PROCESSING AND CHARACTERISATION OF BIOGLASS\textsuperscript{®} COATING ON Ti\textsubscript{6}Al\textsubscript{4}V SUBSTRATES

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PROCESSING AND CHARACTERISATION OF BIOGLASS® COATING ON Ti₆Al₄V SUBTRATES

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Abstract

The goal of his work was to investigate the possibility to coat Ti₆Al₄V substrates with bioglass powder by means of electrophoretic deposition (EPD), subsequently followed by a suitable heat treatment to densify the coating.

Smooth defect free thick (> 1 mm) coatings were obtained on anodised Ti₆Al₄V cylindrical substrates by means of EPD. A mathematical description of the kinetics of the process showed a good correlation with experimental results. The voltage, powder concentration and time during EPD were optimised to produce coatings with the wanted thickness.

Microwave sintering was found to be an efficient method to sinter coatings up to a thickness of 50 μm, obtained free cracks of the coating. Thicker coatings could be obtained by a second EPD and sinter step. After sintering an interaction zone was detected between substrate and coating and a satisfying adhesion was observed with a scratch test. XRD, EPMA, and SEM analysis were performed on the densified coating.

Keywords: Bioglass 45S5®, Epd, Coating glass, Titanium

Resumen

El objetivo de este trabajo es investigar la posibilidad de recubrir Ti₆Al₄V con polvos de vidrio bioactivo por medio Deposición Electroforética (EPD), seguido de un tratamiento térmico de densificación del recubrimiento. Espesores (> 1 mm) de recubrimientos suaves libres de defectos fueron obtenidos con la anodización de probetas cilíndricas de titanio por medio de EPD. Una descripción matemática de de la cinética de los procesos es mostrada con una buena correlación con los resultados experimentales. El voltaje concentración de polvos y el tiempo fueron optimizados durante el EPD con los espesores esperados. Sinterizado por microondas fue el método usado eficientemente para sinterizar recubrimientos con espesores superiores a 50 μm, obteniendo recubrimientos libres de grietas. Espesores mayores podrán ser obtenidos por un segundo recubrimiento de EPD y posterior sinterizado. Después del sinterizado una zona de interacción fue detectada entre el sustrato y el recubrimiento y un adhesión satisfactoria fue observada por medio de un ensayo de rasguño. Análisis de XRD, EPMA, y SEM fueron realizados sobre el recubrimiento densificado.

Palabras Claves: Vidrio bioactivo 45S5®, Epd, recubrimientos de vidrio, titanio

1. INTRODUCTION

One of the limiting factors, affecting widespread application of bioglass is the difficulty on producing well-adhering coating by and industrial feasible process. Different processes are possible for the deposition of a bioactive glass layer on titanium substrates like plasma spraying, chemical vapour deposition, dip coating, electrophoretic deposition (EPD) and electrochemical deposition. The coating process not only influences the cost of the processing, but will also the coating structure, the adhesion with the substrate, the porosity (shape, size morphology), and in this way the bioactivity.

The method, which will be investigated here to coat Ti₆Al₄V substrates with bioglass, is electrophoretic deposition. This is a process in which suspended charged powder particles are deposited on an electrode under influence of an electric field. Some advantages of this technique are high reproductivity, low cost, and the high speed. EPD can produce coatings with a broad thickness from less than 1μm to more than 500μm [1], while
deposition rates vary from seconds to minutes offering an easy control over the thickness and morphology of the coating.

After electrophoretic deposition the obtained coating, which is in fact still a powder compact, has to be densified by a heat treatment. In this work microwave sintering will be investigated. In microwave sintering, electromagnetic waves interact with ceramic materials, leading to volumetric heating by dielectric loss. Such a volumetric heating can help to improve the problems given with conventional heat transfer and to generate a more uniform microstructure [2].

The objectives of this study are to obtain defect-free bioglass coatings with a minimal thickness of 50 µm by means of electrophoretic deposition and to find a suitable heat treatment to densify these coatings.

2. EXPERIMENTAL PART

This part describes the different techniques, which were used for the production of bioglass coatings on Ti6Al4V substrates. These coatings were obtained by electrophoretic deposition (EPD) of bioglass powder on the Ti6Al4V substrates. After EPD, these samples were sintered with conventional and hybrid microwave sintering. Characterisation was performed by means of XRD, Scanning Electron Microscopy (SEM) and Electron Probe Microanalysis (EPMA).

2.1 Substrate Preparation and Anodisation

2.1.1 Substrate preparation

Cylindrical substrates, made from Ti6Al4V, were used. These substrates had a diameter of 10 mm and a length of 25mm. These substrates were degreased before use.

To degrease samples were cleaned by dipping the substrates for 30 min in acetone, dried and dipped again but in an ethanol for 20 min and also dried for 10 minutes with a hair dryer.

2.1.2 Anodisation

To obtain a TiO₂ oxide layer, substrates were anodised by immersing the substrates in an acid solution which contained 10 % H₃PO₄. A DC voltage of 15 V was applied between the substrate and a cylindrical counter-electrode, which surrounded the sample for 2 min. A current of 10mA was measured during anodisation.

2.2 Electrophoretic deposition

2.2.1 Suspension preparation

After adding the proper amount of powder to the suspension medium, the suspension was mixed in a glass beaker by magnetic stirring during 15 minutes and subsequently ultrasonificated in an ultrasonic bath (Branson 2510) during 20 minutes. All suspensions contained 54 vol % Methyl ethyl ketone (MEK) (99%, Acros), 6 vol % n-butyl amine (99.5%, Acros) and 0.2 wt% nitrocellulose (Aldrich). The powder concentration was 60 g/l.

2.2.2 Electrophoretic deposition

Although electrophoretic deposition can be performed by simply immersing two electrodes into a suspension and applying a voltage, the experimental results which are discussed here have almost all been obtained using two specific designed deposition cells, as schematically presented in Figure 1 and Figure 2. For suspension studies, a cell in which two flat disks are put is used as show in Figure 1, for coating the cylindrical substrates; the cell of Figure 2 is used.

The deposition cell in Figure 1 consists of two stainless steel electrodes in a container, which allows positioning the electrodes in a reproducible manner. Furthermore, the deposition electrode is enclosed in non-conducting covers made of polytetrafluorethylene (PTFE) in order to avoid deposition around the edges of the electrode and to have a well defined surface area (9 cm²). The cell can contain 60ml suspension and the electrode separation distance is 2 cm.

In the deposition cell in Figure 2, the cylindrical Ti₆Al₄V substrates are coated. The inner electrode, the substrate is the deposition electrode, the outer electrode is a cylinder = 3.5cm, made from conductive polymer. The substrates are centralized in the cell by a special sample holder, which is clamped on the cell. The suspension is mechanically stirred during EPD.

Electrophoretic deposition at constant voltage was performed with freshly prepared suspensions, using a F.U.G. (type MCN 1400-50) power supply. During deposition, the cell current is automatically recorded [Onron, K3NX] each second. After deposition, the deposit is dried in ambient air. The amount of deposit is determined by weighing the deposit until a constant weight is obtained.
2.3 Sintering

To study the sinter behaviour of the coating on the Ti₆Al₄V samples, three different sinter furnaces were used: a microwave furnace, a high vacuum resistance heated furnace and a Nitrogen flushing furnace. But for this study only the microwave furnace will be mentioned.

2.3.1 Microwave sintering

Different anodised as well as non-anodised samples were sintered in the microwave furnace in a nitrogen (L AIR LIQUIDE Grade N28 99.997%) gas flow of 15 l/h. The microwave furnace used in this work was designed and fabricated by MEAC. The hybrid microwave sintering technique was used as densification technique, because of the fast heating and cooling rate, which can be achieved. A schematic view of the experimental set-up used in the microwave furnace is shown in Figure 3. The coated specimen is positioned on a porous mullite refractory. It is surrounded by a SiC tubular susceptor, which is placed on a mullite support in order to make sure that the coated area is surrounded by the susceptor.

$$\mu_d = \frac{2\varepsilon\xi}{3\eta} \cdot (1 + f) \cdot G(\alpha)$$  \hspace{1cm} (1)

With

$$G(\alpha) = \left[ \frac{1-\frac{1}{9}\left(\frac{\alpha\sigma^2}{\eta} \right)3+2\frac{\Delta\rho}{\rho}}{1+\left[1+\frac{1}{2}\frac{\alpha\sigma^2}{\eta}\right]^{\frac{3}{2}}} \right]^{-1}$$  \hspace{1cm} (2)

With

$\varepsilon$ : the dielectric number of the dispersing medium [-]
$\xi$ : the $\xi$-potential [V]

2.4 Characterisation Methods

2.4.1 Characterisation of suspensions

Electrophoretic mobility and zeta potential measurement in concentrated suspensions were performed with the electro-acoustic measuring technique (ESA 8000, MATEC). The mobility was measured via Electroacoustic Sonic Amplitude (ESA) directly in the suspension to which n-butylamine or nitrocellulose was added stepwise with a titration.

The dynamic mobility, $\mu_d$, is preferred over the ESA-signal, as it represents a value, which is independent from the solids loading of the suspension. It is possible to convert $\mu_d$ to the $\xi$-potential.

$$\mu_d = \frac{2\varepsilon\xi}{3\eta} \cdot (1 + f) \cdot G(\alpha)$$  \hspace{1cm} (1)

With

$$G(\alpha) = \left[ \frac{1-\frac{1}{9}\left(\frac{\alpha\sigma^2}{\eta} \right)3+2\frac{\Delta\rho}{\rho}}{1+\left[1+\frac{1}{2}\frac{\alpha\sigma^2}{\eta}\right]^{\frac{3}{2}}} \right]^{-1}$$  \hspace{1cm} (2)

With

$\varepsilon$ : the dielectric number of the dispersing medium [-]
$\xi$ : the $\xi$-potential [V]
\( \eta \) : the viscosity of the dispersing medium \([\text{Pa}\cdot\text{s}]\)

f: f = 0 for apolar and f = 0.5 for polar media [-]

\( \omega \) : the frequency during measurement \([\text{s}^{-1}]\)

r: the particle radius \([\text{m}]\)

\( \Delta \rho \) : The difference of the densities between particles and liquid \([\text{kg/m}^3]\)

\( \rho \) : The particle density \([\text{kg/m}^3]\)

2.4.2 Particle size measurements
A Coulter LS 100, based on laser diffraction, was used to determine the particle size of the bioglass powder. For the measurements, the bioglass powder was suspended in water, mechanically stirred for 5 minutes and subsequently ultrasonicated for 1 minute.

2.4.3 Other methods
Phase analysis was performed with an X-ray diffractometer. With this apparatus the X-ray diffraction pattern of crystalline materials is measured. Since every crystalline phase has a characteristic set of lattice spacings, the phases present in the specimen can be identified. The height of the recorded peaks increases with the amount of phase present in the specimen. For these measurements, a Seifert 3003 TT goniometer is used.

The scanning electron microscope Philips XL 30 FEG employs a Schottky based gun design using a point-source cathode of tungsten, which has a surface layer of zirconia (ZrO\textsubscript{2}). The brighter electron source possesses both low energy spread and low current fluctuations, with as a consequence higher effective currents in smaller probes.

This equipment was used to investigate the microstructures, compositions and some coating and substrate's characteristics.

For analysis of the coating composition a JXA-733 electron probe is used. This is a high performance X-ray micro analyser for qualitative and quantitative analysis of a variety of specimens and their composing elements.

2.4.4 Sample preparation
Sample preparation of the sintered coated substrates was performed by crosscutting the samples, embedded in a resin (type technovit 4004), grinding, polishing and etching.

Grinding was performed with grinding paper. It started with grinding paper number 320 until the surface was flat, then a number 800 was used for 2 a 3 min, afterwards 1200 and 4000 were used also for 3 minutes.

Polishing was done using a mix (OPS) of 100 ml SiO\textsubscript{2} and 30 ml H\textsubscript{2}O\textsubscript{2}. During 5 minutes, a pressure of 3 bar was applied and subsequently 2 bar for the same time.

Etching was done with a solution of 85 % H\textsubscript{2}O, 5% HNO\textsubscript{3} and 10% HF for 5 seconds on the polishing surface.

2.4.5 Hardness measurements
The Vickers test was used in this project to determine the hardness of Ti6Al4V substrates. A 100-g load was used during 30 seconds with an indenter (diamond point) having an angle of 136°. Diagonals were measured to obtain the hardness value; eighteen points were also measured in the analysis across the transversal section to find the hardness profile.

3. RESULTS AND DISCUSSION
This part presents the experimental results and discussion on how to obtain smooth crack-free bioglass coatings on Ti6Al4V substrates. For this goal, the bioglass powder is firstly characterised. Suspensions based on methyl ethyl keton, n-butylamine and nitrocellulose were prepared and analysed. With these suspensions, a bioglass powder coating was put on the substrates by means of electrophoretic deposition (EPD). Subsequently, the coatings had to be densified by a heat treatment. Finally the obtained coatings were analysed: the interaction of the coating with substrate material, the coating adhesion and the effect of the heat treatment on the substrate material and coating.

3.1 Powder Characterisation
First at all, it is important to have an overview of the main properties of the bioglass powder and substrate (Ti6Al4V) material. Table 1 shows the materials that have been uses for the experiments.
Table 1. Composition, density, hardness, and young’s modulus of bioglass substrate material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Composition</th>
<th>Density (g/cm³)</th>
<th>Hardness (Hv)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45S5</td>
<td>24.5 Na₂O, 24.5 CaO, 45.0 SiO₂, 6.0 P₂O₅</td>
<td>2.66</td>
<td>458 ± 9.4</td>
<td>35</td>
</tr>
<tr>
<td>Ti6Al4V</td>
<td>90 Ti, 6 Al, 4 V</td>
<td>4.42</td>
<td>345</td>
<td>114</td>
</tr>
</tbody>
</table>

By means of the Coulter LS, particles size measurement was performed. The particles size distribution is non-symmetrical and presents a positive bias (see Figures 4 and Tables 2); in spite of this fact, particles were considered to be into the specification parameters given by the supplier (size particle <5μm).

![Particle Size](image)

**Figure 4.** Diameter of the particles in function of the total volume and area.

Table 2. Particles size measurement and distribution

<table>
<thead>
<tr>
<th>Size</th>
<th>10</th>
<th>25</th>
<th>50</th>
<th>75</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mm</td>
<td>1.200</td>
<td>2.240</td>
<td>4.110</td>
<td>6.738</td>
<td>9.310</td>
</tr>
</tbody>
</table>

In order to investigate the amorphous character of the bioglass powder, XRD analyses were carried out on powder compacts. 20 was varied between 20 and 90° (Figure 5).

Only one broad peak was detected around 30°. This peak is the amorphous silica peak [3]. It is clear that the powder is amorphous because no other peaks were obtained.

![XRD Spectrum](image)

**Figure 5.** XDR spectrum of the bioglass powder

The morphology and shape of the powder was analysed by means of SEM, as illustrated in Figure 6. From the SEM pictures, it is observed that the bioglass particles are very angular and have a platelet shape.

![SEM Picture](image)

**Figure 6.** SEM picture of bioglass powder taken at 10 μm
3.2 Suspension characterisation
A high zeta potential and electrophoretic mobility is a necessary request for a “good” suspension. Therefore the zeta potential and electrophoretic mobility of these suspensions was measured by means of the ESA-9800 (Matec Applied Sciences) for a MEK - butylamine - nitrocellulose suspension with 5-15 vol % butylamine (Figure 7). A high zeta potential of -6,5E+13 (cmV) is obtained at 10 vol % butylamine resulting in a high suspension stability.

Figure 7. Zeta potential and mobility as function of the n-butylamine content.

3.3 EPD OF BIOGLASS
In this paragraph, the deposition of bioglass powder by means of EPD is discussed. An optimal powder concentration and voltage was looked for to produce smooth coatings with good adhesion and without cracks. For the optimal parameters, the kinetics of the EPD process was investigated to predict the coating thickness. In such a way, coatings < 50 µm were made in one step. It was also possible to produce coatings with a thickness of even 250 µm, by a multidipping process.

With a suspension of 10 vol % butylamine and 0.2wt % nitrocellulose, the optimal voltage, powder concentration and time was searched for to obtain smooth coatings.

The suspension was stirred in the cell for 1 minute before immersing the Ti6Al4V substrate. Voltages between 100 and 150 V were used, and deposition times between 5 and 30 seconds were applied.

After electrophoretic deposition, the coated samples were dried at room temperature for about 12 hours, resulting in a smooth coating (see Figure 8). During drying, the deposit shrinks on the solid substrate material. Due to the fact that the shrinkage of the coating is inhibited by the substrate, stresses will be built-up in the powder coating that might cause cracking and/or delamination of the coating. However, very thick coatings of more than 1 mm thick could be obtained with the bioglass powder. A possible reason for the crack free deposits is the platelet shape morphology of the powder particles.

Figure 8. Sample coated with bioglass (45S5) by EPD

3.4 EPD - kinetics
To predict the coating thickness in function of the time, Hamaker’s equation [4] is used to describe the kinetics of the EPD process:

\[
\frac{dY}{dt} = f \cdot \mu \cdot c \cdot E \cdot S
\]

with the yield Y (kg), time t (s), the electrophoretic mobility \( \mu \) (cm²/V.s), the electrical field strength E (V/m) between the electrodes, the solids loading C (kg/m³) of the powder in suspension and the surface area A (m²) of the electrode, \( f \) is a factor which takes in account that not all powder brought to the electrode is incorporated in the deposit. In this work, \( f \) is assumed to be 1. In this equation the electric field strength has to be known. Anné [5] found that a potential drop can be created at the depositing electrode or over the deposit, but the extend of this potential drop is determined by the solvent and charging agents. It was found that for suspensions based on methyl ethyl keton and n-butylamine the electric field strength during EPD is constant and no potential drop at the electrodes happened.

For an electrode set-up with flat shaped electrodes as shown in Figure 9, the electric field strength is equal to:
\[ E = \frac{V_{\text{applied}}}{d} \]

(4)

With \( d \) the distance between the electrodes and \( V_{\text{applied}} \) the applied voltage.

The powder concentration \( c \) (kg/m\(^3\)) can also be written in function of the thickness \( d_1 \) of the powder compact at the electrode:

\[ c = \frac{M - Y}{H - d_1 S} \]

(5)

With \( M \) the amount starting powder (kg), \( H \) suspension volume (m\(^3\)).

**Figure 9.** Equivalent electrical scheme of the EPD process [6].

If \( d_1 \) is very small compared with \( d \), equation (3) can also be written as:

\[ \frac{dY}{dt} = k\left(\frac{M - Y}{H}\right) \]

(6)

With

\[ k = f \mu E S \]

(7)

The solution of this differential equation is

\[ Y = M \left(1 - e^{-kt/H}\right) \]

(8)

From this equation, the factor \( k \) can be calculated and in this way the electrophoretic mobility.

For a cylindrical electrode set-up, the electric field strength, has to be changed by:

\[ E = \frac{V_{\text{applied}}}{a \left(\ln\left(\frac{b}{a}\right)\right)} \]

(9)

With \( V_{\text{applied}} \) the applied voltage, \( b \) the radius of the counter-electrode and \( a \) the radius of the deposition electrode.

**Experiment**

EPD experiments were performed at 150 V with solids loading of 2.5 g in 50 ml of suspension at resp. 20 and 60 s (Table 3). From these experiments, a value of the electrophoretic mobility \( \mu \) of 10.5 cm\(^2\)/V.S was calculated, which will be used as input to estimate the thickness of the bioglass coatings on cylindrical substrates.

A good correlation was found between the predicted thickness (yield) and the measured thickness (yield).

**Table 3.** Yield and calculated \( \mu \) for bioglass for flat shaped electrodes.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Yield (g)</th>
<th>El.Mobility (cm(^2)/V.S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.045</td>
<td>11.7</td>
</tr>
<tr>
<td>60</td>
<td>0.099</td>
<td>9.3</td>
</tr>
</tbody>
</table>

**3.5 Sintering**

The sinter behaviour of the bioglass powder was investigated with a dilatometer (Netzch 402 DIL). The experiment was performed in air, the heating speed was 5°C/min to 1000°C. Calibration of the dilatometer was done prior to the actual tests, using an Al\(_2\)O\(_3\) standard.

From Figure 10, one can observe a first decrease at 560°C. This temperature corresponds with the
glass transition temperature. At a temperature of 810°C, the densification starts, at 1000°C the densification is still going on and it continues increasing slowly.

![Figure 10. Result of the dilatometry experiment.](image)

**Figure 10.** Result of the dilatometry experiment.

### 3.5.1 Microwave sintering

Microwave sintering was performed in a nitrogen atmosphere to prevent oxidation of the substrate and to prevent plasma formation during sintering. The goal of these experiments was to find the microwave sintering parameters to get a good defect-free adhering coating.

A solution for the lack of room temperature coupling of the sample coating combination is to use a susceptor to increment the bioglass and substrate temperature during the initial phase of heating. In this project SiC was used, which is an ideal susceptor material because of its high loss factor and good refractory properties. In order to do so, a SiC tube was symmetrically surrounding the sample during microwave sintering. Visual on-line observation through the pyrometer shows that the outline of the specimen is distinguishable from the surrounding environment at temperatures lower than 900°C. At higher temperatures, the difference between specimen and environment fades away, and disappears completely at about 1200°C.

Based on the visual observations concerning coating adhesion and the presence of cracks in the coating after sintering, a heating rate of 180°C/min with a dwell time of 6-8 min at 1000°C and a cooling rate of 150°C/min were found to be most successful under all other investigated conditions, either cracks were formed or the coating delaminated from the substrate. The coating delimitation and crack formation can be due to a too large layer thickness obtained during the EPD process. Other factors to take into account are the thermal expansion coefficient mismatch between the bioglass and the substrate, resulting in thermal stresses during cooling. As an example, the sintered coated substrate, processed for 6 min at 1000°C.

In order to increase the coating thickness, additional experiments were performed in which a second bioglass powder layer was deposited by means of EPD on an already sintered first bioglass layer. The investigated sinter parameters to densify the second coating are summarised in Table 4. A heating rate of 200°C/min with a dwell time of 5-15 min at 1000°C and a cooling rate of 150°C/min were found to be appropriate.

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Heating rate (°C/min)</th>
<th>Dwell time (min)</th>
<th>Cooling rate (°C/min)</th>
<th>Coating adhesion</th>
<th>Crack formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>5</td>
<td>15</td>
<td>Good</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>200</td>
<td>10</td>
<td>150</td>
<td>Good</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Only on the top</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>15</td>
<td>150</td>
<td>Good</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The possibility to apply two layers by consecutive EPD and microwave sintering is shown in Figure 11. Layers with a total thickness between 70 and 100 µm could be obtained by applying a second layer on top of a first one. In some cases, this allowed to get a final average layer thickness of 150-200 µm.

The first goal in this work is to get a good coating consolidation and adhesion by means of microwave sintering, whereas the second goal is the formation of a coating of adequate thickness with a remaining porosity. These objectives were reached as shown
in Figure 11 and 12, where the remaining porosity is homogeneously distributed.

![Figure 11. Application of two bioglass layers on a Ti6Al4V substrate by an alternating EPD and microwave sintering process.](image)

Additional sintering experiments were done to obtain a good interface between the Ti6Al4V and the bioglass substrate. A good layer adhesion and interface formation was obtained by increasing the heating rate and dwell time at 1000°C, as shown in Figure 13.

![Figure 13. Adhesion of bioglass layer.](image)

The Ti6Al4V substrate presented changes in its microstructure due to the rapid cooling after microwave heating, revealing a second phase free interface region as shown in Figure 14 by the absence of the “white” phase in the interface region.

![Figure 14. Microstructure of the Ti6Al4V alloy (bottom) and interaction at bioglass interface.](image)

The interface was investigated in more detail by means of SEM and EDAX point analysis, as shown in Figure 15.

![Figure 12. Porosity Distribution (dark) in the bioglass (bright) coating after sintering, and a detail of the bioglass particles.](image)
3.6 Characterisation of the coatings

As already discussed in the former paragraph, smooth coatings without any defect could be obtained with EPD and subsequently sintering. In this paragraph these coatings will be further characterised: the homogeneity of the coating, the coating adhesion with the substrate material and the interaction of the coating with the substrate material. Also the amorphous character of the coating was investigated.

3.6.1 Homogeneity of the coating

In this paragraph the homogeneity of the coating is analysed. The homogeneity parallel and perpendicular with the substrate material was investigated.

Figure 16 show a detailed SEM picture of the coating surface. A rough surface is observed in which the initial powder particles are still visible. At some places, the powder particles are sintered together to form large grains (Figure 17).

During sintering a graded interaction zone can be created between the coating and the substrate material. This composition of the interaction zone influences the local thermal expansion coefficient and in this way the final residual stress state. Therefore composition profiles were measured by means of EPMA along a cross-sectioned coated substrate after respectively a first and second sintering step (see Figure 18). The second sintering was performed to increase the thickness, improving the adhesion and porosity of the coating. Analyses were performed, based on the following oxides: TiO\textsubscript{2}, SiO\textsubscript{2}, CaO, P\textsubscript{2}O\textsubscript{5}.

From the composition profiles, it was found that an interaction zone exists between the substrate and bioglass. The width of the interaction zone is the same for a first and second sinter cycle, but the width of the diffusion layer is dependent for the analysed elements.
3.6.2 Coating adhesion: the scratch test

The scratch test is designed for the assessment of the mechanical integrity of the coated surface. The test method consists of generating scratches with a stylus of defined shape by drawing it across the surface of the coating substrate system to be tested, under constant a progressive load. The driving force for the failure of the coating-substrate in the scratch test are a combination of elastic-plastic indentation stresses, frictional stresses and residual internal stress present in the coating. The normal load at which failure occurs is called the critical load $L_c$ [7].

In order to investigate the adhesion of the coating to the substrate, selected samples were subjected to the scratch test with a load of 10 N/min and velocity of 0.65 mm/min. From this test, the adhesion strength can be qualitatively determined.

Tests were performed on machined and sandblasted-coated substrates. The coating was densified by microwave sintering with the optimal sinter parameters. A roughness profile ($R_a = 3.5\, \mu m$) of the sandblasted samples is given in Figure 19.
Roughness profile of sandblasted Ti6Al4V substrate.

The micrographs of the scratch tests, taken by SEM, of the coated non-treated and sandblasted samples are given in Figures 20 and 21 respectively.

Figure 19. Roughness profile of sandblasted Ti6Al4V substrate.

3.6.3 Cristallinity of the bioglass coating

By means of XRD the crystalline character of the coating was investigated. As already was discussed in paragraph x, the as deposited powder showed an amorphous character.

After sintering in the microwave with the optimal inter parameters, the amorphous character of the coating disappeared. There are clearly peaks presents in the spectrum $2\theta = 20^\circ-90^\circ$ of some crystalline phase. One of the requests of a bioactive glass layer is the amorphous character [8] of the glass phase. This is not the case and in the future experiments care has to be taken to maintain the amorphous character. Increasing the cooling speed after sintering can perform this below the glass transition temperature. Above this temperature a slow cooling speed is necessary to maintain the equiaxial structure of the substrate material (Figure 22).

Figure 20. Scratch test on a coated non-treated surface substrate.

Figure 21. Scratch test on a coated sandblasted sample surface.

Figure 22. XRD of bioglass (45S5) with second sintering.

4. CONCLUSION

The goal of his work was to investigate the possibility to coat Ti6Al4V substrates with bioglass powder by means of electrophoretic deposition (EPD), subsequently followed by a heat treatment to densify the coating.

The starting powder of these experiments was bioglass powder grade 45S5. It was found that the powder particles were amorphous, very angular and had the shape of platelets. Before EPD, the Ti6Al4V cylinders were anodised to form a TiO$_2$ layer to improve the interaction of the coating with
the substrate.
A suspension based on methyl ethyl keton, n-butylamine and nitrocellulose was a suitable suspension to obtain very smooth bioglass coatings. After drying crack free deposition of more than 1 mm were obtained, but these thick coatings couldn’t be successfully sintered. The absence of cracks was attributed to the shape of the particles.
The kinetics of the EPD process was looked in more detail and a prediction of the coating thickness based on Hamaker’s equation showed a good correlation with the experiments.
A second bioglass layer could be made by EPD on a first already densified layer, which means that the bioglass layer does not work as an electrical insulator.
50 µm thick defect-free coatings could be densified in one step in a microwave furnace under N2. It was found that a fast cooling was beneficial to obtain good coatings, but with cooling rates higher than 150°C/min, cracks appeared at the top of the hemispherical top of the cylinders. Also a second bioglass layer could be successfully sintered and maximum coating thickness of 500 µm was reached.
The heat treatment also affected the microstructure of the substrate material. An equiaxial α/β was present after a sinter treatment in the microwave furnace, but a wildmanstätten structure was present after a second heat treatment in the microwave furnace. Also the hardness was slightly higher after a heat treatment.
Characterisation of the coatings made by microwave sintering showed that an interaction zone was present between substrate and coating, but the thickness was not influenced by the amount of heat treatments. This was also translated in a rather good adhesion between substrate and coating.
XRD analysis were performed on the densified coating and revealed that the bioglass phase was transformed to partial crystalline phase.

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6. REFERENCES
2002.


