Titanium Coating on PEEK Substrate for Medical Devices

By: Armando Salito, Orchid Orthopedics Switzerland GmbH
Aurore Dockter, Orchid Orthopedics Switzerland GmbH
Céline Harnisch, Orchid Orthopedics Switzerland GmbH
Sylvie Ruch, Orchid Orthopedics Switzerland GmbH

ORCHID

A white paper from

ORCHID

TITANIUM COATING ON PEEK SUBSTRATE FOR MEDICAL DEVICES

Salito A., Dockter A., Harnisch C, S. Ruch, Orchid Orthopedics Switzerland GmbH, Baden Dättwil (Switzerland)

Porous titanium coatings onto polymers are of great interest to medical industries. A vacuum plasma spray (VPS) process has been developed to coat PEEK with a micro porous biomimetic titanium coating. This study reports the experimental characterization of the topography and microstructure and of the mechanical strength of the VPS Pure Titanium Coating on medical grade PEEK substrates. These results provide quantitative guides for the design of orthopedic implants for which such coating is used to enhance anchorage to bone tissues.

1 INTRODUCTION

PEEK is a biomaterial used for spine surgery. Its bioinert property, high toughness combined with a Young modulus close to that of bone, make it an appropriate biomaterial for fusion cages. Such implants are designed to match the interspace between two vertebrae [1]. Nevertheless, the hydrophobicity of PEEK surfaces results in poor integration with surrounding biological tissues. This is a significant limitation when strong anchoring to the bone is required, and this prone to the creation of fibrous tissues and inflammation [2]. One solution to these problems may be provided by coating PEEK implants with a hydrophilic rough and microporous layer of titanium.

In this white paper, we report the production concept and the characterization of the topography, microstructure and mechanical performances of the pure titanium coating applied on the PEEK substrate using vacuum plasma spraying technology for spinal implant application.

2 CELL IMPLANT SURFACE INTERACTION

Several studies have assessed the properties of the microporous titanium implant surface structure, which induces osseointegration. Such properties may be summarized as follow:

The hydrophilic implant surface is essential to promote the adsorption of proteins, which will lead to cell attachment and proliferation at the surface of the implants [3, 4, 5].

Surface topography plays an important role and is defined in terms of surface texture, surface roughness and curvature. Surface topography is defined at the millimetre level for the short-term mechanical primary anchoring of the implant, and at the submicrometer level for long term stability. Cells interaction with the implants take place at the submicrometer level. Several studies evidence that an anisotropic structure enhances bone integration significantly. [6, 7, 8]

One hypothesis behind the poor osteointegration of smooth and polished surfaces may be mechanical friction, which does not allow proper mechanical retention. Many other hypotheses relate to cell flattening on such surfaces, which prevent their

proper nutrition. A moderate surface roughness is required to perfect the interconnection of cell tissues. Very rough surfaces may leave such a distance between peaks that cells perceive them as a smooth surface [9].

Surface chemistry can be also used to induce or prevent cell attachment. Surfaces modified with functional groups of varying hydrophobicity and electrical charge have been shown to affect the adsorption of protein and therefore to affect cells' 'proliferation [10].

3 PLASMA SPRAYING PROCESS

During plasma spraying, an electrical arc is generated between two water-cooled electrodes in a gun. The arc heats a gas to an extremely high temperature and partially ionizes it and creates a plasma jet. Since gas temperatures of up to 20'000 °C can be achieved, the ionised gases are accelerated by the tremendous expansion in volume and pass through the jet-shaped anode at high speed. The powder for coating is injected using a carrier gas. In the plasma gas stream the powder particles accelerate to a high speed and are melted and impact the surface of the substrate with high kinetic energy. Porous to dense layers are created on the substrate by adjusting the spray parameters. The optimized dynamic of the coating process may keep the implant below 200°C avoiding alteration of the PEEK substrate. The type of atmosphere and the pressure level are important variables for plasma spraying, various process can be obtained by adjusting these important parameters. When vacuum or inert gas plasma spraying (VPS) is used (Figure 1), the interactions between the melted powder and the surrounding atmosphere are strongly reduced. This is indispensable for coating titanium materials, which are materials sensitive to oxidation and nitrogen absorption. During VPS, the melting grade of particles can be easily managed by changing the chamber pressure. This allows tailoring of the coating porosity while maintaining a very good cohesion and adhesion.

Figure 1: VPS plasma spraying system.

4 Materials and Methods

4.1 Materials

Samples were produced by Orchid Orthopedics Switzerland GmbH in the form of disc of Ø25.4x8 mm2, or of cylinders Ø19.05x25.4 mm2 with PEEK medical grade. For the topography study, some discs had a wave structure at the surface to simulate the typical structure of a cage implant. For mechanical testing, flat discs were used. The discs were coated on one or both sides with titanium VPS layers. All the coatings were performed using the same titanium material and vacuum plasma spray process.

4.2 Manufacturing process

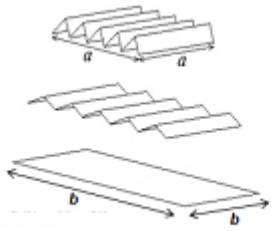
The manufacturing process of the pure titanium coating is based on two distinct steps: a surface preparation and the effective micro porous titanium plasma spraying process. The surface preparation is subdivided in two phases. The first one consists of grit blasting using corundum (Al2O3) the PEEK surface to increase the surface roughness. The second phase of the surface preparation uses a proprietary process of plasma surface activation performed on the PEEK substrate after grit blasting. The aim of this process is to create the conditions for a strong adhesion of the titanium VPS coating. Finally, the second step of the manufacturing process is the effective deposition of a micro porous titanium VPS coating on the plasma activated PEEK surface.

4.3 Methods

An optical profilometer, Altisurf 500, was used to characterize the roughness of the sample. Using the software, Phenix V2, cartographies of the disc surfaces were done with 5x5 mm dimensions. An acquisition with steps of 2 micron, a speed of 400 micron/sec and a double frequency 400/800 Hz. Roughness profiles of a 7 mm length were extracted from the diagonal of the cartographies and their parameter (Ra, Rz, etc.) were calculated with Altimap topography XT software.

The observations of the discs and microscopic pictures were obtained using the Scanning Electron Microscopes (SEM), Zeiss Gemini DSM 982 and FEI Nova Mano SEM 450, with high voltage of 5 kV.

The measurement of the specific surface of the titanium coating is of interest because it defines the potential increase of the contact surface between the bone tissues. This parameter has been determined using the VK-X200 3D Laser Scanning Microscope combined with the VK analyser software of KEYENCE Corporation. The measurement principle is illustrated in Figure 2.



$$Geometric\ surface = a^2$$

$$Effective\ surface \quad b^2$$

$$Specific\ surface = \frac{Effective\ surface}{Geometric\ surface} - \frac{b^2}{a^2}$$

Figure 2: Definition of the specific surface.

To characterize the mechanical strength of the titanium coating on the PEEK surface, tensile and shear static strength and shear fatigue strength were performed. For the tensile strength, the coupons were Ø 25.4x8 mm2 thickness and for shear and shear fatigue strength, the coupons were of Ø19.05x25.4 mm2. These mechanical tests were performed according ASTM F1147 and ASTM F1044 with the MTS Model 50 (DS1 42957 EMT-01) system using load cell Modell 569332-01 – 50 KN and associated with the software Testworks. Fatigue strength measurement according to ASTM F 1160 were performed at CRITT laboratory. (Charleville-Mézières) with the MTS858 Id.Nr. ESM42 system.

5.0 RESULTS

5.1 Surface Topography

The PEEK surface topography has been analyzed at different steps of the coating process. Figure 3a) shows the surface structure before any coating operations. We observed very thin grooves and ligaments due to the machining process.

The surface structure of Figure 3b) is obtained after the grit blasting process of the PEEK sample. We observed a random rough structure, which gives typical roughness parameter Ra of 8 µm. A detailed analysis shows that few corundum particles stay encrusted on the PEEK surface, which is not critical. Figure 3c) highlights the PEEK after the plasma activation process and the first dense bond titanium layer. This step is the key factor to guarantee robust titanium coating adhesion. Increasing the magnification of the layers (Figure 3d), we observe a numerous amount of titanium particles on the surface partially melted of spherical size between 0.5 micron and 5 micron.

Finally, on Figure 3e), we observed the Ti-VPS coating with the micro porosity and micro roughness for an optimized cell adhesion. Some titanium particles of the coating are slightly flattened because of the post coating blasting process, which is needed to reduce coating particles loosening.

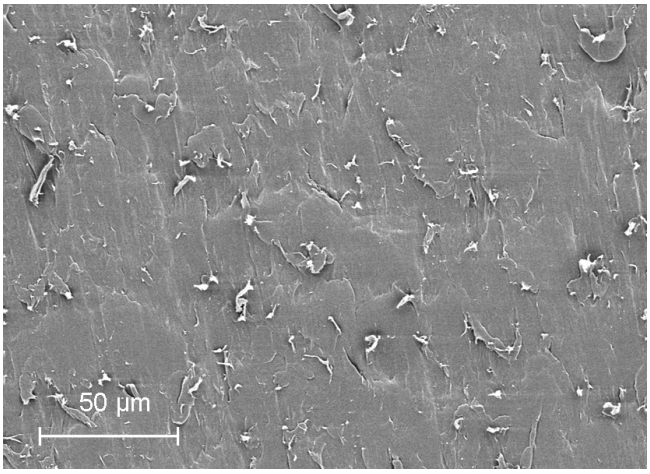


Figure 3a): Pure PEEK surface as machined.

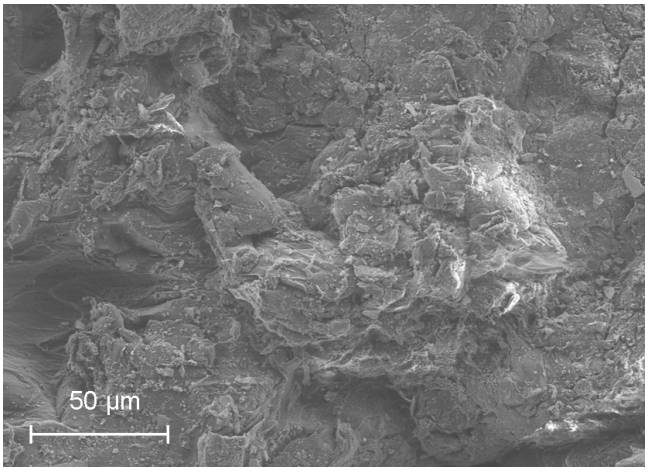


Figure 3b) PEEK surface after the grit blasting.

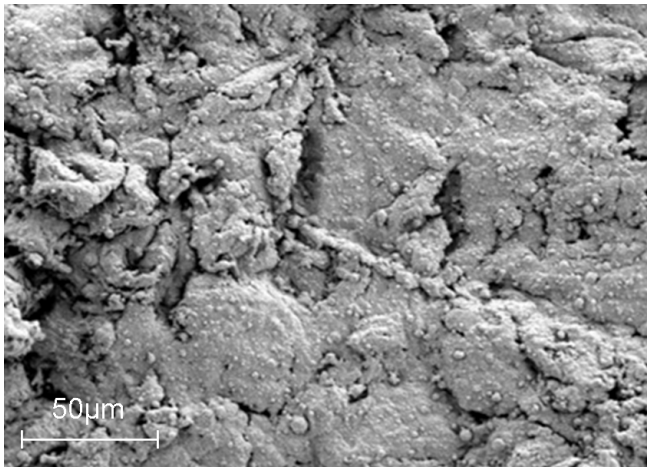


Figure 3c) PEEK surface after surface activation.

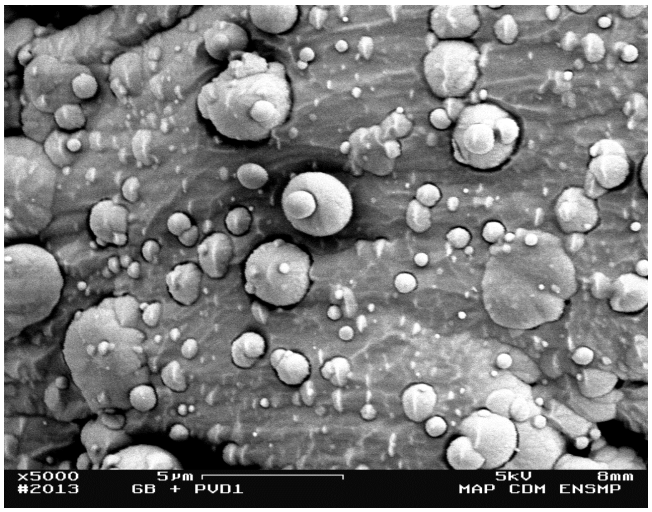


Figure 3d) PEEK surface after surface activation, higher magnification.

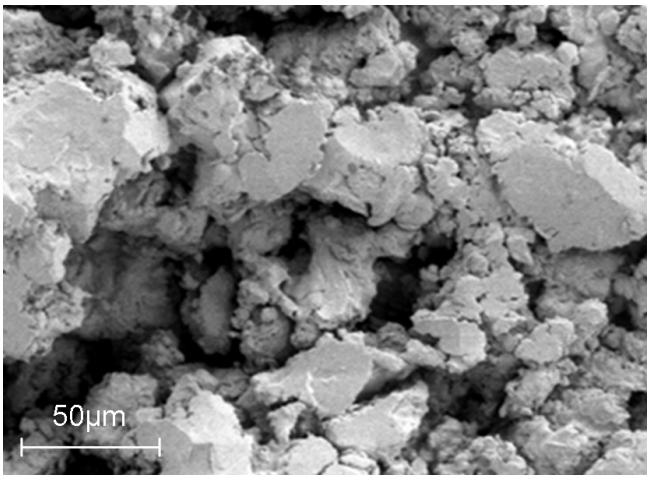


Figure 3e) PEEK surface after titanium VPS coating.

5.2 Specific surface measurement

Table 1 gives the measured specific surface of the titanium coating. Ten (10) measurements were carried out on 10 different positions of the titanium coated sample. For each position, a rectangular area of 1486378.73 µm2 (approximately 1.4 mm x 1.06 mm) has been analyzed. The resulting titanium coating has an average specific surface area 5.47 times larger than an uncoated, theoretically smooth, surface with comparable planar geometry. The standard deviation of the specific surface is measured in this case to 0.10 and the 95% confidence interval is 0.07.

	Effective surface [µm^2]	Geometric surface [µm^2]	Specific surface [--]
Position 1	8239955.26	1486378.73	5.54
Position 2	8312592.83	1486378.73	5.59
Position 3	8089407.99	1486378.73	5.44
Position 4	7850557.51	1486378.73	5.28
Position 5	8030613.84	1486378.73	5.40
Position 6	8256600.07	1486378.73	5.55
Position 7	7960410.23	1486378.73	5.36
Position 8	8099465.75	1486378.73	5.45
Position 9	8291539.09	1486378.73	5.58
Position 10	8203494.41	1486378.73	5.52
Mean	**8133463.70**	**1486378.73**	**5.47**
Confidence Interval	109828.10	0.00	0.07
max CI limit	8243291.80	1486378.73	5.55
min CI limit	8023635.60	1486378.73	5.40
Std deviation	153529.101	0.000	0.103
max	8312592.83	1486378.73	5.59
min	7850557.51	1486378.73	5.28

Table 1: Titanium specific surface measurement by laser scanning microscopy.

5.3 Cross section, porosity and iso-elasticity observation of titanium VPS coating

Figures 4a) and 4b) show the cross section of the microstructure of the titanium coating. We may observe an open porosity in the range of 40% to 50%, which is measured by image analysis. The porosity is built up from pore channels, which are created close to the interface PEEK substrate - coating and develops interconnected branches, which create irregular pores in the size range between 20 to 200 µm Figure 4c). This matches the requirement for an optimized interaction between implant and cells. This type of porosity structure is very important to obtain also an iso-elastic titanium coating, which is able to follow, to a certain level, potential deformation of the PEEK cage when the implant is submitted to different loads. To better emphasize this iso-elasticity property, in Figure 5 we show a dense non iso-

elastic titanium coating applied on PEEK. This type of coating is very sensible to PEEK load; creating internal stress in the coating. Because of the poor porosity, these stresses cannot be released, and would be prone to coating spalling.

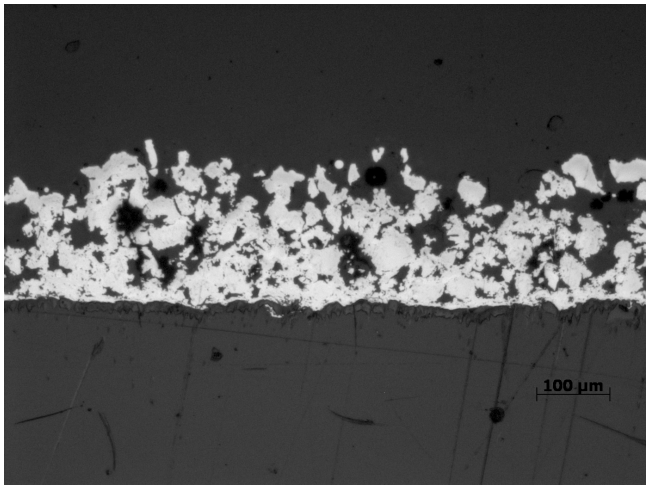


Figure 4a) Ti VPS coating on a flat PEEK samples.

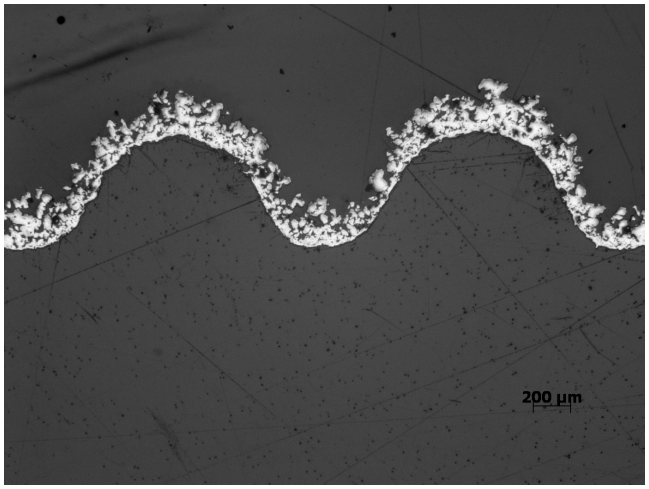


Figure 4b) Ti VPS coating on a wave PEEK implants.

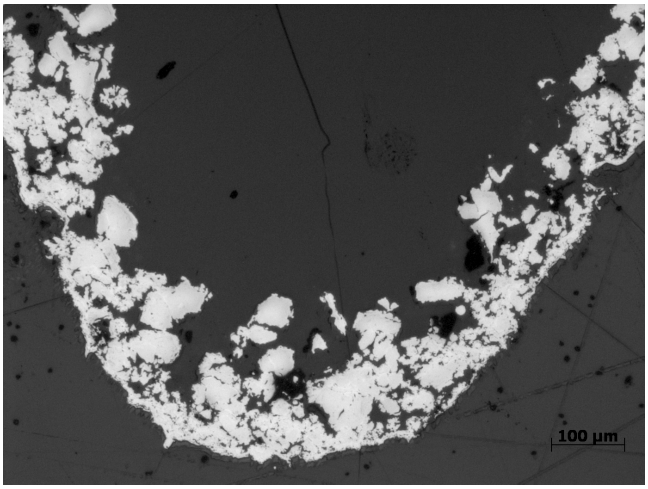


Figure 4c) Ti VPS coating on a wave PEEK implants with pore channel starting close to the interface PEEK implant and titanium coating.

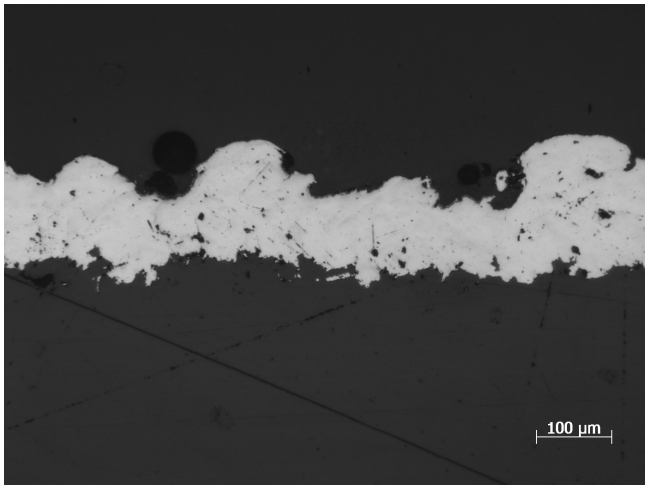


Figure 4d) Dense Ti coating on PEEK implant with poor isoelasticity

5.4 Roughness measurement

5.4.1 Roughness cartography, profile and amplitudes parameters

The surface cartographies and the roughness profiles for each major step of the coating process are displayed in Figures 6a through 6d, the indicated roughness in each figure is based on a profile length measurement of 7 mm [13, 14, 15].

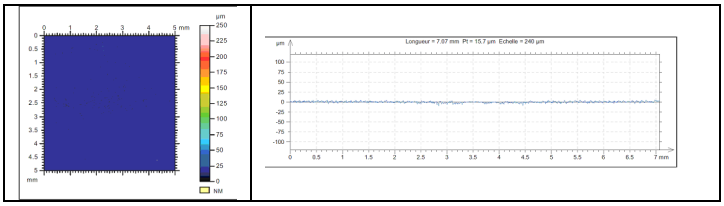


Figure 6a) Roughness profile of the PEEK implant after machining. Ra: 1.28 µm, Rz: 9.29 µm.

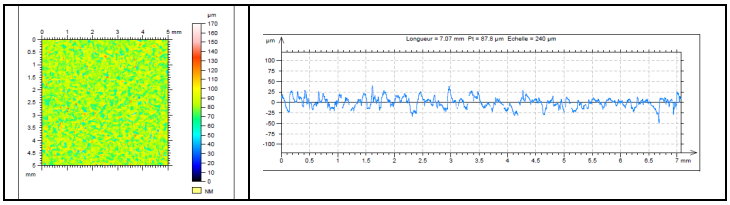


Figure 6b) Roughness profile of the PEEK implant after grit blasting. Ra: 8.86 µm, Rz: 49.9 µm.

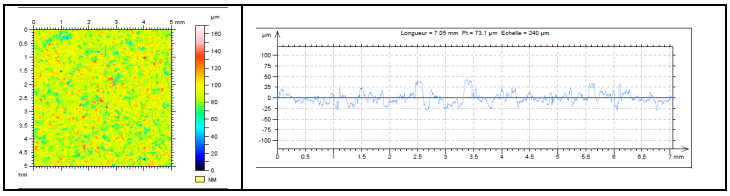


Figure 6c) Roughness profile of the PEEK implant after proprietary activation process. Ra: 8.76 µm, Rz: 48.1 µm.

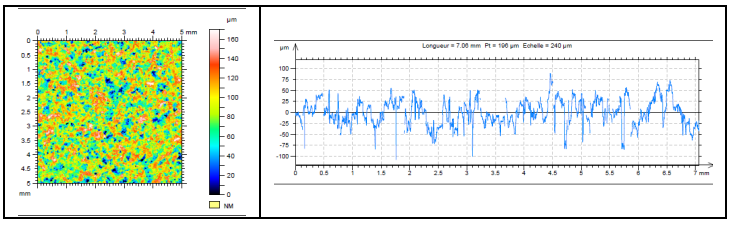


Figure 6d) Roughness profile of the PEEK implant after VPS titanium coating. Ra: 19 µm, Rz: 126 µm.

We observe a marked difference between machined PEEK roughness and grit blasted PEEK roughness. It is clearly visible when looking at the cartographies and the roughness profiles and the amplitude roughness parameters confirm this. The arithmetic mean deviation Ra of the roughness profiles and the maximum height of the roughness profile Rz values for the grit blasted samples are five (5) times higher than those for the machined PEEK. The grit blasted PEEK roughness profile shows similar values and characteristics to the PEEK with the proprietary surface activation. Furthermore, there is a significant difference in roughness between the PEEK surface with the proprietary activation and the PEEK with the titanium coating, the Rz value is increased again by a factor of five (5).

5.3.2 RSm spatial parameter

Another very important parameter that is often omitted in coating specifications is the RSm roughness spatial parameter defined as mean width of a repeatable profile element (Figure 7)[13,14,15]. This parameter is interesting on surfaces having periodic or pseudo-periodic structures, such as turned or structured surfaces.

In case of plasma sprayed titanium coating, the RSm parameter defines the length of two statistical repeatable roughness profile elements. The RSm parameter is interpreted as density of the profile element in a coating structure. If the RSm value is high, the density of the profile element is low. On the contrary, if the RSm value is low, the density of the profile element is high.

This parameter is helpful to differentiate coating roughness profiles for coating topographies that have about the same amplitude between the peaks and valleys, but a difference in the density of those peaks and valleys.

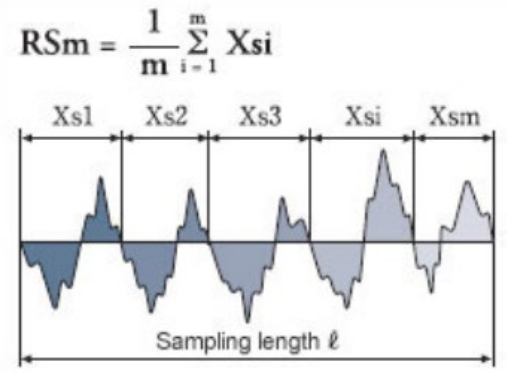


Figure 7. Definition of the RSm parameter.

We may explicit the RSm parameter comparing Figures 4a) and Figure 8 both microstructures have the same range of Rz values (Figure 4)a: Rz 144 µm). In case of the titanium coating (Figure 4 a), the measured Rsm value is of 433 µm, which is about a factor two (2) lower (denser profile element) than the coating of Figure 8 which has a RSm value of 736 µm.

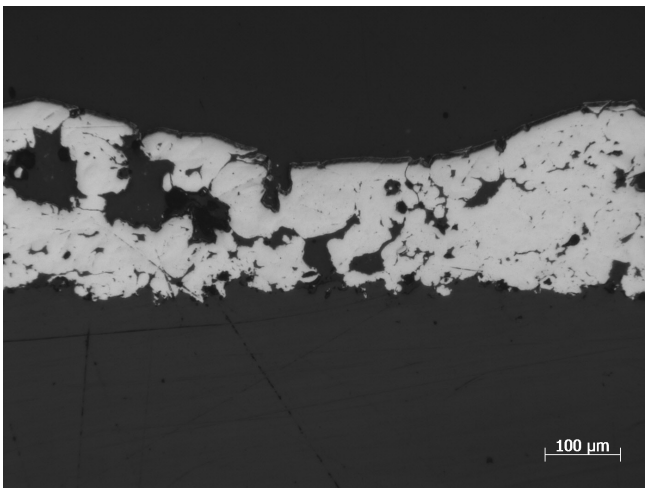


Figure 8: Titanium coating on PEEK substrate Rz: 167 µm, Rsm: 736 µm.

5.5 Mechanical testing

Mechanical testing has been performed according to the FDA ''Guidance for Industry on Testing of Metallic Plasma Spray Coating on Orthopaedic Implants to Support Reconsideration of Post market Surveillance Requirement''.

5.5.1 Tensile strength measurement

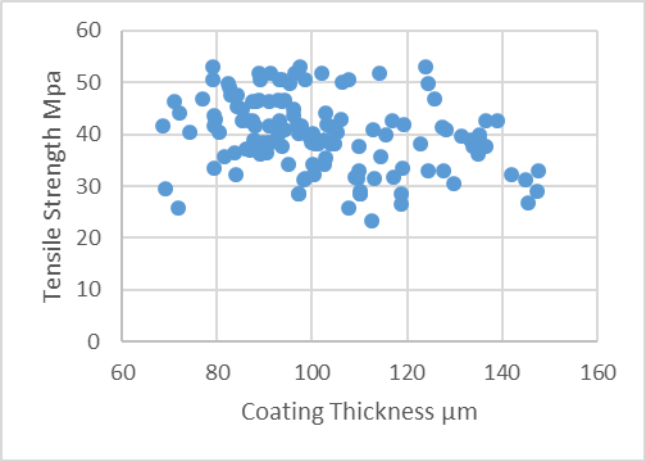


Fig. 9 Tensile strength in function of the coating thickness

Figure 9 shows the adhesion results of 130 measurements as function of the coating thickness, which were carried out for several production runs within one year. These results show that almost all the values are between 30 to 50 MPa, which is quite over the minimum value of 22 MPa required by the FDA guidance. We also notice that there is no clear correlation between coating thickness and adhesion strength.

5.5.2 Shear static strength

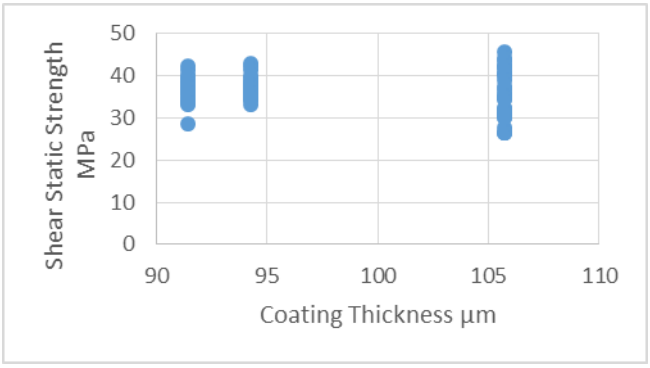


Figure: 10 Shear fatigue strength

Figure 10 shows the shear static strength for different thickness values. These measures were performed during three distinct production phases. A total number of 90 measurements have been performed, e.g. 30 for each phase with values between 25 to 45 MPa. Those values are over the minimum value of 20 MPa requested by the FDA Guidance. In the investigated coating thickness range, no evidence of correlation between the coating

thickness values and the shear static strength values has been evidenced.

5.5.3 Shear Fatigue testing

Shear fatigue testing has been performed according to ASTM F 1160. The measurements have been carried out at CRITT Laboratory (Charleville-Mézières, France). Figure 11 shows the Wohler S-N diagram, which plots the nominal shear strength amplitude versus cycle to failure. Two sets of measurements have been displayed consisting of two measures campaigns. For both sets of measurement, the endurance limit (runout) is situated between 14 MPa to 15 MPa for 10'000'000 of cycles.

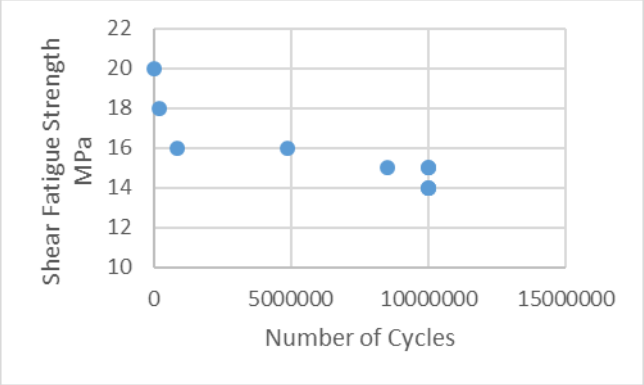


Figure 11: Shear fatigue strength of two (2) measurements campaigns

6 Conclusion

Titanium VPS coating on PEEK has been developed to match biological requirements for cell implant interaction. The coating topography and microstructure have been characterized with SEM analysis and laser scanning microscope. The surface topography change has been studied as a function of the major steps of the coating production process. The average increase specific surface of the titanium coating is 5.47 times larger than an uncoated, theoretically smooth, surface with comparable planar geometry.

The titanium coating PTC described in this study has a typical thickness between 50 to 200 µm, a porosity in the range of 40% to 50% and a roughness parameter Rz between 90 µm to 160 µm and an RSm value of 433 µm.

The coating porosity is built up from the PEEK substrate. Porous channels are created, which expand in several branches creating the coating pores between 20 to 200 µm. The combination of such structured porosity with a low roughness profile parameter RSm creates a very high level of coating iso-elasticity. This allows a better distribution and release of the stresses of the PEEK cage into the coating and this avoids the risk of coating spalling.

Finally, a series of mechanical testing according to the FDA guidance shows that the tensile strength of the titanium coating PTC is in the range of 30-50 MPa with a shear static strength value in the range between 25-45 MPa and shear fatigue strength between 14 to 15 MPa. All of these values confirm the good bonding of the titanium coating on the PEEK substrate.

ENDNOTES

[1] Kurtz SM, Devine JN, PEEK biomaterials in trauma, orthopaedic, and spinal implants. Biomat 2007; 28; 4845-69

[2] Altankov, G.; Grinnell, F. and Groth, T. Studies on the biocompatibility of materials: Fibroblast reorganization of substratum-bound fibronectin on surfaces varying in wettability. Journal of Biomedical materials research 30 (1996), Issue 3, pp. 385/91.

[3] Wertz CF, Santore M.M, Effect of surface hydrophobicity on adsorption and relaxation of kinetics of albumin and fibrinogen: single-species and cpmpetitive behaviour. Langmuir 17(10), 3006-3016 (2001)

[4] Grinnel F. Feld MK, Fibronectin adsorption on hydrophilic and hydrophobic surfaces detected by antibody binding and analysed during cell adhesion in serum-containing medium. J. Biol Chem. 257(9), 4888-4893 (1982)

[5] Lu DR, Park K. Effect of surface hydrophobicity on the conformational changes of adsorbed fibrinogen. J. Colloid & Interface Sci, 144(1), 271-281 (1991).

[6] Gershan H, Rosen J.J., Cell adhesion and cell surface topography and SV40-Virus-transformed 3T3 cells, The Journal of Cell Biology, vol. 76, 1978, 639-651(1978).

[7] Barr S, Hill E, Bayat A, Current implant surface technology: an examination of their nanostructure and their influence on fibroblast alignment and biocompatibility. Eplasty 9, e22 (2009).

[8] Chen S, Jones JA, Xu Y, Low HY, Anderson JM,Leong KW, Characterization of topographical effects on macrophage behaviour in a foreign body response model. Biomaterials 31(13), 3479-3491 (2010).

[9] Keselowsky BG, Collard DM, Garcia AJ, Surface Chemistry modulates fibronectin conformation and directs integrin binding and specifity to control cell adhesion, J. Biomed. Mater. Res. A 66(2), 247-259(2003).

[10] Sanz-Herrera JA, Moreo P, Garcia-aznar JM, Doblaré M. On the effect of substrate curvature on cell mechanics. Biomaterials 30(34), 6674-6686 (2009).

[11] ASTM F1144: Standard test method for shear testing of calcium phosphate and metallic coating. West Conshohocken, PA: ASTM International 2011.

[12] ASTM F1147: Standard test method for tension testing of calcium phosphate and metallic coating. West Conshohocken, PA: ASTM International 2011.

[13] ASTM F1854: Standard test method for stereological evaluation of porous coating on medical implants. West Conshohocken, PA: ASTM International 2009.

[14] ISO 3274:1996 – Geometrical Product Specification (GPS) – Surface texture profile method – Nominal characteristics of contact (stylus) instrument, Geneva, Switzerland, International organization of Standard, 1996.

[15] ISO 4287:1996 – Geometrical Product Specification (GPS) – Surface texture profile method – Terms, definitions and surface texture parameters Geneva, Switzerland, International organization of Standard, 1996.

[16] ISO 4288:1996 – Geometrical Product Specification (GPS) – Surface texture profile method – Rules and procedures for the assessment for the assessment of surface texture, Geneva, Switzerland, International organization of Standard, 1996.

