Porous titanium coatings through electrophoretic deposition of particle stabilized emulsions.

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INTRODUCTION

Nowadays, porous materials are of great interest for a broad range of applications going from polymeric foams for packaging to ceramic soot filters in diesel engines. In the biomedical field, porous materials gain currency as scaffolds for guided bone growth and as coatings on prosthetic devices for an improved implant fixation. The latter being one of the major challenges in implant technology since loosening comprises the main reason for implant revision (65%). By tailoring the surface morphology and controlling the porosity and pore size of the coating, osteointegration can be promoted resulting in an optimal mechanical anchorage. Additional use of bioactive coating materials on the internal surface of this porous coating like bioactive glass (BAG) or hydroxyapatite (HA) can establish a firm chemical fixation between implant and tissue.
In this study, porous titanium coatings on Ti6Al4V substrates are obtained using titanium particle stabilized emulsions. After coating the substrate with the emulsion by means of electrophoretic deposition (EPD), the liquid phases are removed by evaporation and the porous coatings are sintered in a microwave furnace in helium.

OBJECTIVE

The goal of this study is to develop a macroporous Ti-coating with controlled porosity and pore size on a dense Ti6Al4V substrate (figure 1). The envisaged specifications of this macroporous Ti-coating are an overall open porosity of 15-40%, a thickness of 200-400 µm and a spherical macropore size that can be varied from 50 to 150 µm.
Later on, the surface of the macroporous structure will be covered with a second, multilayer coating. First, a TiO_2 -bond coating is created to improve the adhesion between the titanium and the second bioactive layer (BAG, HA,…). On top of this bioactive layer, a microporous amorphous silica layer containing biofilm inhibiting molecules can be applied. The ability of tuning the release of the molecules can reduce the risk of infections.

EXPERIMENTAL PROCEDURE

The development of the titanium coating is actually a three steps process.
In the first stage, an oil-in-water Pickering emulsion is prepared. 40 ml of absolute ethanol with 5 vol% demineralised water serves as the continuous phase and various amounts of paraffin oil (5 or 10 ml) are added. Magnetic stirring for 10 min gives rise to the dispersion of the oil phase into droplets. These droplets are stabilised by adding titanium powder particles.
For electrophoretic deposition the particles have to be properly charged. Since oxidation of the substrate should be avoided, the substrate is required to act as the cathode. This implies a positive charge on the dispersed droplets. 1,2 ml of a solution of polyethyleneimine (PEI, 50 wt% in water diluted with absolute ethanol to 0,01 g/ml) leads to an adequate positive charge at low pH. The desired pH is obtained by adding 0,3 ml of a phosphoric acid solution (85% diluted to 1 M in absolute ethanol) and 0,143 ml acetic acid. After some additional stirring the system is balanced.

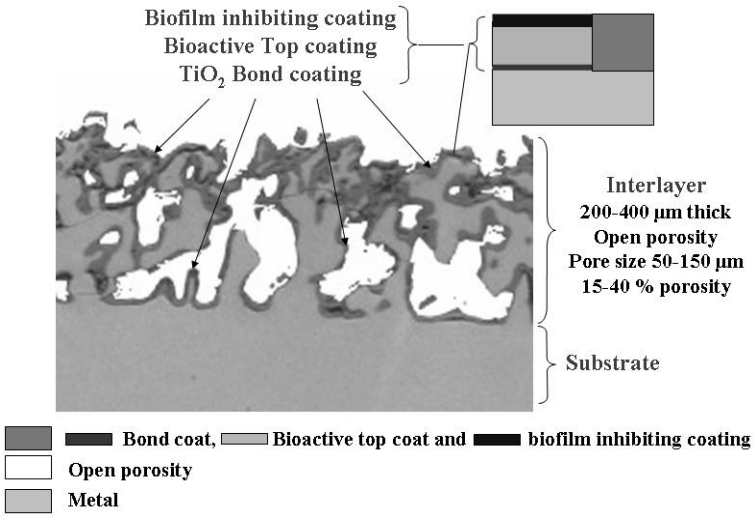


Figure 1. Schematic overview of the targeted coating.

The second step is the electrophoretic deposition of the emulsion on the Ti6Al4V substrates. In the deposition cell, the electrodes are placed vertically at a distance of 3,5 cm and the deposition electrode is coupled as the cathode. The electrical field is applied by means of a controlled voltage F.U.G. (type MCN 1400-50) power supply. Experiments are performed at 90 V and various times (150 s and 300 s).

In the final phase of the processing route, the obtained deposited substrate is dried for at least 24 hours and introduced in the microwave furnace. Since the dielectric loss factor of titanium is too low at room temperature, the principle of hybrid microwave heating is applied. The sample is hereby positioned in a SiC tube. At low temperature, the microwaves couple with the tube and the coating is heated by convection and radiation. At higher temperature, the titanium coating itself starts to couple with the microwaves. All samples are heated at 50°C/min to the sintering temperature. Various sintering temperatures (1000°C, 1050°C and 1100°C) and cooling speeds (2 and 120°C/min) are examined.

The EPD and sintering parameters are summarized in table 1. The surfaces of the coating, as well as the polished and etched cross-sections are analysed by means of scanning electron microscopy (SEM, XL 30 FEG, FEI).

Table 1. Experimental parameters used for the deposition and sintering of the coatings.

Experiment	m_{Ti} [g]	$V_{paraffin}$ [ml]	PEI [ml]	pH [-]	U_{EPD} [V]	t_{EPD} [s]	$T_{sintering}$ [°C]	t_{dwell} [min]	ΔT_{cool} [°C/min]
A	12	0	3,6	4,08	90	300	1100	10	120
B	6	5	1,8	3,97	90	150	1050	30	120
C	6	10	1,8	3,3	90	300	1000	15	120
D	6	5	1,8	3,97	90	300	1050	15	2

RESULTS AND DISCUSSION

The SEM micrograph of an untreated Ti6Al4V substrate is shown in figure 2. The original microstructure consists of an equi-axial α+β structure. To avoid a drastic reduction of the strength and fatigue resistance of the substrate material, this structure should be maintained after sintering. To do this, some characteristic temperatures of the alloy should be taken into account: the martensitic phase transformation starting temperature (800°C), the β-transition temperature (995°C) and the melting temperature (1660°C).

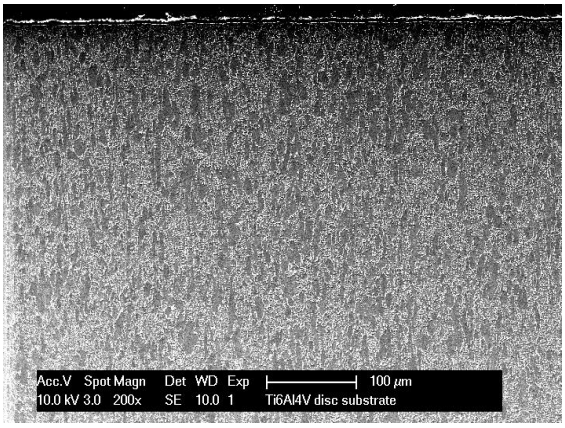


Figure 2. SEM micrograph of an untreated Ti6Al4V substrate: the microstructure consists of an equi-axial α+β structure (α is the dark phase, β is the light phase).

After microwave sintering, a spherical residual porosity is visible. Figures 3 and 4 demonstrate the difference in morphology between a suspension based coating; experiment A (figure 3) and an emulsion based coating; experiment B and C (figure 4a resp. 4b). The emulsion based coatings contain larger cavities, which can be attributed to the presence of the emulsion droplet templates. The coating thickness is about 200 µm and the pore network is mainly open with homogeneously distributed pores of an average pore size of 50 µm.

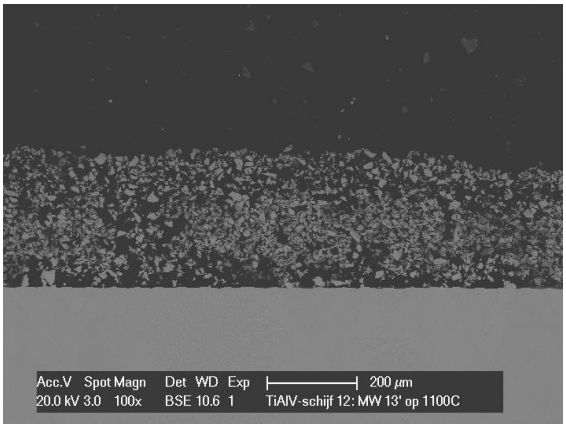
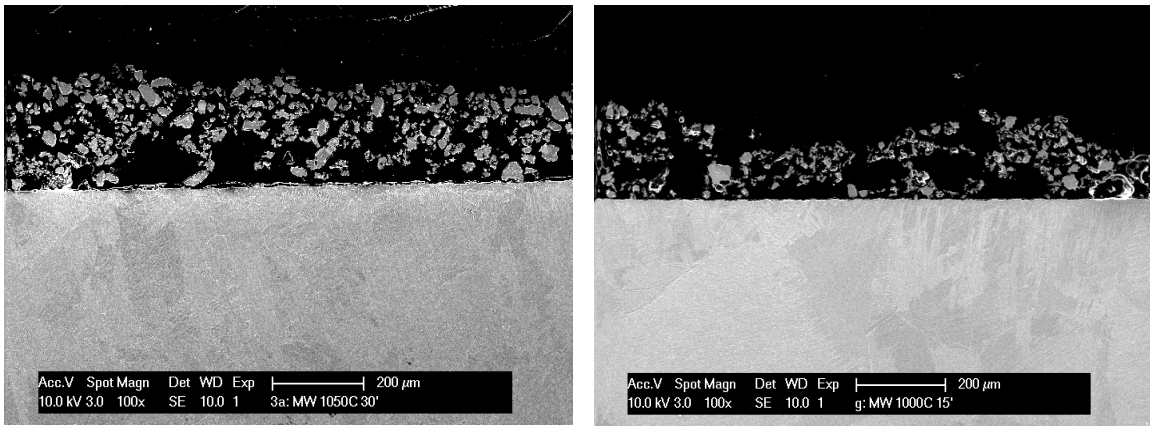


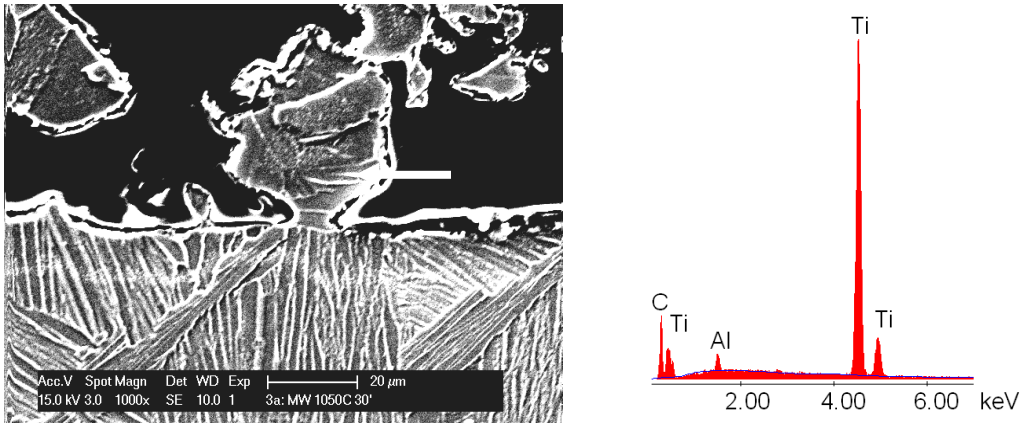
Figure 3. SEM micrograph of a cross section of a coating obtained from a Ti powder suspension; experiment A.



(a) *(b)*

Figure 4. SEM micrograph of a cross section of a coating obtained from a Ti particle stabilized emulsion; experiment B (a) and experiment C (b).

Since powder sintering is a diffusion driven process and the substrate material (Ti6Al4V) differs from the coating material (Ti), V and Al alloying elements diffuse from the substrate into the porous coating at the spots where neck formation occurs. This causes a change in the composition of the coating near the substrate surface (figure 5). Complete diffusion throughout the coating should be avoided to maintain the excellent biocompatibility of the pure titanium coating.



(a) (b)

Figure 5. SEM micrograph of a cross section of a coating after sintering for 30 min at 1050°C (a) and EDS point analysis (indicated by arrow) taken in one of the diffusion bonded particles (b).

In this study, the sintering temperature was raised above the β-transition temperature to establish particle bonding. This resulted in a modification of the original α+β structure (figure 2) after heat treatment. Figure 6 gives a schematic presentation of the final microstructure as a function of the cooling rate. In experiment A, the rapid cooling (120°C/min) during microwave sintering alters the microstructure into a Widmannstätten microstructure (figure 7a). Lowering the cooling rate (2°C/min) results in a more coarse Widmannstätten microstructure in experiment D (figure 7b). In order to preserve the better mechanical properties after sintering, the original α+β structure has to be maintained. Therefore, an even slower cooling rate or an additional heat treatment should be applied.

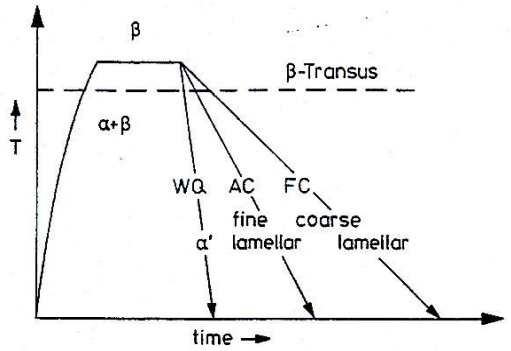


Figure 6. Schematic presentation of the microstructure in a Ti6Al4V alloy as function of the cooling rate.

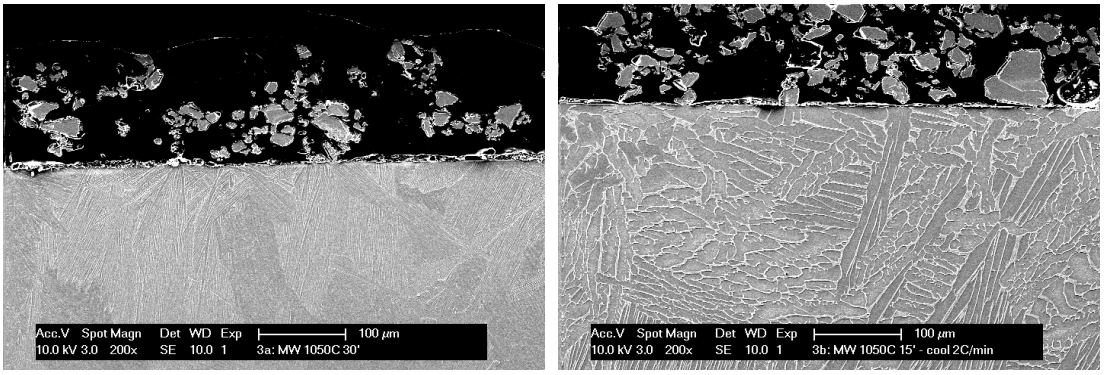


Figure 7. SEM micrograph of a cross section after cooling at (a) 120°C/min;experiment A and (b) 2°C/min, experiment D.

CONCLUSIONS

Macroporous Ti coatings on dense Ti6Al4V substrates were obtained by means of electrophoretic deposition of titanium particle stabilised emulsions followed by microwave sintering of the deposits in helium. The coatings had a final thickness of ± 200 µm with a prevalent open porosity and average pore size of 50 µm. Further work will focus on tailoring the pore volume and size by controlling the emulsion, the Ti particle size, the EPD and sintering parameters.

ACKNOWLEDGEMENTS

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