Preparation and characterisation of titania/hydroxyapatite composite coatings obtained by sol–gel process

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Abstract

In the present work a titania network encapsulating a hydroxyapatite particulate phase is proposed as a bioceramic composite coating. The coating on a titanium substrate was produced starting from a sol containing a mixture of titania colloidal particles and hydroxyapatite submicron particles using the dip-coating technique. The microstructure, the morphology and the surface chemical composition of the coating were characterised using X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS), respectively. Adhesion tests were also performed. These analyses showed that the obtained coating was chemically clean, homogeneous, rough, porous, with a low thickness and well-defined phase composition as well as a good adhesion to the substrate. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Brånemark [1] introduced the term "osteointegration" to describe the contact between the titanium surface and the bone. The term 'bio-integration' has a different meaning: *stimulate the bone growth with a bioactive surface that encourages the direct bond between the implants and the surrounding bone*, where the 'bioactivity' is the ability of a material to attach itself to the living tissues without an interposing fibrous tissue layer [2].

In the recent years many studies have been carried out in order to develop bioactive materials. Hydroxyapatite (HA) coatings are used to promote osteoconductive bonding of metallic implants in the dental and ortho-paedic fields. The plasma spray technique is currently used to fabricate HA coatings [3,4], but the unavoidable HA decomposition due to a high-temperature process [5], the relatively high thickness ($> 30\,\mu m$) and a poor bonding with the substrate [6] are the major problems of this method.

It has been reported that the materials prepared with the sol–gel process are efficient calcium phosphate absorbents in vitro and in vivo studies [7–9] while those of the same composition but prepared by traditional methods at high temperature are biologically inert [10]. Many hydroxylic groups present onto the sol–gel processed coating may be responsible for the bioactivity of these materials [11].

The aim of this study was to prepare a composite film constituted of a titania matrix encapsulating HA by the sol–gel process, in order to obtain a thin, stable, clean and bioactive coating for a titanium substrate.

Since successful bone fixation has been shown to be related to the surface morphology and composition, attention was focused on the microstructural, morphological and surface properties.

2. Materials and methods

2.1. Sol–gel and coating preparation

The sol–gel coating process is illustrated in Fig. 1.

Commercially available HA powders (Fin Ceramica, Faenza, Italy) were added to anhydrous ethanol (Fluka, Buchs, Switzerland) at the ratio of 1:1 by weight.

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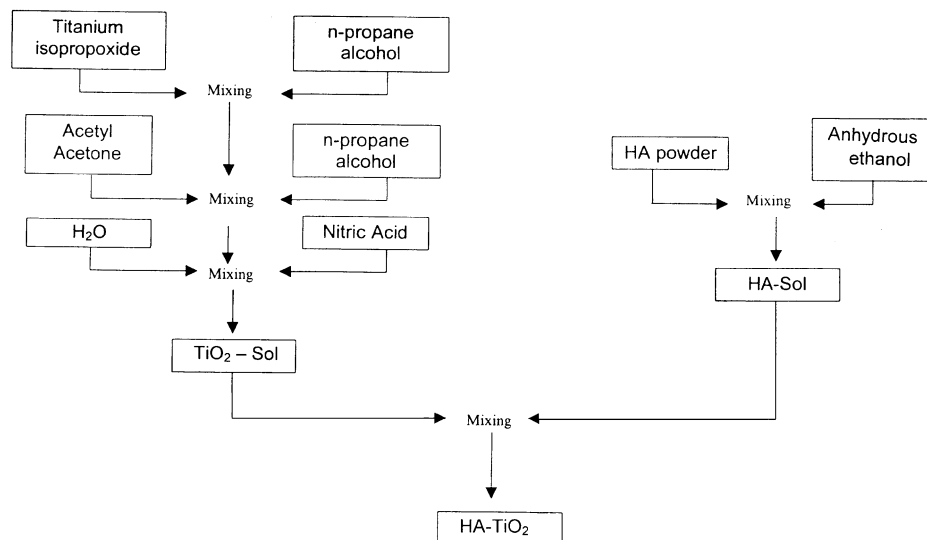
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Fig. 1. Sol–gel process.

The titania sol solution (TiO$_2$ 5% w/w) was prepared by mixing titanium isopropoxide, acetyl, nitric acid, n-propane alcohol and distillated water (molar ratio Ti/AcAc = 2/1 and Ti/H$_2$O = 1/2). The chemicals were supplied by Aldrich, Wisconsin, USA.

The sol–gel solution was obtained mixing the HA–ethanol solution to titania sol at the ratio of HA:TiO$_2$ equal to 1 by weight.

Plates of commercially pure titanium (Goodfellow, Cambridge, UK), ultrasonically cleaned in acetone for 15 min, in 70% ethyl alcohol solution for 20 min and then in distilled water for 20 min were used as substrates.

The coatings were obtained by dipping the substrates in the mixture at a speed of 15 cm/min. A computer-controlled linear positioner (Physik Instruments series 500) was used as a puller. The dipping equipment was located in a box at controlled temperature (25°C) and humidity (<40%). The gel film was then heated at 500°C for 30 min. This process was repeated four times.

2.2. XRD measurements

X-ray diffraction measurements were performed by means of a Philips PW1880 diffractometer equipped with a 3-kW generator. A Cu target was used as X-ray source (Cu Kα radiation) at 40 kV and 40 mA. A graphite monochromator was located in front of the proportional counter in order to reduce the background noise in the detector.

During the measurements related to the HA powder, the incident angle was varied as half of the scattering angle (2θ) in a coupled $2\theta/\theta$ movement. For the analysis

of the film the incident angle was kept fixed at 1° varying only the detector angle (2θ) in a 2θ scan.

2.3. SEM analyses

Scanning electron microscopy (SEM) examinations were performed with a PHILIPS XL40 LaB6, equipped with an energy dispersive spectrometer (EDS) EDAX DX4i. An electron probe at an acceleration voltage of 20 kV was employed. Before the observation, the samples were coated with a 5 nm Au film by sputtering. The analytical investigations were carried out in spot mode.

2.4. XPS measurements

A VG Scientific ESCALAB 210-D spectrometer operating with a non-monochromatic Al Kα radiation at a pressure of $\sim 5 \times 10^{-9}$ mbar was used for the investigation of the surface chemical composition of the coating. The X-ray gun worked at 15 kV and 300 W and the electron take-off (detection angle) was set at 90° for all the measurements.

Survey spectra, in the range of 0–1100 eV, were recorded with a pass energy of 50 eV, while narrow scans in the regions of C1s, O1s, Ti2p, Ca2p, P2p were recorded with a pass energy of 20 eV. All the spectra were corrected for sample charging using, as internal reference, the C–C/C–H, C1s peak at the binding energy of 284.6 eV. The integrated peak areas and the Wagner atomic sensitivity factors were used for quantitative analysis (with an estimated error of $\sim 15\%$).

2.5. Adhesion test

The adhesive bond strength of thin TiO_2/HA film to metal substrate was measured by a tensile test. A commercial nail-shaped aluminium stud-pin (Quad Group Inc., Washington, USA, with epoxy resin adhesive attaching to disk head) was fixed onto the coated specimens by a clip. After heating the specimens in an oven at 150°C for 1 h and cooling to room temperature, the adhesive strength was measured using a tensile test machine (Romulus II Interim Quad Group Inc., Washington, USA). The tensile stress was calculated by normalising it with respect to the contact area:

adhesion stress = maximum pull stress/stud area.

Nine samples were analysed. The surfaces of debonded samples were observed by SEM and EDS.

3. Results and discussion

The used HA powder, analysed by XRD (Fig. 2), was crystalline, with a hexagonal structure [12] and a Ca/P ratio, calculated by XPS measurements, of 1.65.

The X-ray diffraction spectrum of TiO_2/HA coating (Fig. 2) showed peaks related to HA, titanium and anatase phases, confirming that the HA was incorporated in the titania matrix. No amorphous phase was
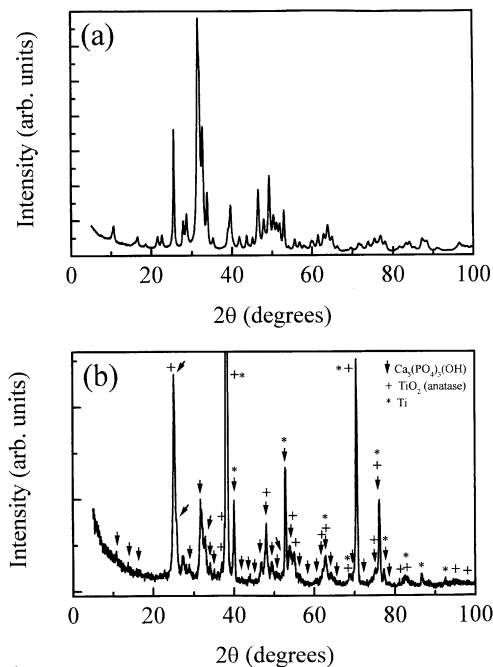
present. In fact, also the initial amorphous titania gel crystallises to anatase during heating. Since it has been demonstrated that the crystalline HA has a considerably lower dissolution rate than amorphous forms [13,14], from a structural point of view a very stable coating results.

With SEM investigation (Fig. 3a), the coating morphology appeared homogeneous, rough and with pores with a size in the range of 250–300 nm. At a higher magnification (Fig. 3b), the coating surface showed cracks due to the shrinkage occurring during the thermal process that could supply points of "mechanical interlocking" [15] to promote osteointegration. These cracks do not influence the mechanical and adhesive properties of the coating, because they are not present in the section of the film as showed in the cross-section SEM micrograph in Fig. 3c. The interface observation evidenced a well-deposited thin film (white layer) and a surface wall effect (grey layer) because the sample section was not perfectly perpendicular. The thickness of the coating was $<10\,\mu m$, even if the exact value could not be calculated due to the surface wall effect.

The EDS analysis confirmed that calcium and phosphorous are present in the coating in a typical ratio 1.6 of HA. The evaluation of the surface chemical composition was carried out by XPS analysis without any cleaning procedure of the sample in order not to alter or to degrade the sample surfaces. As shown in the survey scan (Fig. 4), the only elements detected on the surface were Ti, O, C, Ca and P, whose respective atomic percentages are given in Table 1. No contaminant element was detected and the carbon concentration of 17% is typical for organic contamination levels on "clean" surfaces [16].

In the recorded spectra, the Ca2p and P2p peaks, at the bending energy (BE) of 347.2 and 133.0 eV, respectively, were typical of HA [17]. The Ti2p 3/2 signal (Figs. 4 and 5) showed a single peak centred at 458.3 eV characteristic of titanium (IV). Therefore, the Ti detected on the surface is only the oxide (TiO_2) derived from the titania sol used for the coating preparation.

Further examinations of the asymmetrical broadening of the O1s peak (Fig. 6) indicated that multiple O species were present on the surface. The sub-peak B, at the BE of 529.7, could be assigned to titanium (IV) oxide (TiO_2), while the sub-peak A at the BE of 531.3 eV to the Ca–O and P–O bonds of HA, and to the OH groups adsorbed on the surface.

The Ca/O and Ca/P ratios were calculated to be 0.23 and 1.50, respectively, and compared with the theoretical values of 0.38 and 1.67 for the HA. The Ca/P ratio can be considered very close to the theoretical one, taking into account that the XPS information is mediated on the analysed area ($\sim 5\,mm \times 5\,mm$) constituted by TiO_2 and HA and that, due to the matrix effect, the intensity and
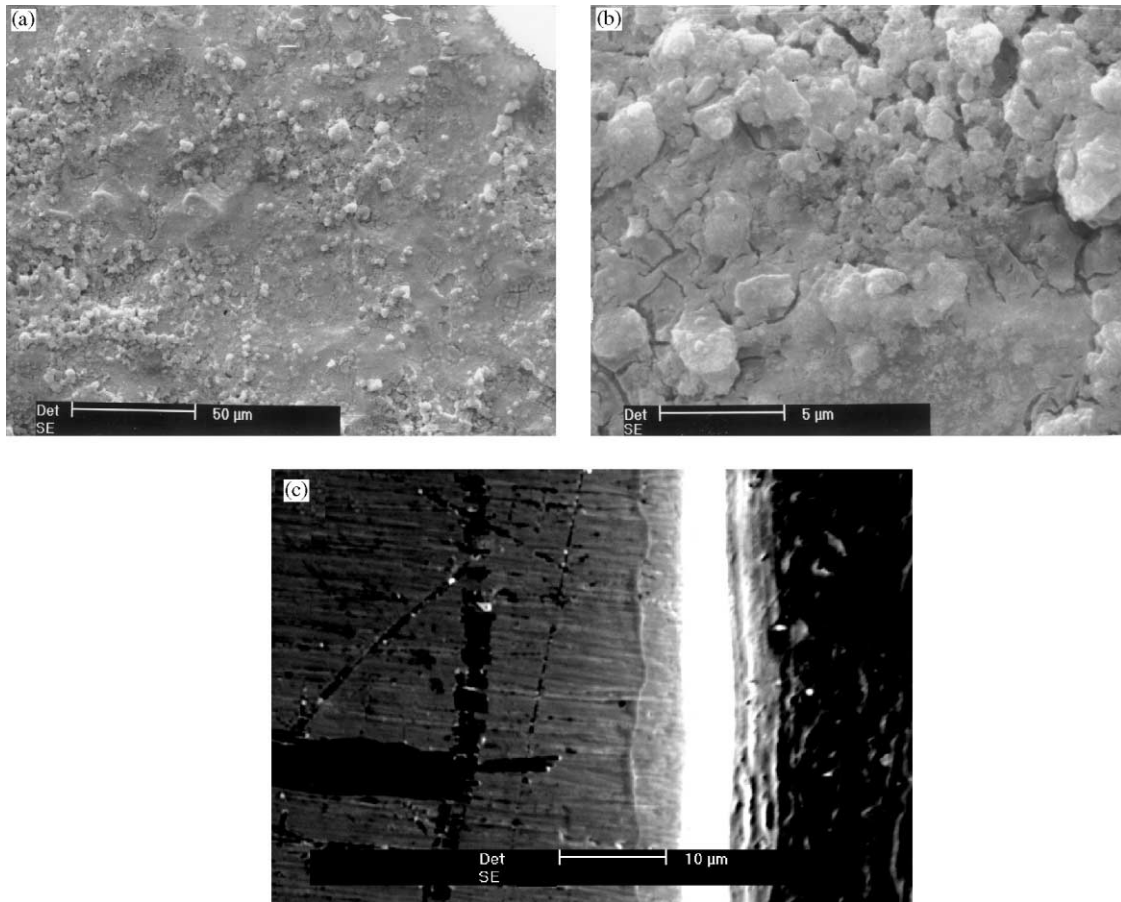

Fig. 2. XRD pattern of (a) HA powder; (b) HA–titania composite coating.

Fig. 3. SEM micrographs: (a) HA–TiO$_2$ coating at 50$\times$ of magnitude; (b) HA–TiO$_2$ coating at 5000$\times$ of magnitude; (c) cross-section.
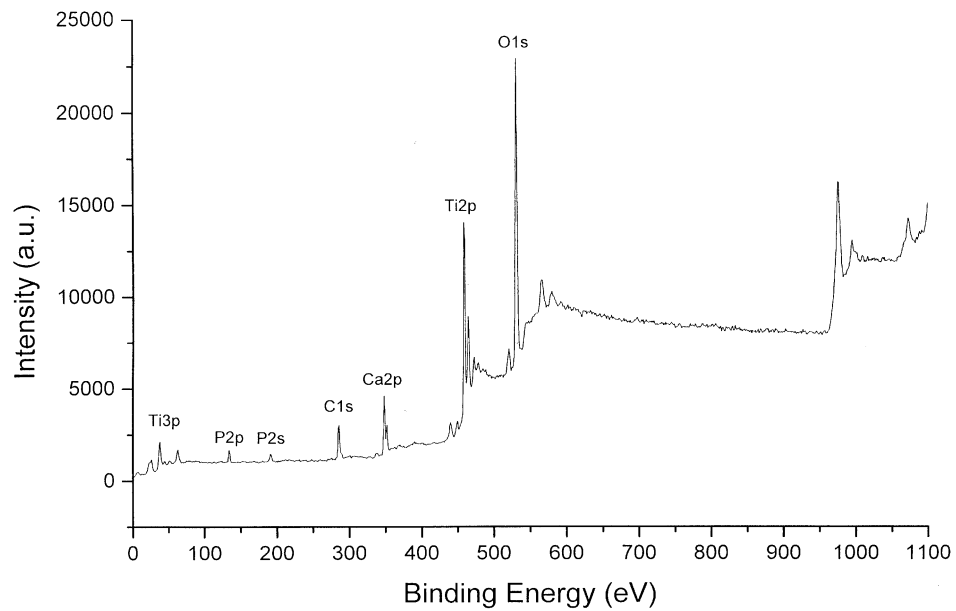

Fig. 4. HA–TiO$_2$ coating: XPS survey scan.

the resolution of the coating's Ca2p and P2p signals were lower with respect to the ones detected for the same elements on HA powder.

Table 1
Atomic percentage of the elements detected at the HA–TiO$_2$ coating surface

	Ti		O	C	Ca	P
Atomic %	17.71		56.6	17.1	5.2	3.4
		TiO$_2$	HA, **OH**			
		34.1	22.5			

The Ca/O ratio indicated oxygen excess that could be attributed to the presence of OH groups on the surface. It is known that hydroxyl groups, such as Ti–OH, remain in the sol–gel prepared materials and promote the osteointegration process [9,18].

In order to confirm the attribution of oxygen excess to Ti–OH bonds at the surface sample, XPS analysis was performed on a pure TiO$_2$ coating prepared with the sol–gel technique in the same experimental conditions. Also in this case, the O1s (Fig. 7) core level showed a peak due to TiO$_2$ contribution, and another at higher binding energy. In this case, the only attribution for the higher energy O1s peak could be the OH contribution because
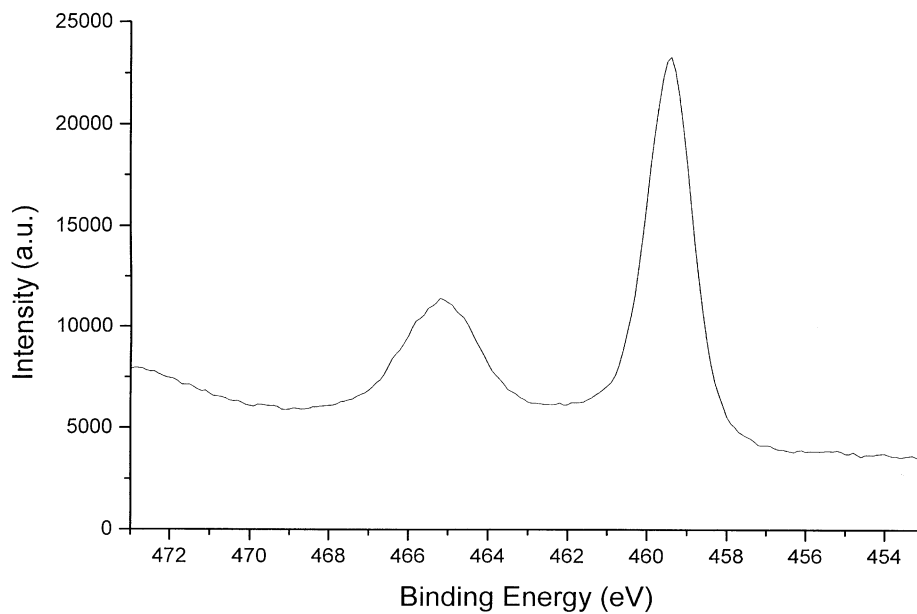

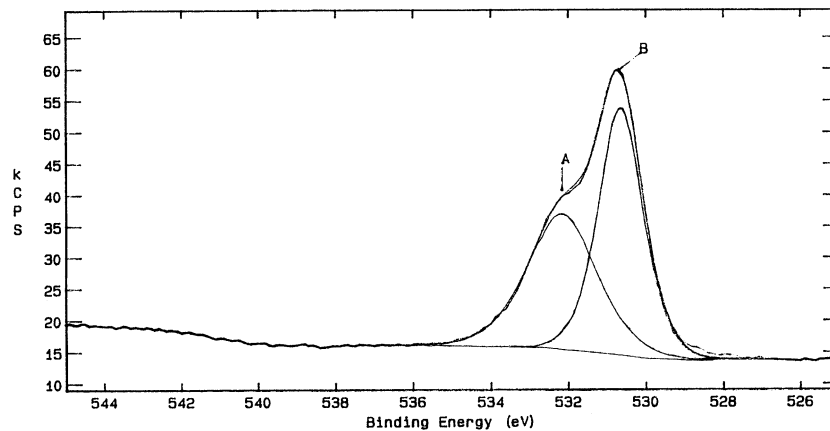Fig. 5. HA–TiO$_2$ coating: XPS Ti2p spectrum.

Fig. 6. HA–TiO$_2$ coating: XPS O1s spectrum.

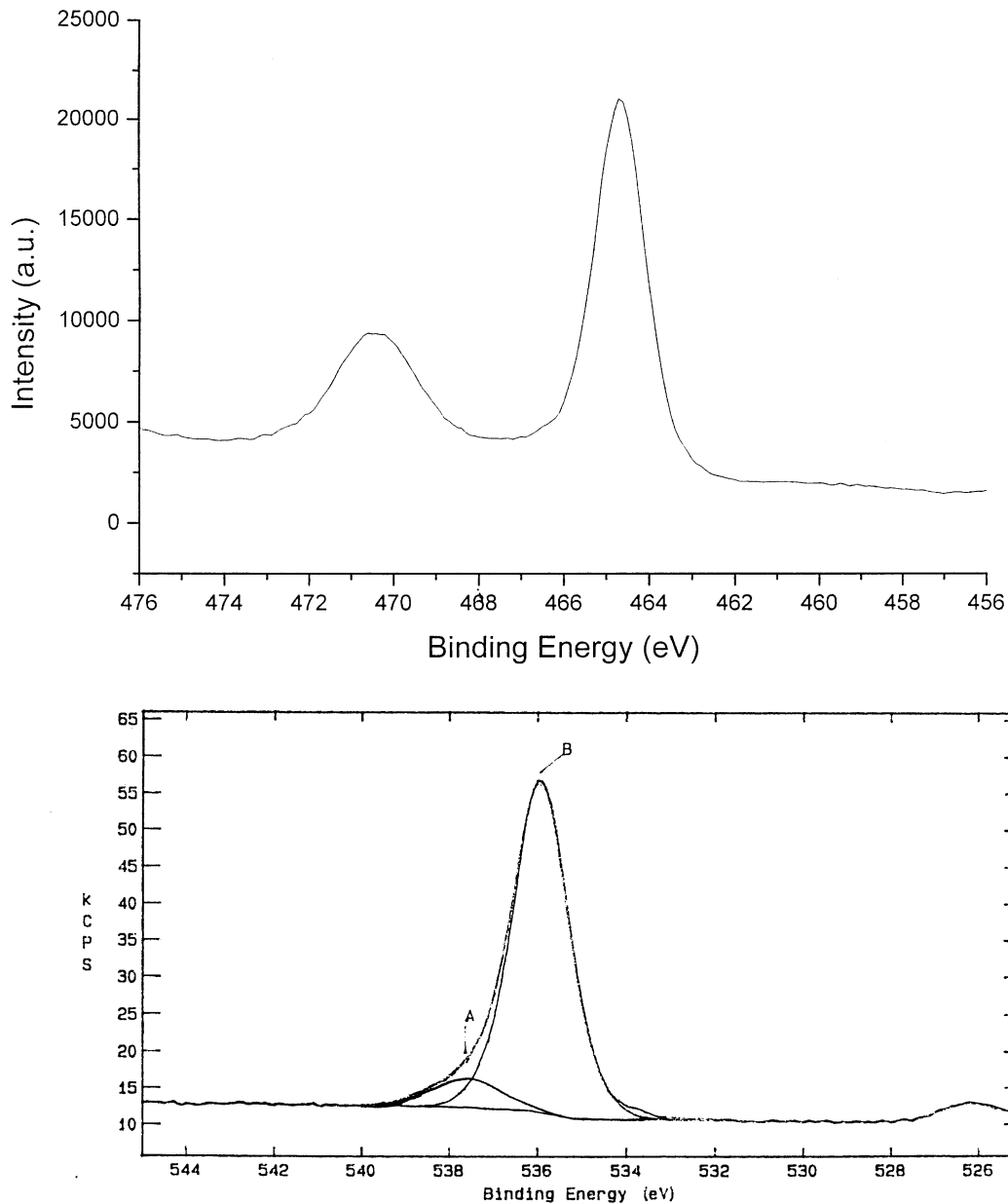Fig. 7. TiO$_2$ coating: XPS Ti2p and O1s spectrum.

no elements other than Ti, O and C were detected at the surface.

Then, the XPS results suggested that the prepared composite coating could show bioactive properties. In order to confirm this hypothesis, in vitro biocompatibility tests are in progress.

Finally, the adhesion strength of the film to the substrate was detected with the pull-test. The obtained value was 39.8 ± 3.75 MPa. The area subjected to the pull-test was examined by SEM (Fig. 8). The presence of the coating and epoxy resin were evident and the EDS analysis showed no signal coming from Ti substrate, indicating that a good adherent coating can be obtained by means of the sol–gel dipping method.

4. Conclusions

A composite coating consisting of titania matrix in which HA particulates were encapsulated was produced. The coating showed defined crystalline phases. The surface was chemically clean and the presence of hydroxylic
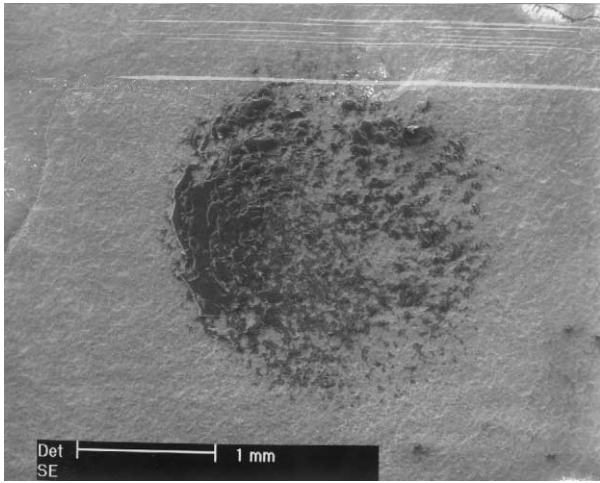
Fig. 8. SEM micrographs of area subjected to the pull-test.

groups as Ti–OH was confirmed by XPS. The morphology appeared rough and porous and the bond strength to the metal substrate was quite good.

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