In vitro and *in vivo* performance of Ti6Al4V implants with plasma-sprayed osteoconductive hydroxylapatite–bioinert titania bond coat "duplex" systems: an experimental study in sheep

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To evaluate the *in vivo* performance of "duplex" hydroxylapatite top coat/TiO_2 bond coat systems, cylindrical Ti6Al4V rods of 130 mm in length and 11–13 mm in diameter were coated by atmospheric plasma spray (APS) technique with both a standard hydroxylapatite (HAp) layer and a HAp + TiO_2 bond coat "duplex" layer. In this pilot study coated and uncoated rods serving as controls were implanted into the femur of sheep so that their distal ends were freely suspended in the medulla of the femur. After an observation time of six months it was found that bone apposition and bone ingrowth were considerably increased in the presence of a osteoconductive coating. In particular, *in vivo* spalling and delamination frequently observed with HAp coatings was virtually absent in duplex coatings owing to the strong adhesion of the bond coat to the HAp top coat that anchored the latter solidly to the metallic surface of the implant. Some tentative mechanisms leading to this improved coating adhesion will be discussed.

1. Introduction

Conventional hip prostheses use a stem manufactured from Ti alloy and an alumina femoral head that articulates with a cup-shaped socket anchored in the acetabulum. This socket, made of commercially pure titanium (cp-Ti) or Ti alloy, is lined with either ultrahigh molecular weight polyethylene (UHMW-PE) or, in recent developments, alumina to assure a low coefficient of friction.

Despite copious research long-term stability still remains a major problem, in particular as the number of cases showing implant loosening increase with increasing number of implantations but with some delay. Furthermore, there is still discussion about the necessity to coat parts of the femoral stem with hydroxylapatite (HAp) as a osteoconductive bone growth-mediating agent or even with a bioinert cp-Ti sponge with or without a HAp coating in order to achieve an optimised integration at the bone–implant interface. In addition there is a controversy concerning the thickness of a HAp coating. A thin HAp layer ($< 50\,\mu m$) shows better adhesion to the metallic substrate compared with a thicker coating owing to reduced residual coating stresses. It is supposed to be resorbed in the course of the bony integration. However, in some instances a thick HAp layer ($\pm$ 150 μm) may be required to ensure a more permanent bond between implant and bone to guarantee implant stability by a lasting biological effect. Such a situation may arise during an endoprosthetic replacement operation with exchange of the implant when the cortical bone matter had been previously damaged, often in concurrence with an undesirable geometric configuration of the implant-supporting bone. In this case a thin, rather quickly resorbed calcium phosphate coating may not be sufficient to sustain the required large scale bone regeneration. Hence thicker coatings may be needed to stimulate bone reconstruction over longer times.

Clinical evidence exists that the probability of survival of uncoated hip endoprostheses is significantly less than that of prostheses with either HAp coatings up to 200 μm thick or bone cement (PMMA) fixation. In particular, no osteolytic lesions and radiolucent lines were observed

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after an observation time of five years in the presence of thick HAp coatings in contrast to uncoated prosthesis stems showing such effects in medial proximal, medial and lateral directions in the mid-third of the femur, and lateral in the distal third [1]. These results suggest that the presence of a long-term stable HAp layer may reduce gap formation between the implant and the living bone [2, 3] with the associated risk of movement of abraded polyethylene particles towards deeper regions of the prosthesis stem and subsequent osteolysis. In addition, since the stability of the coatings also depends on their microstructure, that is, surface roughness and porosity, and their phase content, that is, presence of thermal decomposition products and amorphous calcium phosphate, these properties must be carefully optimised.

It is well known that a osteoconductive HAp coating will elicit a specific biological response at the interface of the implant material by control of its surface chemistry through adsorption of non-collageneous protein that leads to the establishment of a strong and lasting osseoconductive bond. The advantages of such coatings include (i) an optimised bone bridging capacity in case of gaps at the interface and the absence of a fibrous capsule of connective tissue surrounding the implant [4], (ii) fast bone apposition rates through preferential adsorption of proteins [5], (iii) bonding osteogenesis providing a continuous and strong interface between implant and tissue that is able to transmit not only compressive but also tensile and shear stresses [6], (iv) accelerated healing compared to implants without a osteoconductive coating [7], as well as (v) reduced release of titanium ions to the surrounding tissue and thus minimising the perceived risk of a cytotoxic response [8, 9].

Because of the chemical and structural similarities of the osteoconductive HAp coating and the inorganic constituent of the composite material ''bone'', the bond between HAp and living bone is decisively stronger than that between HAp and the Ti alloy. Since there exists a large elastic modulus gradient between the metallic implant and the bone, a gap may develop during prolonged shear loading of the implant in service. Then acellular connective tissue may invade this gap leading to a consecutive loosening of the implant [2, 3]. Thus, it may be desirable to reinforce the implant stability by reducing gap formation through addition of a bioinert bond coat to the osteoconductive HAp coating. It is anticipated that this ''duplex'' system will be able to withstand the high, local tensile and shear stresses occuring during micromovements of the patient during the first stages of the healing phase after implantation.

2. Functions of bioinert bond coats

The purposeful development of specific HAp-bond coat systems started in the early 1990s at the University of Alberta, Edmonton, Alberta, Canada. A thin (15–20 μm) dicalcium silicate (Ca_2SiO_4) bond coat layer was deposited by atmospheric plasma spraying (APS) on Ti6Al4V substrates on to which an up to 200 μm thick HAp coating was applied by the same technique. The adhesive strength of the coating system, measured by the ASTM C633-79 tensile adhesion test was found to have increased by about 25% when compared to a coating without a bond coat [10]. However, the strength degraded rapidly during *in vitro* resorption testing in simulated body fluid owing to the pronounced hydration of hydraulic β-Ca_2SiO_4 formed from (non-hydraulic) γ-Ca_2SiO_4 during plasma spraying.

However, much better performance in terms of adhesion strength and *in vitro* resorption resistance was observed with plasma-sprayed bond coats based on titania, a eutectic mixture of titania and zirconia [11, 12] or zirconia [13] as well as graded HAp/titanium coatings [14]. In particular, the interfacial bond strengths between coating systems and metal implant were found to increase by up to 100% compared to coatings without a titania bond coat [15–18]. To explain this effect it was conjectured that the bond coat will act as a thermal barrier reducing the extremely high cooling rates (10^6–10^7 K/s) of molten powder particles and thus resulting in a HAp layer with increased crystallinity and reduced thermal decomposition. This gives amorphous calcium phosphate (ACP), generally present in plasma-sprayed HAp coatings without a bond coat, the opportunity to convert to crystalline CP phases. On the other hand, the dehydroxylation of the HAp towards oxyhydroxylapatite/oxyapatite [19], and the thermal decomposition of the latter into tricalcium phosphate (TCP) and tetracalcium phosphate (TTCP) will still take place in the hot plasma jet.

In addition, the bond coat will (i) prevent the direct contact between titanium metal and HAp that is thought to catalyse the thermal decomposition of the latter [20–22], (ii) reduce the release of potentially cytotoxic heavy metal ions from the implant body [23], (iii) reduce the steep temperature gradients during plasma spraying leading to ACP formation, (iv) reduce the gradient of the coefficients of thermal expansion between the titanium alloy and the HAp that will induce substantial residual stresses along the interface, and also (v) may act towards cushioning forces induced by cyclic micromotions of the patient during the healing phase [3, 24].

In vitro results on ''duplex'' bond coat-HAp systems suggested that the deterioration of the adhesion strength in contact with protein-containing (human serum albumin, HSA) simulated body fluid (modified Hank's Balanced Salt Solution, HBSS) was noticeably reduced when compared to HAp without a bond coat. Incubation of plasma-sprayed HAp coatings under physiological conditions for 64 days showed a substantial decrease of the tensile adhesion strength (ASTM C633-79) from 15 to 5 MPa whereas HAp coatings in the presence of a TiO_2 bond coat not only showed that the adhesion strength of the as-sprayed coating system was much higher at 52 MPa but also decreased after incubation for 64 days only to about 21 MPa [25, 26].

During *in vitro* testing of the resorbability of HAp coatings in the presence of a TiO_2 bond coat in simulated body fluid after Kokubo [27] it was found that by biomimetic mechanisms a well-crystallised layer of a Ca-deficient defect apatite (''bone-like'' apatite according to Weng [28]) forms at the interface of the HAp coating with the fluid [29]. These HAp microcrystals are thought to serve *in vivo* as absorption sites for non-collageneous proteins such as osteonectin, osteocalcin, silylated glycoproteins and proteoglycanes that

are known to mediate bone remodelling. This would be a precondition of structure-mediated incorporation of the biomimetically formed apatite microcrystals into the collagene I matrix and the formation of bone trabeculae along the main stress directions of the proximal femur. In the present contribution the *in vivo* effects of a HAp-bond coat systems were investigated in an animal (sheep) model.

3. Materials and methods

3.1. Preparation of plasma-sprayed coatings

Cylindrical Ti6Al4V rods of 130 mm in length and diameters between 11 and 13 mm were grit-blasted with alumina grit (grain size 0.5–1 mm) using pressurized air of 4 bars at an angle of 75° and a distance of 100 mm, cleaned ultrasonically in a 7.5% Tickopur™ solution (proprietary formulation) at 60 °C for 5 min, and air dried. Medical-grade HAp powder (AMDRY™ 6021, + 45–165 μm) conforming to the ASTM F 1185 designation, and TiO_2 powder (AMDRY™ 6500, + 5–22 μm) were obtained from Sulzer Metco (Deutschland) GmbH. Plasma spray coating was performed using an APS system (M1000, Plasma-Technik, Wohlen, Switzerland) equipped with an F4 plasmatron (Sulzer Metco (Deutschland) GmbH). The rods were horizontally clamped to a lathe and rotated with 20 rpm, commensurate with the traverse speed of the plasmatron of 4000 mm/min. The plasma spray parameters applied to deposit the TiO_2 bond coat and the HAp top coat are shown in Table I.

In addition to the rods coated with HAp + bond coat two other types were prepared: uncoated but grit-blasted Ti6Al4V rods (control), and rods coated only with HAp but without a bond coat.

3.2. Characterisation of coatings

Investigation of the as-sprayed coatings were performed by X-ray diffraction (XRD; RD7, Freiberger Prazisionsmechanik GmbH) in conjunction with Rietveld refinement as well as laser-Raman spectroscopy (LRS; T 64000 Raman microprobe, Jobin Yvon). ^{1}H- and ^{31}P-MAS-NMR and 2D-HETCOR-CP-NMR spectra were acquired with BRUKER AMX4000 and TECMAG (300 MHz) spectrometers (for details see Heimann *et al*. [30] and Hartman *et al*. [38]). To assess the stability of the coatings against biological resorption *in vitro* dissolution scouting tests under physiological conditions were performed in two kinds of simulated body fluid [27, 37].

TABLE I Plasma spray parameters selected to deposit the HAp top coat and the TiO_2 bond coat

Parameter	HAp	TiO_2
Plasma power (kW)	28	41
Plasma current (A)	500	630
Argon gas flow rate (slpm)	50	40
Hydrogen gas flow rate (slpm)	4	12
Powder gas flow rate (slpm)	3	3
Rotation (%)		
Disk	20	15
Stirrer	40	40
Spray distance (mm)	120	120

3.3. Implantation

3.3.1. Operation technique

The operations were performed on four skeletally mature black- and white-headed meat-type sheep (42–84 kg body weight) under general (55 mg Dormicum i.v.; 700 mg Ketamin i.v.) and peridural regional anaesthesia (4 ml Carbostesin 0.5%, Astra) after an i.m. premedication of 1400 mg Ketamin and 30 mg Dormicum. The sheep were positioned on their lateral sides for surgical skin disinfection (Skinsept G, Henkel Ecolab) and sterile coverage of the area of operation. Through a lateral knee arthrotomy, an osteochondral cuneiform block (14–16 × 14–16 mm) was bilaterally excised from the distal femoral groove. A solid metal cylinder (11–13 mm × 130 mm) was inserted into the femoral canal after reaming and the osteochondral block was replaced into its bed. Subsequently the wound was closed in layers and the sheep received a single shot antibiosis as well as pain medication. All animals were able to fully weightbear until the end of their observation period of six months. It should be emphasised that the selected model of an intramedullary cylindrical rod resembles closely the situation of a endoprosthetic stem replacement operation. The likewise mostly cylindrical prosthesis stem is positioned in the medulla with rather wide distance from the cortical bone wall. Since the establishment of a solid bony bridge between corticalis and implant requires an extended period of time, a thin HAp coating with a short resorption time would not be sufficient to guarantee a sufficient bony integration. Consequently thick coatings exceeding 150 μm were applied to the cylindrical Ti6Al4V rods.

3.3.2. Laboratory preparation

After sacrificing the sheep (15 mg Dormicum i.m.; 700 mg Ketamin i.m.; 20 ml T61 i.v., Hoechst-Rousel vet.) the distal femura were explanted and contact radiographs taken (exposure time 90 s at 50 kV; 43805 X-ray system, Faxitron Series, Hewlett-Packard). To prepare for further testing, the bones were stored in an alcoholic solution with ascending concentration (70%, 80%, 96%, 100%) and xylene substitute (Histoclear, Schandan) for at least three days. Subsequently the specimens were embedded in methylmetacrylate (MMA) according to the manufacturers instructions (Technovit 9100 neu, Heraeus). After polymerisation hardening the implants were sectioned with a diamond circular saw (Exakt) into blocs at proximal, medial and distal positions, and glued to glass slides (Technovit 4000, adhesive device Exakt). Subsequently the implant surfaces were ground and reglued to object slides (Technovit 7210 VLC, adhesive device Exakt). Each specimen was sectioned with a diamond circular saw to a thickness of 100 μm, and ground, polished and finally stained with toluidine blue. Microradiographs were taken with an exposure time of 90 s at 22 kV.

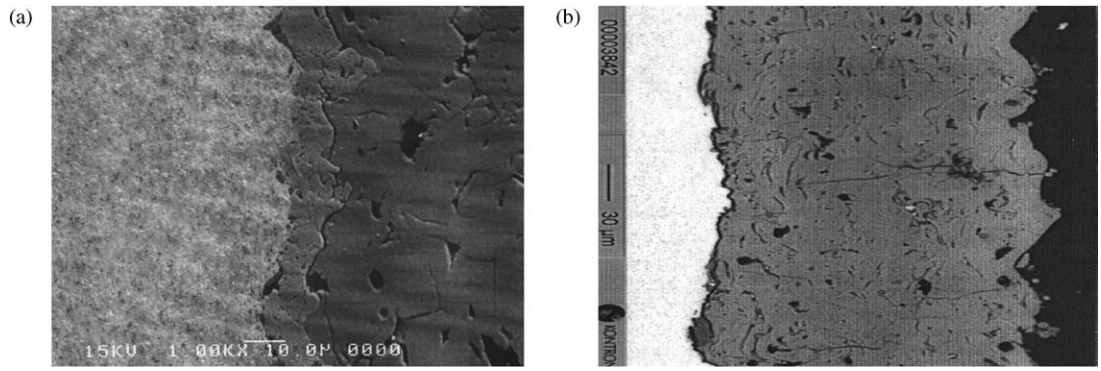

Figure 1 (a) Cross-section of a ''duplex'' TiO_2 bond coat (centre)/HAp top coat (right) system on a Ti6Al4V implant substrate (left). (b) Cross-section of a HAp coating without a bond coat (right) on a Ti6Al4V substrate (left).

4. Results and discussion

4.1. Plasma-sprayed coatings

Fig. 1(a) shows an SEM micrograph of a typical cross-section of a ''duplex'' HAp/TiO_2 bond coat system on a Ti6Al4V substrate. The dense bond coat layer of 10–15 µm thickness (centre) adheres tightly to the titanium alloy (left). The HAp top coat of up to 150 µm thickness (right) shows rather large pores that will aid the ingrowth of bone cells into the coatings. Fig. 1(b) shows for the sake of comparison a HAp coating of about 180 µm thickness without a bond coat.

As expected, comparison of the chemical composition of the coating obtained by XRD, LRS, and NMR shows (Table II) that the presence of a bond coat reduces the thermal decomposition of the osteoconductive HAp coating. *In vitro* dissolution studies with up to 12 weeks exposure to simulated body fluid [27, 37] showed that with increasing incubation time non-HAp calcium phosphate phases disappear. Quantitative phase determination based on XRD with Rietveld refinement revealed that it was not possible by XRD analysis to separate the HAp and the TCP/TTCP contributions in as-sprayed and incubated samples, hence necessitating additional Raman and NMR measurements. On the other hand addition to the samples of Al_2O_3 as an internal standard allowed to determine quantitatively by XRD the amount of ''amorphous'' phases that may be comprised of amorphous calcium phosphate (ACP) and incompletely crystallised ''distorted'' dehydroxylated structures (oxyhydroxylapatite, oxyapatite). The quantitative XRD results of the as-sprayed and incubated coatings with a bond coat are much more in accord with the LRS and NMR results (Table II). This is almost certainly caused by the high proportion of well-crystallised HAp in these samples. While the LRS and NMR data show surprisingly good correlation that to some extent also holds for the XRD data of the samples with a bond coat (**bold** in Table II), there is a clear deviation for the as-sprayed samples (*italics* in Table II).

Raman spectroscopic studies showed that the intensity ratio of the stretching vibrations of (PO_4) groups at 963 cm^{-1} and hydroxyl groups at 3555 cm^{-1} increases from 6 : 1 (as-received HAp powder) to 35 : 1 (plasma-sprayed HAp + bond coat) to 45 : 1 (plasma-sprayed HAp without bond coat) thus indicating that the presence of the bond coat slows down somewhat the thermal decomposition [31]. This conclusion is supported by Fig. 2 that compares the laser-Raman spectra (Ar^+ laser at 514.5 nm wavelength, focus diameter 3 µm) of as-sprayed HAp without (a) and with a TiO_2 bond coat (b) [30].

From the appearance of the spectra shown in Fig. 2 it is evident that the presence of a bond coat significantly alters the phase composition towards the predominance of well-crystallised HAp (A_2 band) with concurrent strong suppression of the complex A_1 band (TTCP + β-TCP + ACP) [38, 30] centred around 950 cm^{-1} and also decrease of the intensity of the A_3 band (β-TCP + ACP) [38, 30] centred around 972 cm^{-1}. The bands A_1 and A_3 may also contain some contributions from oxyhydroxylapatite and oxyapatite, respectively. Since ACP is much more soluble under physiological conditions than HAp and even other crystalline Ca-phosphate phases such as TCP and TTCP [32, 33], suppression of ACP formation will increase the resorption resistance of the coatings and hence their *in vivo* stability.

2D–^{31}P–^{1}H HETCOR-CP-NMR spectra [38] of HAp coatings without (Fig. 3(a)) and with a TiO_2 bond coat (Fig. 3(b)) show after 12 weeks incubation in r-SBF [37] that in the presence of a bond coat the central C–F peak assigned to well-crystallised stoichiometric HAp is substantially sharper than that of a coating without bond coat owing to higher crystallinity and phase purity. The weak ^{31}P-peak D at + 1.2 ppm may be due to

TABLE II Quantitative coating composition in mass% of HAp without and with a bond coat after incubation in r-SBF [37] for 0, 1 and 12 weeks. The data were obtained by XRD, LRS, and NMR [30]

	Without bond coat			With bond coat		
Weeks	0	1	12	0	1	12
XRD	*65**	*75*	73	**68**	**71**	**70**
XRD (amorphous)	35	25	27	32	29	30
Raman	*43*	*53*	75	**66**	**70**	**80**
NMR	*46*	*68*	74	**63**	**81**	**92**

*XRD data ± 5% (± σ).

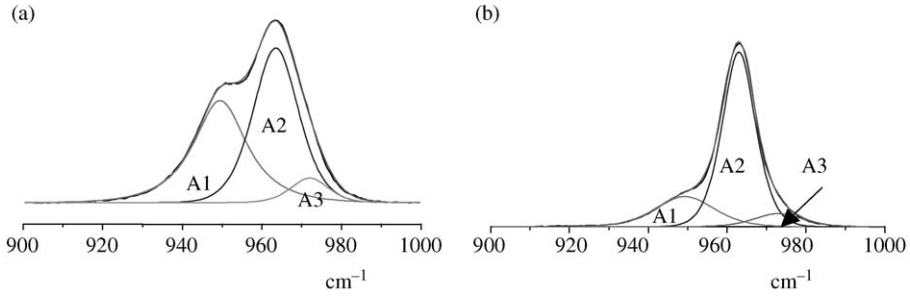

Figure 2 Laser-Raman spectra of as-sprayed HAp coatings without (a) and with a TiO_2 bond coat (b). For an explanation see text.

strongly distorted orthophosphate groups with no nearby OH whereas the ^{1}H-peak E at about +5 ppm can be tentatively assigned to a distorted proton environment [38]. The D–E peak combination attributable to TCP/TTCP disappears completely after an incubation time of 12 weeks in accord with the notion that the easily soluble ''distorted'' structures including oxyhydroxylapatite and oxyapatite near the C–F peak centre will be preferentially removed. Indeed the coating in the presence of a bond coat consists to 92% of well-ordered, highly crystalline HAp (cp. Table II).

4.2. *In vivo* behaviour of the implants

To test the biological performance of ''duplex'' HAp/titania systems coated Ti6Al4V rods were implanted into the femura of sheep. The authors are well aware of the fact that the few animals used to assess the *in vivo* performance of the novel ''duplex'' coating system in no way satisfy statistical requirements but provide only qualitative results. However, this study was aimed at showing that no adverse effects will be produced by utilisation of a titania bond coat. Moreover, the overall performance points to a substantial if not yet statistically proven improvement of the adhesion of the coatings to the titanium alloy substrate.

The results of the microscopic and microradiographic investigations of the samples are shown in Figs. 4–6.

The uncoated rods used as a control reveal in all three sectioning planes (proximal, medial, distal) a layer of connective tissue of varying thickness separating the implant from the bone. In the distal femur this tissue layer is up to 1000-μm-thick (Fig. 4). As direct contact between implant and bone is achieved only punctually in some isolated areas, the implant body is predominantly separated from bone tissue by a gap filled with fibrous connective tissue. This means that no solid implant fixation is to be expected.

In contrast to the uncoated (control) rods, a HAp coating initiates substantial bone growth that appears to anchor the implanted rod tightly to the cortical bone wall (Fig. 5(a)). This can be confirmed in all three sectioning planes characterised by a solid body of newly formed bone securely attached to the corticalis. On the far side towards the marrow-filled centre of the femur a thin lamellar layer of bone can be found. However, parallel to the implant circumference there is frequent gap formation between the metallic implant and the HAp coating that results in a complete separation of the ceramic coating from the metallic substrate and secondary invasion of bone tissue and/or connective tissue into the gap in various places (Fig. 5(b)). In contrast to this, cross-sections of implants coated with HAp in the presence of a TiO_2-based bond coat (Fig. 6) show that in the proximal plane strong bone apposition occurs resulting in a continuous and tight succession of

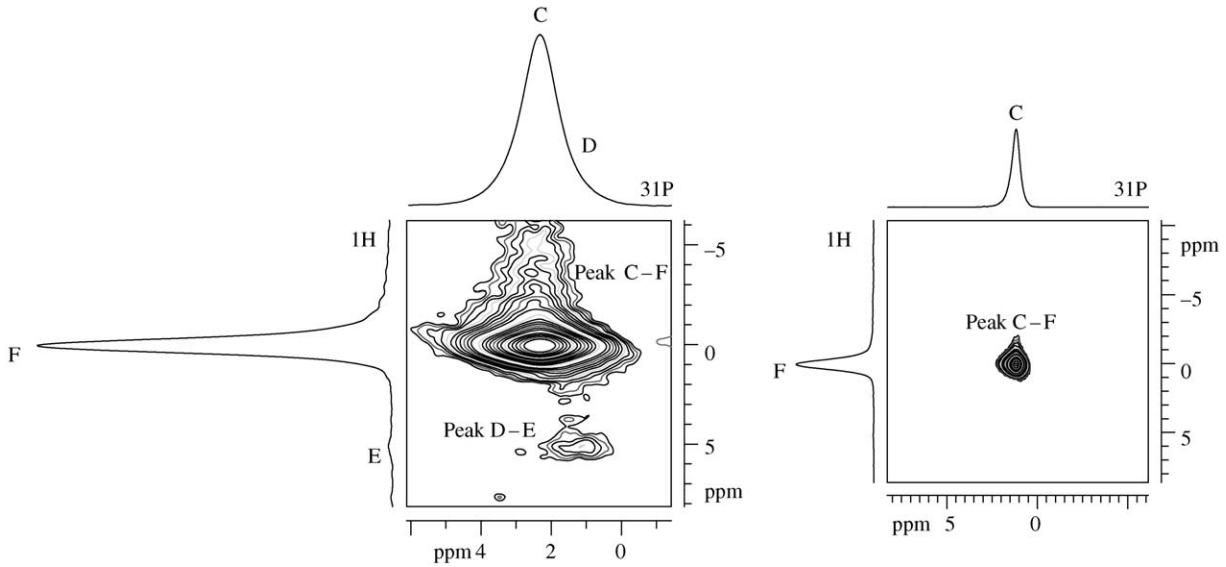

Figure 3 2D–^{31}P (horizontal axis)–^{1}H (vertical axis) HETCOR-CP-NMR spectra of HAp coatings without a bond coat (a) and with a TiO_2 bond coat (b) incubated for 12 weeks in r-SBF [37].

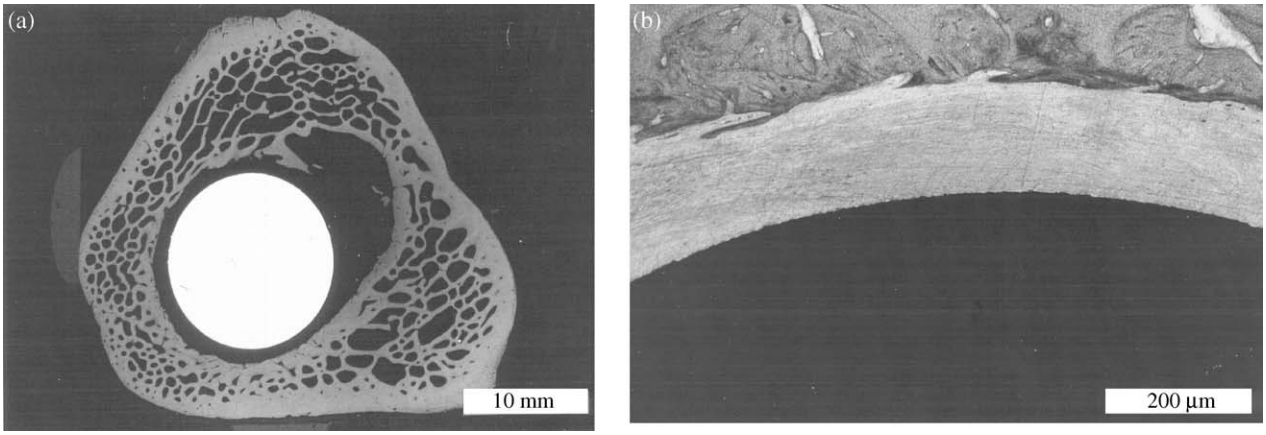

Figure 4 Microradiograph (a) of a cross-section of an uncoated rod (control) lodged in the medulla of a sheep femoral bone and enlarged micrograph (b) of the same sample showing the separation of the implant (bottom) and the bone (top) by a fibrous layer of connective tissue. Distal plane.

implant body (bottom), bioceramic coating (centre), and newly formed bone (top) (Fig. 6(a)). In the distal plane there is strong neoformation of bone in the region close to the corticalis. Moreover, a small bone lamella has formed in close contact and tightly adhering to the osteoconductive ceramic implant at the far side towards the marrow-filled medulla (Fig. 6(b)).

Similar results have been obtained recently in a study on the improvement of osseointegration of Ti6Al4V implants in the presence of a ''duplex'' TiO_2 bond coat/HAp top coat using a dog model. Coated Ti6Al4V cubes $(5 \times 5 \times 5\,mm^3)$ were implanted in the femoral bone of adult dogs via bone sockets created in the lateral femoral condyle and the greater trochanter using a hand drill with a diameter matching the size of the implant. After an observation time of six months it was confirmed that there was a statistically significant $(p = 0.021)$ increase in the bone coverage in the presence of a bond coat ($94.3 \pm 2.2\%$ with a bond coat, $81.6 \pm 2.0\%$ without a bond coat) [34].

These *in vivo* experiments appear to confirm the assumption obtained from previous *in vitro* experiments that a suitable bond coat based on bioinert TiO_2 will substantially increase the adhesion strength of the osteoconductive HAp coating to the Ti6Al4V substrate, forming a mechanically stable implant body. The reason for the excellent adhesion of the bond coat to the metal can be seen in the fact that the 10–15-µm-thick TiO_2[1] layer acts as an extension of the already existing native passivating oxide layer of only several nanometres thickness. However, the reason for the good adherance of the bond coat to the HAp top layer is still obscure but may be related either to the formation of an extremely thin reaction layer consisting of calcium titanate [22, 35] or the formation of a solid solution of titanium oxide with HAp [36]. Both mechanisms are thought to augment by a rather strong ''metallurgical'' diffusive bonding the mechanical interlocking of the coating splats into asperities of the grit-blasted metallic substrate surface typical for plasma-sprayed coatings. Since the rate of biomimetic apatite formation will be strongly increased by functional Ti–OH groups [39] a plasma-sprayed TiO_2 bond coat may also contribute to the mechanism of improved coating adhesion to the surrounding living bone.

5. Conclusion

The *in vivo* behaviour of uncoated, HAp-coated, and HAp/titania-coated rod-shaped implants inserted into the condyle and extending into the medulla of sheep femura leads to the following conclusions.

1. Without an osteoconductive coating there is no bony integration of the implant. The implant is surrounded by a circumferential fibrous layer of connective tissue that prevents solid fixation.
2. Although implants with only a standard HAp

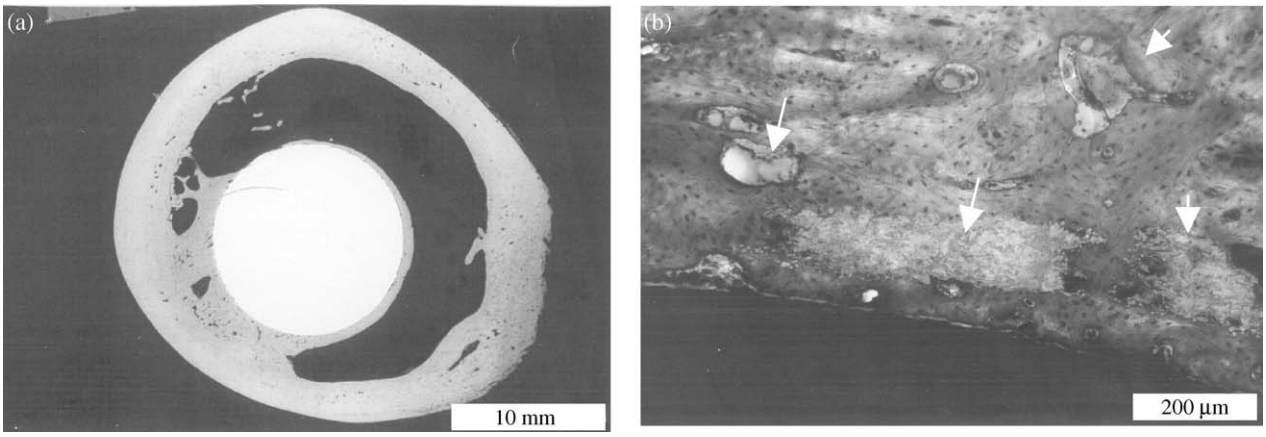

Figure 5 Microradiograph (a) of a cross-section of a HAp-coated rod lodged in the medulla of a sheep femoral bone and enlarged micrograph (b) of the interface between the implant and newly formed bone, showing separation of the HAp layer *in vivo* (arrows). Medial plane.

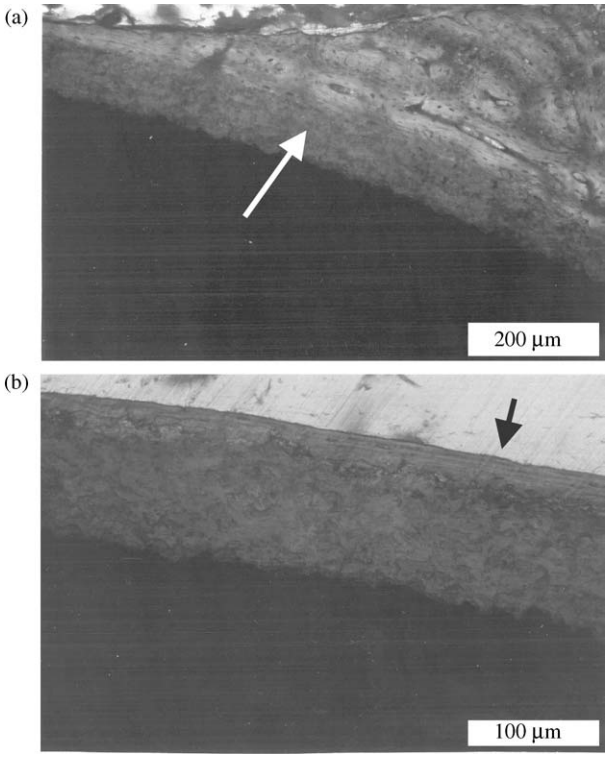

Figure 6 (a) Enlarged cross-sections of an implanted Ti6Al4V rod coated with HAp + bond coat (arrow). The proximal plane shows an intact HAp layer with intense and stable bone ingrowth. (b) Micrograph of the distal plane with a thin lamella of newly formed bone (arrow) in solid contact with the well-adhering and intact HAp coating.

coating show a good gap bridging potential, between the implant and cortical bone frequently *in vivo* delamination is observed of the ceramic coating from the metallic body. This delamination creates a gap into which bone and/or connective tissue can invade thus replacing the desired osteoconductive bonding by a mere osseoinductive contact osteogenesis. While the former is thought to be able to transmit both tensile and shear forces through bony ingrowth the latter results in a bony ongrowth that can transmit only compressive forces.

3. In contrast, the presence of a thin bioinert TiO_2-based bond coat between the metallic implant body and the osteoconductive HAp layer considerably strengthens the interface between ceramic and implant material thus preventing separation of the coating and providing for an undisturbed and continuous interface that is conducive to a strong and lasting integration of the implant. Laser-Raman and 2D-HETCOR-CP-NMR spectroscopy showed that thermal decomposition of HAp in the presence of a bond coat is significantly suppressed, presumably owing to the thermal barrier effect of the intermediate titania layer.

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The animal experiments were performed in full compliance with the current laws existing in the Federal Republic of Germany.

Notes

1 Actually the titanium oxide layer deposited by APS is not a stoichiometric TiO_2 but consists of several Magnéli-type sub-stoichiometric phases Ti_nO_{2n-1}.

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