

## Bioactive coatings of glass-ceramics on metals<sup>1)</sup>

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To combine the mechanical properties of high-strength base metals with the biological properties of bioactive materials, coatings of BIOVERIT® glasses and glass-ceramics on CoCr alloys and titanium have been produced. Different kinds of coating processes have been used: dipping, sputtering, plasma spraying, sintering and pasting. Dipping and pasting seem not to be suitable to produce layers because of cracks and low adhesion strength of the coatings (dipping) and the limitations in relation to the implant shape and the thickness of the layers (pasting). Using sputter techniques it is possible to produce dense layers (<10 µm) with a high adhesion strength. Plasma spraying resulted in layers with a thickness of 50 to 300 µm, but during the plasma spraying process there is a partial evaporation of the highly volatile glass components. Sintering processes are very suitable to produce layers with a high adhesion strength; these layers are long-term stable in simulated body fluid.

### Bioaktive Glaskeramik-Beschichtungen auf Metallen

Es wurden Schichten von BIOVERIT®-Gläsern und -Glaskeramiken auf CoCr-Legierungen und Titan hergestellt, um die mechanischen Eigenschaften der hochfesten Metalle mit den biologischen Eigenschaften der bioaktiven Materialien zu kombinieren. Unterschiedliche Beschichtungsverfahren kamen dabei zur Anwendung: Tauchbeschichten, Kathodenzerstäuben, Plasmasprühen, Sintern und Kleben. Tauchbeschichten und Kleben scheinen für die Schichtherstellung nicht geeignet zu sein auf Grund von Rissen in der Schicht und einer geringen Haftfestigkeit der Schicht (Tauchbeschichten) bzw. durch Einschränkungen bezüglich der Implantatkörpergeometrie und der Schichtdicke (Kleben). Mit Hilfe des Kathodenzerstäubens war es möglich, dichte Schichten (<10 µm) mit einer hohen Haftfestigkeit zu produzieren. Beim Plasmasprühen wurden Schichten mit einer Dicke von 50 bis 300 µm erzielt, allerdings kommt es beim Plasmasprühen zu einer teilweisen Verdampfung der leichtflüchtigen Glaskomponenten. Sinterverfahren sind sehr gut zur Herstellung von Schichten mit hoher Haftfestigkeit geeignet, wobei sich die Schichten in simulierter Körperflüssigkeit als langzeitstabil erwiesen haben.

## 1. Introduction

Nowadays, in modern medicine there is a growing trend to use bioactive materials (tricalciumphosphate, tetracalciumphosphate, hydroxyapatite, bioactive glasses and glass-ceramics) to preserve and restore bodily functions. If implanted into a bone defect, a bioactive material is not encapsulated by a connective tissue, but comes into direct contact with the surrounding bone and forms a tight bond with it. But all bioactive materials have a fundamental problem: poor mechanical properties. Therefore, it has been tried to combine materials in order to achieve the required properties. It is possible to combine the mechanical properties of high-strength base materials (metals and metal alloys) with the biological properties of bioactive materials by using them as coatings. Because of the better corrosion stability, nowadays cobalt alloys and titanium alloys are preferred to high-grade steel.

### 1.1. Coatings of hydroxyapatite

The most applied method to coat metal implants with hydroxyapatite (HA) is the plasma spraying technique [1 to 4]. But within one year these coated implants show biodegradation [5]. This can be attributed to the presence of crystalline phases (tricalciumphosphate, tetracalciumphosphate, calcium oxide) and amorphous phases [6].

Other methods to coat metal implants with HA have been investigated: electrophoretic deposition [7], flame spraying [8], a polymeric route [9] and sputter techniques. Cooley et al. [10] have used a HA target to coat titanium implants via high-frequency sputtering. In-vivo tests result in a better bone contact compared with uncoated implants. Ong et al. [11] also have used a sputter technique to coat titanium implants with HA and yielded amorphous calcium phosphate layers. During a subsequent thermal treatment the layers were crystallized as HA. The heat-treated layers have a lower solubility, but also a lower adhesion strength than the amorphous layers.

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Table 1. Composition (in wt%) of the glass-ceramics BIOVERIT® [19]

	BIOVERIT® I	BIOVERIT® II	BIOVERIT® III
SiO <sub>2</sub>	30.5	44.5	–
Al <sub>2</sub> O <sub>3</sub>	15.9	29.9	10.0
MgO	14.8	11.8	–
CaO	14.4	0.1	14.0
P <sub>2</sub> O <sub>5</sub>	11.4	0.1	51.0
Na <sub>2</sub> O	2.3	4.4	15.0
K <sub>2</sub> O	5.8	4.9	–
F <sup>-</sup>	4.9	4.2	2.0
Cl <sup>-</sup>	–	0.1	–
ZrO <sub>2</sub>	–	–	5.0
TiO <sub>2</sub>	–	–	3.0

Table 2. Composition of the CoCr alloys (in wt%) determined by EDX analysis

	Co	Cr	Mo	Fe	Mn	Si	W	Ni
Prothecast®	63.3	28.1	5.2	1.4	1.0	0.8	–	–
Vitallium®	48.8	19.6	–	1.9	1.6	–	17.9	10.2

Table 3. Coating processes used for the production of BIOVERIT® layers

coating process	substrate	coating material
dipping	Prothecast®, titanium	BIOVERIT® I and III
sputtering	Prothecast®, titanium	BIOVERIT® I and II
plasma spraying	Prothecast®, Vitallium®	BIOVERIT® I and III
sintering	Vitallium®, Prothecast® titanium	BIOVERIT® III
pasting	Prothecast®, titanium	BIOVERIT® I

## 1.2. Glasses and glass-ceramics as coatings

On the other side, different kinds of glasses and glass-ceramics showing bioactive behaviour have been developed [12], and there are studies dealing with the production of thin layers of glasses or glass-ceramics on base materials (metals, metal alloys, alumina ceramics).

Hench and Buscemi [13] have prepared bioglass layers with a thickness of 0.2 to 2 mm on preoxidized metals using a dipping process. Hench and Greenspan [14] have coated alumina ceramics with two bioglass layers, thereby the connection between ceramic and glass is caused by ion diffusion. These are relatively complicated methods, as for example the thermal expansion coefficients have to be adapted. Furthermore, problems with a low adhesion strength, and in relation to the coating of edges of the implants have been reported [15 and 16].

Gabbi et al. [17] have produced layers of BIOVETRO® with a thickness of 60 to 70 µm using a plasma spraying technique. Kaps [18] has described the electrophoretic precipitation of bioactive glass-ceramics BIOVERIT® and ilmaplant-L1® on titanium implants.

## 1.3. Objectives

The purpose of the current study was to produce dense layers with a high adhesion strength on metals using different techniques and employing bioactive glass-ceramics of BIOVERIT® type.

## 2. Experimental procedure

### 2.1. Materials

As coating materials, the glass-ceramics BIOVERIT® were used (table 1). The system SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–MgO was the starting point for the development of the glass-ceramics BIOVERIT® I and II. Both contain mica crystals of phlogopite-type (Na,K)Mg<sub>3</sub>[AlSi<sub>3</sub>O<sub>10</sub>]F<sub>2</sub>. BIOVERIT® I contains also apatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>F<sub>2</sub>) crystals in addition to mica crystals. The machinability of these glass-ceramics depends on the presence of the mica crystals. While in BIOVERIT® I flat mica crystals are precipitated, the glass-ceramic BIOVERIT® II contains a type of curved mica crystals, which allow a better machinability than flat micas. BIOVERIT® II contains also cordierite (Mg<sub>2</sub>Al<sub>3</sub>[AlSi<sub>5</sub>O<sub>18</sub>]) crystals in addition to mica crystals. These glass-ceramic combines machinability and, referring to glass-ceramics, high mechanical strength. The glass-ceramic BIOVERIT® III, comprised of the system P<sub>2</sub>O<sub>5</sub>–Al<sub>2</sub>O<sub>3</sub>–CaO–Na<sub>2</sub>O, contains crystalline phases such as apatite, AlPO<sub>4</sub> (in different modifications) and other phosphates.

Because of its good biological properties and machinability, the commercial material BIOVERIT® is successfully applied as bulk material to human medicine [19]:

- orthopaedics (vertebra substitutes, spacers),
- head and neck surgery (e. g. middle ear implants),
- stomatology (dental root implants).

As substrates, titanium plates supplied by Goodfellow, Cambridge (Great Britain), with a purity of 99.6%, Prothecast® and Vitallium® disks (table 2) with a diameter of 15 mm and commercial slide glasses were used. The slide glasses were coated by sputtering a titanium layer with a thickness of about 500 nm simulating a titanium substrate.

### 2.2. Methods

The coating processes used for the production of BIOVERIT® layers are shown in table 3. The microstructure of the films has been characterized by means of Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM), X-ray and electron diffraction. X-ray diffraction studies (Cu-K<sub>α</sub> radiation and nickel fil-

ter) were carried out using a diffractometer F4 (Siemens, München (Germany)). The TEM investigations were performed on a TEM BS 540 (Tesla, Brno (Czech Republic)) using a replica technique [20]. Both fresh and etched fracture surfaces of the samples were coated with a Pt–Ir–C layer by high-vacuum evaporation. The layers were removed from the surfaces by treating the samples with a 1:1:1 solution of 5% HF, 20% HNO<sub>3</sub> and 20% HCl. The SEM investigations were performed on an SEM JSM-U3 (Jeol, Tokyo (Japan)).

Differences of the compositions between target material and thin films have been determined using SIMS, EDX analysis and Rutherford Backscattering Spectrometry (RBS). The RBS analysis was conducted using 1 to 2 MeV helium ions. The thicknesses of the sputtered layers were determined profilometrically by a Dektak 3030 supplied by Veeco, München (Germany). The adhesion strength of the films on the substrates was examined using pull-off investigations.

For in-vitro experiments, the films have been kept in the simulated body fluid "Hanks medium" (composition (in g/l): 8.00 NaCl; 0.14 CaCl<sub>2</sub>; 0.40 KCl; 0.35 NaHCO<sub>3</sub>; 1.00 glucose; 0.10 NaH<sub>2</sub>PO<sub>4</sub>; 0.10 MgCl<sub>2</sub> · 6H<sub>2</sub>O; 0.06 Na<sub>2</sub>HPO<sub>4</sub> · 2H<sub>2</sub>O; 0.06 MgSO<sub>4</sub> · 7H<sub>2</sub>O) and "tris-buffer solution" (250 ml trishydroxymethylaminomethane ( $c = 0.2$  mol/l) + 428 ml HCl ( $c = 0.1$  mol/l) + 322 ml distilled water). In addition investigations with cellular tissue (MDCK) have been performed.

### 3. Results

#### 3.1. Dipping

Layers of BIOVERIT<sup>®</sup> with a thickness of 1 to 2 mm were prepared by dipping disks of Prothecast<sup>®</sup> and titanium in the melt. Before the deposition of the layers, the metal substrates were sand-blasted. The layers had a lot of cracks, the adhesion strength was very low. An additional pretreatment with an acid-etching technique using phosphoric acid yields the same result.

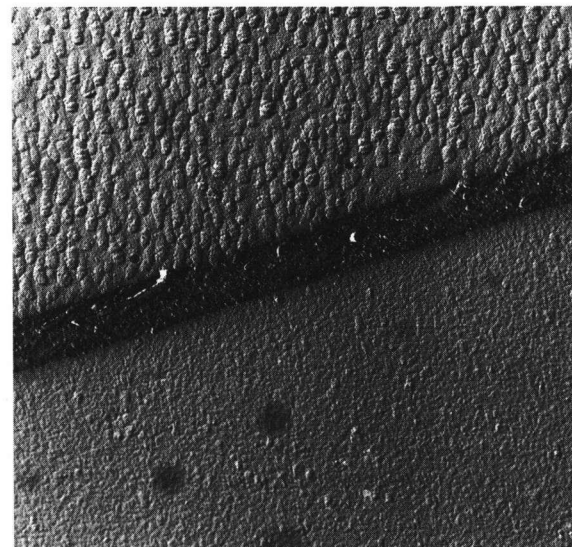
#### 3.2. Sputtering

Thin films have been deposited on various substrates by RF-magnetron sputtering starting from glass targets or glass-ceramic targets of BIOVERIT<sup>®</sup>-type using a Sputron II (Balzers, Balzers (Liechtenstein)) and a home-built sputter equipment. The depositions have been performed in argon and oxidizing ( $p_{\text{argon}} = 0.33$  Pa;  $p_{\text{oxygen}} = 0.07$  Pa) atmosphere.

The films deposited by RF-magnetron sputtering possess a thickness between 0.4 and 2.8  $\mu\text{m}$ . Figures 1a and b show transmission electron micrographs of sputtered layers on slide glasses previously coated with a titanium layer. Figure 1a shows the surface, whereas figure 1b depicts the fracture surface of the sputtered layer. Dense layers possessing a roughness of 100 nm can be obtained.



a) |-----| 1  $\mu\text{m}$



b) |-----| 2  $\mu\text{m}$

Figures 1a and b. Transmission electron replica micrographs of the surface (figure a) and the fracture surface (figure b) of the BIOVERIT<sup>®</sup> coating deposited by RF-magnetron sputtering.

By means of illustration and electron diffraction in the TEM using ion-thinned sections, it can be demonstrated that the cause for the obtained roughness is the well-known influence of the sputter process on the morphology, and not a crystallinity of the layer. In addition, X-ray diffraction patterns using the step-scanning method do not show any crystal phase.

The slide glasses coated with titanium and the glassy layer show different interference colours leading to the conclusion that the thickness of the layer is not uniform. The difference in the thickness was determined to be  $\pm 6\%$ . These differences can be attributed to the position of the substrates in the Sputron II, and to the distri-

Table 4. Composition (in at.%) of the target and a layer deposited

	BIOVERIT® target	BIOVERIT® layer
Ca + K	6.8 ± 0.2	11.0 ± 1.0
P	2.0 ± 1.0	2.0 ± 1.0
Si + Al	17.0 ± 0.5	24.0 ± 1.0
Mg	9.0 ± 1.0	8.0 ± 1.0
F	7.0 ± 1.0	12.0 ± 2.0
O	58.0 ± 3.0	43.0 ± 5.0
Ba (impurity)	0.12 ± 0.02	—
Na	below detection limit	below detection limit

Table 5. Composition (in at.%) of the target and a layer deposited

	BIOVERIT® target	BIOVERIT® layer
Ca + K	8.3 ± 0.4	8.3 ± 1.0
P	3.5 ± 1.0	3.3 ± 1.0
Si + Al	18.6 ± 1.0	19.1 ± 1.0
Mg	6.4 ± 1.0	6.2 ± 1.0
F	not determined	not determined
O	63.2 ± 3.0	63.1 ± 4.0
Na	below detection limit	below detection limit



Figure 2. Bright-field Nomarski interference contrast micrograph of cellular monolayer (MDCK) on the surface of the sputtered layer.

bution of the layer thicknesses of the cathode. Comparative SIMS investigations of the target material and of the glassy layer show the high similarity of the spectra.

The film stoichiometry has been determined by means of RBS. Using a suitable incidence, RBS enables the analysis of layers with a thickness of more than 500 nm without any influences of the substrate. An important advantage of the RBS technique is the ability to accurately determine the composition without the aid of

measurement standards. Attention must be paid to the fact that elements with comparable atomic weight can be analyzed solely as the sum of two elements. The choice of the plasma composition influences the stoichiometry of the deposited films. Table 4 presents the composition of a film deposited in argon atmosphere. The composition of the film is different from that of the target, for example the oxygen content of the film is lower than that of the target. This effect is not found in the sample deposited in the oxygen-enriched plasma (table 5). The RBS analyses are in agreement with the values obtained from EDX measurements.

The adhesion strengths of the films on the substrates have been determined to be  $\geq 25$  MPa. The thin films have been treated with a simulated body fluid (Hanks medium) at 37°C for 1 week. Neither TEM micrographs nor the measured thicknesses of the coatings showed any difference between treated and untreated samples.

Investigations with cellular tissue (MDCK) have shown the biocompatibility of the coatings. After 2 d, a confluent cellular monolayer adhered to the surface of the sputtered coatings (figure 2).

### 3.3. Plasma spraying

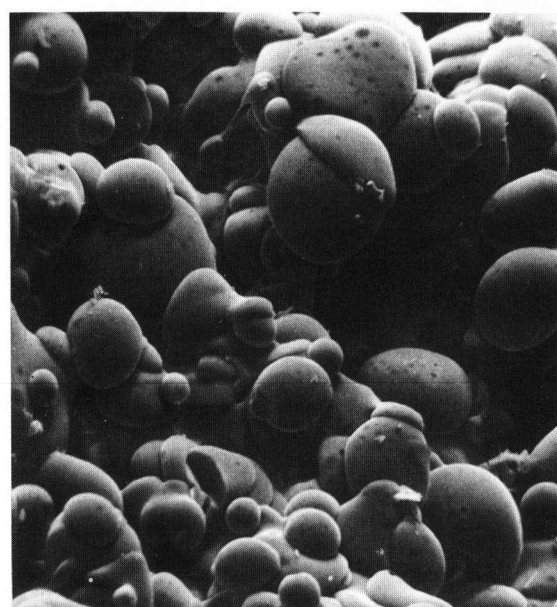
The films have been deposited on various substrates by plasma spraying starting from glass powders or glass-ceramic powders of BIOVERIT®-type using a home-built equipment (plasma gas: N<sub>2</sub>, Ar; I = 200 to 400 A; size of the powder particles: <50 µm).

Glass-ceramic layers of BIOVERIT®-I-type with a thickness of 50 to 300 µm on titanium and Prothecast® substrates have been produced (figures 3a and b). However, the layers are porous (with pores from the surface to the metal substrate). Moreover, during the plasma spraying process there is a partial evaporation of the highly volatile glass components. The fluoride content was determined using the method reported by Pietzka and Ehrlich [21], the phosphorus content (expressed as P<sub>2</sub>O<sub>5</sub>) was determined photometrically [22]. Glass powders and glass-ceramic powders have comparable evaporation losses (table 6). The highly volatile glass components are needed for the formation of the crystal phases. Therefore, the content of the crystal phases is decreased in the layers (also after thermal treatments) in relation to the bulk glass-ceramics.

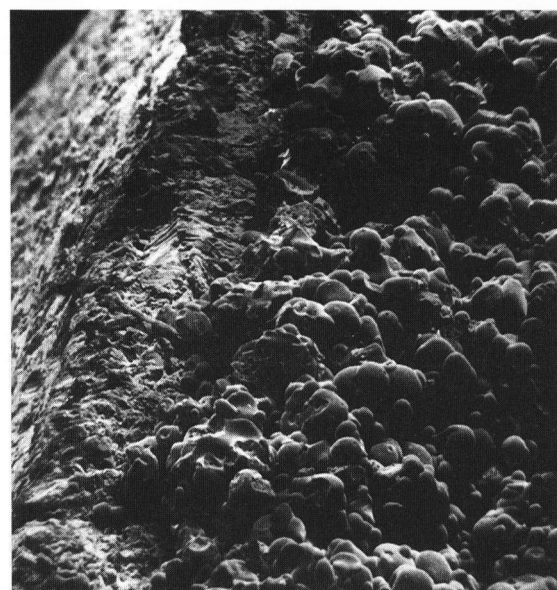
### 3.4. Sintering

A suspension of phosphate glass or phosphate glass-ceramic powder in water or alcohols was brought onto the metal (Vitalium®). The subsequent thermal treatment at about 700°C for a few minutes resulted in a dense and almost glassy coating with a thickness of 150 to 400 µm. Thermal treatment at about 500 to 600°C formed a larger amount of crystalline phases in the coating.

Very thin layers of SiO<sub>x</sub> between metal and glass-ceramic improved the adhesion strength. The adhesion



a) |-----| 100 μm



b) |-----| 300 μm

Figures 3a and b. Scanning electron micrographs of a) the surface of BIOVERIT® layer deposited on a Prothecast® disk by plasma spraying, b) the interface between the metal substrate (Prothecast®) and the BIOVERIT® layer deposited by plasma spraying.

strength between the layer and the metal was measured by pull-off investigations. Shearing strength values of about 30 MPa were measured. The fractures pass through the glass-ceramic layer or through the adhesive, but a total separation of the coating from the metal was never observed.

Tests of long-term mechanical strength yielded the following results for different bending tensions (table 7). The limiting value of 10 millions bending cycles was

Table 6. Content of volatile glass and glass-ceramic components before and after plasma spraying

	P <sub>2</sub> O <sub>5</sub>	F <sup>-</sup>
glass powder	13.3 wt%	5.2 wt%
plasma-sprayed glass powder	12.8 wt%	4.6 wt%
difference	-3.8 %	-11.5 %
glass-ceramic powder	12.8 wt%	5.2 wt%
plasma-sprayed glass-ceramic powder	12.1 wt%	4.6 wt%
difference	-5.5 %	-11.5 %

Table 7. Long-term mechanical strength of layers produced by sintering

bending tension (in MPa)	bending cycle (in 10 <sup>6</sup> N)	result
300	10.2	intact sample
300	10.7	intact sample
300	17.3	intact sample
325	10.7	intact sample
325	6.7	destroyed sample
325	6.5	destroyed sample
350	9.5	destroyed sample
350	8.8	destroyed sample

reached by applying a bending tension  $\sigma \geq 300$  MPa, approximately corresponding to the basic strength of the metal Vitallium® ( $\sigma = (342 \pm 17)$  MPa).

A solubility test in trisbuffer solution during the time of one to eight weeks showed basically the same results as the compact glass-ceramic materials. The solubility decreases during the experiments as can be seen from the examples of sodium, calcium and phosphate ions. Therefore, a protective layer is formed during the corrosion process. This is a prerequisite for long-term stable medical implants.

### 3.5. Pasting

It is also possible to join metals and glass-ceramics using an adhesive technique. The metal substrates (Prothecast®, titanium) and the bulk glass-ceramic were sandblasted, coated with SiO<sub>x</sub> ( $x \leq 2$ ) and a silane and then pasted with EVICROL®. Using pull-off investigations, the adhesion strength was determined to be 20 to 30 MPa. The applications of this method are limited in relation to the implant shape and the thickness of the layers. In addition, the use of organic adhesives is somewhat risky, due to the reported toxicity.

## 4. Conclusions

The current study shows that it is possible to produce layers of BIOVERIT®-type on implant metals using different coating processes. The surface morphology of the coatings varies strongly according to the deposition

technique used and is expected to be of great influence on the long-term stability. Furthermore, the chemical composition, structure and the bonding strength of the deposited coatings depend on the deposition technique.

To produce dense, thin layers ( $<10\ \mu\text{m}$ ), the most promising deposition technique seems to be the sputtering process which enables the economic deposition of these coatings. For the deposition of layers with a thickness of 50 to 400  $\mu\text{m}$  plasma spraying and sinter techniques have to be favoured.

Dipping processes seem not to be useful to produce layers because of cracks and low adhesion strength of the coating. The application of the pasting technique is limited in relation to the implant shape and the thickness of the layers.

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