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Sol-gel derived hydroxyapatite coatings on titanium substrate

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Biomaterials, in particular those used for orthopaedic prostheses, consist of a metallic substrate, exhibiting excellent mechanical properties, coated with a ceramic layer, which guarantees resistance to the corrosion and an elevated bioactivity. In this paper the preparation of sol-gel films of hydroxyapatite, HA ($Ca_{10}(PO_4)_6(OH)_2$), on titanium substrate is described. The samples were obtained through the dip-coating method, starting from a colloidal suspension of hydroxyapatite. In order to increase the adhesion between the HA film and the metallic substrate, the same substrate has been preliminarily coated either with titanium oxide, TiO_2 (in the anatase or rutile phase), or calcium titanate, $CaTiO_3$ (perovskite). Also these latter films have been deposited from a sol-gel solution. The characterization of the films through XRD, SEM, and AFM gave good results for the crystallinity of the deposited HA; for what concerns the sample morphology, the films turned out to be homogeneous and crack-free.

1. Introduction

Bioceramics, which are applied, for instance, in the fabrication of orthopaedic and dental prostheses, in some cases are used in the form of films deposited on metallic substrates or mixed with other materials in order to produce composite biomaterials which possess better mechanical and biochemical properties. In fact, the deposition of ceramic coatings on metallic substrates limits the release of ions by the metallic materials used in the realization of prostheses, which exhibit very good mechanical performances, but are corroded by the physiologic solution which surrounds the implant [1]; furthermore, by means of the ceramic film it is possible to modify the surface features of the metal, increasing the prosthesis biocompatibility or bioactivity.

Due to its similarity with the inorganic component of bones and teeth, one of the first materials used for the fabrication of these coatings on metallic materials has been synthetic hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$]. Moreover, hydroxyapatite (HA) and other materials based on calcium phosphate allow a fast stabilization of the implant with respect of the bony tissue which surrounds them; it has also been demonstrated that the deposition of HA films prolongs the lifetime of prostheses [2].

The categories of metals which are currently used in the realization of orthopaedical prostheses are essentially three: stainless steels, cobalt alloys and titanium alloys [3]. These latter exhibit excellent mechanical properties and a good resistance to corrosion, and this is the reason why they are the most used, particularly for hip prosthesis fabrication.

The method widely applied for the realization of ceramic coating is plasma spray. The main advantage of this technique is that the properties of the metallic substrate are not changed at all, as during the process the substrate remains at temperatures lower than 300°C. There are also other methods to make ceramic coatings: electrophoretic deposition, hot pressing, magnetron sputtering and deposition by means of sol-gel [4].

The aim of this work has been to test the application of the sol-gel technique for the deposition of HA films on a metal substrate in order to obtain a composite biomaterial to be applied in the field of orthopaedic prostheses. The method used for the deposition has been the dip-coating, followed by a suitable thermal treatment.

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According to the studies of Huaxia, Ponton and Marquis [5] the relationship between the substrate and the coatings is due to the reaction:

$$2Ca_{10}(PO_4)_6(OH)_2 + 4TiO_2 \rightarrow +6Ca_3(PO_4)_2 + 2CaTi_2O_5 + 2H_2O \quad (1)$$

This reaction occurs because of two phenomena which can both take place at the substrate-film interface. The first is the diffusion of phosphorous ions within the surface layer, producing a titanium and phosphorous compound: the decrease of phosphorous ions at the interface gives origin to calcium phosphate. The second is the formation on the most external surface of the metal, during the heating, of a very thin layer of titanium oxide which can subtract Ca^{2+} ions from the film to form $CaTi_2O_5$.

In order to favour this latter phenomenon and to increase the adhesion of the hydroxyapatite film with the substrate, the deposition (followed by a thermal treatment) of an intermediate coating of TiO_2, also obtained by "dip-coating", has been experimented. The deposition, always with the same technique, of an intermediate coating of $CaTiO_3$ has also been tested, in order to favour the formation at the interface not only of Ti and P compounds, but also of phosphorous and calcium compounds.

2. Experimental

Three sols have been prepared. The preparation of the solution to use for the deposition of TiO_2 coatings (TiO_2 sol) has been performed starting from titanium tetraisopropoxide ($Ti(OC_3H_7i)_4$), suitably stabilized. Once the optimum solution was prepared, its viscosity was measured (Brookfield Digital Viscosimeter mod. DV-II). The initial value found for the TiO_2 sol was 2.24 centipoise. Maintaining the solution in a closed container, the viscosity did not change much with time, so allowing to obtain good quality films even after few months from the preparation.

For the preparation of the solution used for $CaTiO_3$ films ($CaTiO_3$ sol) calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) was used. This salt causes a considerable increase in the viscosity of the solution (initial value = 5.64 cps), and at the same time decreases its stability: in fact, even keeping the sol in a closed container, after about two months gelation occurs.

For the preparation of the starting solution for hydroxyapatite films (HA sol) $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$ were used. The initial value of the viscosity is 84 cps and the solution exhibits a milky appearance.

To determine the working conditions for the preparation of the coatings a preliminary study has been carried on about the gel behaviour as a function of the treatment temperature. Powders obtained from the gel underwent thermal treatments at various temperatures between 100 and 1000°C, being this the working range to obtain the coatings, and then were characterized by means of X-ray diffraction.

Films were deposited by using the dip-coating method: the withdrawal speed was optimized depending on the composition and the viscosity of the solution used.

The metallic substrates have been carefully cleaned and dried under laminar flow to avoid the deposition of dust. A preliminary treatment at 400°C for 10 minutes allows the complete elimination of organics on the surface. After cooling at room temperature, the dipping operations have been carried out.

To prepare titania films a single layer has been deposited from the TiO_2 sol (optimum withdrawal rate = 9.6 cm/min). The sample was kept at room temperature for 10 minutes to allow the solvent evaporation, always under laminar flow, afterwards a thermal treatment was performed in furnace up to 750°C. Samples were cooled to room temperature always under laminar flow.

Also for the preparation of the coatings of calcium titanate, starting from $CaTiO_3$ sol a single layer has been deposited (optimum withdrawal rate = 7.7 cm/min), operating like in the previous case.

For the preparation of hydroxyapatite films two layers have been deposited. After each deposition the samples have been let for 30 minutes under laminar flow and then heat treated in a furnace. The withdrawal rate used for the first deposition was 19.5 cm/min, and 12.4 cm/min for the second. After the first deposition the film has been completely dried with a preliminary thermal treatment at 200°C, after the second deposition the temperature used for the treatment was 750°C. In this case, to avoid the formation of cracks in the films due to thermal chock, the samples were cooled down slowly inside the furnace.

The thermal evolution of the gels and films has been monitored by means of X-ray diffraction (XRD), while the morphological analysis has been performed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The surface chemical composition of the films was determined by using XPS.

3. Results and discussion

3.1. Structural and morphological characterization

X-ray diffractograms recorded on the powders obtained from the TiO_2 sol treated up to 300°C do not reveal any noticeable peak, and this indicates the presence of one or more amorphous phases. After 300°C the formation of the anatase phase starts. By gradually increasing the temperature, one can note that at 550°C a highly crystalline powder is obtained, completely consisting of TiO_2 in the anatase phase. Varying the temperature up to 750°C (which is the maximum temperature reachable in the realization of the film, as it will be seen further on) the partial transformation of the anatase phase into the rutile phase is taking place.

From the XRD spectra of the powders obtained from $CaTiO_3$ sol, one can see that again no crystalline phases are present up to 300°C. At 300°C the peaks related to the anatase phase appear, similarly to those observed in the bulk TiO_2. The crystallization of calcium titanate in its perovskite form $CaTiO_3$ is completed at 600°C. Increasing the temperature up to 750°C it is seen that besides perovskite another phase of calcium titanate, with formula $Ca_2Ti_5O_{12}$, and a small quantity of TiO_2 in the anatase phase are present.

The diffractograms relative to the powders obtained from the HA sol reveal a certain degree of crystallization already at 300°C, even if the dimensions of crystallites are still very small, thus the peaks are not well defined yet. As the temperature increases, the degree of crystallization progressively increases up to 750°C: over this temperature no more variations are detected. The crystalline phase formed is hydroxyapatite.

After the preparation, the film morphology was studied by means of SEM and AFM.

First the metal substrate was analyzed, and then the coatings of TiO_2, $CaTiO_3$ and hydroxyapatite.

SEM observations revealed that the substrate exhibits a very irregular surface, where one can see spotted flat areas with cavities having an about circular shape with diameters varying between 1 and 10 μm. The depth of such cavities, measured by AFM, varies from 200 to 500 nm.

The high surface roughness of the substrate makes the quantity of solution deposited during the dip-coating process increase, but creates problems of cracks formation in the film: in fact, as will be seen in the following, the films do not completely fill the cavities present on the substrate, but follow its profile.

The evolution of the TiO_2 coating during the thermal treatment has been studied. The sample under examination, drawn from the furnace after 30 minutes of treatment at 550°C, exhibits an amorphous nature. The film treated at 750°C for 1 hour (Fig. 1) shows grains homogeneously distributed over all the surface, whose dimensions are about $0.3 \div 0.7$ μm.

From the AFM image one can clearly note that the film exhibits zones of very high homogeneity, but also some agglomerations of particles. The analysis of the surface shows a decrease of the film roughness with respect to the substrate (and also with respect to the film treated at lower temperature).

The XRD characterization demonstrated that at 550°C in the TiO_2 film only the anatase phase is present (Fig. 2), as it was determined also from the analysis performed on the bulk sample. The presence of a weak and not well defined peak indicates that after only 30 minutes of treatment at 550°C the crystallization of titanium oxide is not complete yet, what was already shown by SEM analysis.

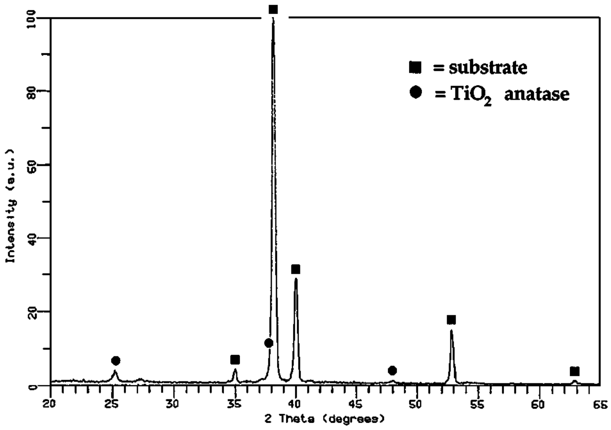

Figure 2 Diffractogram of the TiO_2 film treated at 550°C.

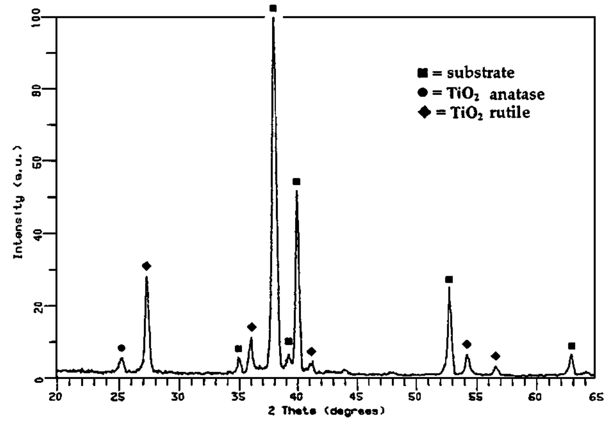

Figure 3 Diffractogram of the TiO_2 film treated at 750°C.

On the other hand, the rutile phase is predominant at 750°C (Fig. 3), even if a small amount of anatase is still present.

Similarly to what was done for the TiO_2 coating, the thermal evolution of the $CaTiO_3$ film was followed. SEM observations show that also the calcium titanate coating is amorphous at 550°C. Also in this case cracks

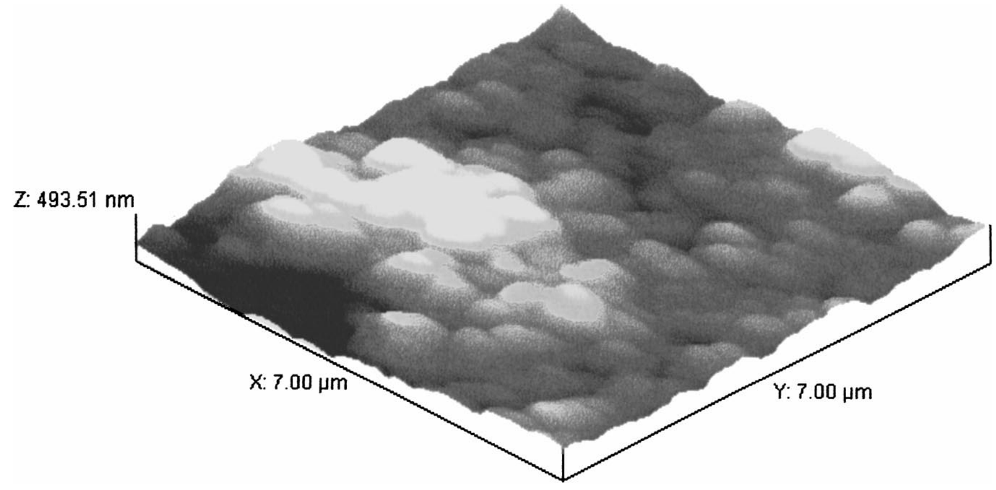

Figure 1 AFM image (70 × 70 μm) of the TiO_2 film after treatment at 750°C for 1 hour.

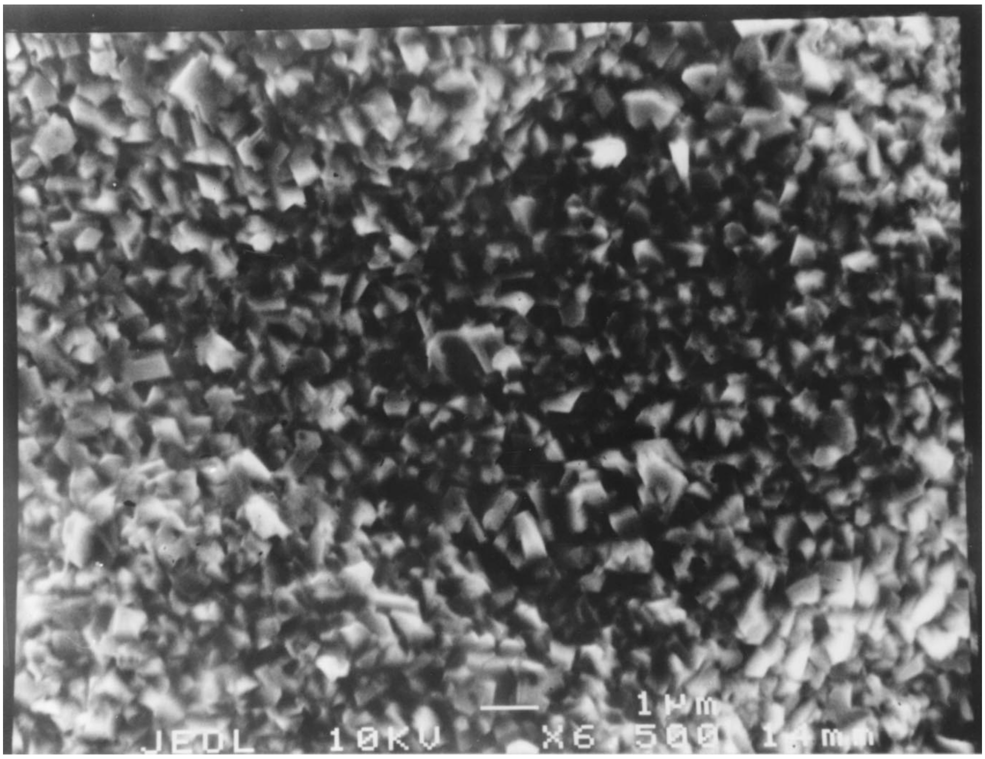

Figure 4 SEM picture of the $CaTiO_3$ film treated at 750°C.

are present, but their amount is much less with respect to those present in the TiO_2 film and their dimensions are small. AFM analysis revealed that the surface roughness is of the same order of magnitude of that of the substrate, and this suggests that the film tends to follow the irregular profile of the substrate. After the thermal treatment at 750°C for 1 hour, also the calcium titanate film is a very homogeneous layer of grains having dimensions varying from 0.4 to 0.8 μm (Fig. 4). The AFM images show that cavities are still present, but their height varies in the range $0.2 \div 0.3$ nm, i.e. a little more than half the depth found for the substrate. The grain distribution is very regular.

Similarly to the film of titanium oxide, also in this case aggregations of particles are present. In particular, it was noted that such agglomerates are mainly formed on the border of the cavities. This must be probably ascribed to the formation of a thicker layer of solution during the withdrawal procedure, with subsequent localized increase of the film thickness.

From XRD analysis (Fig. 5) one can observe that a certain amount of calcium titanate is present already at 550°C, even if the film appears as amorphous, what is confirmed by the SEM image.

At 750°C (Fig. 6) it is possible to see that neither $CaTiO_3$ is present any longer, or the other phase of calcium titanate, $Ca_2Ti_5O_{12}$, already observed during the examination of the thermal evolution of the gel. Another difference is the presence of the rutile phase instead of anatase.

For what concerns the samples coated with hydroxyapatite, XRD measurements performed on the first of the two layers of hydroxyapatite, treated at 200°C, did not give significant data, because the thickness of this film is too small and the degree of crystallization is low at this temperature. SEM observations showed a good homogeneity in the central zone, while the formation of cracks has been noticed near the borders.

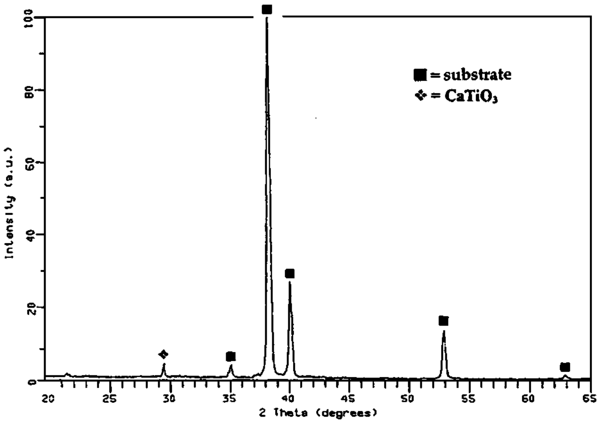

Figure 5 Diffractogram of the $CaTiO_3$ film treated at 550°C for 30 minutes.

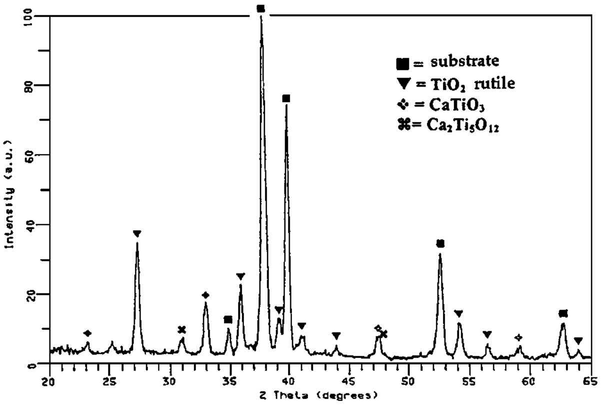

Figure 6 Diffractogram of the $CaTiO_3$ film treated at 750°C for 1 hour.

Again SEM analysis confirms the presence of zones having good homogeneity together with particles with

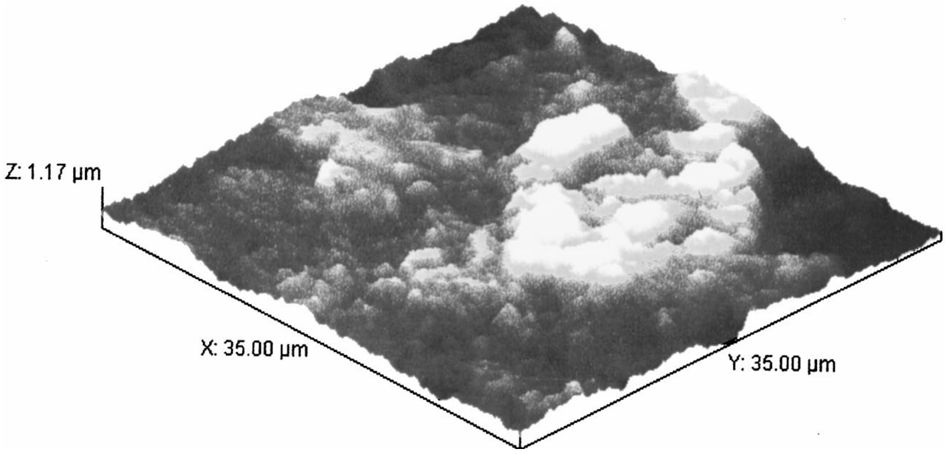

Figure 7 AFM image (35 × 35 μm) of the hydroxyapatite film treated at 750°C for 4 hours.

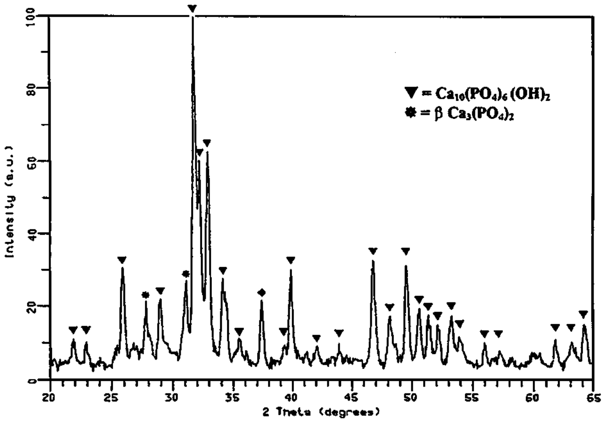

Figure 8 Diffractogram of the HA film, treated at 750°C, deposited on the intermediate TiO_2 coating.

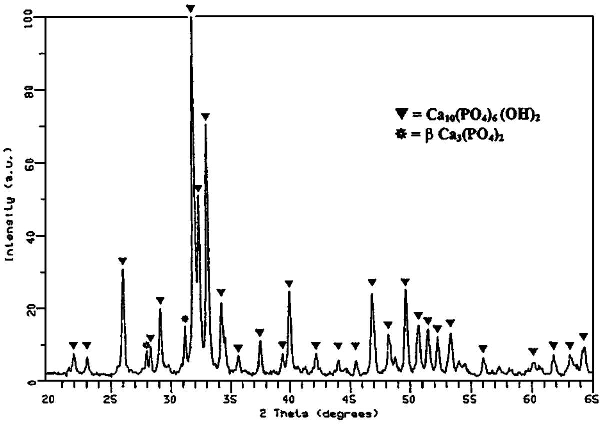

Figure 9 Diffractogram of the HA film, treated at 750°C, deposited on the intermediate $CaTiO_3$ coating.

dimensions of about 1 μm and agglomerations of grains having dimensions up to $3 \div 4$ μm. Good homogeneity was also revealed by AFM analysis, as shown in Fig. 7.

The average height measured through the whole surface is practically the same as the one found for the section. These results indicate a very good homogeneity of the hydroxyapatite film obtained. This fact was also confirmed by XPS depth profiling [6]. It is also worth noticeing that from the point of view of the surface morphology no significant differences were found between the HA films deposited on intermediate TiO_2 or $CaTiO_3$ films.

Figs 8 and 9 show the diffractograms relative to the hydroxyapatite coatings deposited on the intermediate TiO_2 and $CaTiO_3$ film respectively.

In both cases the predominant phase is hydroxyapatite, but a certain amount of β-$Ca_3(PO_4)_2$ (β-TCP) is also present, which did not appear in the analysis of the bulk. The formation of β-TCP can be ascribed to the reaction (1), which involves the migration of Ca^{2+} ions within the intermediate coating with formation of calcium titanate, causing a variation of the Ca : P ratio inside the hydroxyapatite film at the same time and, therefore, the formation of β-$Ca_3(PO_4)_2$.

From the comparison of the spectra it is noticed that the HA coatings deposited on $CaTiO_3$ always show a degree of crystallinity higher than those deposited on TiO_2. This is probably due to the fact that the presence of calcium titanate in the intermediate coating is less favourable for the diffusion of Ca^{2+} ions within the coating, so that the variation of the Ca : P ratio is lower than in the case of the intermediate TiO_2 coating.

3.2. Evaluation of bioactivity for TiO_2 films

Panjian, Kangasniemi and de Groot [7] verified that the TiO_2 coating treated at 500°C for 10 minutes, immersed for several days in a physiologic solution which simulates the plasma contained in the human blood, favours the heterogeneous nucleation of hydroxyapatite on its surface.

The so formed hydroxyapatite exhibits a great similarity to the apatite found in the bony tissue: in fact, it exhibits a not very high degree of crystallization, even if two OH^- groups of hydroxyapatite are substituted by a CO_3^{2-} group. The formation of $Ca_{10}(PO_4)_6CO_3$ on the surface of the TiO_2 coating must be ascribed to the fact that, performing a thermal treatment limited in time and at a not very high temperature, several OH^- groups still remain on the external layer of the film.

The physiologic solution has a $pH = 7.4$ at 37°C (body temperature). Being the isoelectric point of the titania film at pH $\sim$6.8 [8], when the sample is dipped into this solution it exhibits on its most external layer a negative charge able to give rise to ionic pairs with Ca^{2+} ions. In addition, still present OH^- groups can

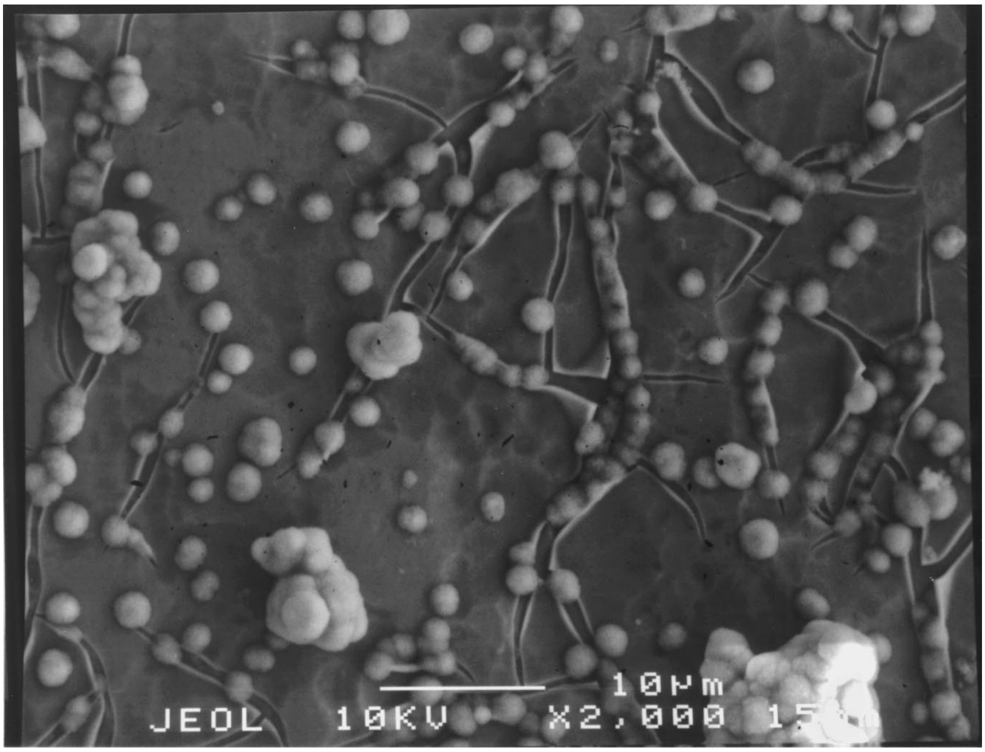

Figure 10 SEM picture of the TiO_2 film after 10 days of immersion in SBF.

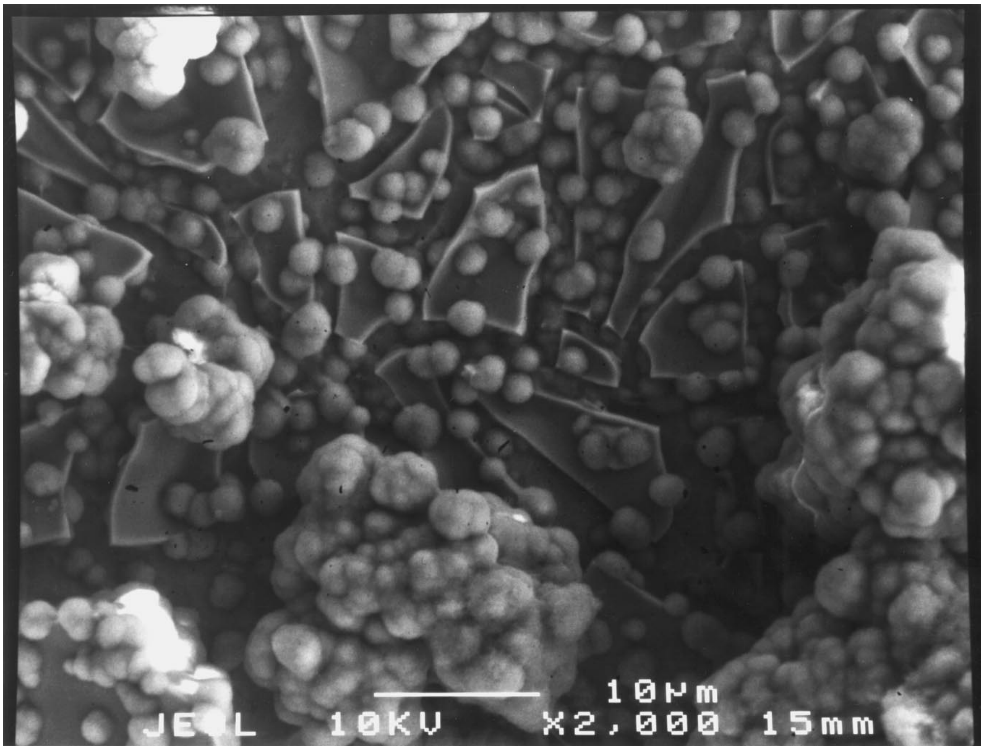

Figure 11 SEM picture of the TiO_2 film of Fig. 10: detail of an area of high inhomogeneity.

form hydrogen bonds with the phosphate groups which are in the solution [9].

The increase of the concentration of both calcium and phosphate ions near the surface brings to a local exceeding of the critical level of saturation beyond which the heterogeneous nucleation of hydroxyapatite starts.

Samples prepared from TiO_2 sol and treated at 500°C for 10 minutes underwent a test *in vitro*.

Following indications reported in literature [10] a physiologic solution (Simulated Body Fluid, SBF) was prepared. For the execution of the test *in vitro* on the TiO_2 coatings, the samples were put in polyethylene containers with 30 ml of SBF. They were then hermetically closed and put in a muffle furnace at 37°C for 10 days.

After this period of time the samples were pulled out and, after drying under laminar flow, analyzed by SEM.

The presence of cracks was revealed on the TiO_2 film. As one can see in Fig. 10, the presence of the fracture seems to have favoured the deposition of the

$Ca_{10}(PO_4)_6CO_3$ particles, as they are mostly distributed on the borders and inside the cracks. Therefore it is probable that the borders themselves act as a center of heterogeneous nucleation for the apatite, which during its growth tends to arrange inside the cracks, filling them completely.

This theory is supported by what observed in Fig. 11, where one can see that, together with spherical particles, with diameters varying between 1 and 2 μm, there are also agglomerations of particles, localized in zones of the film where the greatest number of cracks is found, and therefore also of nucleation centers. In these zones the growth begins before, with respect to the other parts of the coating and, taking advantage of the higher concentration of Ca^{2+} ions and of phosphate groups, soon after the nucleation on the film the growth proceeds rapidly on the deposited particles. As the deposition of $Ca_{10}(PO_4)_6CO_3$ proceeds, the solution becomes poorer of Ca^{2+} and phosphate ions, so that after 10 days no more growth occurs.

4. Conclusions

In this work the application of the sol-gel technique for the realization of ceramic coatings on metals has been studied, with the aim of obtaining composite biomaterials to be used in the fabrication of orthopaedic prostheses. The study was focused on the deposition of hydroxyapatite films by dip-coating on a titanium substrate.

This process did not find industrial applications yet, but allowed to obtain films that from SEM and AFM analyses revealed good homogeneity and a high surface roughness, and this latter parameter is particularly important, as it guarantees a wide contact surface between the prosthesis and the surrounding bony tissue.

XRD analysis revealed the presence of hydroxyapatite having a high degree of crystallinity, quality that gives the film a very good resistance to the degradation which undergoes in the physiologic solution which surrounds the prosthesis plant when inserted in the human body.

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References

1. W. R. LACEFIELD, in “An Introduction to Bioceramics,” edited by L. L. Hench and J. Wilson (World Scientific, Singapore-New Jersey-London-Hong Kong, 1993), p. 223.
2. M. INOMOTO *et al.*, in “Bioceramics, Vol. 8,” edited by J. Wilson, L. L. Hench and D. Greenspan (Pergamon-Elsevier, Oxford, 1995), p. 186.
3. L. L. HENCH and Ö. ANDERSSON, in “An Introduction to Bioceramics,” edited by L. L. Hench and J. Wilson (World Scientific, Singapore-New Jersey-London-Hong Kong, 1993), p. 241.
4. C. J. BRINKER and G. W. SCHERER, “Sol-Gel Science - The Physics and Chemistry of Sol-Gel” (Academic Press, London, 1990).
5. J. HUAXIA, C. B. PONTON and P. M. MARQUIS, *J. Mater. Sci. Mater. in Med.* **3** (1992) 283.
6. F. CIRILLI, S. KACIULIS, G. MATTOGNO, G. RIGHINI, F. FERRARI, A. MONTENERO and G. GNAPPI, *J. Electron Spectrosc. Related Phenom.* **95** (1998) 61.
7. L. PANJIAN, I. KANGASNIEMI and K. DE GROOT, *J. Am. Ceram. Soc.* **77** (1994) 1307.
8. G. A. PARKS, *Chem. Rev.* **65** (1965) 177.
9. D. E. C. CORBRIDGE, “The Structural Chemistry of Phosphorus” (Elsevier, Amsterdam 1974), p. 247.
10. L. L. HENCH, in “An Introduction to Bioceramics,” edited by L. L. Hench and J. Wilson (World Scientific, Singapore-New Jersey-London-Hong Kong, 1993), p. 332.

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