

Experimental analyses of surface treatment on titanium samples

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ABSTRACT

The roughness of the dental implant surface will influence the behavior of osteoblastic cells regarding the spread, proliferation, differentiation and synthesis of proteins on the surface of titanium. Depending on its characteristics, roughness can be macro-, micro- and nano-roughness

Material and method. We achieved the obtaining of thin layers of biomaterials by the pulsed laser deposition method (PLD, Pulsed Laser Deposition) on the titanium samples and the deposition has been made by Spin coating method of a thin film based on hydroxyapatite, respectively hydroxyapatite-maleic copolymer, only on one side of the sample.

Results. From a microscopic point of view, the qualities of bio-glass are remarkable. Thus, bio-glasses are amorphous materials and are successfully used as covering material for metallic and polymeric implants, to significantly increase their biocompatibility.

Discussion. The biological properties of the materials for implants are of fundamental importance for the success of the treatments and they are reflected along with other characteristics of the implants, in the tissue reaction they cause under the conditions of their insertion in biological systems.

Conclusion. Osseointegration could be impaired in people with diabetes, osteoporosis, with bone metabolism disorder where therapeutic success depends on the biomimetic and functional topography of the dental implant.

Keywords: implant surface, spin coating method, Pulsed Laser Deposition, hydroxiapatite, bioglass

INTRODUCTION

The nano functional surface design of the dental implant favors a biological response to the cell-implant interface causing the creation of a new generation of dental implants. In this way there will be a biological response on the surface of the titanium implant where proteins, blood, immune cells and osteoprogenitor cells interact with the surface of the biomaterial in the early stages of healing [1], being dependent on surface roughness and can affect osteoblastic differentiation, cell maturation, matrix formation and osseointegration of the dental implant [2]. Adsorption of proteins on the surface of the implant leads to cell attachment signaling where

active inflammatory cells, monocytes, lymphocytes, granulocytes participate in the healing process and the mechanism of osteoconduction, osteoinduction and osteogenesis [3,4].

The process of osseointegration of dental implants depends on: its shape and size, the material from which it is made, the design of the rotational spire, the abutment-implant connection, the surface topography and treatment, its wetness, the cylindrical or conical shape, existing today about 1300 different dental implants [5].

All this influences the healing process of bone tissue after the insertion of the implant. The initial stage begins with plasma hemostasis, stimulation of

cellular mechanisms, polymerization of fibrin and the formation of a blood clot that constitutes an extracellular matrix for neo angiogenesis, with the appearance of osteogenic cells. They act at the edge of the cavity, remote osteogenesis, and on the surface of the implant, contact osteogenesis [6].

The reparative phenomena of peri-implant bone tissue are lasting and follow the formation of bone tissue around the dental implant and the adaptation of the bone structure to pregnancy [7].

The roughness of the dental implant surface will influence the behavior of osteoblastic cells regarding the spread, proliferation, differentiation and synthesis of proteins on the surface of titanium. Depending on its characteristics, roughness can be macro-, micro- and nano-roughness [8,9].

Surface treatments of dental implant are macrotopography and microtopography. Microtopography have physiochemical surface treatments, morfophogenetic treatments (additive, subtractive and nano-modified) and biochemical treatments [10].

In order to increase the osteointegration and biomechanical fixation of the dental implant, morphological changes have been made on the surface of titanium by additive methods of coating with other biomaterials (titanium plasma spraying, hydroxyapatite, calcium phosphate) or by subtractive methods to increase the rough surface of the implant (blasting with aluminum oxide, ceramics, anodizing). Thus:

Galvanostatic anodic oxidation at high current values, with strong acids, sulfuric acid, phosphoric acid, nitric acid.

Sandblasting with particles of silicon, alumina, titanium dioxide which produce cavities of 1-3 μm and blasting of 250 μm -300 μm . The contact area between the dental implant and the bone is enlarged with an important role in anchoring the bone cells and connecting it to the surrounding tissues favoring preimplant osteogenesis [4].

Single or double engraving with acid with strong acids, sulfuric acid, phosphoric acid, nitric acid at high temperatures. This removes the post sandblasting residues, increases the surface energy of titanium and the adsorption of bone matrix proteins, and the proliferation and migration of bone cells that stimulate the osteoconductive process [3,4].

The microroughness obtained from simple, single-acid etching causes roughness on the implant surface with values between 0.5 μm and 2.5 μm in diameter. Double acid etching, in a concentrated acid mixture heated to over 100°C, stimulates rapid osseointegration [11].

Sandblasting with Al_2O_3 and TiO_2 granules with a particle diameter between 80 μm -300 μm followed by acid etching on the titanium surface, acid that removes the residues left after sandblasting [12].

Plasma spraying when a film of 30 μm thickness and 7 μm roughness is formed, increasing the surface of the implant 6 times [13].

Hydroxyapatite (HA) coating of dental implant where plasma spraying of HA is used as the method. HA is heated with a plasma flame at a temperature of about 15,000-20,000 K and propelled onto the implant in an inert environment making an additional thickness of the implant of about 50 μm -100 μm and its surface area increases by about 600%.

It thus stimulates osteogenesis, improves primary stability, increases tensile strength at the bone-implant interface, stimulates osteo-conductivity and osteogenesis. As a disadvantage we mention the fracturing of HA from the surface of the dental implant, the dissolution of HA, delamination from the implant and favors the retention of the dental plaque [14].

There is an increase in the number of people with advanced clinical conditions leading to secondary failure of dental implant treatment. Numerous methods of treating the surfaces of dental implants aim at a standardization of the physic-chemical surface morphology that is favorable to peri-implant bone mineralization and the strength of the bone-implant interface.

Osseointegration could be impaired in people with diabetes, osteoporosis, with bone metabolism disorder where therapeutic success depends on the biomimetic and functional topography of the dental implant [15,16].

MATERIAL AND METHOD

Round samples with a diameter of 10 mm and a thickness of 1 mm were made. They are subject to surface conditioning by sandblasting. Titanium belongs to the delivery company ANCIS International, ISO 9001-00 certified by LRQA with no. 354125, TITANIUM T40 Grade 2, and the samples were made at Tehnomed Impex Bucharest. The sandblasting of the samples will be carried out with corundum particles, aluminum oxide, of different granulations: with 50 μm powder, with 80 μm powder of 110 μm powder, 150 μm powder, 250 μm powder.

The deposition has been made by Spin coating method of a thin film based on hydroxyapatite, respectively hydroxyapatite-maleic copolymer, only on one side of the sample, from 20 to 80 deposits [17,18].

The powders used are obtained in hydrothermal conditions, and the maleic copolymer was obtained at the Institute of Macromolecular Chemistry "P. Poni" (ICMPP) Iasi. At the National Institute of Research and Development for Non-Ferrous and Rare Metals (IMNR) Bucharest, the structural "biomimetic" strategy on the titanium samples was realized.

We achieved the obtaining of thin layers of biomaterials by the pulsed laser deposition method

(PLD, Pulsed Laser Deposition) on the titanium samples. This allows multi-structures to be obtained and the thickness of the layers is controlled accurately (0.1 nm) [19,20].

The biomaterials used to cover the samples are: Hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})$; Tricalcium phosphate in crystallographic forms β ; Bio-glass, materials used today in the medical field as bioactive/bio-functional materials for biomimetic implants [21].

RESULTS

A. Analysis of Spin Coating hydroxyapatite deposits on blank titanium sample, non-swapped, using Hitachi S-2600 N scanning electron microscope, equipped with a dispersive energy analysis system (EDS).

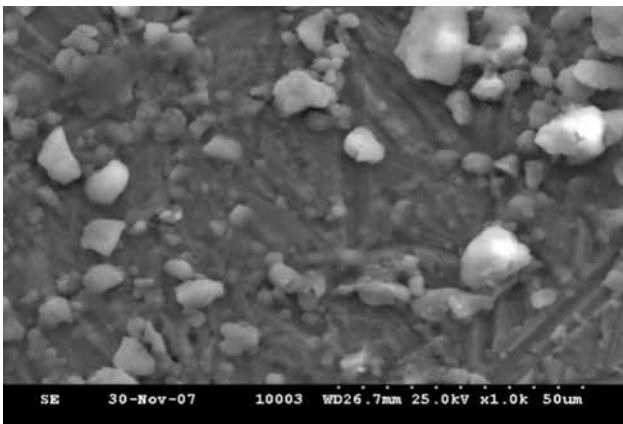


FIGURE 1. The distribution mode of hydroxyapatite particles and the tendency of formation of some X 1000 films

The qualitative chemical microanalysis is presented in the graphs of the peaks of the X-ray intensities, characteristic of the chemical elements, present in the sample. The concentration of the constituent elements of Ca and P is shown in the images with the distribution maps in Fig. 2,3,4.

B. Analysis of spin coating hydroxyapatite deposits on sandblasted titanium sample. 50 deposits were made. The distribution of hydroxyapatite particles is contained in a large dispersion spectrum in the range of $0.1\mu\text{m}$ – $25\mu\text{m}$, predominating the micron and submicron fraction of $0.1\mu\text{m}$ – $3\mu\text{m}$ (Fig. 5).

The presence of the Ti peak is due to the small size of the analyzed particle, which allowed its penetration by the electron beam, which has a penetrating power of about. $2\mu\text{m}$ (Fig. 6,8).

C. The analysis of the sandblasted titanium samples and the HA biofilm by the pulsed laser deposition method was carried out using the scanning electron microscope QUANTA INSPECT F, equipped with a field emission electron gun (FEG - Field Emission Gun) with a resolution of 1.2 nm and with energy dispersive X-ray spectrometer (EDS), with the resolution at MnK of 133 eV (Fig. 9,10).

A non-uniform deposition of HA determined by the surface roughness, slight discontinuities of the deposition is achieved, the pores having sizes between $5\mu\text{m}$ – $10\mu\text{m}$. The morphology of the superficial layer is granular, with agglomerations of particles with submicron sizes (Fig. 10).

D. Analysis of the sandblasted titanium sample and the tricalcium phosphate β biofilm (Fig. 12)

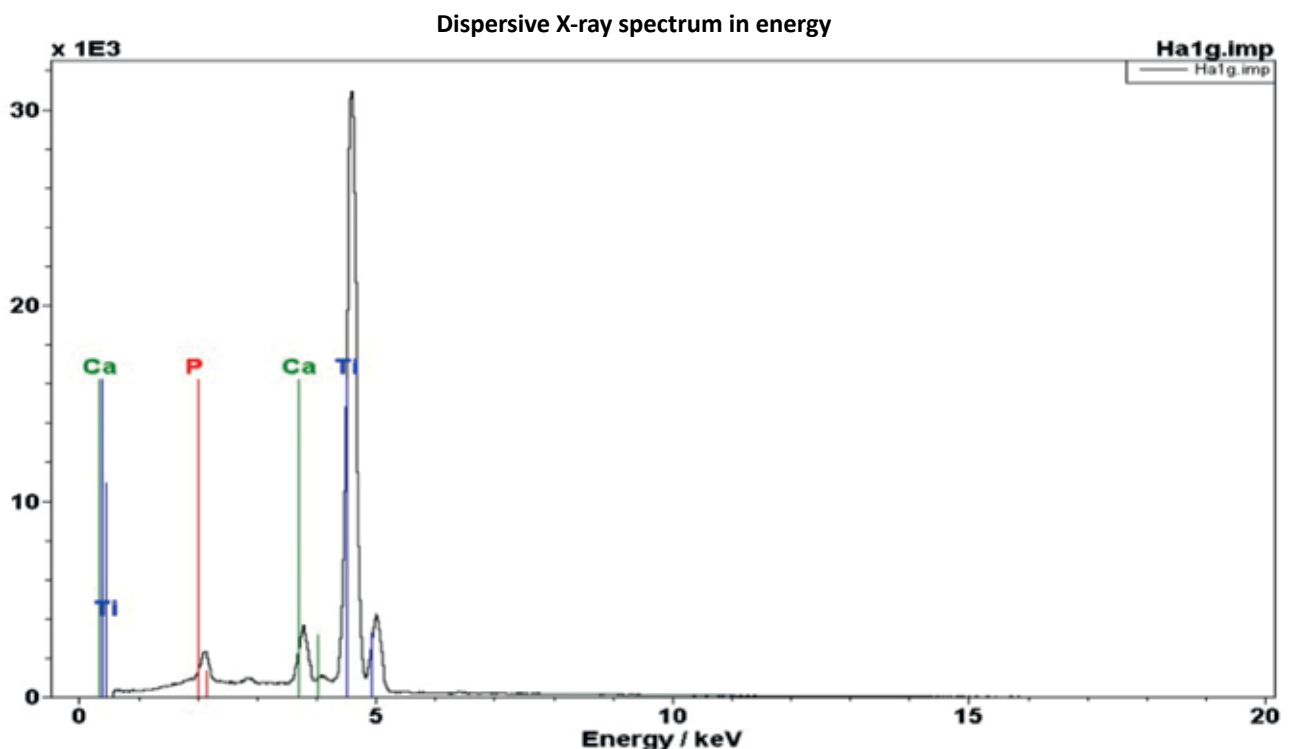


FIGURE 2. Qualitative chemical microanalysis globally

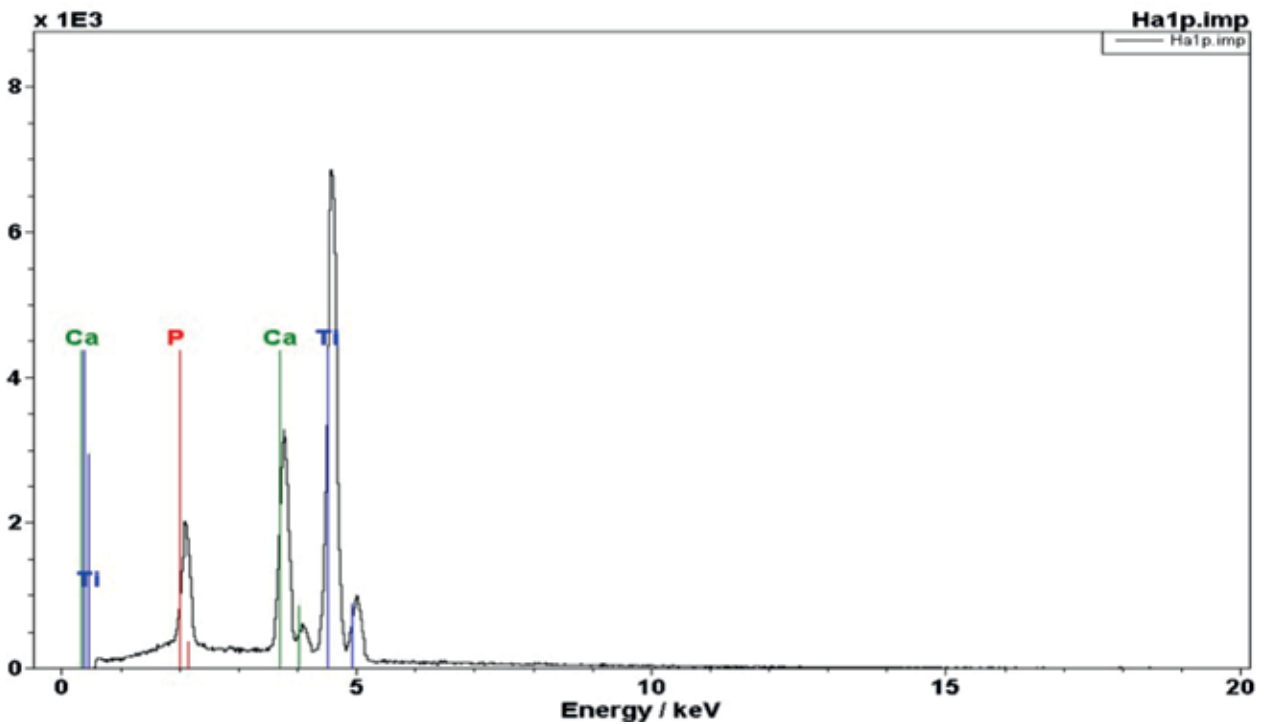


FIGURE 3. Qualitative chemical microanalysis on a particle

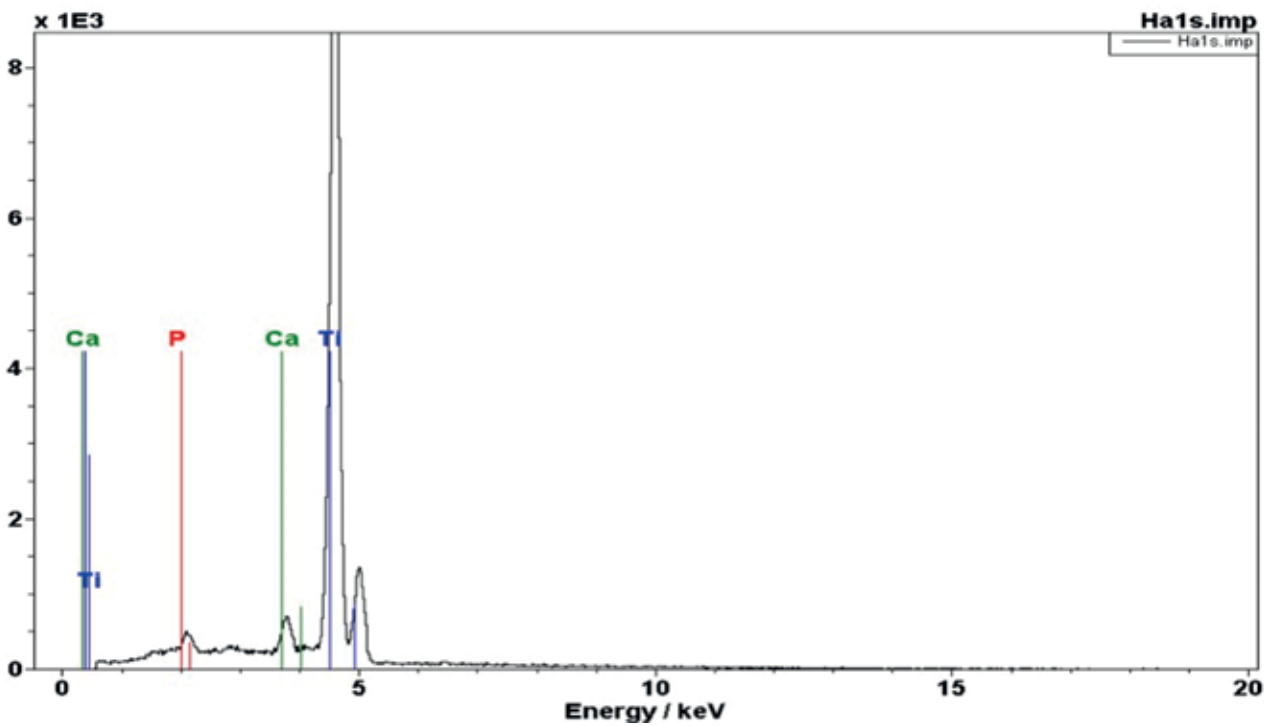


FIGURE 4. Qualitative chemical microanalysis on film

E. Analysis of the sandblasted titanium sample with bio-glass deposition (Fig. 14)

The deposition of bio-glass is uneven, with porosities, the pores having sizes between 5 μm -10 μm . The morphology of the superficial layer is granular, with agglomerations of particles of submicron size

and with round, smooth particles with a glassy appearance (in the form of splashes) with a maximum average diameter of 5 μm . These particles are uniformly distributed on the bio-glass film. It has a nanostructured appearance with grains of approximately 14 nm - 25 nm.

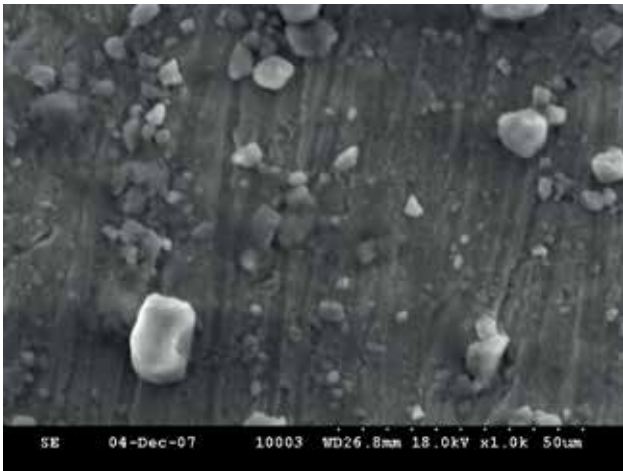


FIGURE 5. It can be seen the distribution of hydroxyapatite particles and the tendency to form films in the center of the X 1000 image

DISCUSSIONS

During the coating processes, through the Spin coating method, due to the increased temperature, HA degradation products also appear, so on the surface we will have, in addition to the HA ceramic particles, tricalcium phosphate, tetracalcium phosphate, as well as calcium oxide.

From a chemical point of view, in some cases, the obtained layer can be represented by a mixture of de-

hydroxylated hydroxyapatite and tri/tetracalcium phosphate. It should be noted that the type of layer obtained by the Spin coating method can significantly influence the quality of the surface of the titanium implant.

SEM examination of thin biofilms of HA, β tricalcium phosphate, bio-glass obtained by the pulsed laser deposition (PLD) method on the surface of titanium samples shows images of a granular, rough surface morphology for all depositions. The depositions for HA and β tricalcium phosphate are not uniform, they show roughness with the dimension of $5\ \mu\text{m}$ - $10\ \mu\text{m}$ for HA and bio-glass and the double dimension for β tricalcium phosphate. The bio-glass film is uniformly distributed on the surface of the sample.

CONCLUSIONS

The biological properties of the materials for implants are of fundamental importance for the success of the treatments and they are reflected along with other characteristics of the implants, in the tissue reaction they cause under the conditions of their insertion in biological systems.

For this reason, biomaterials assume certain changes over time of their surface - bioactive coating - which influence for a longer or shorter period the reactivity of the tissues in which they are in-

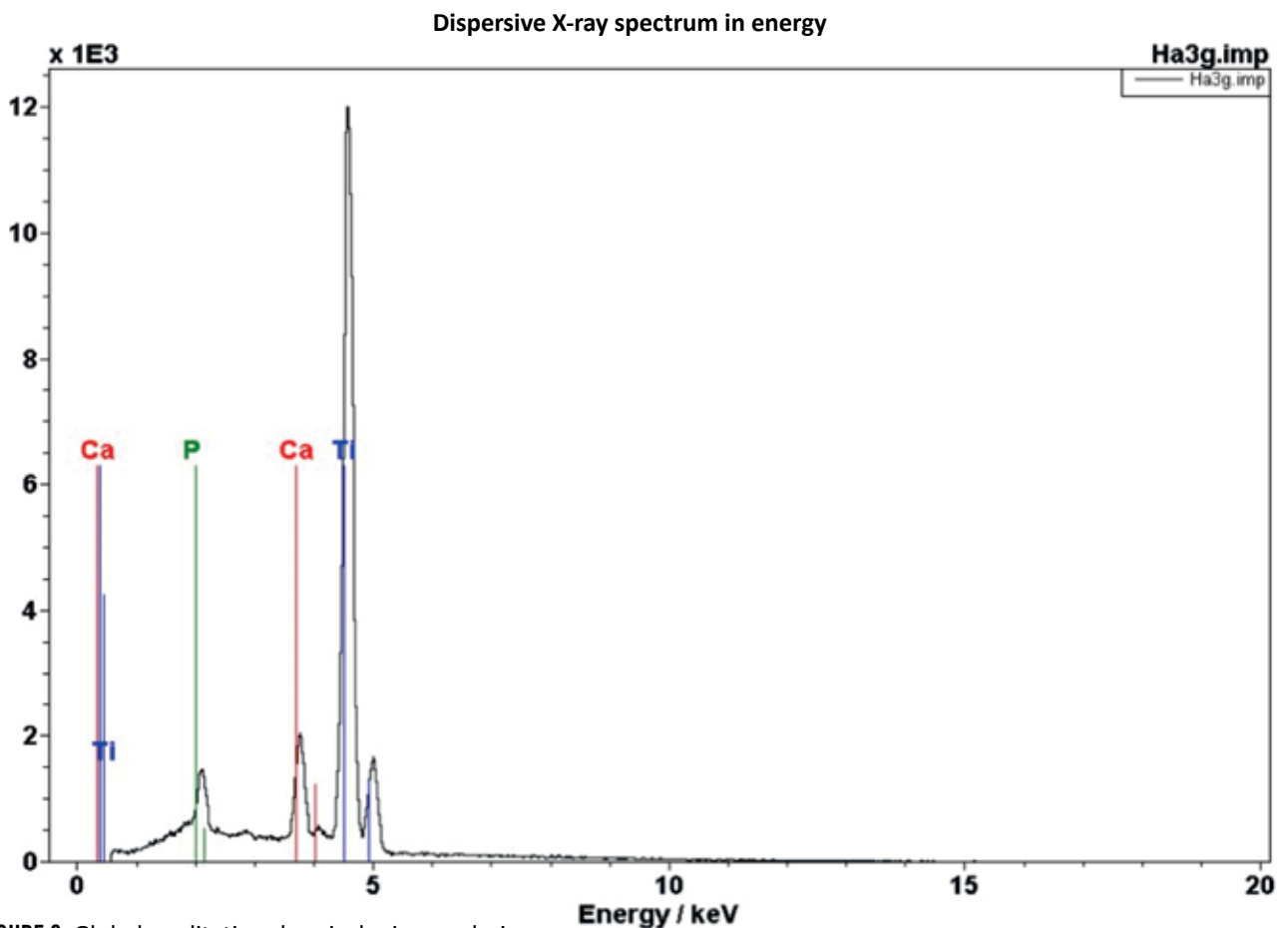


FIGURE 6. Global qualitative chemical microanalysis

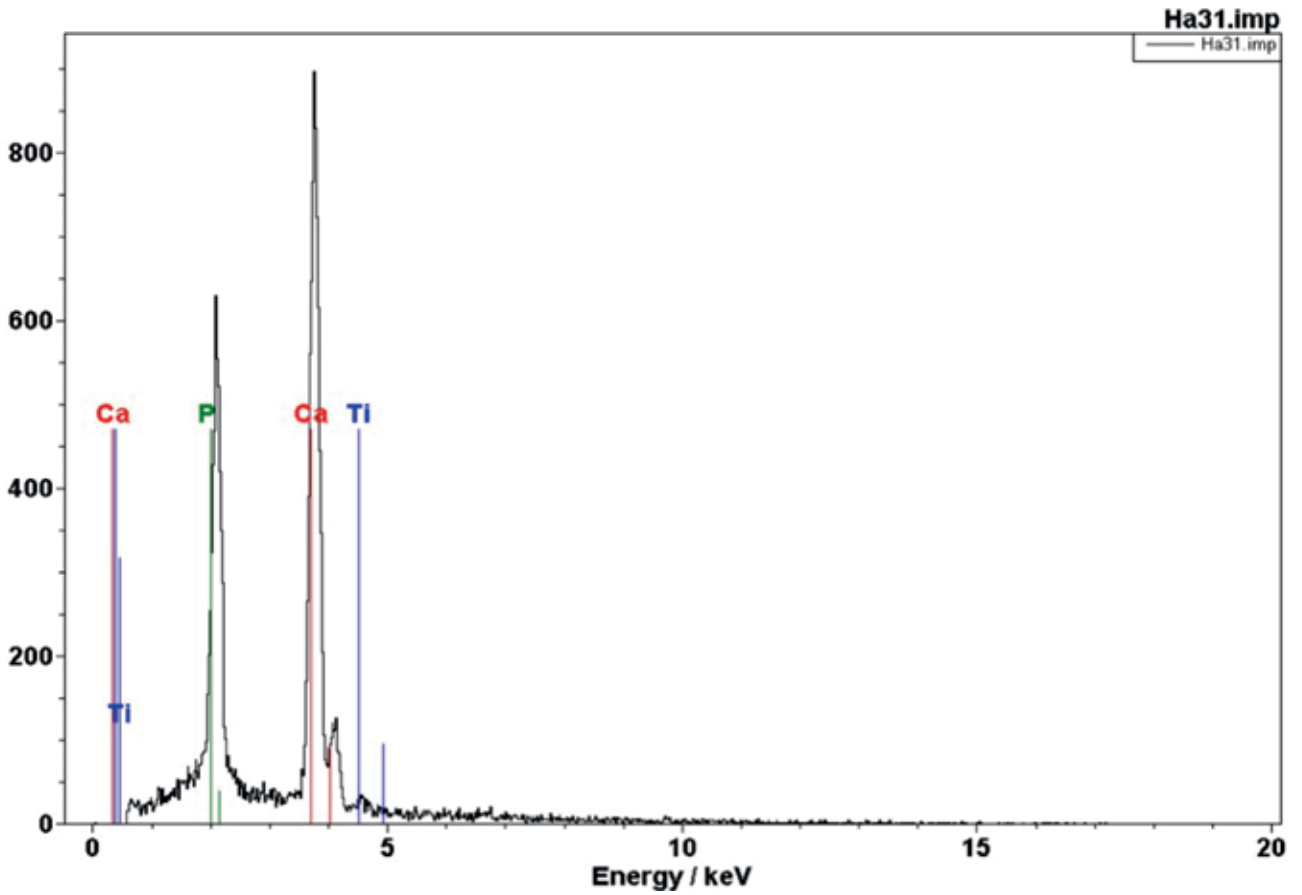


FIGURE 7. Qualitative chemical microanalysis on large particles

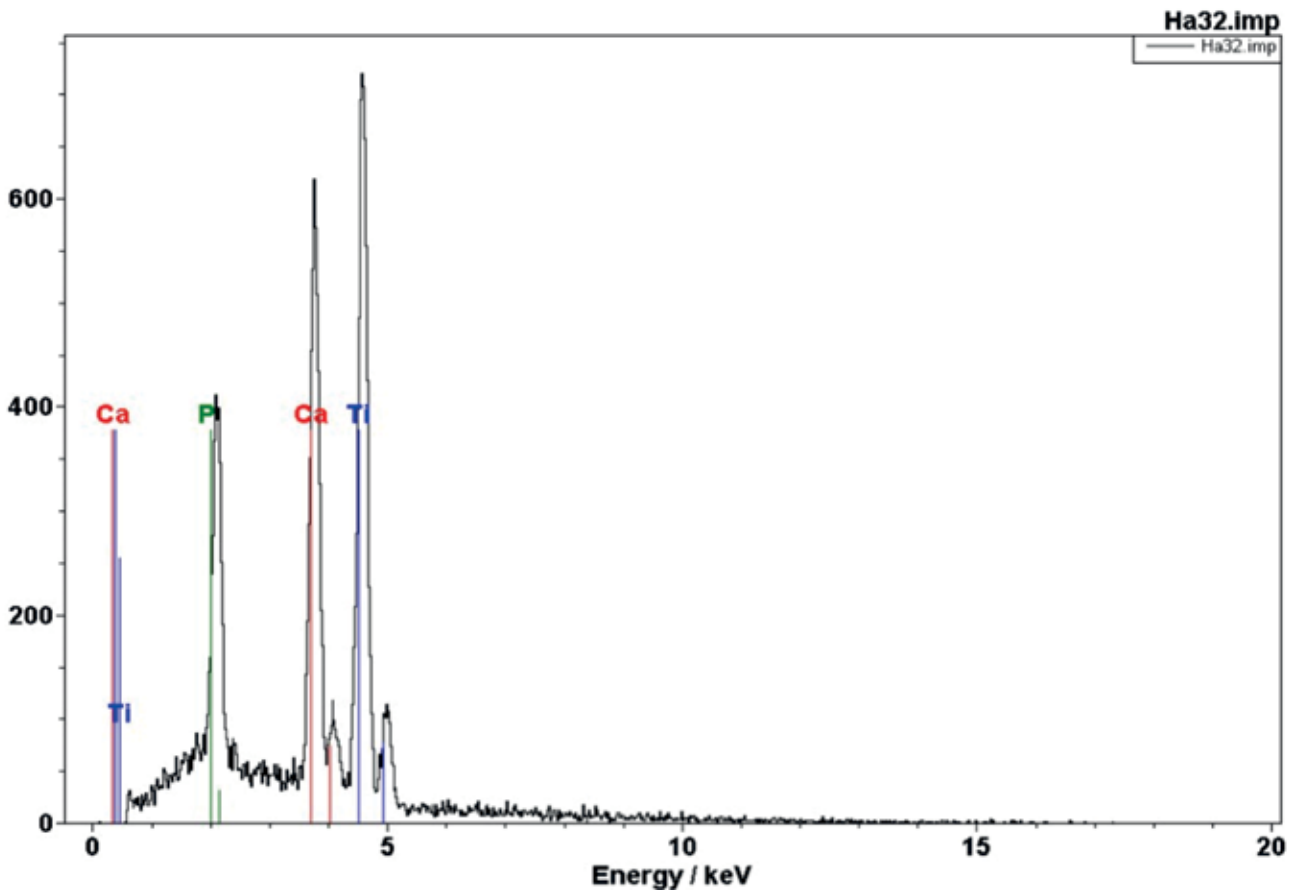


FIGURE 8. Qualitative chemical microanalysis on small particles

served. Thus, the surface texture and the quality of the biofilm on the titanium are of particular importance in the osseointegration of the implant.

From a microscopic point of view, the qualities of bio-glass are remarkable. Thus, bio-glasses are amor-

phous materials and are successfully used as covering material for metallic and polymeric implants, to significantly increase their biocompatibility.

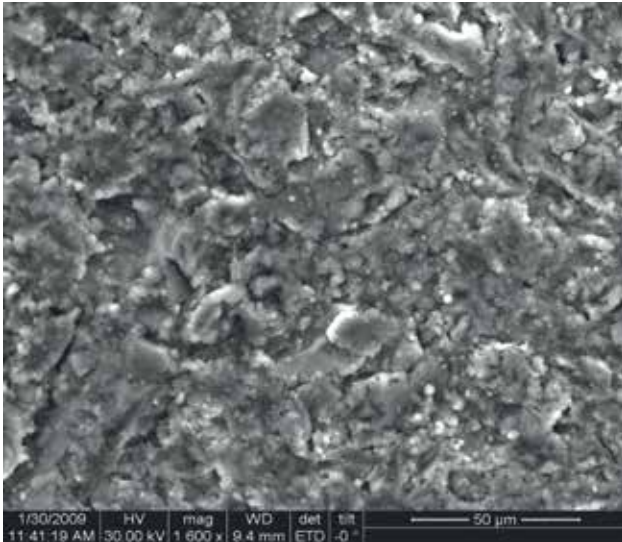


FIGURE 9. HA deposition with the rough relief of the sandblasted surface. X 1600

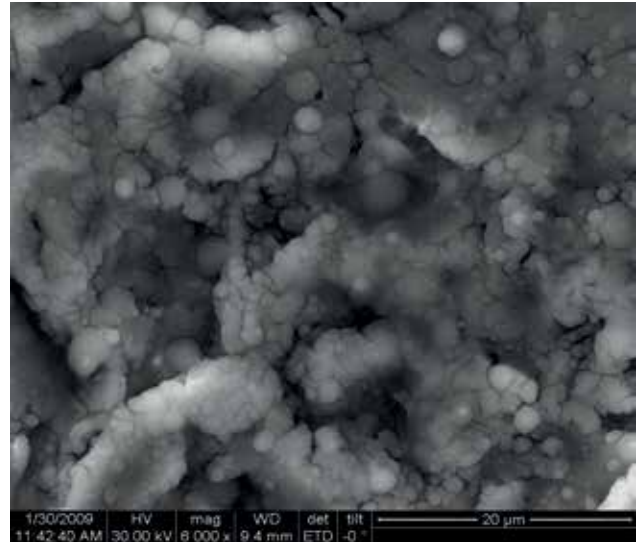


FIGURE 10. HA provides a uniform appearance on roughness and sandblasted cavities X 6000

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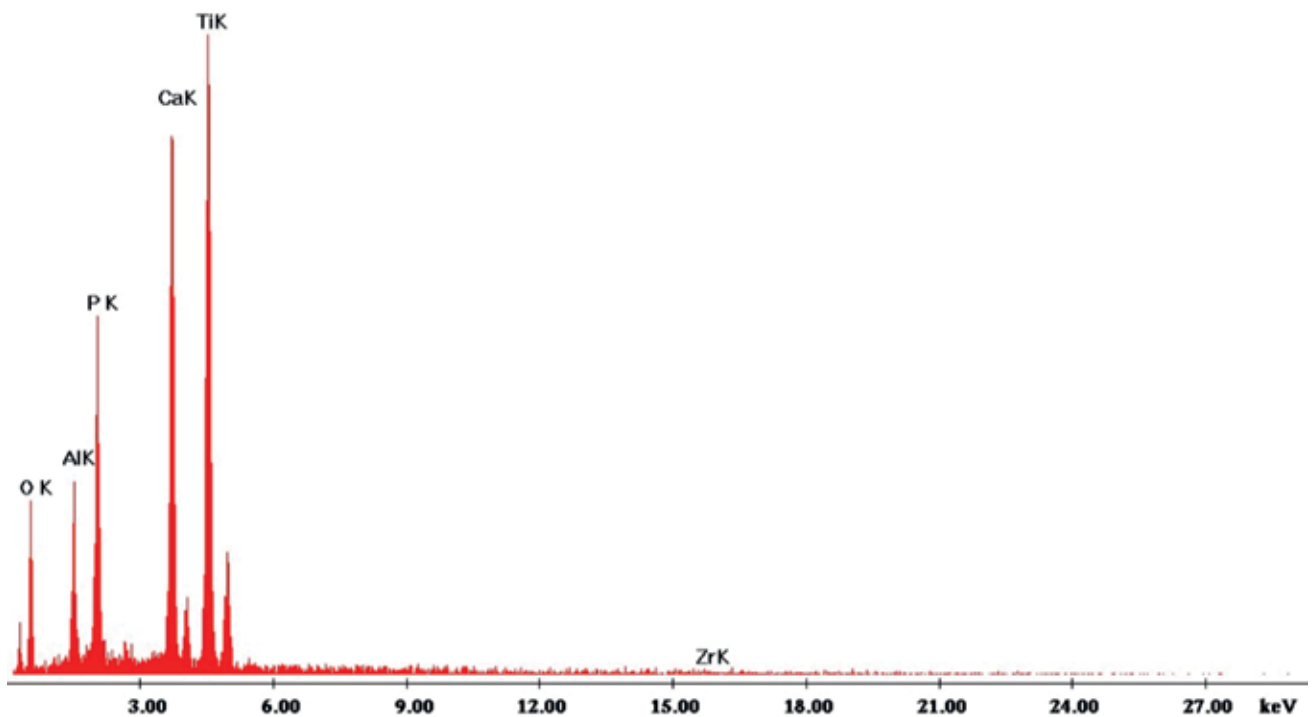


FIGURE 11. Energy dispersive X-ray spectrum (EDAX). The sample contains Ti, Al in the substrate and Ca, P, O2 and traces of Zr

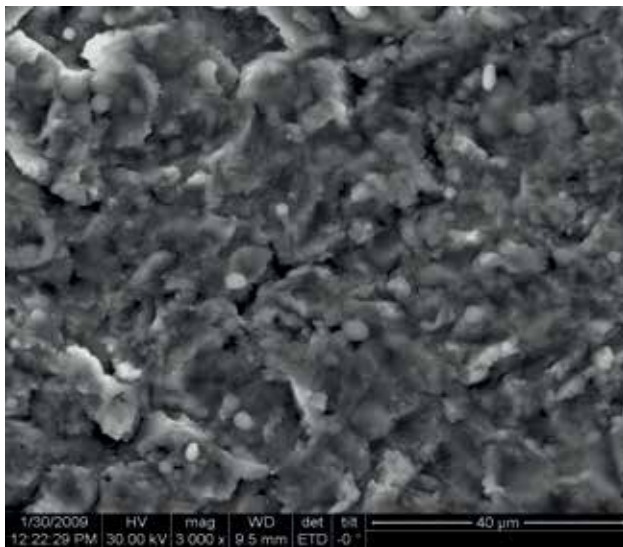


FIGURE 12. The deposited tricalcium phosphate β layer does not appear well highlighted X3000

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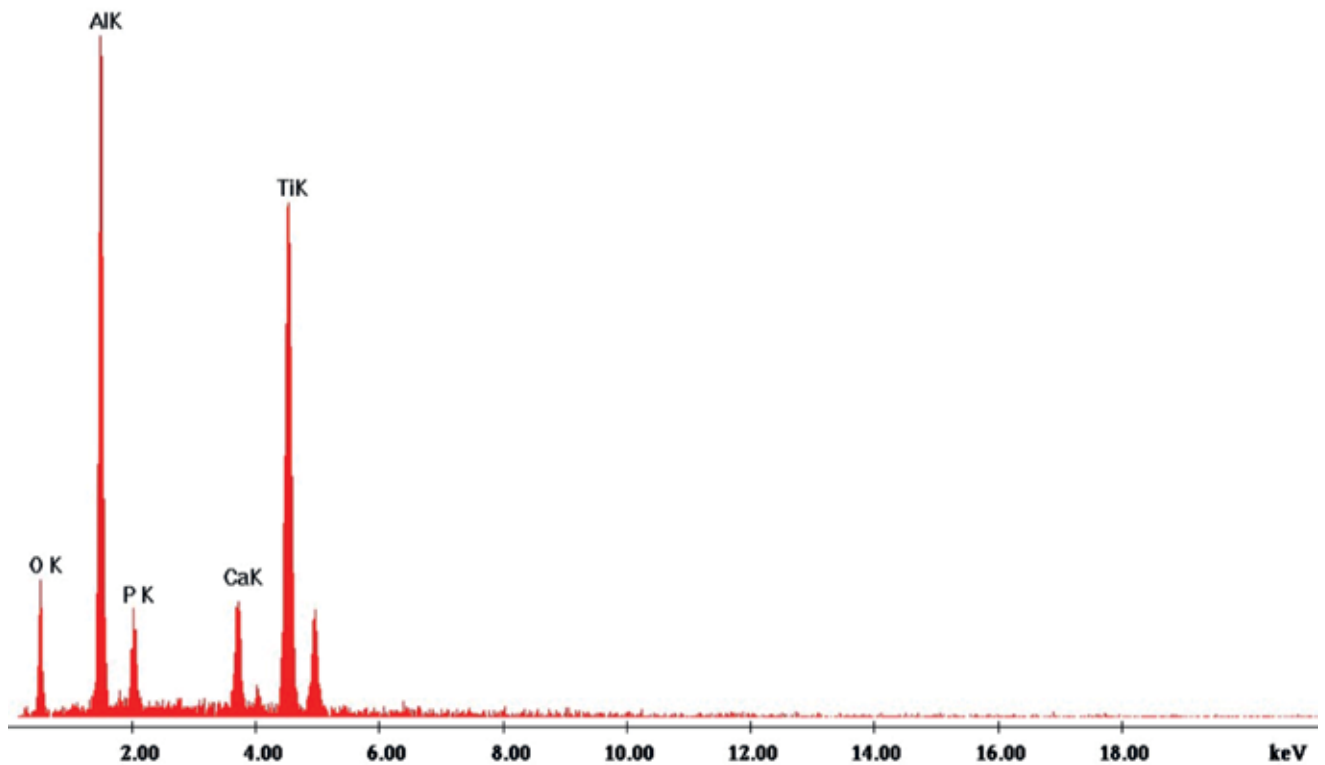


FIGURE 13. Energy dispersive X-ray spectrum (EDAX) with chemical elements: Ti, Al in the substrate and Ca, P and O2 in the deposited layer

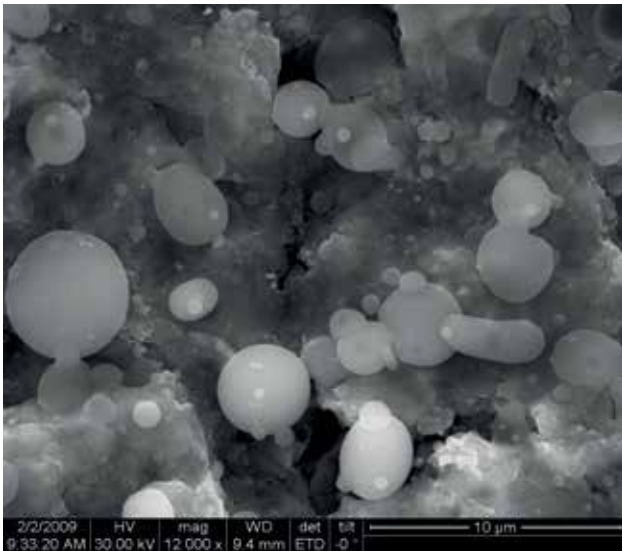


FIGURE 14. The relief of the substrate are well covered by the bio-glass film with a granular appearance, with agglomerations of particles. X 12,000

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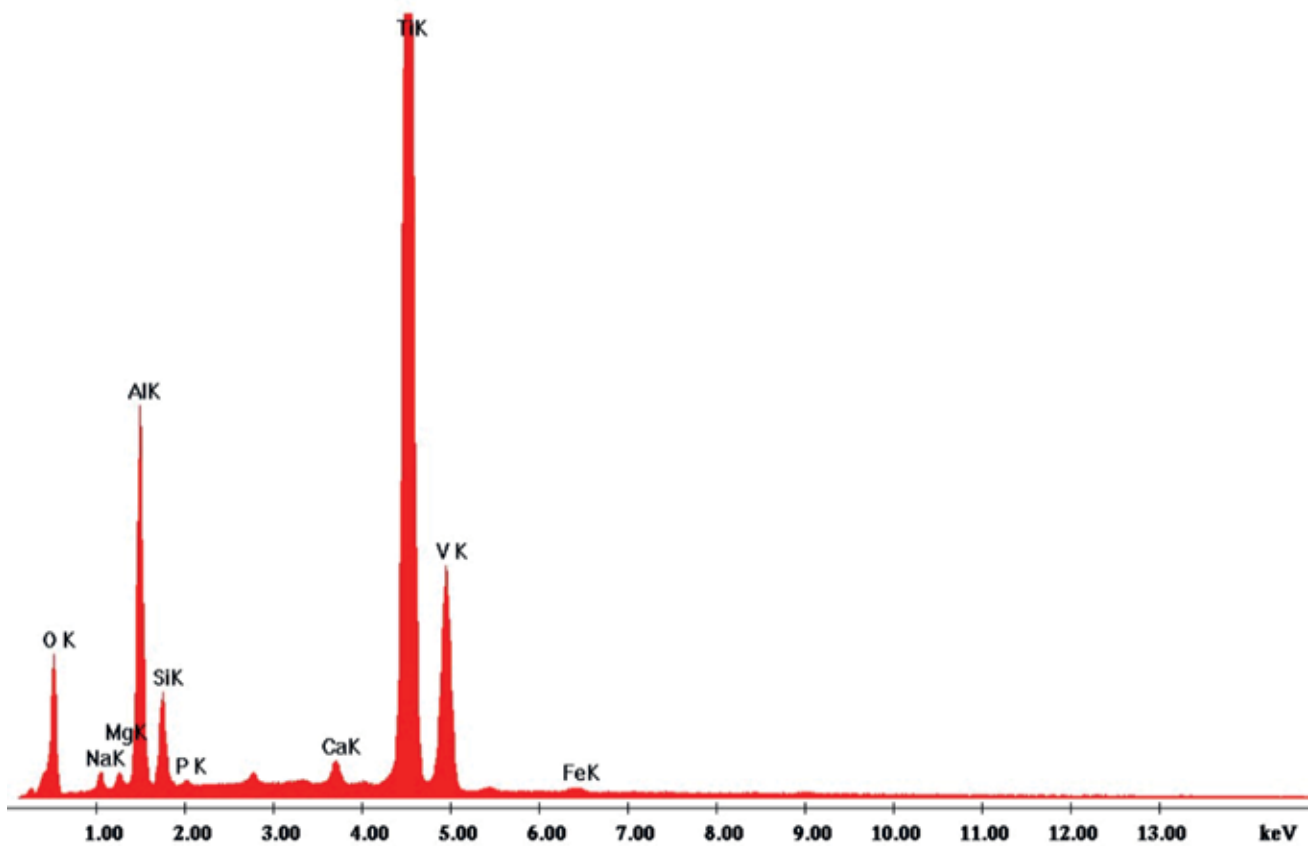


FIGURE 15. The energy dispersive X-ray spectrum shows chemical elements: Ti, Al, V in the substrate and Si, Ca, P, Na, Mg, Fe and O₂ in the deposited layer

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