CERAMIC COATINGS ON TITANIUM FOR BONE IMPLANTS

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INTRODUCTION

Among metals, titanium and its alloys are mostly recommended for bone implants because of their favourable mechanical properties, biocompatibility and resistance to corrosion by body fluids. However, these materials are not capable of forming a direct bond with the living tissue.

On the other hand, inorganic non-metallic materials have been developed exhibiting bioactivity, i.e. the ability to form bone-like apatite in contact with body fluids, without any non-adhering fibrous tissue arising at the interface. Such specific behaviour of bioactive materials is the prerequisite to direct bonding with bone tissue. Because of their inferior mechanical properties as compared to those of metals, the bioactive materials so far developed cannot be used as bulk materials for routine bone replacements. The main groups of bioactive materials are the following: bioactive glasses, bioactive glass-ceramics and hydroxyapatite materials (see e.g. Hench, 1991).

A combination of the two types of materials, i.e. of a metallic substrate provided with a bioactive coating, can utilize the advantageous properties of both the metallic as well as of the non-metallic component of the composite.

Nowadays, plasma spraying of hydroxyapatite (HA) coatings onto titanium and Ti-alloys is succesfully used for dental implants and for orthopaedic replacements. The main disadvantages of this technique are as follows: limitations arising from the shape of the coated articles, low and variable adhesion of HA to the substrate, and a variable phase composition due to poor reproducibility of the spraying process which affects the behaviour of the composite in the live tissue. Therefore, several other methods and materials for coatings have been studied and reported in the literature.

In this review, various materials for coatings on titanium will be considered, arranged according to preparation methods and to the nature of chemical systems, with the main emphasis laid on the composition and properties of the coating proper. Only ceramic coatings prepared by high temperature processes will be discussed. Electrochemical techniques of titanium surface treatment will be dealt with in a separate review.

THERMAL SPRAYING

In principle, fine particles of an inorganic substance are heated above its melting temperature and deposited, after leaving the high temperature zone, on a substrate. Decomposition, melting, vaporization and crystallization are the main phenomena participating in the formation of the coating. Plasma spraying and flame coating are the basic methods of thermal spraying.

Plasma sprayed apatite coatings

Since the time of the early publications on the subject in the eighties (e.g. de Groot et al., 1987), plasma spraying of HA has become a standard method of Ti surface modification for bone implants. Powdered HA is introduced into the air plasma torch. During a short exposure to a very high temperature (above 5 000 K), the particles melt at their surface and are deposited on the cooler metal substrate. Owing to the quenching effect, the product is partly amorphous. Hydroxyapatite decomposes at high temperatures so that the coating contains, besides HA, dehydrated products such as crystalline oxyapatite, TCP etc. The thickness of the layer (0.050 - 0.250 mm) is a compromise between a stronger thin layer and the longer time of resorption of a thick layer. According to the conditions in the plasma torch, the properties of the layers can differ widely in terms of crystallinity and porosity.

Above 850 °C, HA dehydrates first to oxy-hydroxyapatite with a variable content of OH groups, at higher temperatures to oxyapatite $Ca_{10}(PO_4)_6O$ which is very reactive at ambient temperature and rehydrates in air to $Ca_{10}(PO_4)_6(OH)_{0.5}O_{0.75}$ (Rey et al., 1991). Above 1200 °C, oxyapatite decomposes to tri- and tetracalcium phosphate $Ca_3(PO_4)_2$ and $Ca_4P_2O_9$, respectively.

A calcium titanate phase $CaTi_2O_5$ was detected by Ji et al. (1992) at the metal-ceramic interface, produced by chemical reaction of HA with Ti. The authors conclude that in addition to mechanical interlocking, some chemical bonding occurs at the interface. The adhesion of the layer to a Ti-Al-V alloy can be improved by additional heat treatment, the main effect being the transformation of amorphous phosphate phases to crystalline ones (Ji and Marquis, 1993). Titanium

phosphide was found at the interface after heat treatment of the coating at 950 °C in vacuo, as a result of phosphorus diffusing into the Ti alloy.

The structure of the plasma sprayed HA coating was found to be non-uniform. Crystalline phases were observed on the surface by a TF-XRD study, while an amorphous phase was present in the interior layers of the coating close to the substrate (Ohgaki et al., 1997).

The main characteristics of satisfactory HA coatings were summarized by Willmann (1997). The thickness of the coating may be in the range of 0.050 - 0.250 mm. The coating is always porous, with interconnected pores. The lower the thickness, the higher the bonding strenth to the substrate (typical pull-off strength above 35 MPa for a thickness of 200 microns). The composition, the content of mineral phases and crystallinity should comply with ASTM F 1185 (ISO/DIS 13799). Willmann also predicts possible future development: HA coating may be used as a carrier for the bone morphogenetic protein which accelerates osseointegration of an implant more than any bioactive material alone.

In order to improve the resistance to in-vivo degradation and the osteoconductivity, a double-layer coating was developed, composed of more stable fluorohydroxyapatite covered by a poorly crystalline carbonated HA layer (Ranz et al., 1997). Plasma sprayed coatings of a mixture of alumina and HA powders on Ti6Al4V are reported to have a better inner cohesion as well as adhesion to the substrate (Demonet et al. 1997).

Submicron particles of Y_2O_3-stabilized zirconia were incorporated in a plasma sprayed HA coating in order to increase the bonding strength to the Ti6Al4V substrate (Chang et al., 1997). The coating obtained exhibited increased porosity. The cubic phase of zirconia remained stable during plasma spraying. Due to a chemical reaction of a part of ZrO_2 with HA, $CaZrO_3$ was formed accompanied by increased alpha-TCP content. The bonding strength was only slightly improved.

Silva et al. (1997) prepared double-layer coatings by plasma spraying: the undercoat of pure HA was covered by a top layer composed of HA/4% phosphate glass composite. Owing to the glass addition the top layer was less crystalline than the HA one. The authors conclude that well adherent double-layered coatings can be obtained capable of inducing a fast response after implantation and showing reduced long-term dissolution.

Other plasma sprayed coatings

Kuroyama et al. (1991) prepared titanium coated with single-phase alpha-TCP by plasma spraying of beta-TCP powders. According to tests on animals, the pull-out strengths were lower than those of HA within 3 months of implantation, and comparable after 6 months. Considerable resorption of the TCP layer was observed.

Smucler-Moncler et al.(1992) reported that coatings of $CaTi_4(PO_4)_6$ and $CaZr_4(PO_4)_6$ show bioactive behaviour. Plasma sprayed coatings of $CaTi_4(PO_4)_6$ were prepared by Lugscheider et al. (1995). Berger et al. (1996) found that substitution of Ti by Zr in plasma sprayed compositions of the quasi-binary system formed by these compounds improves the long term stability of the material, which is higher in comparison with HA (concluded from solubility tests in a TRIS-buffer solution).

Several attemps were made to coat titanium with a bioactive glass or a glass-ceramic layer. Gabbi et al. (1992) produced layers of Biovetro^R 0.060 - 0.070 mm thick by plasma spraying. Glass-ceramic layers of Bioverit (glass-ceramic in the system SiO_2-Al_2O_3-MgO containing phlogopite and fluoroapatite crystals) 0.050 - 0.300 mm thick were produced on Ti by Carsten et al. (1995). The layers were porous, with pores connecting the external surface with the metal. Because of partial evaporation of volatile components, the crystallinity of the layers was reduced.

Three different glasses (two of them biodegradable and resorbable, the third one biocompatible non-resorbable) based on the system Na_2O-CaO-SiO_2 with a minor content of K_2O, MgO and P_2O_5 were plasma sprayed on the TiAl6V4 alloy in controlled atmosphere (Merolli et al., 1996). The coatings were microporous, without any evidence of crystalline phases. The response of the organism was evaluated by animal tests.

Ferraris et al. (1996) prepared vacuum plasma-sprayed coatings of two bioactive glasses based on the system CaO-SiO_2-B_2O_3 and of a glass-ceramic composite reinforced with Ti particles on the TiAl6V4 alloy. All the coatings were bioactive (tested by soaking in SBF) and well bonded to the substrate. The composite layers containing Ti particles showed better mechanical properties than the pure glass matrices and than HA coatings prepared by the same technique. The formation of HA on these coatings was remarkable in terms of changes in concentration of P, Ca and Si, already in the first day of soaking in SBF. The authors conclude that coatings of this type represent a bioactive and mechanically improved alternative to HA coatings.

Flame coating

Flame spraying,i.e. heating and partial melting of particles by a combustion process, is an alternative to plasma spraying.The combustion fuels include hydrogen, acetylene, propane, etc. The process can be controlled by the flame temperature, which is much lower than in the case of the plasma technique, and by the velocity of combustion gases, i.e. the residence time of particles in the hot zone.

High velocity oxyfuel spraying (HVOF) is a more recent development ot the thermal spraying process, with hypersonic gas velocities and combustion temperatures of above 2 800 °C (Sturgeon, 1996). Coatings of HA were prepared using HA powder with a particle size of 0.025 - 0.045 mm. Both with acetylene and hydrogen fuel, well adherent layers on titanium were formed. The only crystalline phase found in the coatings was HA accompanied by a variable amount of an amorphous phase.

A high velocity flame spraying (HVFS) technique was reported by Oguchi et al. (1992) as a development from the late 1980s. In a more recent study, Oguchi and Hastings (1994) compared the behaviour of HA coatings on Ti, prepared by plasma spraying and by the HVFS process. The tests in vivo did not show any considerable biological differences between the two products. The same authors summarize also their earlier results obtained by in vivo and in vitro tests as follows: the layers of both plasma sprayed and HVFS hydroxyapatite showed structural characteristics of that compound, with preferential orientation of the plasma sprayed HA to the C axis. The HVFS-HA was more porous and showed microbreakage due to rapid reduction of temperature. The solubility of Ca^{2+} ions was higher for plasma-HA.

A comparison of three spraying methods markedly differing in temperatures and velocities was made by Knowles et al. (1995). The methods investigated were: flame spraying, plasma spraying and the HVOF technique. All three methods induced a distortion into the HA structure. Small changes were also detected on the chemical level: carbonate and hydroxyl groups were removed during the spraying process.

MAGNETRON SPUTTERING

The radio frequency (RF) magnetron sputter process has been proposed as an alternative to thermal spraying. In principle, high-energy gas ions impinge upon a target which has been previously coated by the desired material. The atoms of the material are released and transferred from the target to a substrate. The results obtained so far were summarized by Ducheyne and McGuckin (1990). It was repeatably found that RF sputtering of HA onto a metallic substrate produces a well adherent, dense coating with a thickness of 0.001 - 0.010 mm. Some details of the technique were described by de Groot and Wolke (1995). The target consists usually of a copper disc with a plasma-sprayed HA layer. The authors conclude that magnetron sputtering is an excellent method for producing stable, dense, adherent and homogeneous Ca/P thin films on metal substrates. No grit blasting of the substrate surface is needed. The product can be obtained as either amorphous or crystalline. The thickness of about 0.010 mm of HA is considered sufficient for

incorporating the Ti implant by the generally accepted mechanism.

Hamagami et al. (1997) prepared coatings of poly-crystalline HA of 0.002 mm thickness, by RF magnetron sputtering from targets of a calcium phosphate glass with a Ca/P ratio lower than 1.67. The coatings were annealed at 140 °C under high water pressure. Whereas the as-sputtered films were amorphous, the annealed films were found to be of non-stoichiometric oxy-hydroxyapatite exhibiting HA deposition after 6 days in SBF.

CHEMICALLY PREPARED LAYERS DENSIFIED BY SINTERING

A new method of Ti surface modification was developed a few years ago (Miyaji et al., 1994). The authors utilized an earlier finding that titania hydrogel can form bone-like apatite on its surface when soaked in SBF (Kokubo et al., 1990). Commercially pure Ti was treated with 10M NaOH aqueous solution at 60 °C. After washing and drying, the specimens were heated to 400 - 800 °C. At the most favourable temperature of 600 °C, a well adhering and mechanically stable layer was obtained consisting of amorphous sodium titanate (or titania hydrogel with adsorbed alkali), crystallizing to non-reactive $Na_2Ti_5O_{11}$ and rutile at higher temperatures. The 600 °C layer was reactive enough to form 0.005 - 0.010 mm thick HA layer when soaked in SBF for 3 weeks. Similar behaviour was found also with KOH treatment. The authors suggest that the layers are firmly bound to the metal surface because of a compositional gradient from the outer apatite to the metal. During exposure to SBF, alkali is released from the layer into the solution and a titania hydrogel is formed. Dissolved alkali increases pH and the degree of supersaturation of the solution with respect to HA. Titania hydrogel then induces the apatite nucleation.

A similar behaviour was found for Ti-alloys whereas alloys not containing Ti did not show these properties (Miyaji et al., 1995 and Kokubo et al., 1996). The authors conclude that the compositional gradient from the outer apatite layer to the metal surface can result in a uniform gradient of stress transfer from the bone to the implant.

Adhesive strength and fracture behaviour of a deposited HA layer on alkali- and heat-treated titanium was investigated in vitro, in comparison with A-W glass-ceramics (Kim et al., 1996). The adhesive strength of apatite to the Ti substrate was appreciably higher than to the A-W substrate. Therefore, Ti and its alloys subjected to alkali- and heat treatment are believed to bond and integrate tightly with the living bone. This conclusion was verified by in-vivo animal tests comparing the behaviour of pure non-treated Ti with alkali- and heat-treated titanium (Yan et al., 1996).

The strong bonding of apatite and of the living bone to Ti metal has been attributed to a graded structure across the interface: the structure changes from HA to the metal surface via hydrated titania and TiO_2, with no distinct boundary (Kim et al., 1997a). The graded structure implies a gradient of chemical composition, crystallinity and mechanical properties.

Amorphous sodium titanate layer, as formed by alkali treatment only (i.e. without heat treatment), can induce HA formation in a very short time - one day, whereas the alkali- and heat-treated layer (densified at 600 °C) showed a 3-day induction period in SBF (Kim et al., 1997b). This is still comparable with bioactive A-W glass-ceramics. The authors point out that non--densified layers are mechanically unstable, with poor adhesion to the substrate, so that they are not suitable for clinical applications.

A similar conclusion was reached by a study on the effect of heat treatment on the bone bonding ability of alkali-treated titanium (Nishiguchi et al., 1997). On the basis of in vivo tests it was concluded that alkali treatment produces an unstable surface layer which can be lost during preservation or implantation. Therefore, both alkali- and heat-treatment are considered essential for preparation of bioactive titanium in practical use.

Yan et al.(1997) performed detachement tests of Ti-alloy after implantation in rabbit tibiae. They concluded that an alkali- and heat-treated surface can acquire improved bone bonding ability by deposition of a thin HA layer from SBF prior to implantation.

ENAMELLING TECHNIQUES

Enamelling techniques consist of applying a raw mixture on the metal surface by dipping, spraying etc. and of successive firing in order to densify the coating and to establish a strong bond between the two materials.

The main prerequisites for successful enamelling are:

1. equal or similar coefficients of thermal expansion to avoid formation of stresses between coating and metal during cooling from the firing temperature,

2. the capability of the two quite different materials (metal and oxidic coating) to form a strong adhesive or chemical bond which can be supported by mechanical anchoring in the uneven surface of the metal.

The first demand is especially important in the case of thick coatings. The layers of traditional enamels usually have the thickness of tenths of mm, whereas advanced sol-gel methods produce thin films which can attain microns in thickness.

The literature reports on the following systems for enamelling titanium: titania, hydroxyapatite, bioactive glass or glass-ceramics and combination of glass with HA.

Titania coatings

Thin titania coatings were prepared via sol-gel by hydrolysis of Ti-alkoxide and by the dipping technique followed by firing at 400 - 600 °C (Li et al., 1993). The resulting layer was found to be bioactive but the adhesion to the Ti substrate was poor. Müller-Mai et al. (1994) found that a coating of titania prepared by a similar method exhibited only biocompatible, not bioactive behaviour in vivo. The thickness of the twice dipped coating was 0.002 mm after firing at 600 °C.

Hydroxyapatite coatings

It should be noted that quite a large difference between the coefficients of thermal expansion between Ti and HA (87 and 133×10^{-7} K^{-1} respectively) can produce stresses at the interface with a negative effect on the adhesion of the layer, in particular in the case of thick coatings.

Coatings of HA about 20 microns thick were deposited electrophoretically on Ti-alloy discs and sintered at 930 °C in vacuo (Radin, 1992, see also Ducheyne, 1990). The resulting phases were oxyapatite and TCP. In earlier experiments, a well adhering Ti-P compound was found at the coating-metal interface which could not be identified from recorded diffraction patterns (Ducheyne et al., 1986).

Li et al. (1996) prepared hydroxyapatite coatings on titanium rods by the dipping method using a HA-sol. Microcrystals of HA were synthetized by neutralization of calcium hydroxide suspension with phosphoric acid solution. The crystals were dispersed in distilled water or physiological saline solution. The thickness of the layer, after several dipping cycles, ranged from 0.010 to 0.200 mm. Microcrystals of HA quickly induce new bone formation and disappear by resorption. However, the bonding strength between HA layer and Ti was very poor.

Deptula et al. (1996) reported preparation of HA coatings on Ti by a water extraction variant of the sol-gel process modified by addition of ascorbic acid to calcium acetate and phosphoric acid solutions. The substrate was immersed in the sol and withdrawn at a constant speed. Only sols containing ascorbic acid formed homogeneous films on the substrate as a result of improved wetting. After gelling at room temperature, sintering of the coating was performed at 900 °C, resulting in the formation of HA according to electron probe and X-ray analyses. The coatings were uniform, adherent and mechanically resistant. The thickness of the coatings formed by a single dipping was several tenths of microns.

Mizushima et al. (1996) investigated application of HA coatings using calcium nitrate, ammonium hydrogen phosphate and EDTA chelating agent as starting materials. EDTA-derived solutions were very viscous and behaved like a Newtonian liquid up to high concentrations. By drying, the viscous solution turned into a transparent gel free from cracks and precipitates. Coating was carried out by dipping using Ti metal substrates. After drying, densified coatings were obtained by firing at 800 °C in Ar. The gel crystallized into a single-phase HA without any other phases. Vickers indentation tests did not result in peeling off. The densification temperature of 800 °C was by 200 °C lower than that of the conventional alkoxide method and the development of microcracks during drying and firing was considerably prevented, presumably due to the fine and dense structure resulting from rheological characteristics of the coating solutions.

About 0.001 mm thin films of HA on Ti can be obtained by coating with solutions containing organo--metallic compounds, followed by heating at 650 - 1050 °C (Zhou et al., 1996). The product contained HA and TCP. The percentage of HA, as well as the crystallinity and average particle size, increased with increasing temperature.

For the first step of enamelling techniques, i.e. application of HA onto the metal substrate, also direct crystallization of HA from a supersaturated solution can be considered.

Thin films of HA fine crystals (0.010 - 0.020 mm thickness) can be deposited on iron or titanium plates by a precipitation technique using hydrothermal reaction in $Ca(EDTA)_2$ - NaH_2PO_4 solutions at 150 - 250 °C (Fujishiro et al. 1995, 1996).

Bioactive glass coatings

The first attemps to provide Ti with a bioactive glass layer were carried out by dipping the Ti-alloy implants in molten Bioglass[R]. The technique was elaborated by Hench and Buscemi (1979). In vivo bone-bonding study of Bioglass[R]-coated Ti-alloy implants was performed by West (1990). Precoating of implants was made by boric acid in a reducing flame to minimize the effect of the reaction between Ti and glass which produces bubbles weakening the glass-to-metal bond. Precoating results in the formation of $TiBO_3$ glass. Implants coated with glass and with plasma sprayed HA were tested in dog femurs. The push-out strength of Bioglass[R]-coated samples was slightly lower than that of HA-coated samples. The failure of Bioglass[R]-coated implants occurred at the glass-metal interface. Solid implants of Bioglass[R] showed slightly higher strengths than both groups of coated samples.

Kim and Kwon (1997) reported the preparation of titanium coated with bioactive glass using a double coating method. Two glasses were prepared by melting at 1500 °C containing 55 and 50 wt.% of SiO_2. After pulverizing, the powder was dispersed in acetone and applied to the metal by spraying at room temperature. The first glass was used for the ground coat and fired at 1150 - 1300 °C in Ar. A thin layer of Ti_5Si_3 was formed at the interface which enabled adhesion of the coating. Wollastonite and fluoroapatite were found in cooled samples after firing. The cover coat made of the second glass was fired at 750 - 900 °C. The formation of HA in SBF was observed only on the cover coats fired under 800 °C.

Bioactive composite coatings on Ti-alloy were reported by Wu and Sun (1995). The coating was prepared using a mixture of bioactive glass and glass-ceramic powders and densified by firing. Enhancement of the adhesion strength was observed after 24 - 40 weeks of implantation.

In an earlier work, in connection with slip-cast coating of HA on porous stainless steel, also enamelling with bioglass was mentioned which altered the bioglass composition in a detrimental way (Ducheyne et al., 1980).

Glass-ceramic coatings

Takatsuka et al. (1992) reported an attempt to coat Ti-alloy with a modified apatite-wollastonite bioactive glass-ceramic layer. The mother glass powder mixed with an acrylic binder was applied onto the metal surface and sintered at 950 °C in vacuo, after presintering at 400 °C to eliminate the binder. On the average, the layers were 0.075 mm thick. The shear strentgh between the coating and the metal substrate was 200 MPa. The bioactivity was examined by implantation into rabbit tibiae. The bone bonding strength was significantly higher than that of HA after 3 - 4 weeks and it was maintained at least up to 25 weeks.

A multicomponent phosphate glass precursor was prepared by a sol-gel method and filled with TiO_2 and Al_2O_3 (Deffontaines et al., 1992). After spreading on the Ti-alloy surface, the samples were sintered in Ar at 900 °C. The need of adjustment of thermal expansion and creation of chemical interface is mentioned in connection with alpha-beta transition in TiAl6V4 alloy at 975 °C and with Ti-oxygen reactivity. The system allowed thermal expansion of the coating to be adjusted. A complex chemical bonding was achieved at the interface.

A coating based on a glass-ceramic material of the system P_2O_5-Al_2O_3-CaO-Na_2O-F was reported by Frigge et al. (1994). Mother glass powder was mixed with isopropanol, brought onto the metal surface and sintered at 700 °C in an oxidizing atmosphere which produces a Ti and oxygen rich layer at the interface. The oxidized

layer brought about good adhesion whereas heat treatment in vacuo resulted in a weak bond between metal and coating.

The difference in expansion coefficients of Ti (87×10^{-7}) and A-W glass-ceramics (107×10^{-7}) was dealt with by Zhu and Huang (1996). A transition layer of a boron-aluminosilicate phosphate glass (exp. coeff. 77×10^{-7}) was applied as a ground-coat and sintered at 900 °C under controlled atmosphere. Oxyapatite and a small proportion of wollastonite were the main phases in the coating with a thickness of 0.015 mm and 20-30 % porosity. A firm and dense TiO_2 layer was found between the coating and substrate which is assumed to improve the adhesive strength of the coating.

Composite coatings

Maruno et al. (1992) developed a coating consisting of HA-containing glass, suitable for Ti as well as for Ti-alloys. The concentration of HA in the coating gradually increased towards the surface. The slips prepared as a mixture of an alumina-borosilicate glass and of HA powders were applied onto the metal surface and fired at 800 - 900 °C. By repeating the coating procedure, layers 0.050 - 0.150 mm in thickness were produced. Finally, the surface was etched by a solution of HF and HNO_3 to remove the surface layer of glass surrounding the HA particles which thus became directly accessible to the body fluid. It was found that the coating had good adhesion to the substrate and that a strong bond between the coating and substrate was preserved after 31 months of implantation (see also Maruno et al., 1994).

A modified HA-glass coating was developed later under the name Cullet method (Yamada et al., 1996). The powders of HA and of a borosilicate glass were mixed and presintered at 900 °C. After pulverization, the powders obtained were used for coating in the same manner as in the former method. The Cullet method resulted in an superior strength and stability of HA-glass layers due to elimination of large voids and pores. The implants were well integrated into dog femora. The bonding strength of the implant to the bone was increased, in the early stage of implantation, by electrochemical deposition of a calcium phosphate layer covering the HA-glass coating.

Coatings of a similar nature were reported by Wang and Li (1995). A boron-aluminosilicate glass was used as ground coat on Ti-alloy. The overcoat consisted of 3 layers prepared from the matrix glass mixed with 30 - 70 % of HA powder. The content of HA increased towards the surface. The application methods used were spraying, dipping and brushing. Firing of the coating was performed at 900 - 950 °C. Finally, the surface was treated with an acid solution to promote bioactivity by uncovered HA particles. Strong adherence to the bone was achived after 1 - 3 months of implantation into dog leg bone, 3 times as high as for the coating of plasma sprayed HA.

CONCLUSION

Among surface treatments and modifications of titanium for bone implants, plasma spraying of hydroxy-apatite is the most common method used commercially. However, some disadvantages or week points of this method initiated continuing efforts to offer some other alternatives, more suitable at least in special cases. Over the last years, considerable attention has been paid to chemical treatment of Ti by NaOH solution followed by densification of the sodium titanate layer at high temperature. There are still some questions connected with this method to be clarified. Many attemps have been made to provide titanium with a bioactive coating based on glass or glass-ceramics by enamelling techniques. More detailed studies are needed concerning adjustments of expansion coefficients, metal surface treatment prior to enamelling and methods of achieving sufficient adhesive strength at the metal-coating interface.

Ackowledgement

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Abbreviations

A-W	-	anorthite-wollastonite
HA	-	hydroxyapatite
SBF	-	simulated body fluid
TCP	-	tricalcium phosphate
TF-XRD	-	thin film X-ray diffraction

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