Topographical characterization and microstructural interface analysis of vacuum-plasma-sprayed titanium and hydroxyapatite coatings on carbon fibre-reinforced poly(etheretherketone)

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In the present study, topographical characterization and microstructural interface analysis of vacuum-plasma-sprayed titanium and hydroxyapatite (HA) coatings on carbon fibre-reinforced polyetheretherketone (CF/PEEK) was performed. VPS-Ti coatings with high roughness values ($R_a = 28.29 \pm 3.07$ μm, $R_z = 145.35 \pm 9.88$ μm) were obtained. On this titanium, intermediate layer HA coatings of various thicknesses were produced. With increasing coating thickness, roughness values of the HA coatings decreased. A high increase of profile length ratio, L_r, of the VPS-Ti coatings ($L_r = 1.45$) compared to the grit-blasted CF/PEEK substrate ($L_r = 1.08$) was observed. Increasing the HA coating thickness resulted in a reduction of the L_r values similar to the roughness values. Fractal analysis of the obtained roughness profiles revealed that the VPS-Ti coatings showed the highest fractal dimension of $D = 1.34 \pm 0.02$. Fractal dimension dropped to a value of 1.23–1.25 for all HA coatings. No physical deterioration of the CF/PEEK substrate was observed, indicating that substrate drying and the used VPS process parameter led to the desired coatings on the composite material. Cross-section analysis revealed a good interlocking between the titanium intermediate layer and the PEEK substrate. It is therefore assumed that this interlocking results in suitable mechanical adhesive strength. From the results obtained in this study it is concluded that VPS is a suitable method for manufacturing HA coatings on carbon fibre-reinforced PEEK implant materials

1. Introduction

Plasma-spraying has become an established method for the manufacturing of calcium phosphate coatings for clinical applications [1–4]. High reproducibility and economic efficiency of the process are outstanding advantages. By variation of process parameters, such as particle-size distribution, spraying distance and the power-level of the plasma coating density, morphology, composition and crystallinity can be varied. The vacuum-plasma-spraying (VPS) technique enables the preparation of coatings of a broad variety of coating materials, including oxygen-sensitive materials like titanium. Dense, crack-free and crystalline HA-coatings are achieved with the VPS technique. Many studies of plasma-sprayed HA coatings on metallic substrates have been performed and described in the literature [5–9]. However, only a few studies exist concerning the application of the VPS process on thermoplastic polymers and composite materials. In this investigation, a systematic approach for the application of the VPS process on pure and carbon fibre-reinforced PEEK has been chosen. Existing technology and know-how for the deposition of crystalline VPS-HA coatings, which have been achieved with metallic substrates [4], were used as a basis for the optimization of the method to the new substrate material. The objectives of this study were (a) the development of an improved process setup for the applications of VPS on carbon fibre-reinforced PEEK, and (b) the topographical characterization and

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microstructural analysis of the interface between the composite substrate and the VPS coatings.

2. Materials and methods

2.1. Plasma-spraying parameters

Extruded carbon fibre-reinforced PEEK discs were cut into discs of 10 mm diameter and 4 mm height. The specimens were grit-blasted with alumina, cleaned with ethanol and pure water and dried in a vacuum oven at 200 °C for at least 7 days. The dried specimens were placed in copper sample holders and positioned in the VPS chamber. Programming of the plasma flame movement was performed with the central control unit of the VPS system. An oscillating movement of the plasmaburner was performed to minimize the thermal impact on the substrate. Substrate temperature was measured with an infrared sensor. Vacuum-plasma-spraying was carried out with the parameters listed in Table I [10]. In a first step, fine titanium powder with an average grain size of $d_{50} = 25$ μm was sprayed on to the substrates, and subsequently rough titanium powder with an average grain size of $d_{50} = 120$ μm was applied. HA coatings were produced on an intermediate layer of titanium as described above, using HA powder with an average grain size of $d_{50} =$ μm. HA coatings of three different thicknesses, 50, 100 and 150 μm, were produced. After VPS coating, the specimens were gently rinsed in deionized water and dried in air.

2.2. Topographical and microstructural interface analysis

2.2.1. Coating morphology

General coating morphology was examined by scanning electron microscopy (SEM, Hitachi S-2500C) to analyse coating integrity, porosity and microcracks. Additionally, backscattering electron (BSE) analyses were performed to study the optical density of the VPS-Ti coating on the composite substrate. The samples were coated with platinum in a Balzers SCD 004 Sputter coater before SEM analysis.

2.2.2. Cross-section analysis and coating thickness determination

Cross-section analysis of the coated samples were performed using SEM to analyse the substrate after vacuum-plasma-spraying and to investigate the interface between the composite substrate and the VPS-Ti-HA coating. For cross-section analysis, the specimens were cut perpendicular to the coating with a diamond-coated wire saw (Well, Switzerland) and embedded in epoxy resin. Grinding and polishing were performed with a Struers grinding machine to a 4000-grit SiC finish. The coating thickness values of titanium and hydroxyapatite were measured in the backscattering mode in an image analysis system (Voyager, Noran Instruments).

2.2.3. Surface roughness analysis

Roughness of the VPS-Ti and HA coatings was measured by using an optical autofocusing profilometer (Laser UBM). Measurements were performed with a scan length of 6 mm and a point density of 50 points/mm. Roughness values R_a, R_q, R_z and R_{max} (DIN 4762 and 4768) were measured and the arithmetic means and standard deviations of five measurements were evaluated for each specimen. Additionally, profile length ratio, L_r of the coatings was determined.

2.2.4. Fractal analysis

Fractal geometry is a natural description for disordered objects [11]. Fractal analyses of the examined roughness profiles were performed with the box counting method, which is the simplest way to evaluate fractal dimensions [12]. The surface roughness profile is covered with boxes of side length d. If the profile is completely covered with N squares, the fractal dimension, D can be evaluated according to the rules of fractal geometry

$$N(d) = \alpha d^{-D} \tag{1}$$

$$\log N(d) = \log \alpha - D \log d \tag{2}$$

By continuously changing the magnification scale through changing the size, d, of the boxes, the number of squares, N, covering the roughness profile is counted. The fractal dimension, D, is obtained by plotting log N versus log d. With this method the fractal dimensions, D, of the VPS-Ti and VPS-Ti-HA coatings of different thicknesses were examined.

2.3. Chemical characterization

2.3.1. X-ray diffraction

X-ray diffraction of the VPS-HA coated samples was performed with an X-ray diffractometer (PADX, Scintag, USA) with CuK_α radiation in the Bragg-Brentano mode. To place the coated sample into the diffractometer, a special sample holding device was

TABLE I VPS process parameters for the preparation of HA coatings on CF/PEEK substrates

Process parameter	Value
Chamber pressure	140 mbar
Spraying distance	300 mm
Plasma gas Ar	33 l min^{-1}
Plasma gas He	7 l min^{-1}
Voltage	45 V
Plasma energy	33.8 kW
Powder feed rate	16 g min^{-1}

TABLE II Experimental setup of XRD analysis with the PADX diffractometer

Parameter	Value
2θ	15°–55°
Modus	Step scan
Step size	0.02°
Measuring time per step	2 s
Total measurement time	2 h
Voltage	45 kV
Current	45 mA
Wavelength (CuK_α)	0.154 06 nm

fabricated, which allowed the coating surface to be placed at the calibrated reference line. The 2θ positions of the measured hkl signals were corrected by using a silicon standard. The experimental setup of the XRD investigations are listed in Table II. The X-ray data were collected in the 2θ range of 15°–55° in steps of 0.02°.

3. Results and discussion

3.1. Coating characterization

Fig. 1 shows a photograph of a non-coated, grit-blasted CF/PEEK substrate and a VPS-HA-coated specimen. It can be seen that the obtained VPS-HA coatings completely covered the underlying substrate material. In Fig. 2 the SEM and BSE images of the VPS-Ti coatings on the composite substrate are displayed. The coating showed a rough and porous topography built-up by the coarse titanium particles. The BSE image of the VPS-Ti coating revealed a dense titanium layer, suggesting that the fine titanium particles completely cover the underlying composite substrate surface. The achieved coating thickness of the titanium layer varied between 10 and 150 μm. Fig. 3 shows the VPS-HA coatings, revealing a smoother topography compared to the rough and porous titanium coating. No cracks were observed in the VPS-HA coatings. Cross-sections of the VPS coatings showed a close contact at the interface between substrate and titanium coating (Fig. 4). The titanium layer was fully covered with HA and the close contact between titanium and HA suggested a good mechanical interlocking at the HA/Ti interface. The thermoplastic composite substrate showed no formation of voids and cracks indicating that the coating process had no adverse effects on the substrate material.

3.2. Roughness measurements and fractal analysis

The different roughness profiles of the non-coated and VPS-coated substrates are shown in Fig. 5. Roughness of the VPS-Ti coatings was significantly increased compared to the grit-blasted carbon fibre-reinforced PEEK substrate. The VPS-HA coatings revealed a smoother profile compared to the VPS-Ti coatings.

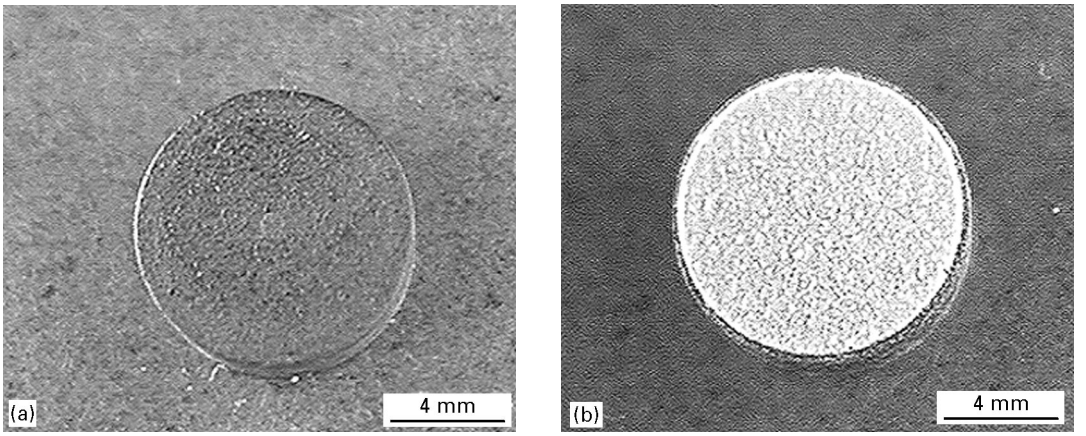

Figure 1 Photographs of a grit-blasted, (a) non-coated and (b) VPS-HA-coated CF/PEEK specimen. The produced VPS-HA coatings completely covered the underlying substrate.

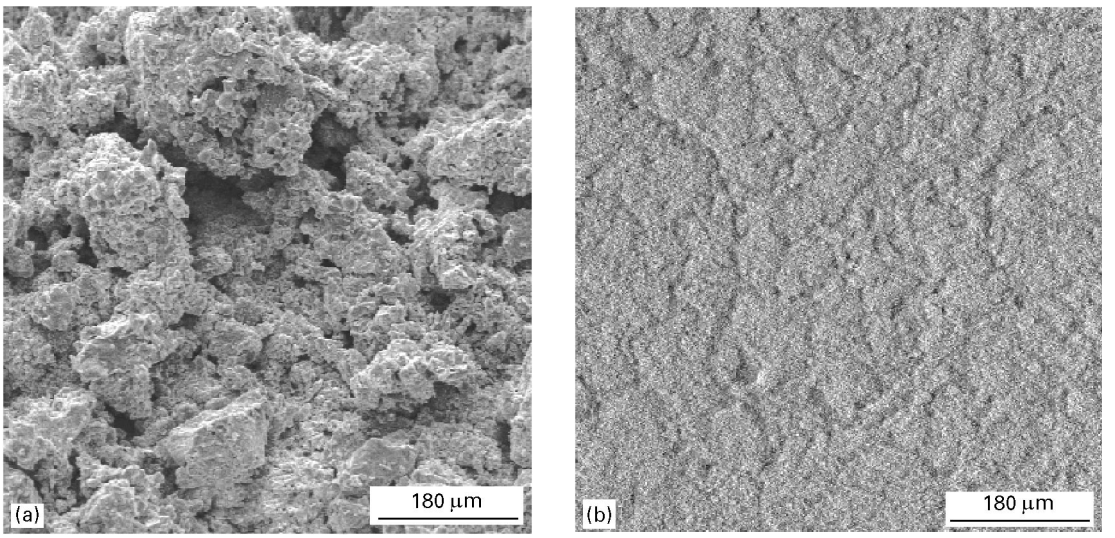

Figure 2 (a) Scanning electron micrographs of the VPS-Ti coatings revealed a very rough surface topography. In the corresponding back-scattering electron image (b) a complete coverage of the VPS-Ti coatings on the CF/PEEK substrate was observed.

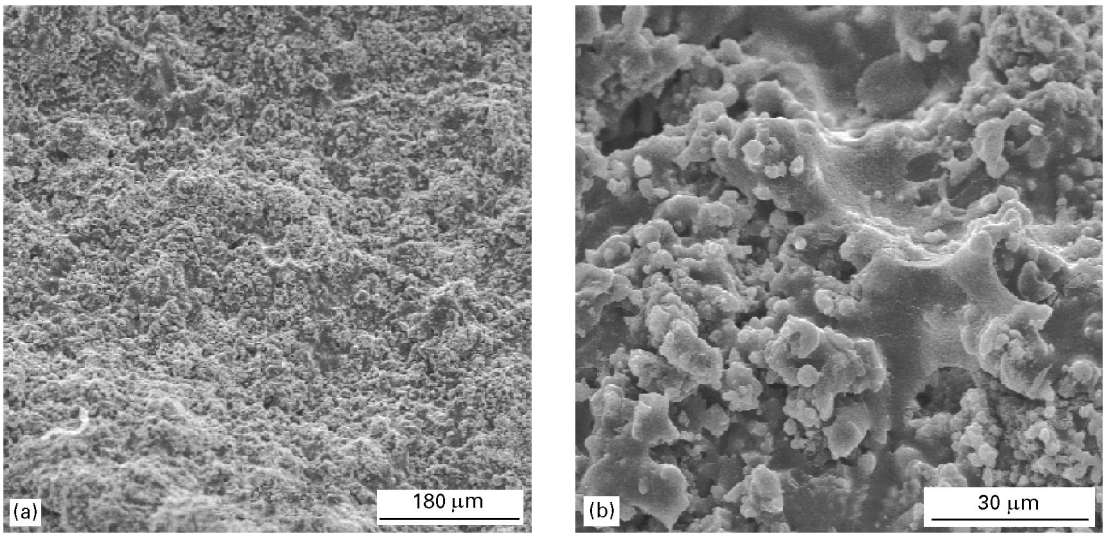

Figure 3 Scanning electron micrographs of VPS-HA coatings showing the typical morphology with molten particles (a) in an overview and (b) in higher magnification. No cracks were observed in the VPS-HA coatings.

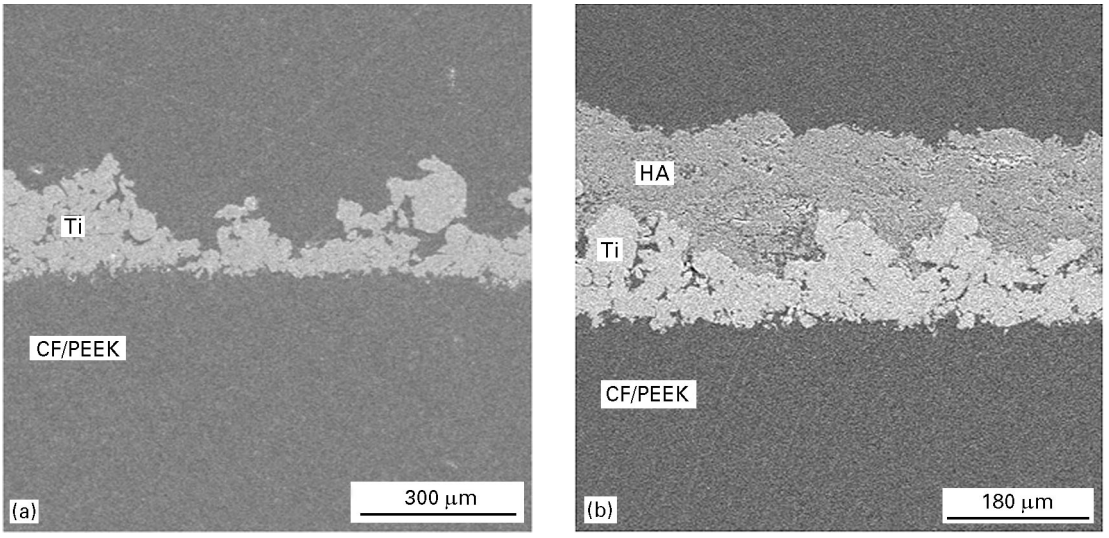

Figure 4 Scanning electron micrographs of cross-sections of (a) VPS-titanium coatings and (b) VPS-hydroxyapatite coatings with an intermediate titanium layer.

The various roughness values of VPS-Ti and HA coatings measured with an optical profilometer (Laser UBM) are displayed in Table III and in Figs 6 and 7. The rough topography of the VPS-Ti coatings showed average roughness values of $R_a = 28.29$ μm, $R_q = 36.61$ μm, $R_z = 145.35$ μm and $R_{max} = 179.21$ μm. With increasing HA coating thickness, roughness values significantly decreased. Profile length ratio, L_r, was significantly increased from a value of 1.08 to 1.45 after coating the grit-blasted CF/PEEK substrate with titanium. Increasing HA coating thickness resulted in a reduction of the L_r values, similar to the roughness values. The 150 μm thick HA coating showed an L_r value of 1.09.

Fractal analysis of the obtained roughness profiles revealed that the VPS-Ti coatings showed the highest average fractal dimension of $D = 1.34 \pm 0.02$. Fractal dimension dropped to a value of 1.23–1.25 after applying the HA coating. No significant difference in fractality was determined between the various HA coating thicknesses (Fig. 8). The results of the fractal analysis showed that the HA coatings with different roughness values and coating thicknesses have a similar fractal dimension. Because all HA coatings were formed by the same coating powder using the same process parameters, this could be an explanation for the equivalence of the fractal dimension. The titanium coating powder had a different grain-size distribution and a different morphology resulting in a higher fractal dimension compared to the VPS-HA coatings.

The influence of surface topography on biological response is still a matter of investigation. One major difficulty is to find those surface topography parameters which are relevant for the interactions between the material surface and the surrounding biological environment.

Fractal analysis might be a useful tool to examine these interactions and to elucidate the complex mechanisms occurring at the implant material surface in contact with the surrounding biological tissue.

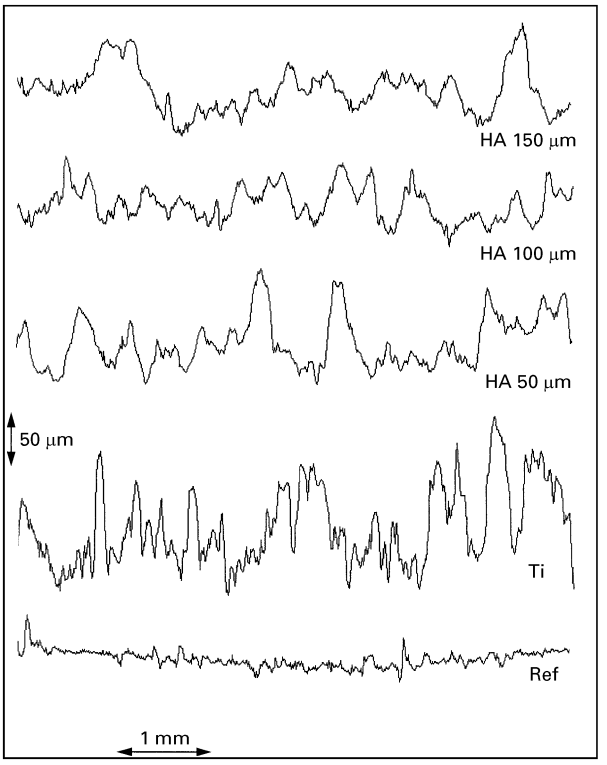

Figure 5 Roughness profiles of VPS-Ti and HA coatings obtained with optical autofocusing profilometer.

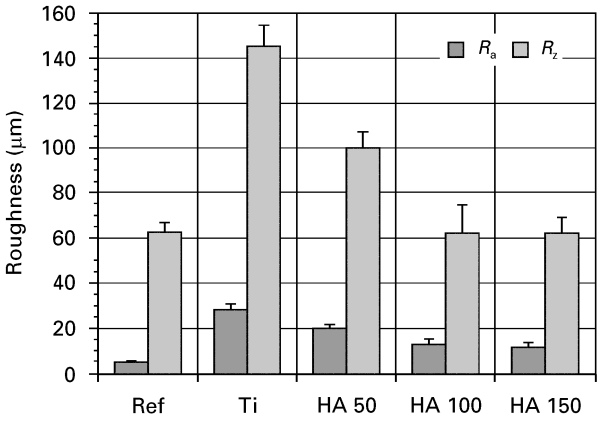

Figure 6 Average values (± S.D.) of roughness values R_a and R_z ($n = 5$) of VPS-Ti and HA coatings measured with an optical autofocusing profilometer (Laser UBM). The HA coatings have different coating thickness values (Ref = CF/PEEK, HA 50 = 50 μm, HA 100 = 100 μm, HA 150 = 150 μm).

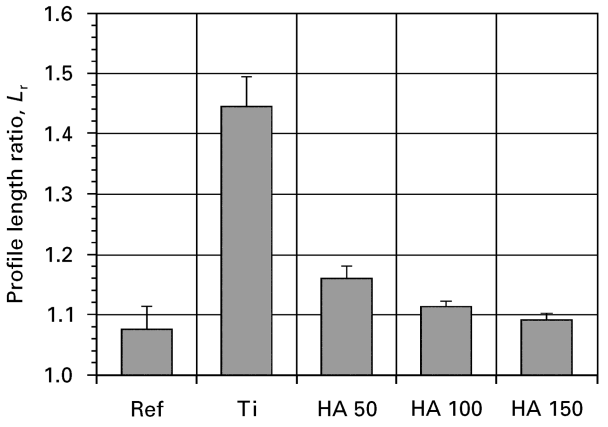

Figure 7 Average values (± S.D.) of profile length ratio L_r of VPS-Ti and HA coatings measured with an optical autofocusing profilometer (Laser UBM).

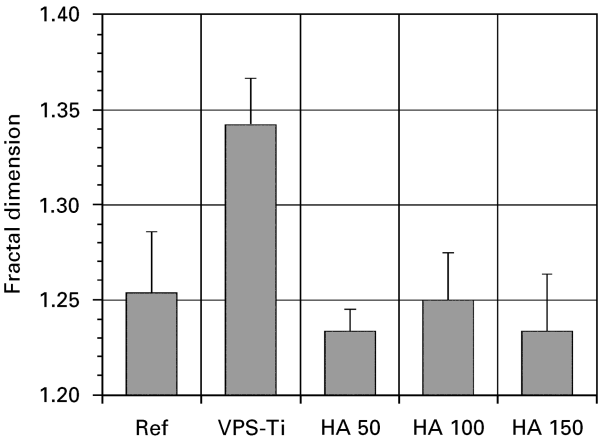

Figure 8 Average values (± S.D.) of fractal dimension, D, of VPS-Ti and HA coatings measured with an optical autofocusing profilometer (Laser UBM).

3.3. Chemical composition

The chemical composition of the VPS-HA coatings was investigated by X-ray diffraction. The spectrum showed hydroxyapatite (PDF 9-432) as main component and a small β-tricalcium phosphate peak at $2\theta = 31.16^\circ$ (Fig. 9). No other phases were determined. This is in good accordance to the results obtained on VPS-HA coatings on titanium alloy substrates [13]. It is, therefore, concluded that the changing in the VPS

TABLE III Roughness values, R_a, R_q, R_z and R_{max} and profile length ratio, L_r, of carbon fibre-reinforced PEEK substrates before and after coating with titanium and HA using VPS. The VPS-Ti coating showed the highest roughness values. With increasing HA coating thickness, roughness values decreased

Specimen	R_a (μm)	R_q (μm)	R_z (μm)	R_{max} (μm)	L_r
CT/PEEK	4.64 ± 0.69	6.68 ± 1.06	62.71 ± 4.49	53.65 ± 9.02	1.08 ± 0.01
Ti	28.29 ± 3.07	36.61 ± 2.92	145.35 ± 9.88	179.21 ± 9.30	1.45 ± 0.05
HA 50 μm	20.18 ± 2.31	26.30 ± 2.65	99.94 ± 8.24	147.19 ± 17.73	1.16 ± 0.02
HA 100 μm	13.25 ± 2.95	15.24 ± 1.19	62.71 ± 13.26	80.08 ± 13.41	1.12 ± 0.01
HA 150 μm	12.25 ± 2.45	15.30 ± 2.95	62.71 ± 7.80	79.08 ± 16.30	1.09 ± 0.01

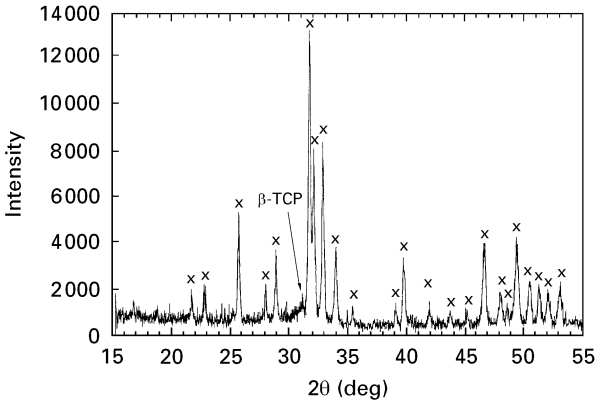

Figure 9 XRD-spectrum of the VPS-HA coatings showing HA (×) as the main component and small concentrations of β-TCP.

process for the carbon fibre-reinforced PEEK substrate did not affect the chemical composition of the HA-coating, as analysed with XRD.

4. Conclusion

With the VPS coating setup which was optimized for carbon fibre-reinforced PEEK substrates, crack-free titanium and hydroxyapatite coatings were obtained. Cross-section analysis showed that the titanium layer completely covered the CF/PEEK substrates, which is assumed to be an important factor for the biological performance of CF/PEEK. The achieved coating thickness of the titanium layer varied between 10 and 150 μm and with this underlying rough titanium layer, HA coatings of various roughness and profile length ratio values were achieved, depending on coating thickness. No physical substrate deterioration was observed indicating that the applied VPS process parameters led to the desired coatings on the composite material. Cross-section analysis revealed a good interlocking between the HA- and titanium coating and between the titanium intermediate layer and the PEEK substrate. It is therefore assumed that this interlocking results in suitable mechanical adhesive strength. From the results obtained in this study it is concluded that VPS is a suitable method for preparing HA coatings on carbon fibre-reinforced PEEK implants. It is suggested that the evaluation of fractal dimensions of VPS-Ti and VPS-HA surfaces and their correlation to cell response may lead to more profound knowledge about the influence of surface structures on *in vitro* and *in vivo* biological performance.

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