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(71) Applicants: **UNIVERSITA' DEGLI STUDI DI TORINO** [IT/IT]; Via Verdi 8, I-10124 Torino (IT). **CONSIGLIO NAZIONALE DELLE RICERCHE** [IT/IT]; Piazzale Aldo Moro 7, I-00185 Roma (IT).

(72) Inventors: **COLUCCIA, Salvatore**; Piazza Bernini 11, I-10138 Torino (IT). **ALTRUDA, Fiorella**; Strada del Cantello 9/2, I-10131 Torino (IT). **CAROSSA, Stefano**; Corso Rosselli 1, I-10128 Torino (IT). **MARTRA, Gianmario**; Via Trattenero 8, I-10053 BUSSOLENO (Torino) (IT). **MUSSANO, Federico**; Corso Peschiera 300, I-10139 Torino (IT). **TOLOSANO, Emanuela**; Via Sospello 11B, I-10147 Torino (IT). **BELLOSI, Alida**; Via Marcucci 32, I-48018 FAENZA (Ravenna) (IT). **FAGA, Maria Giulia**; Via Madama Cristina 57, I-10125 Torino (IT).

(74) Agents: **VANZINI, Christian** et al.; c/o Jacobacci & partners S.p.A., Corso Emilia 8, I-10152 Torino (IT).

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(54) Title: DENTAL OR BONE IMPLANT, IN PARTICULAR OF ALUMINA-ZIRCONIA NANOCOMPOSITE

(57) Abstract: A dental or bone implant comprising a post and a thread made on the outer surface of the post, through which the latter can be anchored to bone tissue. The implant is of a ceramic nanocomposite based on Al_2O_3 and ZrO_2.

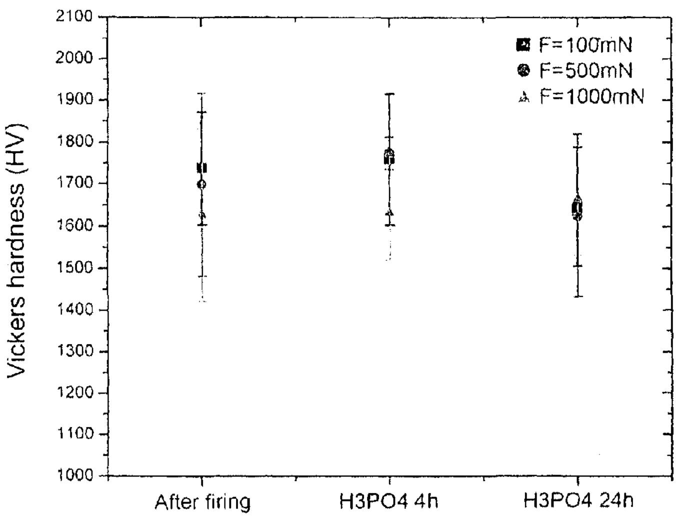

FIG. 3

WO 2013/108203 A1

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Dental or bone implant, in particular of alumina-zirconia nanocomposite

This invention relates to a dental or more generally bone implant comprising a post and a thread made on the outer surface of the said post, through which the latter can be anchored to bone tissue.

A dental implant is a device designed to be surgically located within the mandibular bone or maxillary bone to support a dental prosthesis which will provide the patient with proper biofunctionality. The essential requirements for dental implants currently in use are biocompatibility, the ability to integrate with the bone, their lifetime and functional restoration of the organs (teeth) replaced, while possibly complying with aesthetic harmony.

The shape and components of dental implants are dictated by the mechanical characteristics of the basic material most commonly used for their manufacture, titanium, which together with its alloys accounts for approximately 97% of the market in this sector.

Generally pure titanium of grade 4 is used to make the fixture, that is the part of the implant within the bone, while the abutment, the part which will be covered by the dental prosthesis, and the connecting screw between the abutment and the fixture are made of grade 5 titanium. Titanium of grade 4 is considered to be pure (4 is an indicator of the presence of oxygen, carbon, iron and other impurities in residual percentages within the titanium matrix), while grade 5 titanium is an alloy comprising 6% by weight of aluminium and 4% by weight of vanadium plus other impurities as in grade 4 titanium.

The use of commercially pure titanium arises from the requirement to avoid the release of metal ions in contact with biological tissues, while ensuring the required mechanical properties. The use of grade 5 titanium is only desired by implant manufacturers to ensure a wide margin of mechanical safety for the implant system in relation to the action of chewing loads. The association between the build-up of metal such as aluminium and serious degenerative diseases such as Alzheimer's disease is of more than academic interest in this context, as the prosthetic components of implants are subject to the erosive action of the mouth's environment. Given the manifest need to control the bioavailability of potentially toxic elements, this requirement has been responded to, hitherto only experimentally, through containment barriers (e.g. surface coatings) or the choice of different materials. In this respect solid ceramic materials such as alumina (Al_2O_3) and zirconia (ZrO_2) have recently been proposed as an alternative to metal materials. Furthermore, from the biomechanical point of view the use of ceramic materials is particularly indicated to prevent force being transferred between the prosthesis and the surrounding biological tissue.

Successful development of a dental implant not only depends on the use of the right material, but also on its integration into the tissue in which it is placed. In fact a dental implant should not be regarded as a device that is merely capable of replacing natural teeth, but a system for rehabilitating the entire oral and mandibulatory apparatus. For the patient's quality of life it is therefore important that this rehabilitation should take place in the shortest time possible, and then persist for the longest time possible. A key aspect for the nature of integration is the application of anatomical, biomechanical, bioengineering and surface chemistry knowledge to the design and construction of devices.

Because of the particular mechanical stresses to which a dental implant must respond and the complexity of the physiological responses at the interface between the implant and tissues, the development of innovative devices having adequate structural characteristics capable of quickly and permanently integrating with the host tissue is now an aim of primary importance in the dental field.

In view of the requirements indicated above, the object of the invention comprises a dental or bone implant of the type defined in the introduction, in which the post and the composite ceramic material are based on Al_2O_3 and ZrO_2.

A process for the production of a dental or bone implant comprising the following steps:

providing a mixture of Al_2O_3 and ZrO_2 powders;

pressing the said mixture so as to obtain a green body;

processing the said green body so as to obtain a semi-finished product comprising a post and a thread provided on the outer surface of the said post, and

sintering the said semi-finished product

also constitutes an object of the invention.

According to a preferred embodiment of the process, after sintering the semi-finished product is subjected to bioactivation surface treatment with heat and pressure, keeping the said semi-finished product in contact with a solution of at least one compound selected from the group comprising oxyacids, hydrohalogen acids, alkaline metal bases and alkaline earth bases.

As will be appreciated, the implant according to the invention will find application not only in the dental field, but also in other medical sectors, for example orthopaedics.

Further characteristics and advantages of the implant according to the invention will be apparent from the following detailed description made with reference to the appended drawings provided purely by way of a non-limiting example, in which:

- Figure 1 is a graph showing the content by volume of m-ZrO_2 as a function of ageing time, in fired ATZ;
- Figure 2 is a graph showing the content by volume of m-ZrO_2 as a function of ageing time, in ATZ treated with H_3PO_4 for 4 hours;
- Figure 3 is a graph showing the Vickers microhardness (HV) of fired samples treated with acid, with different applied loads;
- Figure 4 is a graph showing the Vickers hardness of aged samples (fired ATZ) with different applied loads; and
- Figure 5 is a graph showing the Vickers hardness of samples aged for 4 hours treated with acid, with different applied loads.

A dental implant comprises a post, commonly known as the "fixture", which when in use constitutes the endosseous part of the implant, and a head portion, commonly known as the “abutment”, which when in use is covered by the dental prosthesis. In the case of an implant for a different application, for example for orthopaedic use, this implant may be shaped differently according to requirements. The shape of the implant is not however essential for the purposes of the invention.

The post has a thread provided on its outer surface through which the device can be anchored into bony tissue.

According to the invention this implant is made of ceramic composite material based on Al_2O_3 and ZrO_2. Preferably this composite material is a nanocomposite.

For the purposes of this invention, by "nanocomposite" is meant a solid multiphase material in which the Al_2O_3 and ZrO_2 phases comprise grains having dimensions smaller than 100 nm.

The composite obtained has properties which are appreciably better than those of the components alone.

As far as this aspect is concerned, it must be borne in mind that oxide ceramics have good mechanical properties in terms of hardness and, consequently, resistance to wear, as well as established compatibility with biological systems. Pure alumina is in fact used in the biomedical field to make the heads of hip prostheses, while zirconia is not used for this purpose because despite greater toughness which makes it less brittle than alumina it tends to undergo a phase transition from tetragonal to monocline in vivo, with a consequent increase in volume and the initiation of fractures which result in breakdown of the prosthesis. Zirconia is however potentially more effective for biological applications because in addition to being tougher it has a potentially more reactive surface which makes it useful for the purposes of anchoring to bone.

Preferably the percentage by weight of ZrO_2 is 80% or above, the percentage by weight of Al_2O_3 being less than or equal to the 100-complement of the percentage by weight of ZrO_2.

The insert according to the invention is obtained by techniques that are conventional in the ceramics industry, such as linear pressing and isostatic cold pressing to obtain a green ceramic, and a subsequent sintering process. Before sintering the green body is processed by milling under digital control to obtain the desired profiles for the implant.

Preferably the implant so obtained undergoes surface heat treatment to optimise integration with bone tissue (bioactivation). In fact, in addition to their excellent mechanical properties, oxide ceramics tend to be bioinert. It has been established that following treatment with adequate concentrations of phosphoric acid solution under hydrothermal conditions implant surfaces have proved to be active in inducing the deposition of hydroxyapatite, according to the "Kokubo test" normally used to assess the osteointegration possibilities of a biomaterial. In addition to this it has been established that the abovementioned surface treatment does not adversely affect the mechanical properties of the oxide nanocomposites considered. Furthermore, ageing tests under conditions in which the chemical/physical phenomena which can occur under physiological conditions can be accelerated have indicated that after bioactivation treatment nanocomposites should maintain their structural properties unaltered for residence times in host tissue which would correspond to the normal life expectancy of patients, even young ones.

Another important aspect is that of biocompatibility, which has been established through tests of the survival and adhesion of human osteoblast and epithelial cells to the oxide nanocomposites used, including when treated for the purposes of bioactivation.

More generally, surface treatment of the implant in an autoclave may take place in the presence of solutions of oxyacids, hydrohalogen acids, alkaline and alkaline earth metal bases under temperature conditions over 50°C, for times of more than 15 minutes.

Experiments

1. Preparation and characterisation of the ceramic material

High purity powders were used to produce the materials: a mixture of Al_2O_3 and ZrO_2 containing 16% by weight of ZrO_2 marketed by Taimei under the name Taimicron, and a mixture of Al_2O_3 and ZrO_2 containing 20% by weight of Al_2O_3 marketed by Tosoh under the name TZ-3Y20AB. Examples of green bodies were obtained by linear pressing at 80

MPa followed by cold isostatic pressing at 200 MPa. The best conditions for the sintering process were heating at 50°C/hour up to 700°C, residence at 700°C for 2 hours, heating at 100°C/hour to the sintering temperature of 1500°C and residence at that temperature for 2 hours. Thermal expansion coefficients were measured up to 1300°C; the densities of the sintered bodies were measured using Archimedes' method.

The following mechanical properties were also considered: 4-point bend strength on a test bar of 45×5×5 mm (at least five samples for each lot) for the materials after firing, and on 35×2,5×2 mm bars for materials which had undergone ageing and surface treatment; hardness using the Vickers point indentation method, with a load of 9.8 N for 10 seconds on at least five samples for each lot of the materials after firing; in the case of treated and aged materials micro-hardness was measured using an indentation tester (FISCHERSCOPE HM-2000) varying the load up to 0.5 N to determine surface hardness. Here again a Vickers indenter comprising a square base diamond pyramid was used. Toughness was measured using an indentation method with a Vickers point, a load of 98 N for 10 seconds, with at least five measurements on each material, and Young's modulus was measured by the resonance frequency method on at least three samples for each lot, of dimensions 43×5×2 mm, using an H&P gain and phase analyser. Bend strength and hardness were measured on samples after firing and after ageing and treatment.

The microstructure of the samples was analysed using a Zeiss EVO 50 scanning electron microscope provided with an energy dispersion spectroscopy analyser to detect elemental composition.

XPS analyses were also performed using a SPECS X-ray photoelectron spectrometer (Phoibos MCD 150). The source was Mg-Kα radiation (1253.6 eV). The X-ray source was excited by a 150 W electron beam (12 mA, 12.5 kV). The spot dimensions of the irradiated region were 7×20 mm. Photoelectron emissions from the sample were analysed at a take-off angle of 90° under UHV conditions. No load compensation was applied during acquisition. After acquisition binding energies were calibrated on the Al 2p signal of Al_2O_3 with a binding energy BE = 74 eV. The accuracy of the binding energies reported was estimated to be ±0.1 eV. The areas of the XPS peaks were measured after subtracting a background. Atomic ratios were calculated after standardisation using Scofield factors for element "X". The spectra were processed using the Casa XPS v2.3.13 software package (Casa Software Ltd.) and Origin 7.1 software (Origin Laboratory Corp.). Spectral resolution was performed using Gaussian-Lorenzian functions (70%/30%) and the FWHM for each peak was determined.

2. Treatment of samples

The samples were washed using ultrasound in acetone, ethanol and deionised water and then immersed in a solution of H_3PO_4 or NaOH solution in different concentrations at 80°-100°C for times of between 4 and 24 hours in an autoclave or at atmospheric pressure. When treatment was complete the samples were taken from the hydroxylated solution, washed in deionised water and then dried at ambient temperature.

3. Bioactivation

The bioactivity of untreated and treated samples was assessed by merging the samples in a modified simulated body fluid (1.5×SBF). The 1.5×SBF was prepared with an ion concentration of 1.5 times that of the SBF proposed by Kokubo et al., and its pH value was adjusted to 7.4 through the addition of HCl and tri-hydroxymethylaminomethane. Each sample was immersed in 40 ml of 1.5×SBF and held at a constant temperature of 36.5°C for 2 and 4 weeks. Observation of a layer having a Ca/P ratio typical of simulated apatite forms by SEM-EDS was used as a criterion for the bioactivity of the samples.

4. Ageing experiments

The ageing experiments were carried out in autoclaves at a temperature of 134°C and a pressure of 2 bars for increasing times up to 20 hours (1 hour in an autoclave is theoretically equal to 3-4 hours in vivo).

The samples were laid out on a grid in the autoclave so that they were not in contact with the water during ageing, but only subjected to an atmosphere of water vapour. The effect of hydrothermal treatment on the tetragonal-monocline transformation was assessed quantitatively by X-ray diffractometry. The samples were scanned with Cu-Kα radiation (45 kV-40 mA) at a Bragg angle varying from 26° to 34° using a PAN analytical X Pert PRO X-ray diffractometer. The fraction of monocline phase was calculated using the Garvie and Nicholson method.

Transformation of the zirconia phase was observed using an atomic force microscope (AM) and a scanning electron microscope (SEM). The same area of the sample was photographed before and after the ageing process. The AFM (Park System XE100) was observed in non-contact mode. The dimensions of the scanned area were 5×5 μm^2, with a scanning frequency of 0.4 Hz. Measurements were made on a sample which was smooth and treated with thermal etching in air. Measurements of average roughness (R_a) were made using images of five random areas on the sample.

5. Results

5.1 Microstructure

Both the materials Al_2O_3-16wt%ZrO_2 (alumina matrix reinforced with zirconia particles, ZTA) and ZrO_2-20wt% Al_2O_3 (zirconia matrix reinforced with alumina particles, ATZ) comprise sub-micrometre grains. In particular Al_2O_3 grains of 0.881 ± 0.297 μm and ZrO_2 grains of 0.317 ± 0.103 μm were present in ZTA, while in ATZ the dimensions of the alumina and zirconia grains were similar (0.469 ± 0.174 μm). In both cases the alumina and zirconia grains were uniformly distributed. In the case of ZTA the alumina grains were larger, probably because of the low percentage of zirconia, which has a pinning effect on alumina grains.

5.2 Physical and mechanical properties

The properties of the composites are summarised in Table 1, which also provides properties of the monolithic materials for comparison.

Table 1

Composition	**Density (%)**	**Thermal expansion coefficient (m °C)**	**Hardness (GPa)**	**Toughness (MPa $m^{1/2}$)**	**Bend strength (MPa)**	**Young's modulus (GPa)**
Al_2O_3-16wt%ZrO_2	100	8.2	21.3 ±1.5	3.9 ±0.05	441±24	363±5
ZrO_2-20wt% Al_2O_3	99.9	10.0	15.3 ±0.9	7.1±0.1	633±127	245±9
Al_2O_3[1]	99.9	7.8	24.0 ±1.6	3.0 ±0.1	229±34	362±4
ZrO_2[2]	100	11.0	14.5 ±0.4	6.0 ±0.3	615±93	206±4

1- Al_2O_3 Taimei

2- ZrO_2 Tosoh, stabilised with 3 wt% of yttria

In general it will be seen that the compounds offer a good compromise in terms of hardness and toughness in comparison with the monolithic material.

In particular the ATZ composite has a similar hardness to pure zirconia and greater toughness. This indicates that ATZ is more tolerant to fractures than zirconia. This is an advantage because pure zirconia has a problem of tending to fracture, despite its promising mechanical properties.

The toughness and bend strength of ZTA are considerably better than those of the monolithic material, even though it is harder. Toughness and bend strength are however poorer than that for the other composite, thus resulting in greater brittleness. A significant standard deviation was observed for ZTA, in particular for strength values, an indicator of the presence of defects.

5.3 Surface characterisation

Before chemical treatments the surfaces of the oxides were characterised by XPS. The results obtained for ZTA and ATZ samples reveal the presence of atoms of aluminium, zirconium, yttrium, oxygen and contaminants (in small quantities) on the surfaces.

The spectra were calibrated on the Al 2p signal of Al_2O_3 having a binding energy BE=74 eV. The zirconium peak showed a doublet with the Zr $3d_{5/2}$ component at 181.8 ± 0.1 eV. The difference of 2.4 eV in binding energy between the Zr $3d_{5/2}$ and Zr $3d_{3/2}$ peaks is consistent with the binding energy of Zr4+ in pure zirconia. The Y $3d_{5/2}$ component of the yttrium doublet found at 157 ± 0.1 eV, with a difference of 2 eV from the Y $3d_{3/2}$ peak, is characteristic of the stabiliser for the tetragonal phase of ZrO_2 in YSZ.

The O 1s peak is the result of four contributions at 529.7, 530.8, 532.0 and 533.3 ± 0.1 eV corresponding to the O^{2-} in the zirconia matrix, the O^{2-} in the alumina matrix, hydroxyl groups due to solutions from the chemisorption of water, and the hydrated surface layer of the material respectively.

The quantitative proportions of aluminium, zirconium, yttrium and oxygen expected for the ZTA and ATZ samples were calculated considering the quantities of ZrO_2, Al_2O_3 and Y_2O_3 used in the mixture of precursors (see Table 2).

Table 2

Element	**Atomic % in ZTA (calculated)**	**Atomic % in ZTA (XPS)**	**Atomic % in ATZ (calculated)**	**Atomic % in ATZ (XPS)**	**Atomic % in ATZ treated with H_3PO_4 for 4 hours (XPS)**
Al	**36.6**	37.9	**13.4**	13.5	13.7
Zr	**2.8**	3.7	**21.8**	19.9	21.0
O	**60.5**	57.5	**64.1**	63.4	61.8
Y	**0.1**	0.9	**0.7**	3.2	3.5

The calculated values considering the stoichiometric ratio are very close to the experimental values. This demonstrates that the surface chemical composition of ZTA and ATZ is very close to that of the bulk. It will also be noted that the experimental percentage of Y is greater than expected, indicating that the Y atoms segregate out at the grain boundaries in Y-TZP.

5.4 Chemical treatments

Various chemical treatments with H_3PO_4 and NaOH at different concentrations and temperatures for different treatment times were considered for inducing bioactivity on the surfaces of both the composites. The ability of these treatments to induce the formation of apatite on surfaces was tested by immersion in SBF. As a reference, untreated and treated ZTA and ATZ materials were immersed in a solution of SBF for 2 and 4 weeks.

No apatite formation was observed in the case of ZTA, indicating that there is a threshold percentage of zirconia below which bioactivity is not induced.

Of the various treatments, only one (42% by weight H_3PO_4 solution, 80°C, 4 hours in an autoclave) resulted in the formation of simulated apatite in the case of ATZ after four weeks immersion in SBF, using both static and dynamic methods. The surface was almost completely covered with a layer of calcium phosphate, in which the ratio between Ca and P was 1.6, as was to be expected for forms of apatite. An acicular morphology was observed in each test (both the static and the dynamic). The apatite began to grow preferably on the zirconia grains, confirming that this oxide is more effective for the nucleation of apatite. In addition to this, this aspect explains why the composite containing a low percentage of zirconia did not have the same ability to encourage the formation of apatite. To check the effect of phosphoric acid on ATZ, XPS spectra were obtained on samples after treatment. The spectra were calibrated in the same way as for the samples after firing. No significant differences were found between treated ATZ and fired ATZ in terms of Zr/Al ratio. In addition to this no phosphorus peak was observed, indicating that no phosphate phase had formed. Deconvolution of the 0 1s peak revealed interesting differences between fired ATZ and ATZ treated with phosphoric acid (see Table 3).

Table 3

O1s components	**ZTA**	**ATZ**	**ATZ 4h H_3PO_4**
%O_2- (ZrO_2)	9.3%	48.7%	43.7%
%O_2- (Al_2O_3)	65.2%	27.2%	23.4%
%OH	19.2%	20.0%	24.6%
%H2O	6.3%	4.1%	8.3%

In the case of treated ATZ an increase in OH and the percentage of water were noted. The bioactivity observed in this sample must probably be correlated with an increase in OH species on the surface due to a base-acid reaction between zirconia and phosphoric acid. The fact that the same treatment did not result in a similar effect in a sample rich in alumina confirms that alumina grains are not effective in the nucleation of apatite.

It is also important to note that the same treatment in a beaker did not produce any effect on bioactivity after the same treatment time; this indicates that pressure has an important part to play in accelerating the kinetics of surface modification.

5.5 Effect of ageing on ATZ

Various studies have demonstrated that when the percentage of ZrO_2 is below 22% by weight no ageing phenomena occur in similar composites, regardless of the grain size. The process of ageing on the ATZ composite was therefore studied to calculate the actual magnitude of the phase transition and its effect on mechanical properties to check the actual possibility of applying it in vivo. Figures 1 and 2 show the percentage by volume of the phase transition (calculated by the Garvie and Nicholson method) in relation to ageing time (up to 20 hours, corresponding to 80 years in vivo, a sufficiently long time for the service life of a prosthesis) for fired ATZ and ATZ treated with phosphoric acid. As in the case of the fired sample it can be seen that the quantity of monocline zirconia increases with ageing time and the correlation is almost linear. It will be seen that the phase transformation does not exceed a value of 28% by volume. Ageing did not reduce the strength of the ceramic after 20 hours and treatment with phosphoric acid in any event produced an increase in bend strength (see Table 4).

Table 4

Material	**4 pt bend strength (MPa)**
Fired ATZ	1075 ± 190
ATZ aged in an autoclave for 20 hours	1113 ± 142
ATZ aged in an autoclave for 90 hours	1002± 40
ATZ treated with phosphoric acid and aged in an autoclave for 20 hours	1246±124

The effect of treatment and ageing on hardness is illustrated in Figure 3. Three different loads were used to determine any differences between the bulk and the surface; no such differences were however found. The main effect of ageing is a progressive decrease in hardness (Figure 4), but no trend was observed in the case of aged materials after treatment in phosphoric acid up to 20 hours. A significant fall can clearly be observed after 90 hours (Figure 5). SEM observations have shown that there is growth of micrograins on the surface of the zirconia grains with ageing, while AFM observations have demonstrated a phase transformation from tetragonal to monocline during ageing; these measurements have however shown that this transformation gives rise to a very small increase in mean roughness, which can explain their small influence on the mechanical properties of the material.

CLAIMS

1. A dental or bone implant comprising a post and a thread formed on an outer surface of the said post by means of which the latter may be anchored to bone tissue, characterised in that the said implant is of a composite ceramic material based on Al_2O_3 and ZrO_2.

2. An implant according to Claim 1, in which said composite ceramic material is a nanocomposite.

3. An implant according to Claim 1 or 2, in which the percentage by weight of ZrO_2 in said ceramic material is greater than or equal to 80%, the percentage by weight of Al_2O_3 being less than or equal to the 100-complement of the percentage by weight of ZrO2.

4. A method for producing a dental or bone implant, comprising the following steps:

providing a mixture of powders of Al_2O_3 and ZrO_2;

pressing said mixture to obtain a green body;

machining said green body to obtain a semi-finished product comprising a post and a thread formed on an outer surface of the said post; and

subjecting said semi-finished product to sintering.

5. A method according to Claim 4, in which the percentage by weight of ZrO_2 in said mixture of powders is greater than or equal to 80%, the percentage by weight of Al_2O_3 being less than or equal to the 100-complement of the percentage by weight of ZrO_2.

6. A method according to Claim 4 or 5, in which after sintering said semi-finished product is subjected to a bioactivation surface treatment with heat and pressure, including maintaining said semi-finished product in the presence of a solution of at least one compound selected from the group comprising oxyacids, hydrohalogen acids and alkali metal and alkaline earth metal bases.

7. A method according to Claim 6, in which said bioactivation surface treatment further includes holding the said semi-finished product at a temperature above 50°C.

8. A method according to Claim 7, in which said bioactivation surface treatment includes holding said semi-finished product at a temperature above 50°C for longer than 15 minutes.

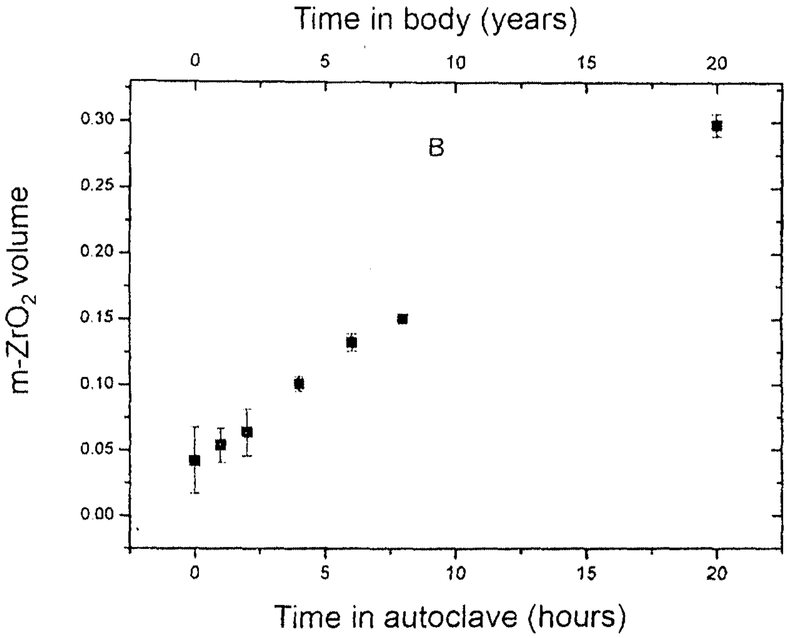
Time in body (years)
0
5
10
15
20
B
m-ZrO$_2$ volume
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
5
10
15
20
Time in autoclave (hours)

FIG. 1

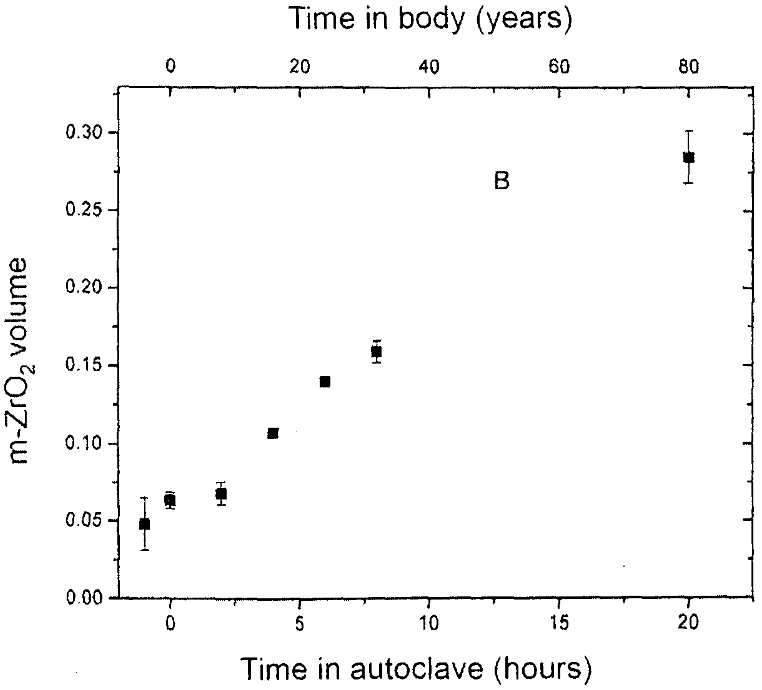
Time in body (years)
0
20
40
60
80
B
m-ZrO$_2$ volume
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
5
10
15
20
Time in autoclave (hours)

FIG. 2

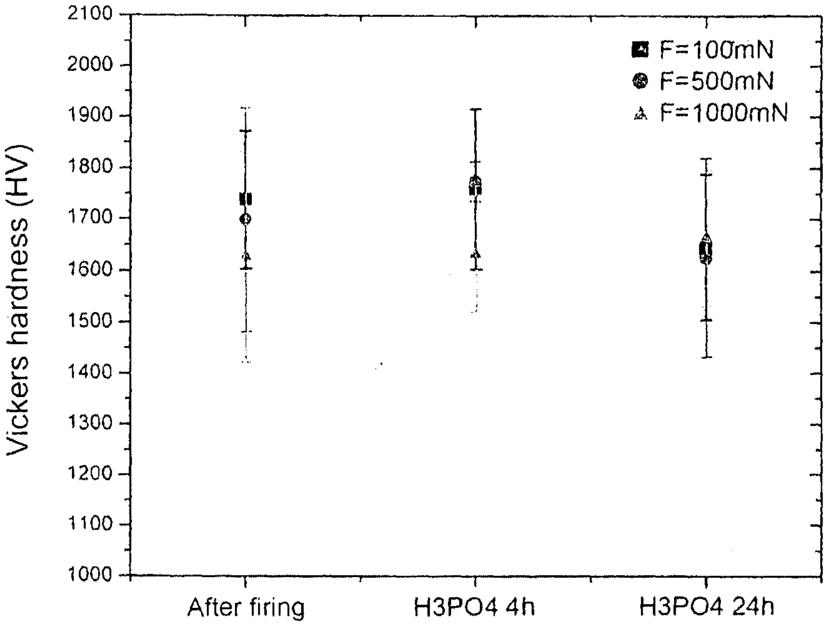
Vickers hardness (HV)
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
F=100mN
F=500mN
F=1000mN
After firing
H3PO4 4h
H3PO4 24h

FIG. 3

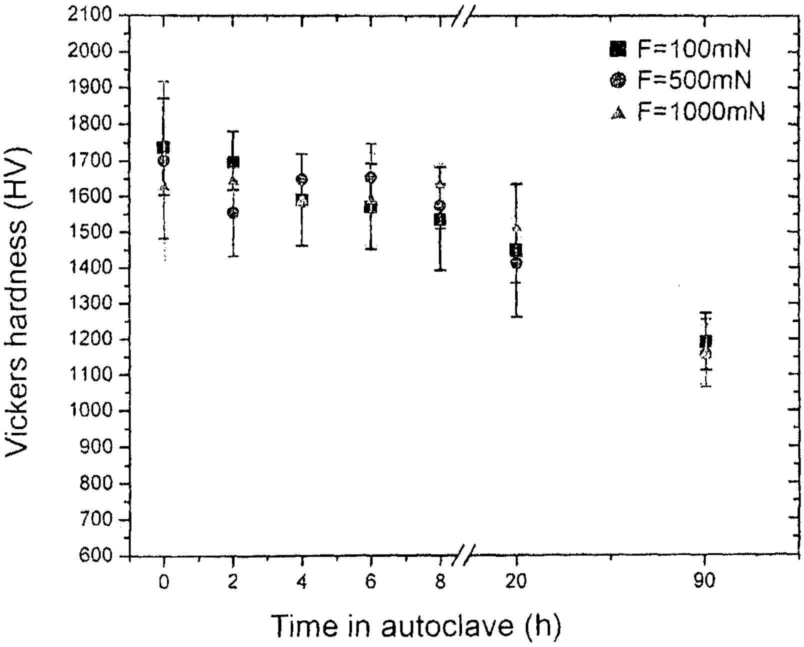
Vickers hardness (HV)
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
F=100mN
F=500mN
F=1000mN
0
2
4
6
8
20
90
Time in autoclave (h)

FIG. 4

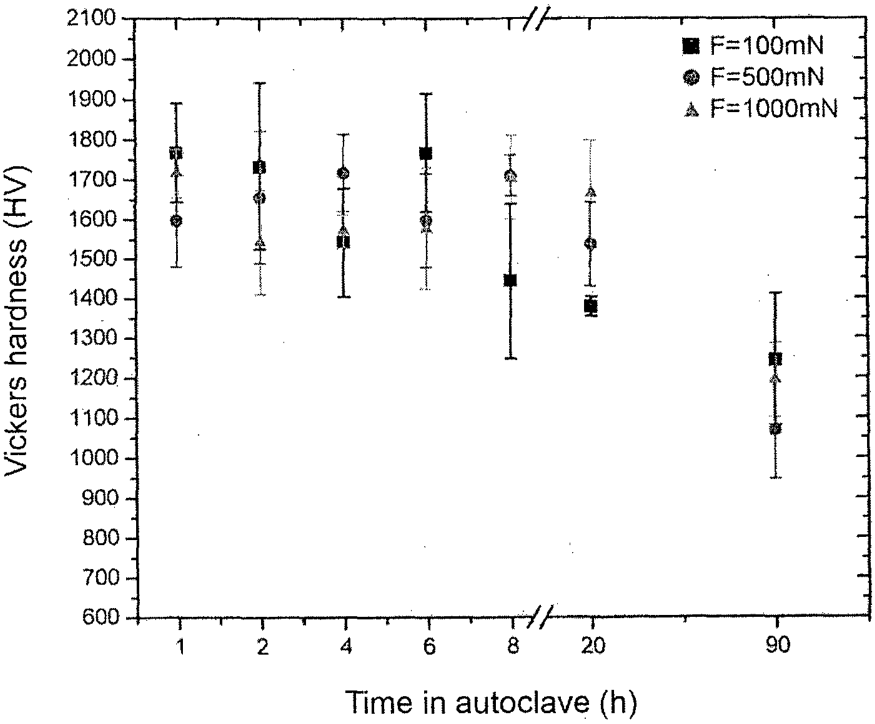
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Vickers hardness (HV)
■ F=100mN
● F=500mN
▲ F=1000mN
1
2
4
6
8
20
90
Time in autoclave (h)

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2013/050425

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61C8/00 A61C13/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A61C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/003083 A1 (YANG QUANZU [CA] ET AL) 6 January 2011 (2011-01-06) paragraph [0009] paragraph [0024] paragraph [0040] -----	1-5
X	US 2006/084035 A1 (VOLZ ULRICH [DE]) 20 April 2006 (2006-04-20) paragraph [0008] the whole document -----	1,3
X	US 2011/183281 A1 (JENSEN PEDER [US]) 28 July 2011 (2011-07-28) paragraph [0030] - paragraph [0031] -----	1

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search 24 April 2013	Date of mailing of the international search report 06/06/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Salvatore, Claudio

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2013/050425

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 2011183281 A1	28-07-2011	NONE	