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NaOH treatment of vacuum-plasma-sprayed titanium on carbon fibre-reinforced poly(etheretherketone)

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Carbon fibre-reinforced polyetheretherketone (CF-PEEK) substrates were coated with titanium by vacuum-plasma-spraying and chemically treated in 10 M sodium hydroxide (NaOH) solution. After NaOH treatment, the specimens were immersed in simulated body fluid (SBF) containing ions in concentrations similar to those of human blood plasma. Scanning electron microscopy, energy-dispersive X-ray analysis and diffuse reflectance Fourier transformed–infrared spectroscopy were used to analyse the NaOH-treated VPS-Ti surface and the calcium phosphate layer formed during immersion in SBF. It was observed that a carbonate-containing calcium phosphate layer was formed on the NaOH-treated VPS-Ti surface during immersion in SBF, whereas no calcium phosphate precipitation occurred on the untreated surfaces. It is therefore concluded that vacuum-plasma-spraying with titanium and subsequent chemical modification in 10 M NaOH solution at 60 °C for 2 h is a suitable method for the preparation of bioactive coatings for bone ongrowth on CF-PEEK.

1. Introduction

Pure and carbon fibre-reinforced polyetheretherketone (CF/PEEK) are currently being investigated for applications in medicine due to the high chemical stability, high chemical purity and biocompatibility of these materials [1–4]. *In vitro* and *in vivo* results which can be found in the literature indicate that mild tissue reactions occur around PEEK implants [2, 5]. Nonetheless, the establishment of PEEK as implant material for reconstructive orthopaedic surgery is still the subject of further investigation. It is believed that the observed tissue reactions can be avoided by coating PEEK with materials known for their favourable response in bone tissue, such as titanium or hydroxyapatite (HA). Vacuum-plasma-sprayed titanium (VPS-Ti) coatings have been successfully applied on CF/PEEK [6]. In the present study, CF/PEEK substrates were first coated with titanium by vacuum-plasma-spraying. Then, chemical modification using an alkaline treatment in sodium hydroxide (NaOH) solution was carried out. This treatment has recently been established by Kokubo and co-workers [7, 8] on abraded titanium and titanium alloy substrates. They showed that an apatite layer was formed on titanium substrates subjected to NaOH and potassium hydroxide (KOH) treatment and subsequent heat treatment at 600 °C, whereas no apatite formation was observed on the untreated titanium substrates. In the present study, the process as described by Kim *et al.* [8] was slightly modified: the VPS-Ti surfaces were treated in 10 M NaOH at 60 °C for 2 h and no additional heat treatment was performed due to the limited thermal stability of PEEK. The characteristics of the modified surface and the induction of *in vitro* biological apatite formation were investigated.

2. Materials and methods

Extruded carbon fibre-reinforced polyetheretherketone (PEEK, Ensinger GmbH, Germany) rods were cut into cylinders with a diameter of 10 mm and a height of 4 mm. The specimens were grit-blasted with alumina, cleaned with ethanol and deionized water and dried in a vacuum oven at 200 °C for at least 7 d. Vacuum-plasma-spraying (VPS) was performed in a plasma spraying chamber (Medicoat AG, Mägenwil) with process parameters described elsewhere. First,

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fine titanium powder with an average grain size of $d_{50} = 25\,\mu\text{m}$ was sprayed on to the substrates. Subsequently, rough titanium powder with an average grain size of $d_{50} = 120\,\mu\text{m}$ was applied. After VPS coating, the specimens were gently rinsed in deionized water and dried in air.

Chemical treatment was performed in 10 M sodium hydroxide (NaOH) solution at 60 °C in a laboratory shaker (Infors AG) rotating with 80 r.p.m. for 2 h. After chemical treatment, the specimens were washed in deionized water. Biomimetic coating was performed in simulated fluid (SBF) with ion concentrations similar to those of human blood plasma. SBF was prepared as described by Kokubo *et al.* [9] by dissolving reagent-grade $CaCl_2$, $KH_2PO_4 \cdot 3H_2O$, NaCl, KCl, $MgCl_2 \cdot 6H_2O$, $CaHCO_3$ and Na_2SO_4 in deionized water. The solution was buffered at pH 7.4 with tris(hydroxylmethyl) aminomethane (Tris) and hydrochloric acid (HCl). The pH was measured with a pH-meter at the end of each investigation. The specimens were placed in sealed polypropylene bottles and immersed in 25 ml SBF for 1, 4, 10 and 24 days. The experiment was performed in a laboratory shaker (Infors AG) rotating with 80 r.p.m. at a temperature of 37 °C. After immersion, the specimens were gently rinsed in deionized water and dried in air. Additionally, NaOH treatment was carried out on polished commercially pure titanium cpTi samples with 10 M NaOH at 60 °C for 2 h and immersed in SBF at the same conditions as the VPS-Ti specimens.

Scanning electron microscopy with a secondary electron detector was performed to analyse the topographical characteristics of the VPS coatings and with a backscattering electron detector to visualize the density of the titanium layer on the substrate. Energy-dispersive X-ray (EDX) analysis was performed at an acceleration voltage of 25 kV with a X-ray microanalysis system attached to the SEM (Voyager, Noran Instruments). EDX spectra were acquired with an acquisition time of 100 s. The specimens were coated with platinum in a sputter coater before SEM and EDX analysis. Calcium and phosphorus concentrations in the solutions were measured after immersion by inductively coupled plasma atomic emission spectroscopy (ICP-AES), using an Applied Research Laboratories 3580B ICP-AES "Minitorch" spectrometer. Chemical changes of the substrates after immersion in SBF were examined by diffuse reflectance Fourier transformed–infrared (DRIFT) analysis (Perkin–Elmer System 2000). Infrared spectra were obtained in the wave number range of 4000–400 cm^{-1}.

3. Results

3.1. NaOH treatment

Fig. 1 shows SEM images of untreated and NaOH treated VPS-Ti surfaces. It was observed that a new layer consisting of small, needle-like structures was formed on the NaOH treated VPS-Ti coatings. Control experiments with polished cpTi surfaces showed that after NaOH treatment pores were formed in the titanium surface and topography was significantly changed (Fig. 2) compared to the untreated polished surface which revealed a very smooth topography. Needle-like shapes were formed on the NaOH-treated cpTi surfaces. Fig. 3 shows the EDX spectra of the VPS-Ti coatings without chemical modification and

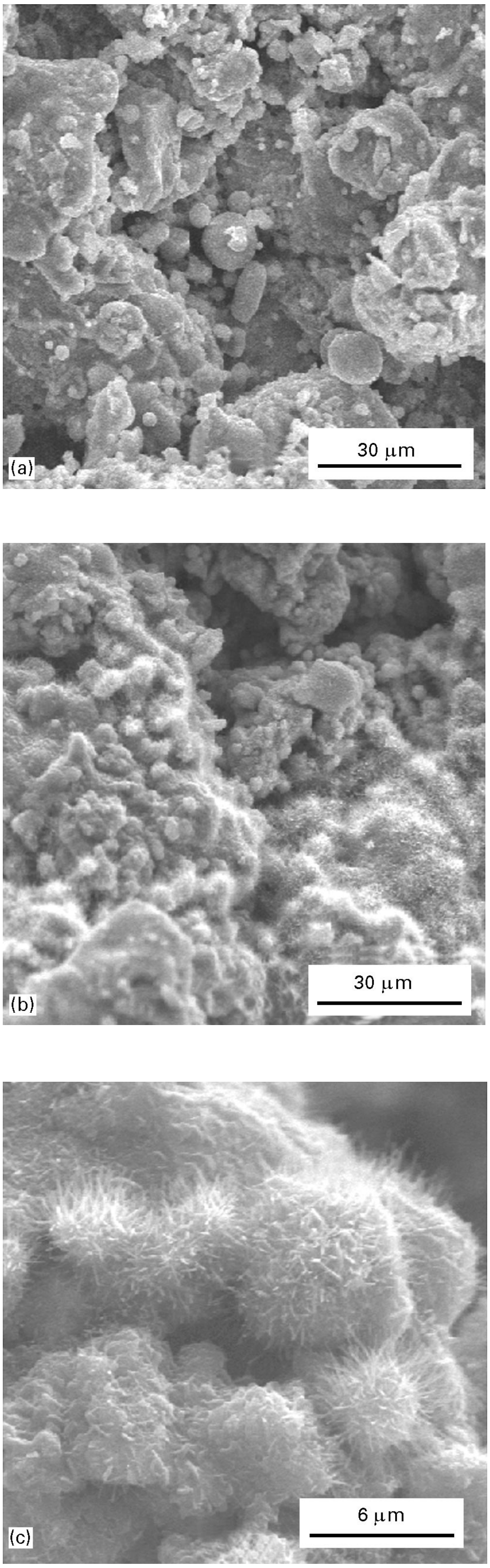

Figure 1 SEM images of (a) untreated (above) and (b, c) NaOH-treated VPS-Ti coatings. It can be observed that the morphology has changed after NaOH treatment revealing a fibrous, needle-like structure.

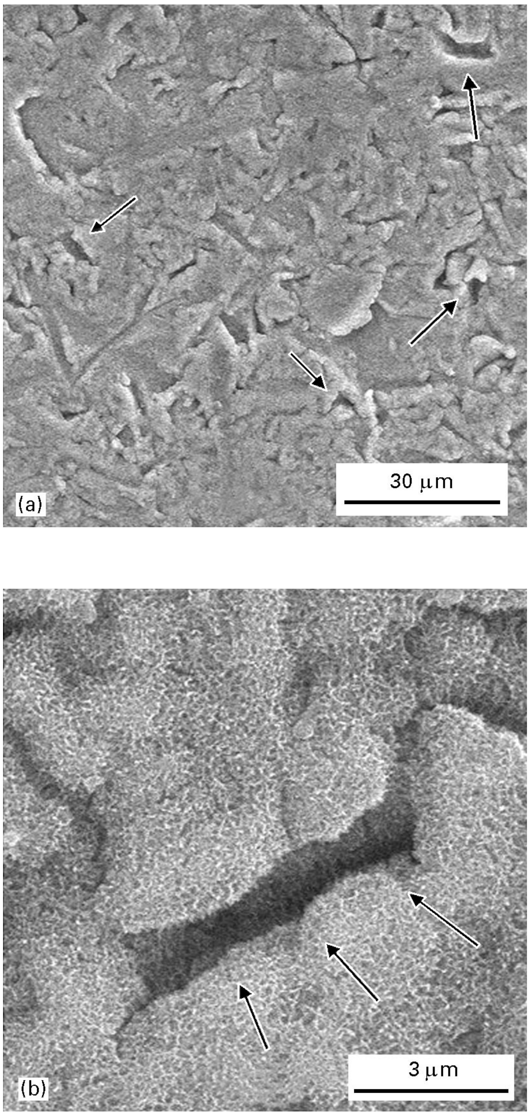

Figure 2 SEM images of (a) a polished cpTi surface after 10 M NaOH treatment at 60 °C for 2 h in an overview and (b) in higher magnification. It can be observed that large pores (arrows) are formed during the NaOH treatment (b). Furthermore, surface morphology was significantly altered (a).

after treatment in 10 M NaOH solution. The spectra indicate that after NaOH treatment, sodium was incorporated into the VPS-Ti coating. It is assumed that this sodium is incorporated within the crystal lattice of the newly formed crystallites which were observed by SEM. Besides sodium, no additional elements were discerned on the NaOH-treated samples.

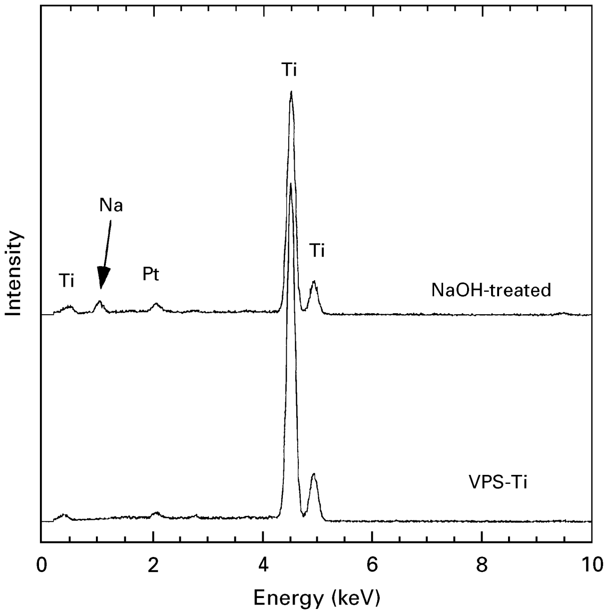

Figure 3 EDX spectra of VPS-Ti coatings on carbon fibre-reinforced PEEK before and after chemical modification in 30% H_2O_2 at room temperature and 10 M NaOH at 60 °C, both for 2 h. On the NaOH-treated surfaces, sodium was detected, while no change in the chemical composition was observed on the H_2O_2-treated specimens.

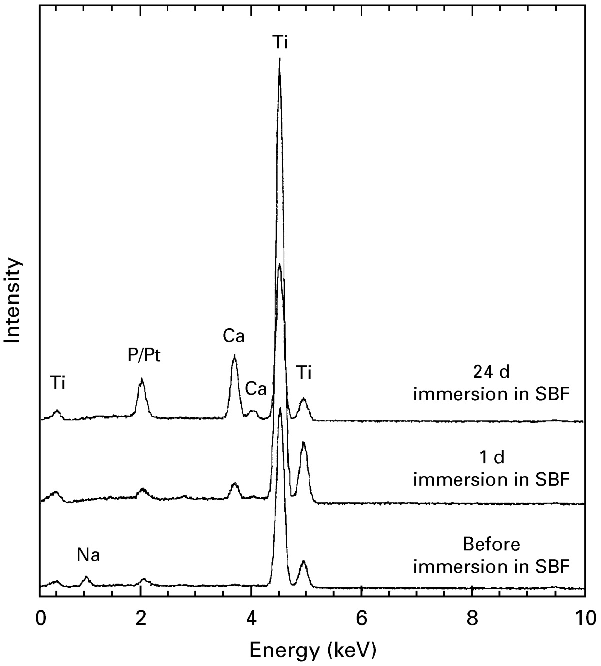

Figure 4 EDX spectra of VPS-Ti coatings treated with 10 M NaOH at 60 °C showing that a calcium phosphate layer was formed after 1 day soaking and which continuously grew up to 24 days immersion time.

3.2. Immersion in SBF

After immersion in SBF, the untreated and NaOH treated VPS coatings were analysed with EDX and SEM. Fig. 4 shows the EDX spectra of the NaOH-treated VPS-Ti coatings before and after immersion in SBF. On the NaOH-treated samples, formation of calcium phosphate was observed after 1 day immersion in SBF. The EDX spectrum showed the appearance of calcium. SEM analysis showed the formation of a layer with some crystallites which displayed the typical morphology of precipitated calcium phosphate (Fig. 5). After 10 and 24 days immersion in SBF, the VPS-Ti surface was completely covered with calcium phosphate crystallites. Control experiments with cpTi showed the formation of calcium phosphate precipitates after NaOH treatment and immersion in SBF at 37 °C for 1 day (Fig. 6).

Calcium and phosphorus concentrations in SBF during immersion of untreated and NaOH-treated VPS-Ti coatings were measured with ICP-AES (Fig. 7). After the first day of immersion in SBF,

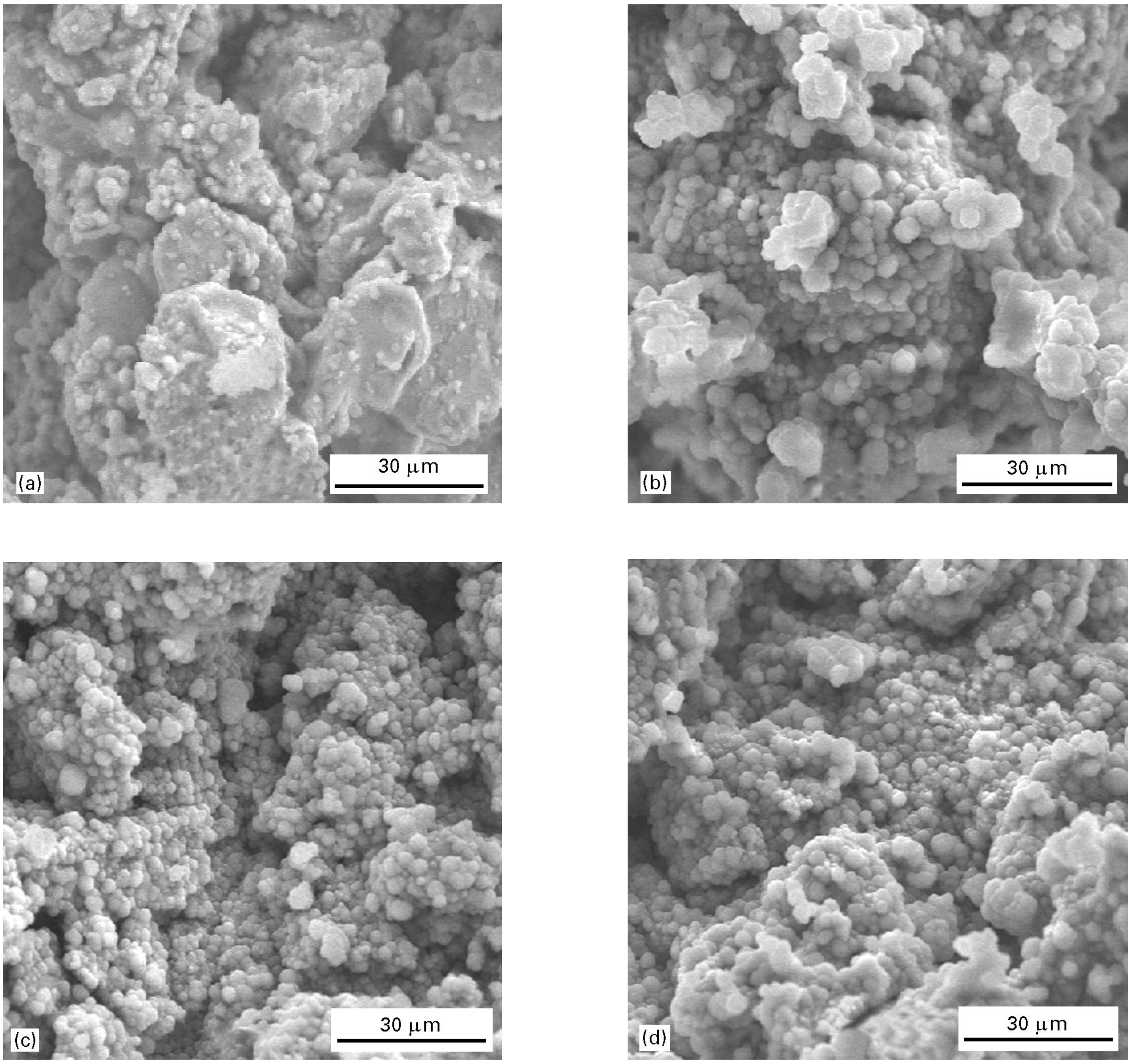

Figure 5 SEM images of VPS-Ti coating treated with 10 M NaOH at 60 °C for 2 h after immersion in SBF for (a) 1, (b) 4, (c) 10 and (d) 24 days With increasing immersion time the number of calcium phosphate precipitates was enlarged suggesting a continuous precipitation.

NaOH-treated VPS-Ti coatings showed a significant drop of both calcium and phosphorus concentrations indicating the precipitation of calcium phosphate. During further immersion, continuous precipitation of calcium and phosphorus on the NaOH-treated VPS-Ti coating was observed. On the untreated samples, only little precipitation of calcium and phosphorus occurred during the first day of immersion in SBF.

Fig. 8 shows the FT–IR spectra of the VPS-Ti substrates treated with 10 M NaOH at 60 °C for 2 h and immersed in SBF for 1, 4 and 24 days. After 1 day immersion, two IR bands at wave numbers 1037 and 1110 $\mathrm{cm^{-1}}$ were observed, which can be attributed to the ν_3 P–O stretch vibration mode in the PO_4^{3-}-group [10]. A faint peak at wave number 559 $\mathrm{cm^{-1}}$ was assigned to the ν_4 P–O bending mode of the PO_4^{3-} group. The observed phosphate signals indicate that a calcium phosphate layer was formed on the NaOH-treated substrates, which is in accordance with the obtained scanning electron micrographs and EDX profiles. After 4 days immersion in SBF, the ν_3 and ν_4-PO_4^{3-} peaks became more distinct. Additionally, a weak shoulder at wave number 963 $\mathrm{cm^{-1}}$ was determined, which was assigned to the ν_1 P–O stretching mode [10]. The presence of CO_3^{2-} groups at wave numbers at 1458/1420 $\mathrm{cm^{-1}}$ and 874 $\mathrm{cm^{-1}}$ was observed. The splitting of the carbonate peaks at 1458 and 1420 $\mathrm{cm^{-1}}$ is observed in all carbonate-containing, naturally occurring apatites [11]. After 24 days immersion, all peaks became more distinct and the transmission values decreased, indicating that the concentration of phosphate and carbonate groups increased. The infrared spectra obtained in the present study indicate the growth of a carbonate-containing calcium phosphate layer, which is similar to the chemical composition of biological apatite in the natural bone [11–13]. This indicates the continuous growth of the biological apatite layer with increasing immersion time. The IR bands at about 1620–1640 $\mathrm{cm^{-1}}$ can be attributed to adsorbed H_2O groups, which can also be observed in human enamel and precipitated apatites [14]. In accordance to IR spectra of bone mineral after removal of the organic phase [15], no infrared bands of OH-groups were observed, which

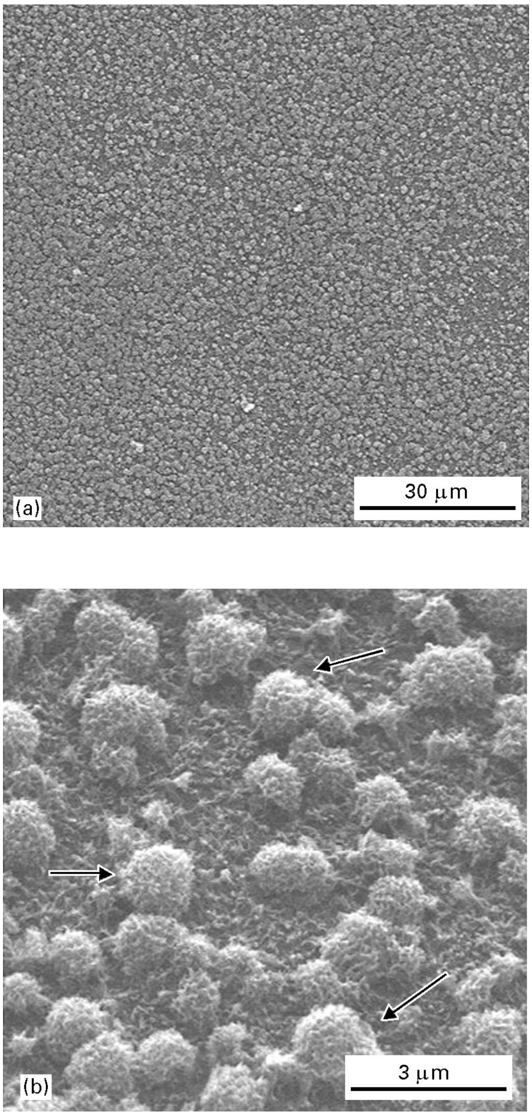

Figure 6 SEM image of a polished cpTi surface after 10 M NaOH treatment at 60 °C for 2 h and immersion in SBF at 37 °C for 1 day. In an overview (a) the formation of calcium phosphate precipitates occurred in a regular manner. In higher magnification (b), the spherulitic calcium phosphate precipitates are clearly recognizable (arrows).

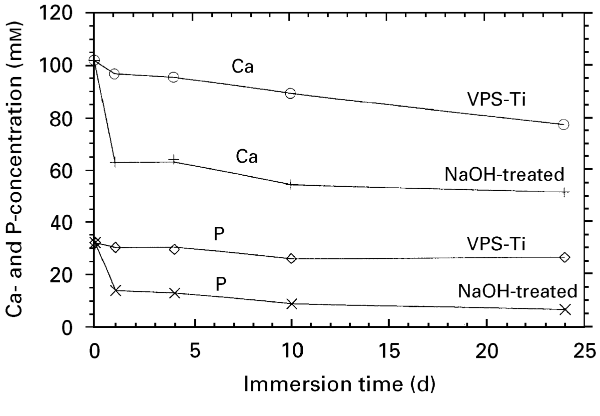

Figure 7 Calcium- and phosphorus-concentration of the untreated and NaOH-treated VPS-Ti coatings during immersion in SBF. Calcium- and phosphorus-concentration in the soaking solution was significantly reduced on the NaOH treated surfaces after 24 days immersion time. The untreated VPS-Ti coatings showed a much smaller reduction of calcium and phosphorus-concentration than the NaOH-treated specimens.

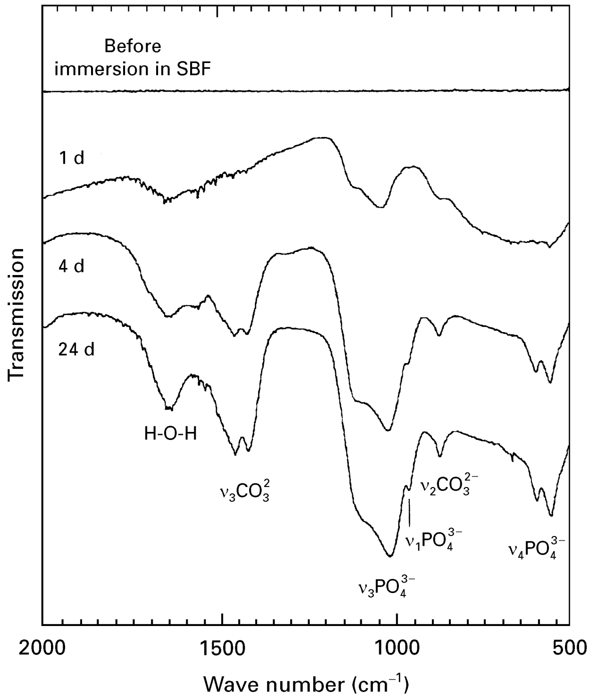

Figure 8 FT–IR spectra of VPS-Ti coatings on CF/PEEK after NaOH treatment and immersion in SBF at 37 °C, obtained in the diffuse reflectance mode. With increasing immersion time, phosphate and carbonate bands became more distinct indicating the continuous precipitation of a carbonate-containing calcium phosphate.

are situated at wave number 633 and around 3570 cm^{-1}, respectively [14]. Bone mineral is a carbonate-substituted apatite and it is therefore assumed that the hydroxyl sites are mostly replaced by carbonate ions.

4. Discussion

After treatment in 10 M NaOH at 60 °C for 2 h and subsequent immersion in SBF, the precipitation of calcium phosphate was observed on the modified VPS-Ti surfaces. EDX- and DRIFT analysis indicated that a biological apatite was formed during immersion in SBF. Two different mechanisms for the formation of biological apatite on NaOH-treated VPS-Ti coatings are suggested.

1. In alkaline solutions, dissolution of the oxide film of titanium surfaces was observed [16]. The rate of titanium oxide film dissolution was shown to be very sensitive to the concentration of alkaline solutions. The dissolution reaction of the TiO_2 film in alkaline solutions was proposed by Dudin and Kolotyrkin [17]

$$TiO_2 + OH^- \rightarrow HTiO_3^- \qquad (1)$$

Thus, after immersion of the titanium surface in NaOH, dissolution of the TiO_2 layer and corrosion could occur, resulting in the formation of an amorphous oxide layer and the formation of large pores (Fig. 2). This has also been observed [16] after immersion of an electropolished titanium surface in dilute solutions of potassium hydroxide. The authors suggested the presence of a large quantity of OH^- ions enclosed within this layer. Owing to the presence of OH^- ions, Ca^{2+} cations could diffuse into the amorphous oxide layer, which could be the initial step for the formation of calcium phosphate on the NaOH-treated VPS-Ti coatings.

2. In this study the formation of small fibrous structures was observed (Figs 1 and 2). The question arises, which chemical composition these crystallites have. Although the analysis of these structures was not the primary goal of the present study, the obtained results allow us to conclude that these structures consist of a sodium titanate modification. EDX spectra showed the formation of a sodium peak. The small amount of sodium could result from the formation of Na_2TiO_3 according to the following reaction

$$HTiO_3^- + 2Na^+ + OH^- \rightarrow Na_2TiO_3 + H_2O \quad (2)$$

The preparation of sodium titanate at low temperature with anatase-type hydrous titanium oxide and 10 M NaOH was reported by Clearfield and Lehto [18]. They showed the formation of needle-shaped crystallites of $Na_4Ti_9O_{20} \cdot x\ H_2O$ at temperatures below 280 °C. Therefore, some sodium titanate modification could be formed on the NaOH treated VPS-Ti surface. During immersion in SBF calcium phosphate formation could have occurred due to an ion-exchange process, since $Na_4Ti_9O_{20} \cdot x\ H_2O$ has a high ion-exchange capacity and all the Na^+ ions are exchangeable [18].

5. Conclusion

It has been shown in the present study that vacuum-plasma-spraying of titanium and subsequent chemical modification in 10 M NaOH at 60 °C for 2 h is a suitable method for the preparation of bioactive coatings on carbon fibre-reinforced PEEK. A carbonate-containing calcium phosphate, which has nearly the same morphology and chemical composition as biological apatite in natural bone, has been formed on the NaOH-treated VPS-Ti coatings during immersion in SBF. The VPS-Ti coatings show a very rough topography and thus a high surface area. This is assumed positively to affect the chemical modification of the titanium surface by NaOH treatment and the *in vitro* calcium phosphate deposition on the modified VPS-Ti surface.

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