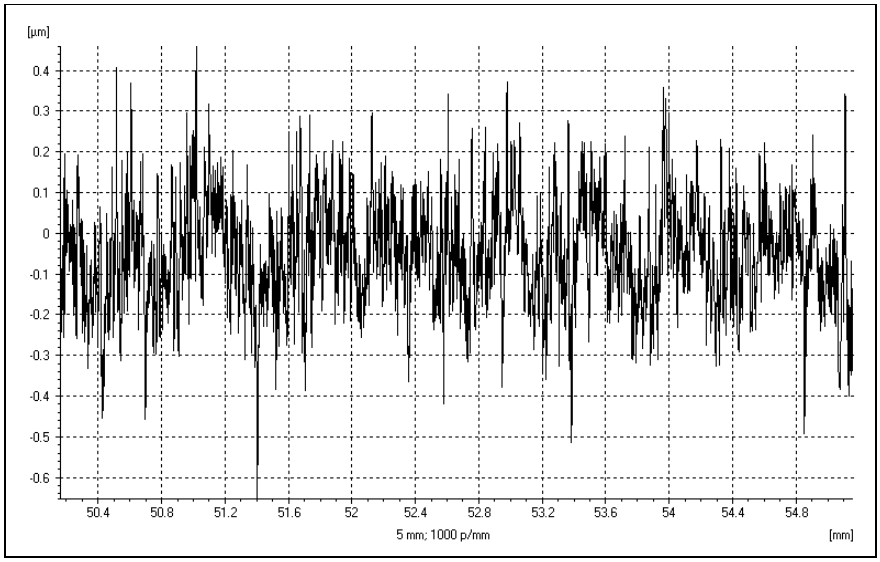


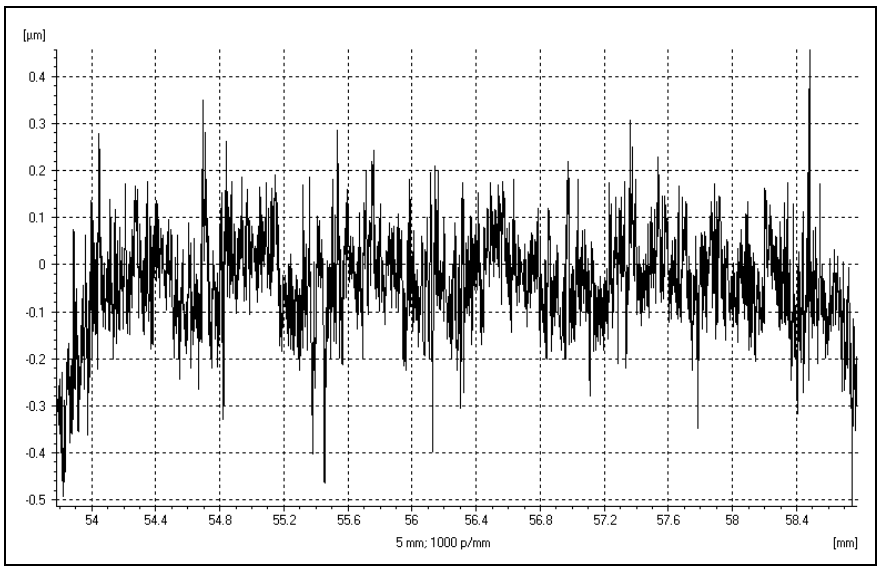
Fig. 9. Surface of AISI 316L specimens coated with sol-gel layers No. 4 to 6 after adherence testing. No sign of cracking proves good adherence to the base. SEM

to DIN 4776. To evaluate the surface roughness of the two-dimensional measurements, the following quantities were selected: the arithmetic average roughness R_a, the root mean square roughness R_q, the 10-point height of roughness profile R_z.

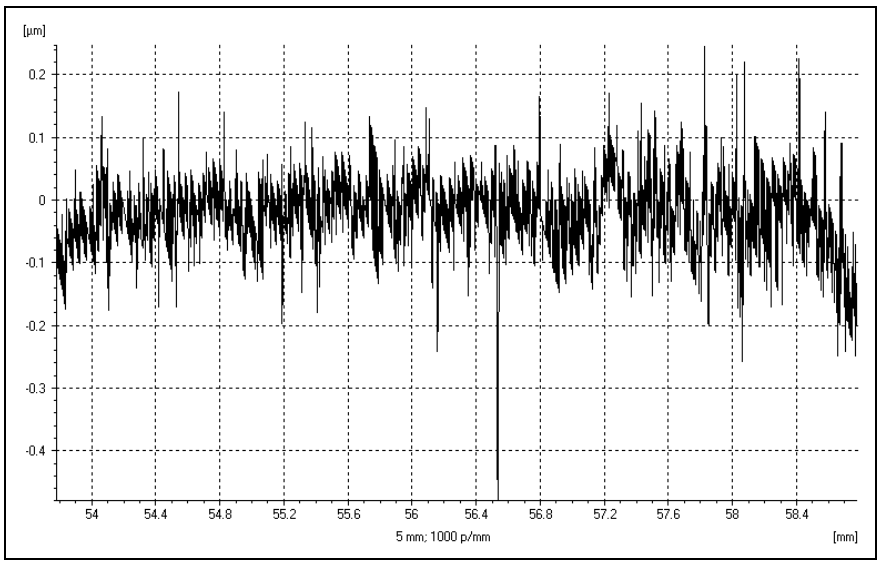
a)


[µm]
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
50.4 50.8 51.2 51.6 52 52.4 52.8 53.2 53.6 54 54.4 54.8
5 mm; 1000 p/mm
[mm]

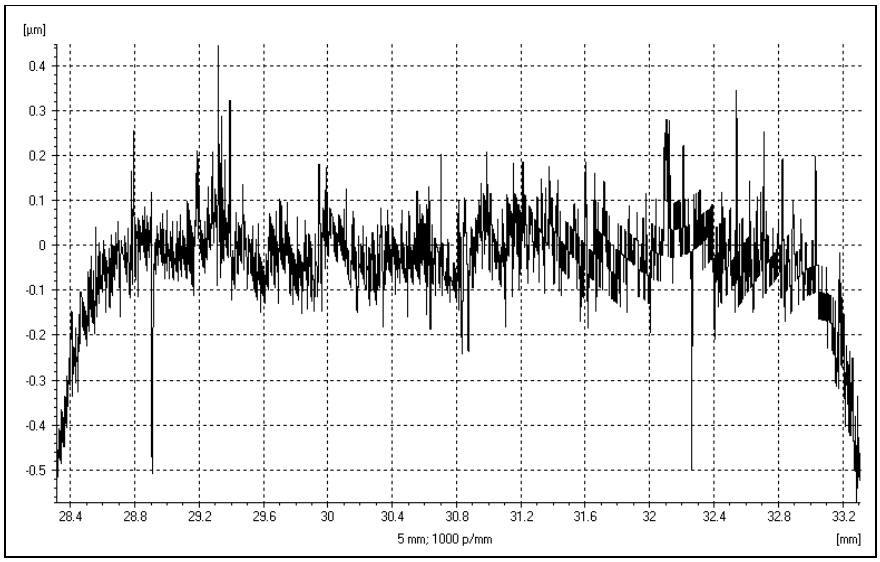
b)


[µm]
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
54 54.4 54.8 55.2 55.6 56 56.4 56.8 57.2 57.6 58 58.4
5 mm; 1000 p/mm
[mm]

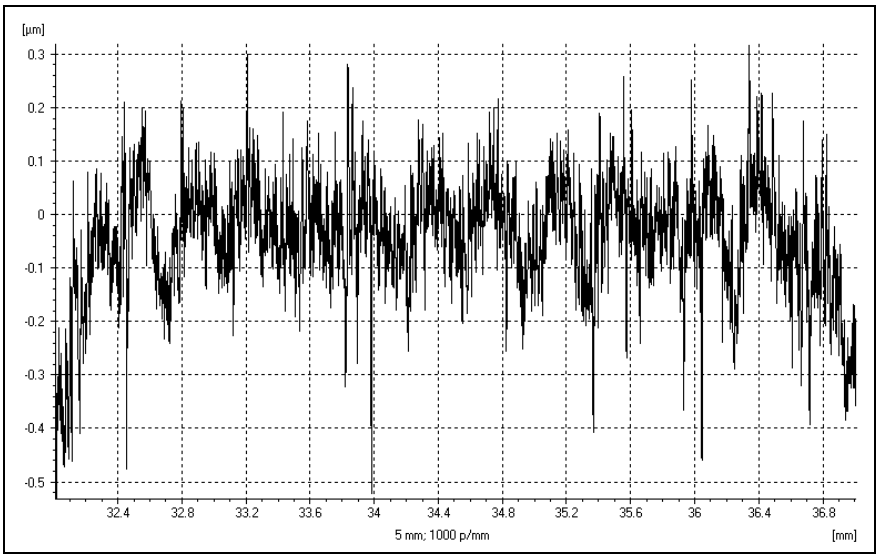
c)


[µm]
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
54 54.4 54.8 55.2 55.6 56 56.4 56.8 57.2 57.6 58 58.4
5 mm; 1000 p/mm
[mm]

d)



e)



f)

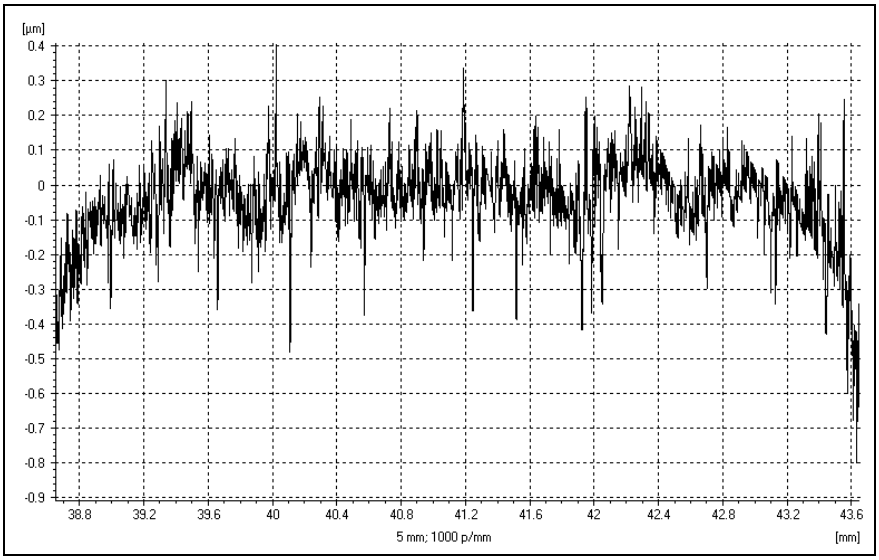


Fig. 10. Two-dimensional surface profilograms of steel specimens coated with silica sol-gel layers

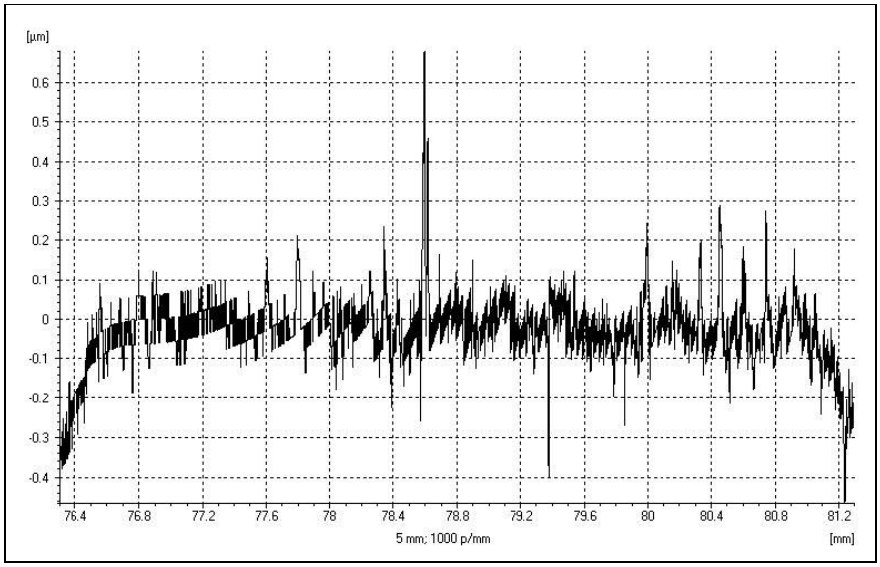


Fig. 11. Surface profilogram of a steel specimen

5. Conclusions

The present research proved that a proper selection of silicon precursors permits obtaining continuous and smooth sol-gel coatings being resistant to plastic deformation. Additionally they are characterised by very close adherence to the base, nanometric thickness and low degree of surface development. At the same time, either in microscopic or topographic examination, no clear discrepancies were observed between individual layers synthesised from sols of different molar compositions. In the layers examined, defects were found in the form of numerous, uniformly distributed pores. These defects made the specimens surface more rough. The probable cause of the defects is the extensive shrinkage of the sol-gel coatings during their gelation and drying. The only way to prevent this destructive phenomenon is by prolonging the times of drying and burning the coatings. Such a change results in a longer time of liquid evaporation and a reduced volume of the liquid that is drained off the pores into the coating, hence the pores at the surface can be filled with air.

A definitive evaluation of the usability of the coatings synthesised by the sol-gel method in the manufacture of surface layers designed for intravessel implants requires additional examinations of physicochemical properties, corrosion resistance and bioconformity in the environment of live tissues. Moreover, attention should be paid to developing such a manufacturing process that would eliminate defective coatings but maintain the mechanical properties obtained.

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