SOL-GEL SILICA-BASED Ag–Ca–P COATINGS WITH AGRESSIVE PRETREATMENT OF TITANIUM SUBSTRATE

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The aim of the experiment was the obtaining of thin silica coatings on titanium by sol-gel method, using mechanical (SiC - paper No.180) and chemical (leaching in HF) pretreatments of the titanium substrates. The solutions were based on TEOS. For the sol-gel dipping process 4 different solutions were prepared: silica, silica with $AgNO_3$ and silica + $AgNO_3$ with brushite ($CaHPO_4 \cdot 2H_2O$) or monetite ($CaHPO_4$) powders. The solutions were aged for 7 and 14 days at laboratory temperature. After sol-gel dip-coating process the samples were dried and fired. The adhesion of fired coatings was measured by tape test according to ASTM procedure and the bioactivity of the coatings was tested using in vitro test. The surfaces of the samples after firing, tape test and in vitro test were observed with the optical and electron microscopes. The firing results showed that silica-silver coatings did not change, brushite sol-gel coatings have cracked and the monetite sol-gel coatings have cracked also, but less than brushite ones. In spite of coating´s crackings, the square's frames made on the surfaces were without any breakdowns after tape tests and the adhesion of all coatings was very good, classified by the highest grade 5. The results of in vitro tests showed that all coatings interacted with simulated body fluid (SBF). After exposition in SBF the new layer formed on substrates. In case of 7 days aged coatings containing brushite the new layer was uniform and compact. In case of 7 days aged coatings containing monetite the new layer was formed by crystals aggregated tightly together. The monetite and brushite coatings prepared from 14 days aged sol were the same as previous ones, but they were thicker. X-ray analyses after in vitro test confirmed dellaite, titanate and hydroxyapatite phases.

INTRODUCTION

There is a number of metals, which are used in medicine: stainless steel, cobalt-chromium alloys, nickel-titanium alloys, titanium and titanium-based alloys. Increased interest in implant with bioceramic coatings can be explained by the fact that metal implants are not without a number of drawbacks. For example, titanium, which has very good mechanochemical properties, tends to seize when it is in sliding contact with itself or another metal [1], also sometimes it can corrode and some patients can have an allergic reactions [2]. The most effective way to increase the compatibility of metallic implants and prostheses with living bone tissue is covering them by inorganic biologically active coatings.

One of the most applied material is hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), which is the analogue of the natural mineral hydroxyapatite (HA). It acts as an intensification in hard tissues and is responsible for stiffness of enamel, bone, dentin and has excellent biocompatibility. Thus it can form a direct chemical bone with hard tissues [1].

To solve the problems of implanted structures biocompatibility, the most important questions are the choice of effective and optimal technology for bioactive coatings preparation. The most popular ways of obtaining coatings are the plasma spraying method [3,4], pulsed laser-deposition [5,6], electrophoretic deposition [7,8], electrochemical deposition [9,10] etc. But they are not without some shortcomings (in particular the high cost of equipment, inability to obtain coatings for materials of different shapes, the extremely high temperature used in plasma spraying process may lead to decomposition of HA etc.).

That is why the most critical question is the development of other application methods. Sol-gel technology is one of them. Sol-gel method is a promising direction that gives a new scientific basis for solving problems to accelerate the surface reaction of bioceramics. The advantages of sol-gel technology for inorganic biomaterials include: new formulations, higher homogeneity and purity levels, hardening of pure form of monoliths, a low-temperature coating of substrates, regulating the size of the powders and almost zero environmental influence [11-13].

Characteristics of the bioactive coating include an antibacterial tests, evaluation of their bioactivity and evaluation of adhesion.

There are several methods for adhesion measurement such as scratch [14, 15], pull-out [15], bending [16] and tape tests [17]. The disadvantages of these methods are

that some of them cannot be used for brittle coatings where cracking is prevalent and some of them require special equipment. Tape test (ASTM D3359) is a simple initial adhesion evaluation method. It is cheap and low-cost method.

There are two common tests for bioactivity measurement: *in vivo* tests (in living organism) and *in vitro* tests. In vitro tests are carried out outside the human body, for it is preparing a special solution, which simulates body fluid is made. The main advantages of *in vitro* tests are that they are fast, relatively inexpensive and they can give the first information about possible bioactivity of obtaining coatings [18].

The aim of the present work was the obtaining of thin, antibacterial, bioactive silica coatings on titanium by sol-gel method, using aggressive mechanical and chemical pretreatments of the titanium substrates.

EXPERIMENTAL

The samples of pure titanium (grade 2, ASTM, B 265) with the size of 10 mm × 30 mm × 1 mm were ground on both sides with SiC paper No. 180 (mechanical pretreatment). The samples were ultrasonically cleaned with acetone and demineralized water for 10 min. After drying on the air at laboratory temperature the samples were subjected to chemical pretreatment: leaching in HF (diluted by *demineralized* water, 1:5 volume ratio) for 30 seconds, then washed 3 times in demi water). Further they were dried at laboratory temperature.

For the sol-gel dipping process 4 different solutions were prepared: silica (S), silica with $AgNO_3$ (due to antibacterial properties, SA) and silica + $AgNO_3$ with brushite ($CaHPO_4 \cdot 2H_2O$, Sigma-Aldrich, SAB) or monetite ($CaHPO_4$, Merck, SAM) powders (due to bioactive properties). The solutions were aged for 7 and 14 days at laboratory temperature. All solutions were based on tetraethyl orthosilicate ($C_8H_{20}O_4Si$, Sigma-Aldrich, TEOS, puriss. ≥ 99,0%). The titanium samples were dipped into 30 ml of stirred sol at $v_{dipping}$ = 6 cm/min, $v_{withdrawing}$ = 20 cm/min, dwell time = 30 s.

After sol-gel dipping process the samples were dried in the air for 24 hours at room temperature, then in the oven at 60 ºC during 30 minutes. Then they were fired at heating rate 2°C/min to 250°C and subsequently 5°C/min to 500°C. The holding time at this temperature was 1 hour. The samples were cooled slowly in oven up to the next day.

After firing one group of samples the tape test was conducted. 6 stripes were made to the coating in a form of net (cross-cut), the distance between each stripe was 1 mm. Then pressure-sensitive adhesive tape was applied to cross-cut area of the coating for 30 seconds and then it was removed. Adhesion was considered to be adequate if no coating is pulled off by the tape when it was removed. The adhesion was evaluated by the following classification, which is shown in Table 1.

Another group of samples was subjected to *in vitro* test by immersing the samples to simulated body fluid (SBF). The concentration of ions in SBF and human blood plasma is shown in Table 2.

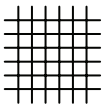
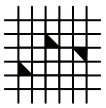
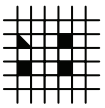
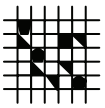
The samples were placed into plastic bottles and exposed to SBF: S/V = 0.1 cm^{-1} (S-surface of samples, V- volume of SBF). *In vitro* test was performed at static conditions (with the same solution during the experiment), bottles were located into incubator with temperature 36.5 ± 0.5 ºC and pH = 7.4. The rate of stirring was 136 rpm and experiment took 14 days.

After *in vitro* and tape tests the samples were observed by optical microscope (OM, Jenapol with NIS Elements), electron microscope (EDS - Thomson Scientific UltraDrySilicon Drift Detector) and X-ray diffractometer (PANanalytical X'PertPRO, the measurement was conducted in Institute of Chemical Technology Prague in Department's of Glass and Ceramics laboratory). Samples were analysed by program HighScore, version 1.0d, PANalytical, Almelo, 2003 and matched with data in database JCPDS PDF2, Sets 1-54, International Centre of Diffraction data, Newtown, Pensylvania, USA, 2004 (in the Institute of Inorganic Chemistry of the Czech Academy of Science, v.v.i., Řež u Prahy).

Table 2. Ion concentrations of SBF-5 and human body plasma [19].

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	HCO_3^-	HPO_4^{2-}	SO_4^{2-}
	(mmol l^{-1})							
Plasma	142	5.0	1.5	2.5	103.0	27.0	1.0	0.5
SBF-5	142	5.0	1.0	2.5	131.0	5.0	1.0	1.0

Table 1. Classification of measuring adhesion by tape-test (ASTM D 3359-02) [17].

Classification	5	4	3	2	1	0
Removed area (%)	0	5	5-15	15-35	35-65	over 65
Cross cut area						

RESULTS AND DISCUSSION

The first observing of the surface after leaching of the titanium samples in HF (Figure 1) showed that the surface was rough and cracked. The reason is aggressive property of HF, which increases the surface roughness of the metal samples.

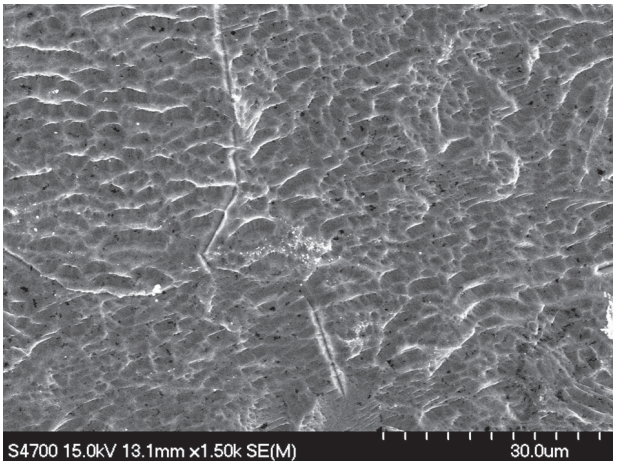
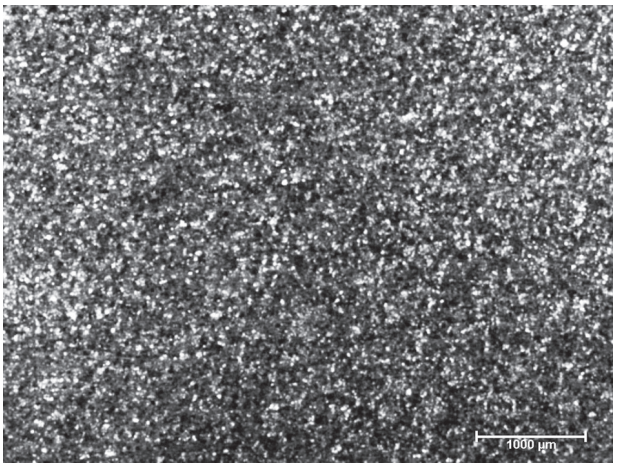


Figure 1. SEM The surface of the titanium sample after chemical pretreatment.

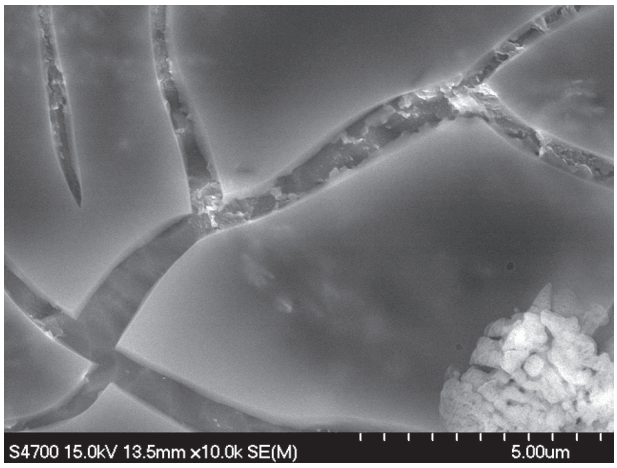
The following images (Figures 2, 3) from optical and electron microscopes show the surfaces of the samples after burning. The images indicate that both SAB-7d and SAM-7d sol-gel coatings have cracked. However, monetite coatings have cracked less than brushite ones. It can be explained by the water content in brushite powder. The particles of monetite and brushite were distributed uniformly on the surfaces.

With a help of optical and electronic microscope it is possible to notice that the coatings from 14 days aged sols: SAB-14d (Figure 4) and SAM-14d (Figure 5) were thicker than the 7 days coatings because of longer sol dwell time. Again the particles of brushite and monetite were distributed uniformly on the surfaces.

In spite of layer cracking, the square's frames made on the surfaces were without any breakdowns after tape tests and the adhesion of all coatings was very good, classified by the highest grade 5.

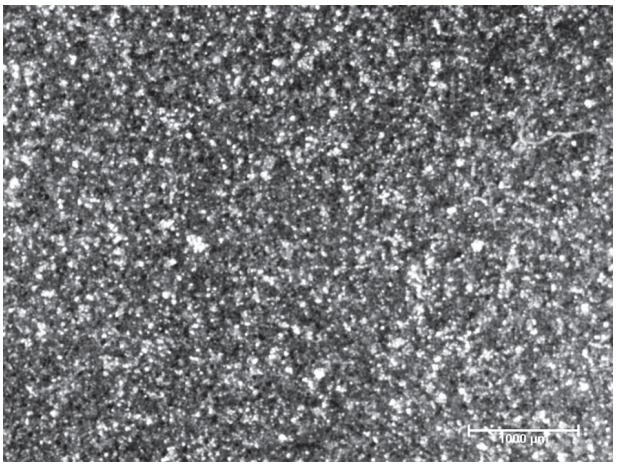


a) OM

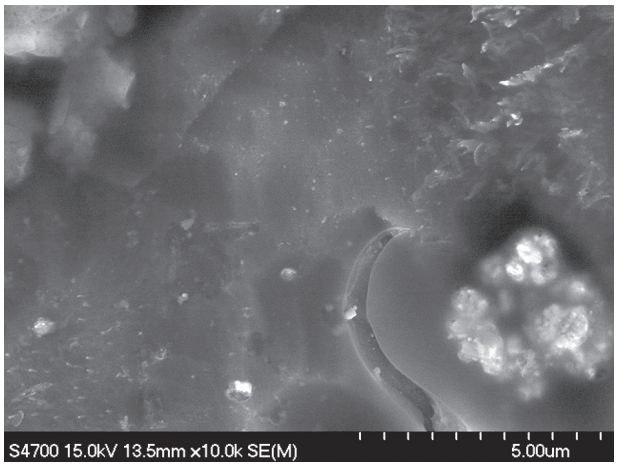


b) SEM

Figure 2. The surface of the titanium sample SAB-7d after burning.



a) OM



b) SEM

Figure 3. The surface of the titanium sample SAM-7d after burning.

The results of *in vitro* tests showed that all the coatings interacted with SBF. After exposition in SBF the new layer formed on the substrates. In case of 7 days aged brushite coatings (SAB-7d) the new layer was uniform and compact (Figure 6). In case of 7 days aged monetite coatings the new layer was formed by crystals aggregated tightly together (Figure 7). The monetite and brushite coatings prepared from 14 days aged sol were the same as previous ones, but they were visually thicker (Figures 8 and 9).

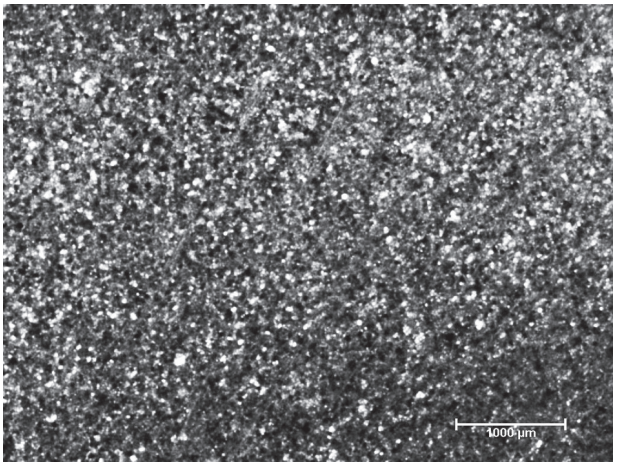


Figure 4. OM The surface of the titanium sample SAB-14d after burning.

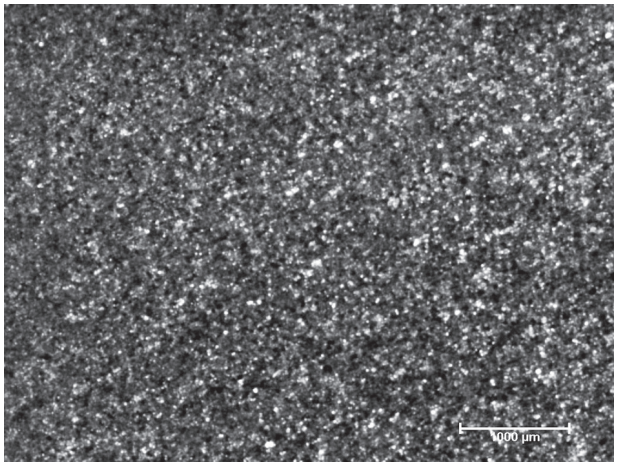


Figure 5. OM The surface of the titanium sample SAM-14d after burning.

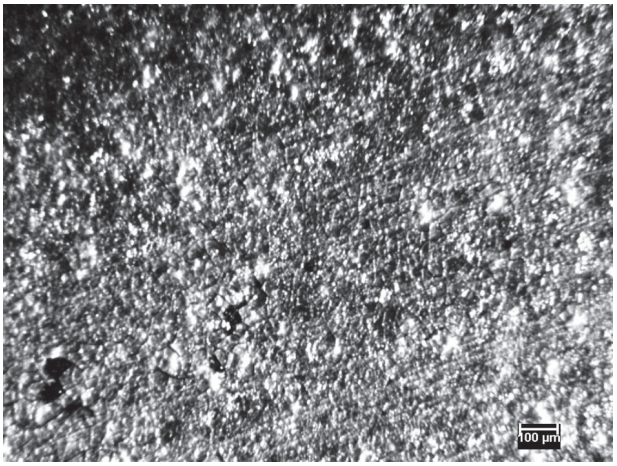


Figure 6. OM The surface of the titanium sample SAB-7d after *in vitro* test.

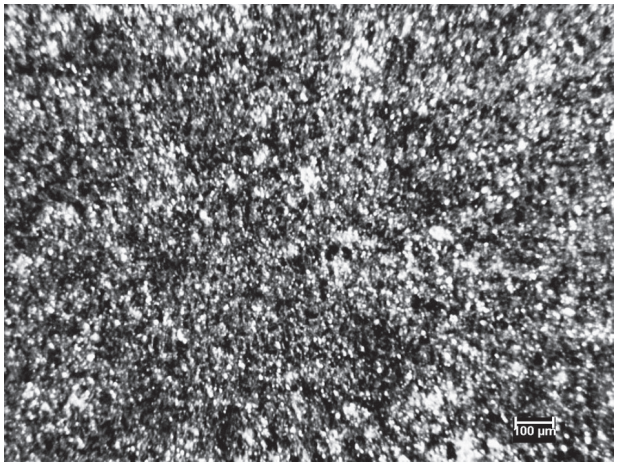
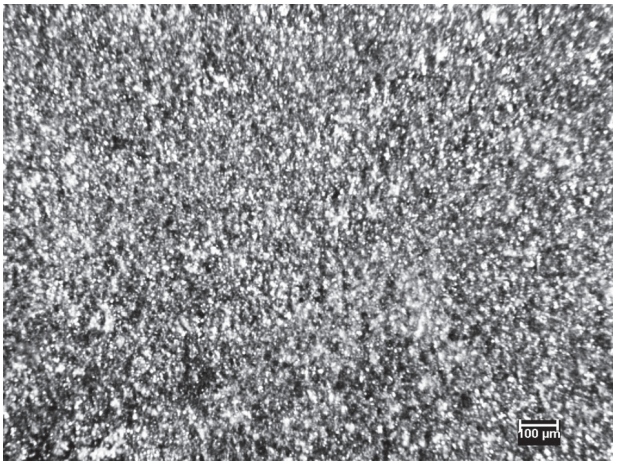
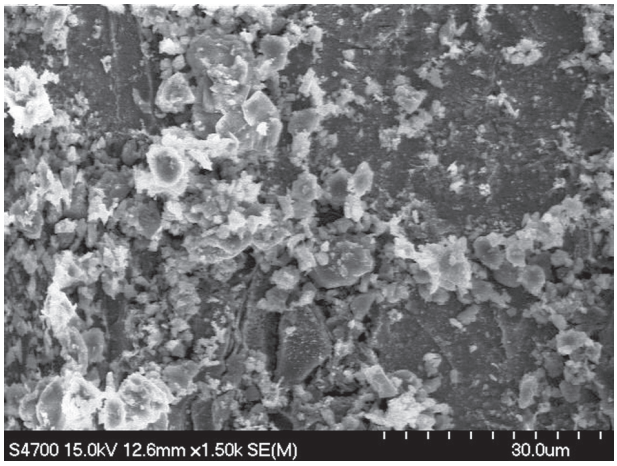


Figure 7. OM The surface of the titanium sample SAM-7d after *in vitro* test.

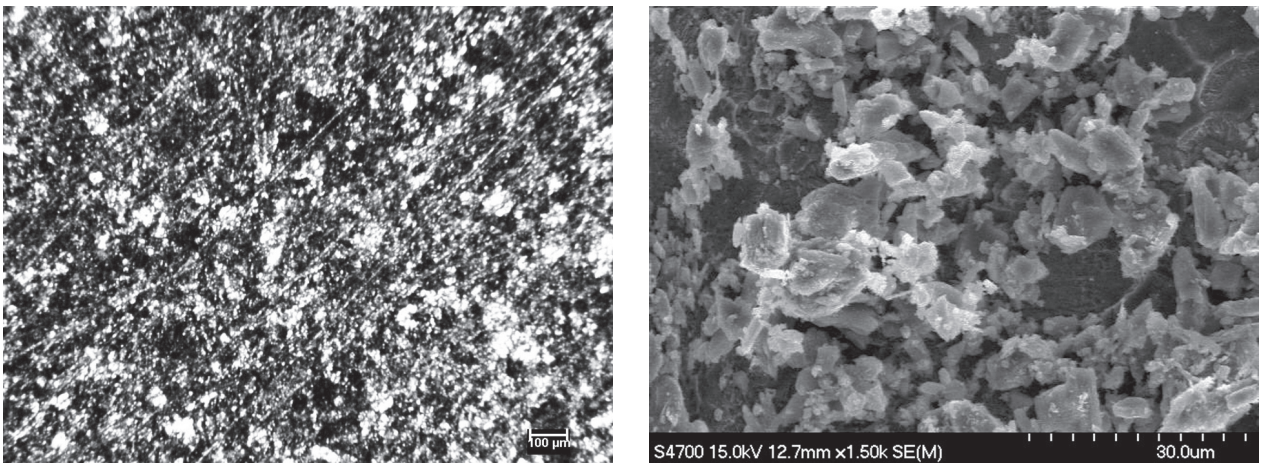


a) OM



b) SEM

Figure 8. The surface of the titanium sample SAB-14d after *in vitro* test.



a) OM b) SEM

Figure 9. The surface of the titanium sample SAM-14d after *in vitro* test.

The figure 10 demonstrates the results of X-ray analysis after in vitro test. The first higher line shows the behavior of 14 days aged coatings containing monetite, the second lower line demonstrates the behavior of 14 days coatings containing brushite. Besides of Ti (pdf N° 44-1294) and Ag (87-0720), the titanate ($CaTiOSiO_4$, 86-2262) and dellaite ($Ca_6(Si_2O_7)(SiO_4)(OH)_2$, 72-1907) were detected. Small peaks of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, 24-0033) promise the possible bio-activity of both monetite and brushite containing layers.

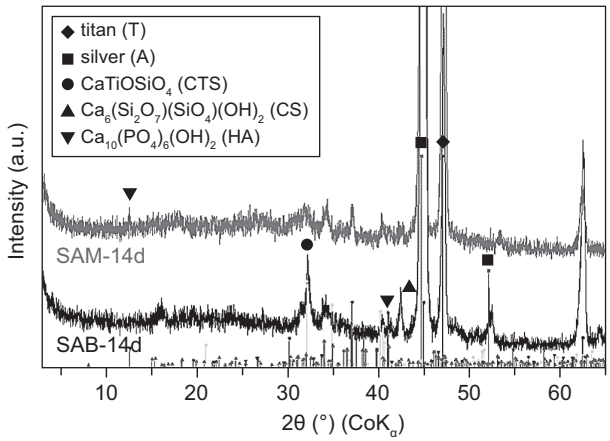


Figure 10. The results of x-ray analysis of SAB-14d and SAM-14d coatings after *in vitro* test.

CONCLUSIONS

1. The observing of the surface after leaching in HF showed that the surface was rough and cracked.
2. The firing results showed that the surface of silica-silver coatings did not change, brushite silica sol-gel coatings have cracked and the monetite silica sol-gel coatings have cracked also, but less than brushite ones.
3. The square's frames made on the surfaces were without any breakdowns after tape tests and the adhesion of all coatings was very good, classified by the highest grade 5.
4. After exposition in SBF the new Si–Ca–Ti–P layer formed on substrates. In case of 7 days aged coatings containing brushite the new layer was uniform and compact. In case of 7 days aged coatings containing monetite the new layer was formed by crystals aggregated tightly together.
5. The SEM results showed that the surface of 7 days aged monetite containing coatings has better results, the surface is smooth with no visible chips or cracks.
6. X-ray analyses after *in vitro* test found the silica-calcium, titanium-calcium and hydroxyapatite phases.
7. The next step of our work is preparation of silica coatings with addition of Ca_3PO_4 powder and measurement of antibacterial properties of layers containing silver.

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