Sol-gel synthesis of calcium phosphate coatings on Ti substrate using dip-coating technique

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The sol-gel chemistry route has been developed to prepare calcium phosphate / hydroxyapatite thin films on titanium substrate by dip-coating technique. The final composites were obtained by calcination of coatings for different time at 1 000 °C. It was shown that adjustment of heating time and dip-coating conditions can be used to control the synthesis processing, phase purity and morphology of thin films. It was concluded that the formation of calcium phosphate / hydroxyapatite composites in some cases is promoted by dipping time.

Key words: calcium phosphates, sol-gel chemistry, thin films, Ti substrate, dip-coating

INTRODUCTION

Calcium hydroxyapatite $(Ca_{10}(PO_4)_6(OH)_2$; CHAp) coatings have received considerable attention because they exhibit excellent biocompatibility, bioactivity and osteoconductivity [1–4]. CHAp coatings on different substrates (Ti-6Al-4V alloy, NiTi alloy, Mg, Ti, Si, steel) are being widely used in orthopaedics and dentistry [5–8]. Many preparation techniques are used currently in coating CHAp onto different substrates [9]. However, some metastable and amorphous phases appear in the CHAp coating with poor adhesion during the plasma spraying process, pulsed laser deposition or biomimetic processes [10–12]. The sol-gel methods are cost effective, low temperature routes for coating hydroxyapatite on various substrates [3, 9].

Sol-gel processing also provides a convenient method for applying tricalcium phosphate (TCP) films [13, 14]. Calcium phosphate ceramic is well known for its osteoinductive properties, good degradability, high hydrophilicity [15–18].

Calcium phosphate cements have been used in medical and dental applications for many years. For example, tricalcium phosphate is one of the major powder components of self-setting orthopaedic and dental cements [19]. However, the low strength and high brittleness of calcium phosphate cements prohibit their use in many stress-bearing locations, which would require an improvement in mechanical properties [20].

Calcium phosphate ceramics, which are commonly used as implants for bone reconstruction, appear to be good candidates for biocompatible drug carriers since they can be resorbed by cells and they promote new bone formation by releasing calcium and phosphate ions [21]. Drug-loaded polymers and calcium phosphate composites were also tested as cell and drug carrier materials [22, 23]. Recently calcium phosphate systems, including both hydroxyapatite and tricalcium phosphates (CHAp-TCP), have attracted significant interest as drug delivery vehicles. It was demonstrated that protein loading and release behaviour of CHAp-TCP can be controlled by tailoring particle size and surface area. The CHAp-TCP cement was suggested as a carrier for different

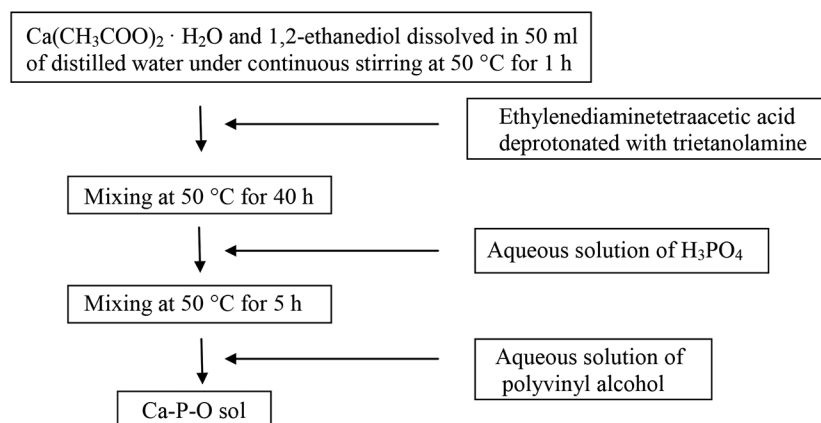* Corresponding author. E-mail: aivaras.kareiva@chf.vu.lt

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┌─────────────────────────────────────────────────┐
│ Ca(CH₃COO)₂ · H₂O and 1,2-ethanediol dissolved  │
│ in 50 ml of distilled water under continuous     │
│ stirring at 50 °C for 1 h                        │
└─────────────────────────────────────────────────┘
                    │        ┌──────────────────────────────┐
                    │ ◄──────│ Ethylenediaminetetraacetic   │
                    ▼        │ acid deprotonated with        │
          ┌──────────────────┐│ trietanolamine               │
          │ Mixing at 50 °C  │└──────────────────────────────┘
          │ for 40 h         │
          └──────────────────┘
                    │        ┌──────────────────────────────┐
                    │ ◄──────│ Aqueous solution of H₃PO₄    │
                    ▼        └──────────────────────────────┘
          ┌──────────────────┐
          │ Mixing at 50 °C  │
          │ for 5 h          │
          └──────────────────┘
                    │        ┌──────────────────────────────┐
                    │ ◄──────│ Aqueous solution of          │
                    ▼        │ polyvinyl alcohol             │
          ┌──────────────────┐└──────────────────────────────┘
          │   Ca-P-O sol     │
          └──────────────────┘
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Fig. 1. Schematical diagram used for the preparation of Ca-P-O sol

drugs, proteins and chemotherapeutic agents [24, 25]. Many preparation techniques were suggested for the preparation of CHAp-TCP films coating, such as microplasma spray, high-power ion beam ablation plasma, rf-magnetron sputtering or electrochemical/hydrothermal method [26–32]. In this paper we report on the sol-gel synthesis and characterization of CHAp-TCP thin films on the titanium substrate using the dip-coating technique.

EXPERIMENTAL

Aqueous sol-gel chemistry route based on phosphoric acid as the phosphorus precursor and calcium acetate monohydrate as the source of calcium ions have been developed to prepare Ca-P-O gel samples. These gels were used as precursors for the deposition of $Ca_{10}(PO_4)_6(OH)_2$-$Ca_3(PO_4)_2$ (CHAp-TCP) composites onto commercial titanium (Ti, 1.5×1.5) substrates by the dip-coating technique. In the sol-gel process, 2.6425 g of calcium acetate monohydrate, $Ca(CH_3COO)_2 \cdot H_2O$ (99.9%; Fluka), were dissolved in 50 ml of distilled water under continuous stirring at 50 °C and mixed with 2 ml of 1,2-ethanediol (99.0%; Alfa Aesar) for 1 h. To this solution 4.82185 g of ethylenediaminetetraacetic acid (EDTA; 99.0%; Alfa Aesar) were slowly deprotonated with 9 ml of triethanolamine (99.0%; Merck). After stirring at 50 °C for 40 h, appropriate amount of phosphoric acid, H_3PO_4 (85.0%; Reachem) was added to the above solution. Finally, after stirring at 50 °C for 5 h, 10 ml of 3% polyvinyl alcohol (PVA7200, 99.5%; Aldrich) solution was added. The obtained solution was stirred in a beaker covered with watch glass at the same temperature and was used for coating of Ti substrates. A schematical diagram for the preparation of Ca-P-O sol is presented in Fig. 1.

The dip-coating technique [33] was employed to produce sol-gel derived calcium phosphate coatings. The main stages of surface preparation of Ti substrate before coating are shown in Fig. 2. Titanium surface was polished with fine sandpaper till the surface became bright. After washing with acetone, ethanol and distilled water, the Ti substrates were storied in 5 M solution of NaOH at 60 °C for 24 h. Again, before dipping the substrates were washed abundantly with distilled water and finally dried in air. The standard immersing (85 mm/min) and withdrawal rates (40 mm/min) for dip-coating process (20 s) were applied for all the samples. The dipping procedure was repeatedly performed 5, 15 and 30 times. After evaporation of solvent the substrates were dried in an oven for 10 min at 110 °C and heated at 1 000 °C for 5 h with a heating rate of 1 °C/min.

For the characterization of surface properties, the X-ray powder diffraction (XRD) analysis, Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and the contact angle measurements were recorded. The FTIR spectra were recorded on a Perkin-Elmer FTIR Spectrum BX II spectrometer. The XRD studies were performed on a Rigaku miniFlex II diffractometer operating with Cu K_{a1} radiation (step size: 0.01, time per step: 0.06 s). In order to study the morphology and microstructure of the samples a scanning electron microscope Hitachi SU-70 was used. For the characterization of surface hydrophobicity of coatings, the measurements of a contact angle on an apparatus KVS Instrument CAM 100 were performed. A micro-droplet of water (volume 6 μl) was allowed to fall onto the sample from a syringe tip to produce a sessile drop.
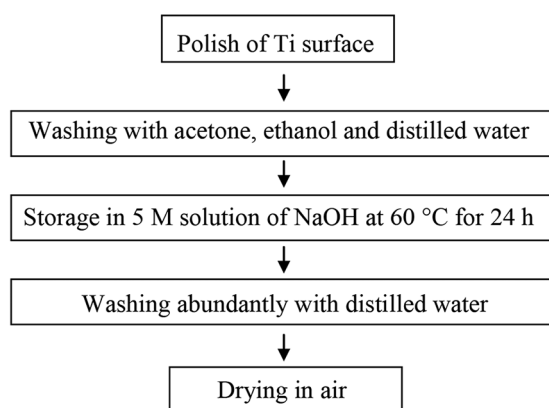
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          ┌─────────────────────┐
          │ Polish of Ti surface│
          └─────────────────────┘
                    │
                    ▼
┌───────────────────────────────────────────────┐
│ Washing with acetone, ethanol and distilled    │
│ water                                           │
└───────────────────────────────────────────────┘
                    │
                    ▼
┌───────────────────────────────────────────────┐
│ Storage in 5 M solution of NaOH at 60 °C for   │
│ 24 h                                            │
└───────────────────────────────────────────────┘
                    │
                    ▼
┌───────────────────────────────────────────────┐
│ Washing abundantly with distilled water         │
└───────────────────────────────────────────────┘
                    │
                    ▼
          ┌─────────────────────┐
          │   Drying in air     │
          └─────────────────────┘
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Fig. 2. The main stages of surface preparation of Ti substrate before coating

RESULTS AND DISCUSSION

Figure 3 represents the XRD patterns of films obtained from Ca-P-O gel using the dip-coating technique. As seen from Fig. 3, after the first immersing, withdrawal and annealing procedure the peaks attributable to the $Ca_{10}(PO_4)_6(OH)_2$ ($2\theta \approx 31.8$ and 32.2; PDF [9-432]), $Ca_3(PO_4)_2$ ($2\theta \approx 35.0$; PDF [18-303]) and CaO ($2\theta \approx 24.2, 29.8$ and 44.3; ICSD [028-0775]) crystalline phases are observed. The XRD diffraction pattern also contains very sharp diffraction lines attributable to TiO_2

(rutile; PDF [21-1276]) crystalline phase, and no formation of any traces of anatase (PDF [21-1272]) could be observed. The formation of TiO_2 during heat treatment of Ti substrate at elevated temperatures is very likely. The additional experiments evidently confirmed this assumption. Figure 4 shows XRD patterns of Ti substrates repeatedly heated at 1 000 °C for 5 h with a heating rate of 1 °C/min. As seen, the surface of Ti is fully converted to the rutile oxide phase after heating at 1 000 °C. According to the literature data, the formation of TiO_2 during the synthesis of CHAp thin films on Ti substrate usually also

Fig. 3. XRD patterns of the Ca-P-O gel samples annealed at 1 000 °C after each dipping procedure for 5 h in air. Diffraction lines are marked: * – $Ca_{10}(PO_4)_6(OH)_2$, + – $Ca_3(PO_4)_2$ and x – CaO. ? – unidentified
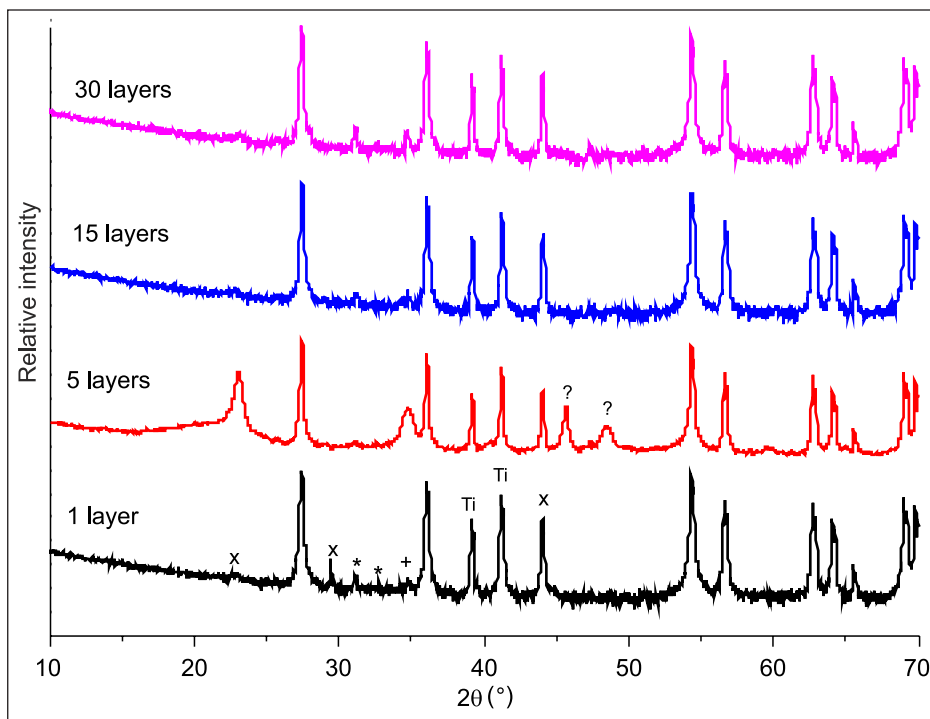
Fig. 4. XRD patterns of Ti substrates repeatedly heated at 1 000 °C for 5 h with a heating rate of 1 °C/min
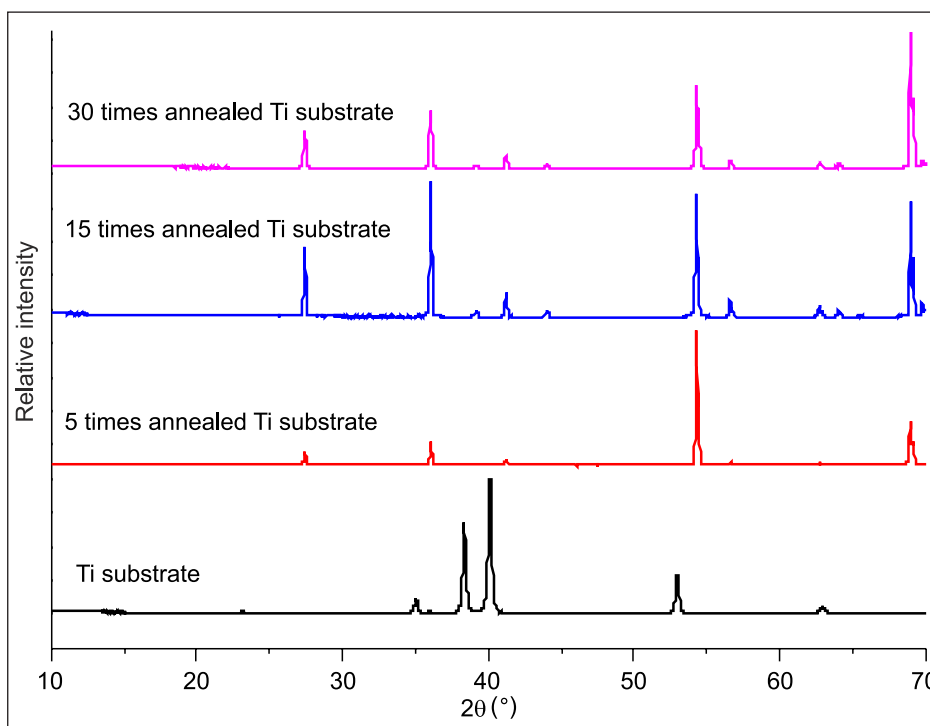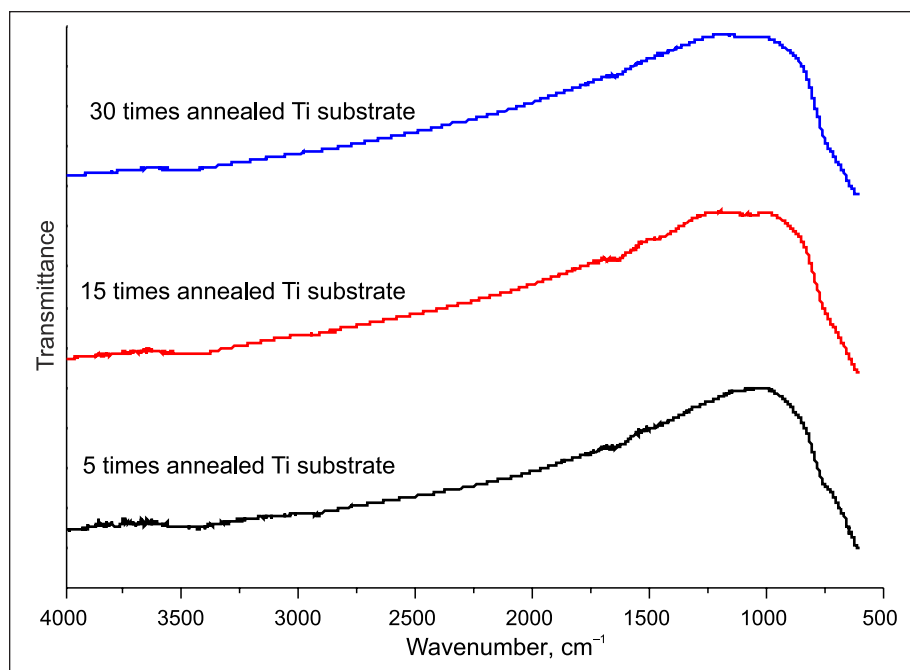
Fig. 5. FTIR spectra of Ti substrates repeatedly heated at 1000 °C for 5 h with a heating rate of 1 °C/min

proceeds [34, 35]. Apparently, characterization of Ti substrates repeatedly heated at 1000 °C using FTIR spectroscopy confirms the XRD analysis results (see Fig. 5). FTIR spectra of the Ti samples calcined at 1000 °C contain low intensity broad bands at 3450 cm^{-1} and 1610 cm^{-1}. The intensities of these bands, which could be assigned to the adsorbed water during the exposure of dried samples to air [36], remain unchanged with calcination temperature. In addition, there is a broad band at 1000–550 cm^{-1} which is assigned to the characteristic metal-oxygen (Ti–O) vibrations. Contrary to the non-coated substrates, the reflections of Ti substrate ($2\theta \approx 38.4$ and 40.2; PDF [44-1294]) are also visible in the XRD patterns of films obtained from Ca-P-O gel. Interestingly, the repetition of immersing, withdrawal and annealing procedures for 5, 15 and 30 times did not change the phase composition of coating dramatically. No characteristic peaks to other phosphate or titanate crystalline phases appear in the XRD patterns. However, such repeating slightly increased the intensity of peaks attributable to the phosphates. Thus, the suggested sol-gel chemistry route could be used for the preparation of CHAp-TCP coatings containing titanium dioxide onto Ti substrate. Surprisingly, these results demonstrate that the number of coating procedures do not influence the crystallization of calcium phosphate coatings.
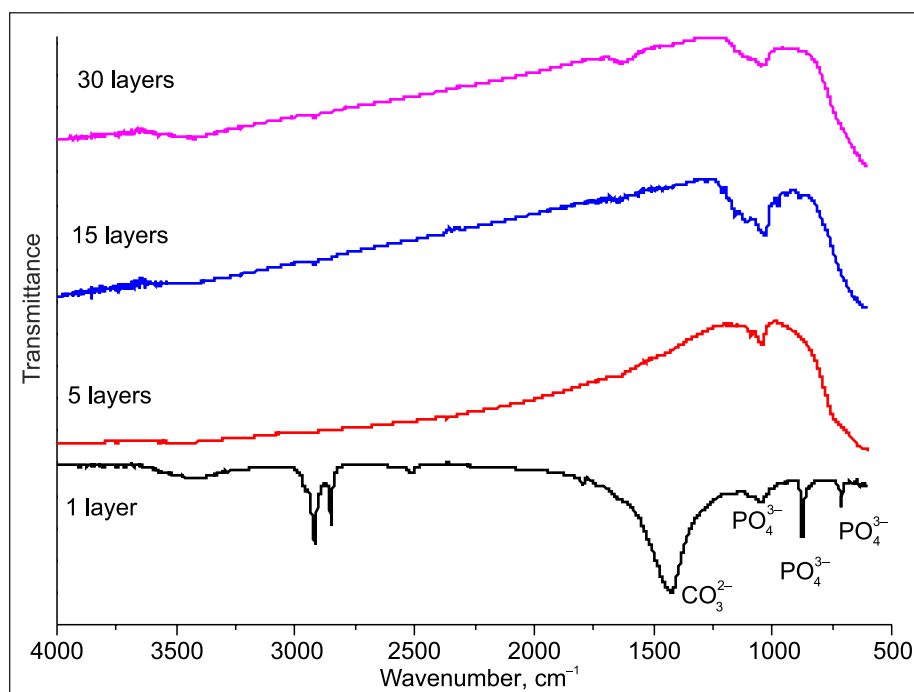

Fig. 6. FTIR spectra of the Ca-P-O gel samples annealed at 1000 °C after each dipping procedure for 5 h in air

The FTIR spectra of the corresponding films obtained from Ca-P-O gel using the dip-coating technique are presented in Fig. 6. In the spectrum of the sample obtained after one immersing, withdrawal and annealing procedure the peaks in the range of $1\,100–575$ cm^{-1} attributable to the P-O vibrations in PO_4^{3-} ($Ca_{10}(PO_4)_6(OH)_2$ and $Ca_3(PO_4)_2$) [37] are visible. The corresponding characteristic bands of stretching vibrations of CO_3^{2-} are at $\sim 1\,450$ cm^{-1} [38]. Also, very intensive peaks in the range of $3\,000–2\,250$ cm^{-1} could be observed in the FTIR spectrum of this sample. However, the origin of these vibrations is not clear. During long-range heating the peaks at $3\,000–2\,250$ cm^{-1} and $1\,450$ cm^{-1} disappeared. Besides, in all spectra the bands at $3\,450$ cm^{-1} and $1\,610$ cm^{-1} are visible as well. Therefore the FTIR spectra indicate the presence of phosphates in the samples.

The textural properties of different specimens were investigated by scanning electron microscopy (SEM). Figure 7 shows SEM micrographs (secondary electron images) of pure titanium substrates heated at $1\,000$ °C and obtained at different magnifications. As seen from Fig. 7, the surface of titanium substrate consists of the regular shaped crystallites with a size of $3–10$ μm. It is obvious that these grains are rhombohedral titanium dioxide crystallites formed during annealing of Ti substrate in air. The size of TiO_2 crystallites increases with increasing the duration of annealing. However, quite different surface morphology was determined for the sol-gel synthesized phosphate films on the titanium substrate. The SEM micrographs of the corresponding CHAp-TCP samples are displayed in Figs. 8 and 9. The SEM micrographs clearly show that already the first layer contains CHAp-TCP products which consist of aggregated spherical particles less than 300 nm in size. According to the SEM micrographs presented in Fig. 8 the coatings of 1 and 5 layers have similar structural characteristics. A progressive change in the morphology of specimens is evident with the increased immersing time. The formation of smaller and very homogeneously distributed spherical particles with an average grain size of 200 nm is evident for the coatings with 15 layers (see Fig. 9). The coatings of 30 layers have similar structural characteristics. However, the size of spherical particles increased significantly up to $0.6–0.8$ μm with increasing amount of the layers on the substrate. Finally, the micrographs of Ca-P-O gel calcined at $1\,000$ °C show highly uniform and crystalline particles with smooth surfaces. There are no macro cracks or pores. Therefore, the proposed sol-gel technique appears to be a very attractive way to make high density, homogeneous CHAp-TCP coatings on Ti substrate.

In order to estimate hydrophobic properties of the produced thin films the contact angle measurements (CAM) were performed [39]. Surprisingly, the hydrophobicity of CHAp-TCP films was found to be slightly dependent on the number of coating procedures. The representative results are presented in Table. As seen, the contact angle of the Ti substrate coated with 5 layers from Ca-P-O gel showed the highest contact angle ($\sim 35°$). The contact angle of specimens produced with 15 and 30 dipping times has very similar values
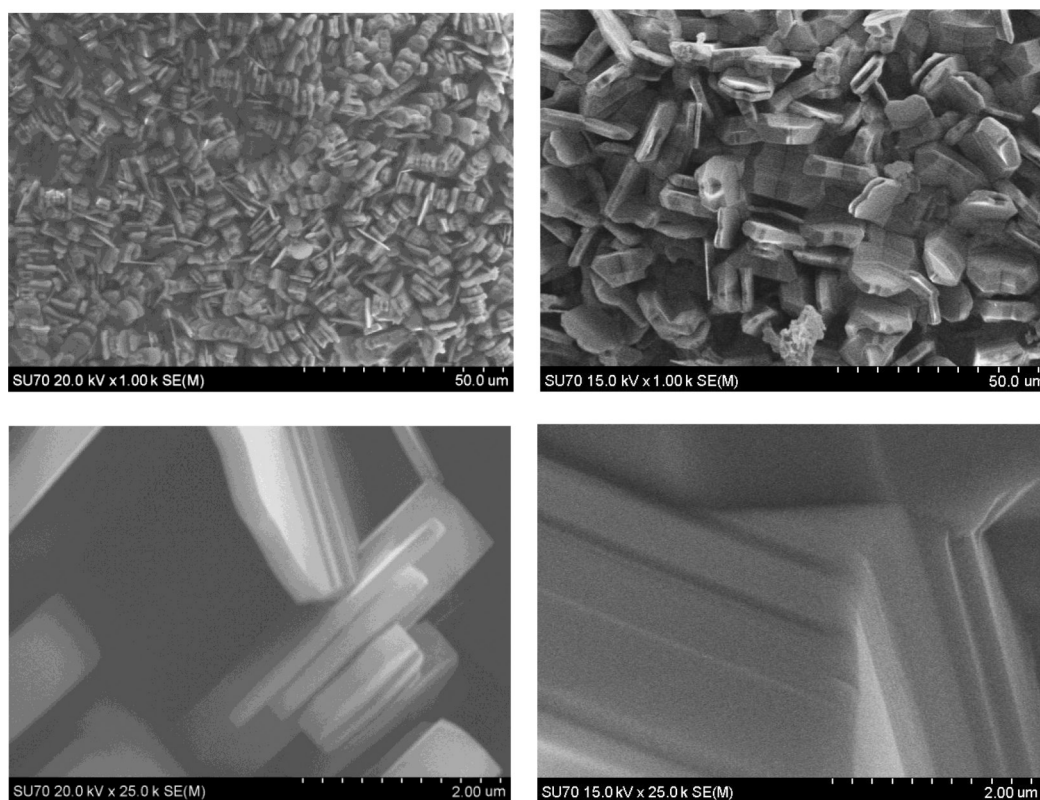

Fig. 7. SEM micrographs of Ti substrates repeatedly heated at $1\,000$ °C for 5 h with a heating rate of 1 °C/min: 5 times (at left) and 15 times (at right)
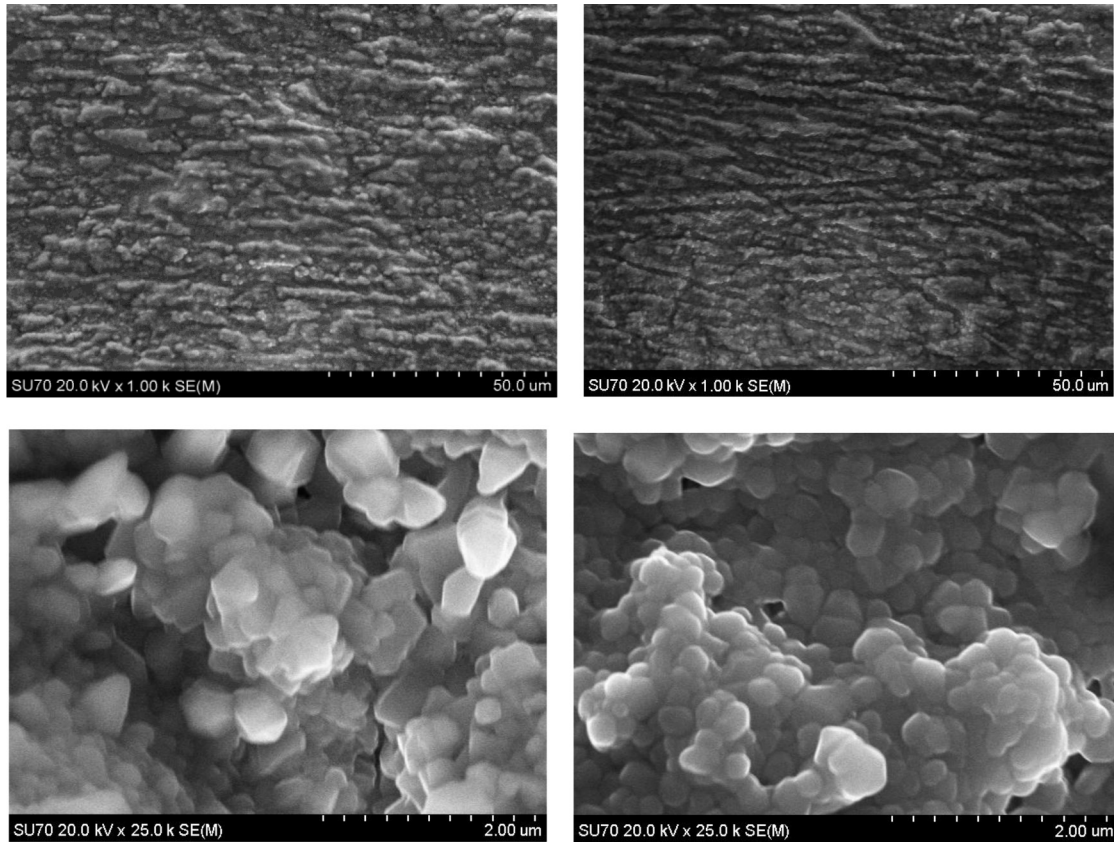
Fig. 8. SEM micrographs of samples containing 1 layer (at left) and 5 layers (at right)
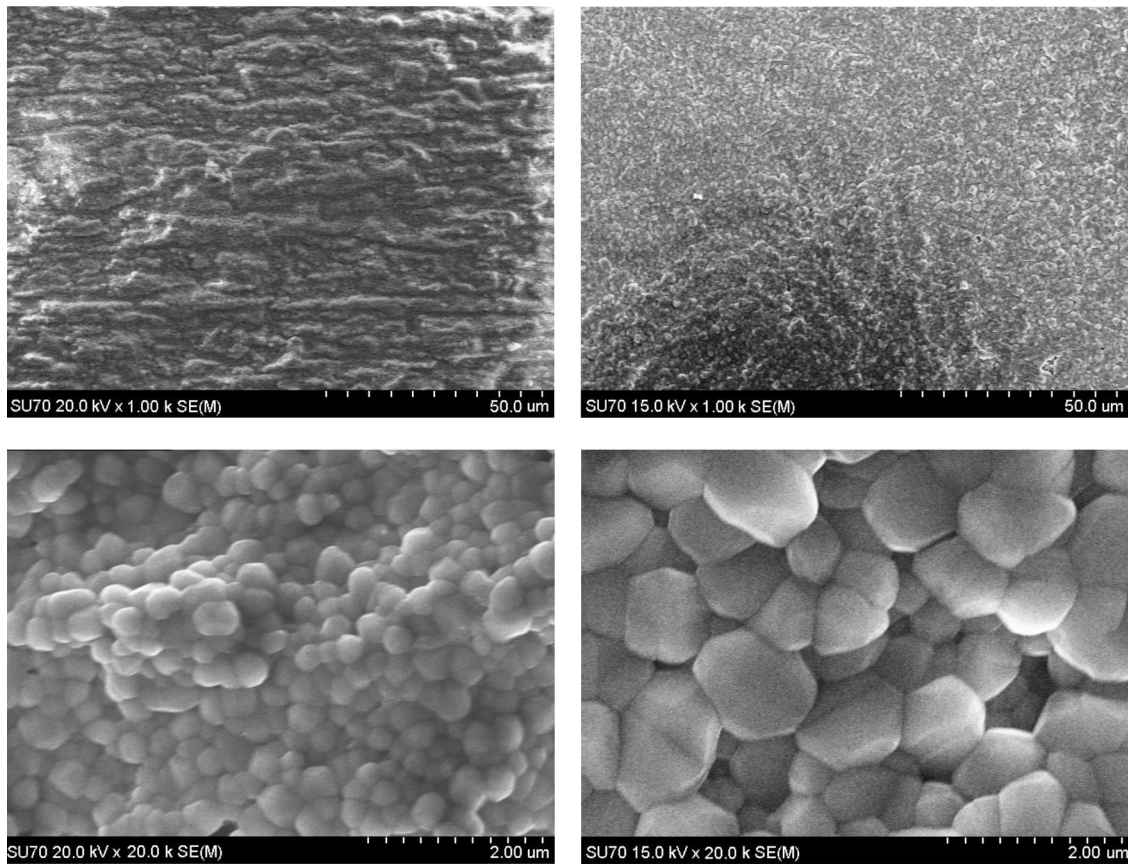

Fig. 9. SEM micrographs of samples containing 15 layers (at left) and 30 layers (at right)

Table. Surface properties measured by CAM on phosphate / hydroxyapatite samples deposited using different dipping times

Number of layers	Mean contact angle, degrees	Average surface tension, mN/m
0	67.2	
1	13.7(4)	27.9(6)
5	35.3(1)	64.6(9)
15	30.0(2)	26.9(1)
30	26.4(2)	11.3(1)

(~26–29°). The hydrophobicity of such films clearly should be dependent on the chemical composition of the coating. The composite materials containing the highest amount of the crystalline $Ca_{10}(PO_4)_6(OH)_2$ phase should be more hydrophilic as only calcium hydroxyapatite contains hydroxy groupings. Since the hydrophobic properties of the samples are relatively the same, the amount of $Ca_{10}(PO_4)_6(OH)_2$ and $Ca_3(PO_4)_2$ should be comparable. These results of contact angle measurements are in a good agreement with the results of XRD analysis.

CONCLUSIONS

A new sol-gel method for the preparation of calcium phosphate / hydroxyapatite thin films on titanium substrate using the dip-coating technique has been developed. For the first time to the best of our knowledge, it was demonstrated that an aqueous sol-gel technique is suitable for the formation of calcium phosphate / hydroxyapatite composite coatings containing $Ca_{10}(PO_4)_6(OH)_2$ and $Ca_3(PO_4)_2$. The XRD and FTIR measurements confirmed that the samples also contain TiO_2 (rutile). Interestingly, the repetition of immersing, withdrawal and annealing procedures for 5, 15 and 30 times did not change the phase composition of the coating dramatically. The SEM micrographs clearly showed that already the first layer contained CHAp-TCP products which consist of aggregated spherical particles less than 300 nm in size. The micrographs of Ca-P-O gel calcined at 1 000 °C show highly uniform and crystalline particles with smooth surfaces. There are no macro cracks or pores. The hydrophobic properties of thin films measured by CAM were associated with the phase composition of CHA-TCP coatings. Finally, the proposed sol-gel technique appears to be a very attractive way to make high density, homogeneous CHAp-TCP coatings on Ti substrate.

ACKNOWLEDGEMENTS

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KALCIO FOSFATINIŲ DANGŲ ANT Ti PADĖKLO SINTEZĖ ZOLIŲ-GELIŲ METODU NAUDOJANT PAMERKIMO TECHNIKĄ

S a n t r a u k a

Zolių-gelių metodu susintetintas Ca-P-O gelis, kuris panaudotas kalcio fosfato / hidroksiapatito ($Ca_3(PO_4)_2$ ir $Ca_{10}(PO_4)_6(OH)_2$) ploniems sluoksniams ant titano padėklo gauti. Infraraudonųjų spindulių spektroskopijos ir Rentgeno spindulių difrakcinės analizės tyrimų rezultatai patvirtino, kad, sintezę atliekant 1 000 °C temperatūroje, ant titano padėklo formuojasi ir TiO_2 (rutilas) fazė. Įdomu pažymėti, kad pamerkimo procedūrų kartojimas 5, 15 ir 30 kartų beveik neveikia dangų fazinės sudėties. Gautų junginių morfologija tirta skenuojančios elektroninės mikroskopijos metodu. Nustatyta, kad jau pirmą kartą pamerkus ir pakaitinus susidaro <300 nm dydžio sferinės kalcio fosfato / hidroksiapatito dalelės. Susiformuoja labai tolygios, neporėtos, be įtrūkimų, lygios dangos. Ištirtos kalcio fosfato / hidroksiapatito dangų hidrofobinės savybės koreliavo su nustatyta fazine sudėtimi. Rezultatai parodė, kad pasiūlytas zolių-gelių sintezės metodas yra labai patraukli technologija gauti tankioms ir homogeniškoms kalcio fosfato / hidroksiapatito dangoms ant Ti padėklo.