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Characterization of hydrothermal–electrochemical calcium titanate coatings on titanium and biomedical titanium alloy

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Abstract

Polycrystalline calcium titanate films up to 300 nm in thickness were grown on titanium and Ti6Al4V substrates by the hydrothermal–electrochemical technique in an autoclave at 200 °C. The films examined by x-ray diffraction exhibited reflections from orthorhombic calcium titanate on both substrates. The analysis by x-ray photoelectron spectroscopy showed calcium, titanium and oxygen at binding energies consistent with calcium titanate. The films grown on Ti6Al4V exhibited a small aluminium content but no vanadium. All films showed magnesium incorporation equivalent to a few per cent of the calcium content, which can be useful for the eventual use of the coating for biocompatible applications.

1. Introduction

Because of their mechanical properties titanium and titanium alloys are used as implant materials. However, titanium with its native oxide is a bioinert material, which is tolerated by the organism but not integrated [1]. There are several approaches to enhance the biocompatibility of the titanium surface. One of them is the direct coating of the titanium substrate with hydroxyapatite (HAp) by sol–gel [2, 3] and plasma spray [4]. However, a dominant concern is the dissolution of the coating. An alternative coating procedure was proposed by Kuroda *et al* [5]. They took advantage of the decreasing solubility of HAp with increasing temperature: a titanium foil immersed in a hydroxyapatite solution was heated by the Joule effect to a temperature higher than the surrounding solution, causing HAp to deposit on the substrate. This method seems difficult to apply to substrates of complex geometry.

A second approach has been the incorporation of calcium ions into the titanium substrate, under the hypothesis that calcium will enhance osteointegration. One method is sol–gel coating of titanium substrates with CaTiO_3 [2, 6]. Manso *et al* used sol–gel to deposit 4 μm thick amorphous CaTiO_3 films on silicon substrates, which crystallized after annealing at 800 °C. After immersion in simulated body fluid (SBF), the films exhibited microstructural changes. Kaciulis *et al* [2] used the CaTiO_3 as an intermediate layer to improve the adhesion of HAp to the substrate.

The hydrothermal–electrochemical preparation of perovskites on titanium metal was introduced by Yoshimura *et al* in 1989 [7]. Basically, a titanium foil immersed in a $\text{Ba}(\text{OH})_2$ solution is anodized under hydrothermal conditions, leading to a polycrystalline BaTiO_3 coating. It was later shown that solid solutions such as $(\text{Ca}, \text{Sr})\text{TiO}_3$ could be prepared on titanium substrates [8]. The use of a substrate with two metals leads to different results: a layered Ti–Zr substrate gave rise to a homogeneous $\text{Ba}(\text{Ti}, \text{Zr})\text{O}_3$ film after a pure hydrothermal treatment in $\text{Ba}(\text{OH})_2$, [9] whereas the hydrothermal–electrochemical treatment of a TiAl alloy in a $\text{Ca}(\text{OH})_2$ solution produced a CaTiO_3 film [10]. Hamada *et al* [11] treated titanium plates hydrothermally, i.e. with no electrochemical activation, in saturated $\text{Ca}(\text{OH})_2$ solutions without adding mineralizers at 121 °C. They reported XRD reflections from anatase but not from CaTiO_3 . XPS showed the Ca 2p photoelectron peaks of calcium at an energy near 347 eV, consistent with CaTiO_3 . The surface examined by scanning electron microscopy did not exhibit significant modifications. Their results are consistent with a very thin layer or an amorphous CaTiO_3 layer.

The hydrothermal and hydrothermal–electrochemical methods exhibit some distinct features: (a) comparatively low processing temperatures, (b) films are polycrystalline, not requiring further annealing, (c) the films present good adherence and (d) it is possible to coat substrates of complex geometry, even inside cavities. All of these features are desirable for eventual biomedical applications. In the present paper we report on hydrothermal–electrochemical CaTiO_3 coating on titanium and Ti6Al4V alloy.

2. Experimental details

The substrates were either titanium plates (99.6%, Goodfellow TI000430/21) or biomedical titanium alloy (Ti6Al4V, Goodfellow TI010500/8) plates cut to 10 × 10 × 1 mm. They were cleaned using acetone, ethanol and deionized water in an ultrasonic bath.

A saturated $\text{Ca}(\text{OH})_2$ (J T Baker, 97.8% and 0.3% of magnesium, Lot T08353) aqueous solution was prepared in hot deionized water, after boiling it to eliminate dissolved CO_2 . Thermodynamic modelling by Riman *et al* [12] of the hydrothermal synthesis of BaTiO_3 at 90 °C indicates that a pH larger than 11 is required to obtain the BaTiO_3 and the pH is even larger if the barium concentration is smaller. There are no similar studies regarding CaTiO_3 but, because of the chemical similarity a high pH might be required. Therefore excess $\text{Na}(\text{OH})$ was added as a mineralizer to the $\text{Ca}(\text{OH})_2$ solution until a pH near 13.5 was obtained. The hydrothermal–electrochemical (HE) process was performed at 200 °C, under a pressure of 2 MPa, generated by the water vapour itself. A dc current density 25–30 mA cm^{-2} was applied during 10–60 min, with an electrode separation around 15 mm. The work electrodes (anode) were both Ti and Ti6Al4V plates whereas a Ti6Al4V cathode was used as the counter electrode (figure 1).

The samples were characterized by x-ray diffraction (XRD) in a $\theta/2\theta$ Siemens D5000 diffractometer, using Cu $K\alpha$ radiation and a 0.02° scan step. X-ray photoelectron spectroscopy (XPS) was performed in a Physical Electronics 1257 system with hemispherical analyser. The measurements were performed using a pass energy of 44.25 eV and assisted with argon

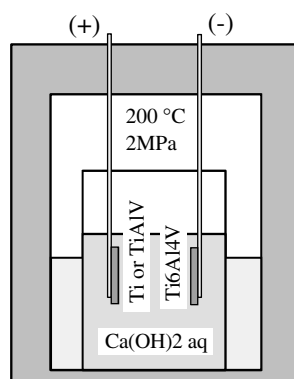


Figure 1. Experimental set-up.

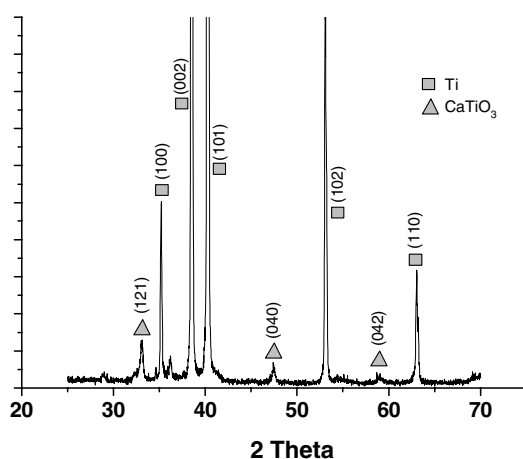


Figure 2. XRD pattern of a CaTiO_3 film on titanium.

erosion at 4 keV and $2 \mu\text{A}$ (estimated erosion rate around 2 nm min^{-1} in SiO_2). A Tencor surface profilometer (model Alpha-Step 500) was used to determine the surface roughness of the samples. A scanning electron microscope (SEM), model JSM-JEOL 6301F with field emission gun, was used to observe the surface morphology.

3. Results

The samples exhibited different colours (yellow, green and violet) depending on the substrate and the duration of the treatment. The colours are attributed to interference from films of different thicknesses.

The XRD analysis of the HE-treated samples exhibited a set of reflections from orthorhombic calcium titanate, CaTiO_3 , (JCPDS 22-0153), superimposed on the polycrystalline substrate, revealing the growth of a polycrystalline CaTiO_3 film, as shown in figure 2. The diffractograms obtained from films prepared on both substrates, titanium and Ti6Al4V , were similar.

The XPS analysis (figure 3) showed calcium, sodium, titanium, oxygen and magnesium on the titanium surface. The relative concentration of calcium, titanium and oxygen was similar to their concentrations in calcium titanate even after erosion to an estimated depth of 20 nm.

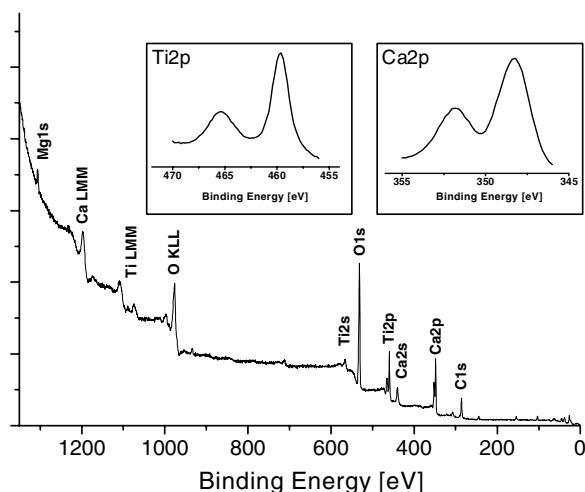


Figure 3. XPS spectrum of a CaTiO_3 film on titanium grown with a 30 min treatment. The insets are the high resolution $\text{Ti}2p$ and $\text{Ca}2p$ photoemission peaks.



Figure 4. SEM micrograph of a CaTiO_3 film on titanium.

The peak energies were consistent with Ca(II) , Ti(IV) , Mg(II) and oxygen as an oxide. The incorporation of magnesium, present as an impurity in the starting Ca(OH)_2 , estimated from the XPS measurements to be as high as 6%, is remarkable because of the low solubility of its hydroxide as compared with other alkali-earth hydroxides: 0.77 g l^{-1} for Ca(OH)_2 and 0.04 g l^{-1} for Mg(OH)_2 , both in hot water [13]. We do not know of any previous report on magnesium incorporation on CaTiO_3 hydrothermal films.

The SEM micrographs (figure 4) showed a microstructure with plate-like growth, and with a few star-like, calcium-rich, structures. A few rhombohedral crystals, identified as calcium carbonate, were observed on the surface. Some nanometre-sized pinholes, randomly distributed, were found in the CaTiO_3 coating (see the inset to figure 4). The film thickness was measured on cross sections of the samples, leading to values in the range from 100 to 300 nm CaTiO_3 , when the treatment time was increased from 10 to 60 min, respectively, see figure 5.

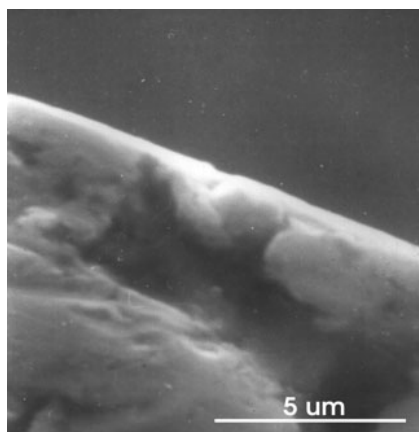


Figure 5. Cross section of a CaTiO_3 film on titanium. The thickness was around 300 nm.

Table 1. Measurements of average roughness parameters.

	Ti (μm)	Ti6Al4V (μm)	Ti/CaTiO ₃ (μm)	Ti6Al4V/CaTiO ₃ (μm)
R_a	4.0 ± 1.1	0.3 ± 0.1	5.2 ± 1.2	0.3 ± 0.1
R_q	5.4 ± 1.1	0.4 ± 0.1	6.8 ± 0.9	0.4 ± 0.1

Profilometry measurements showed different roughness parameters R_a (absolute roughness) and $R_{w(\text{rms})}$ values depending on the substrate used, see table 1.

4. Discussion

The behaviour of the electric current during anodization, performed under galvanostatic conditions, did depend on the substrate. On the titanium substrate it was difficult to maintain a constant current density, requiring periodic manual adjustment. This is probably due to the formation of a good insulating CaTiO_3 film. On the other hand, the electrical current was constant on the Ti6Al4V substrates during the process, indicating that this substrate is never completely sealed by the film. Consequently, the coating showed dramatic differences upon optical inspection. The green colour of the films grown on titanium was always homogeneous, but the films grown on Ti6Al4V exhibited different colours on the same sample (yellow to violet), indicating an inhomogeneous film. Since the mechanical properties of the Ti6Al4V are better than those of pure titanium [14], a good compromise between bulk and surface properties can be obtained by coating the Ti6Al4V substrate with titanium.

Hamada *et al* [11] used a similar procedure, but he did not find reflections from CaTiO_3 by XRD and their SEM micrographs did not show evidence of a film. The difference with the present work relies on three factors: we used a higher temperature (200 °C), a higher pH and electrochemical activation. Our own experiments performed under the same hydrothermal conditions with no electrochemical activation did result in calcium incorporation of an amount larger than in CaTiO_3 , rich in calcium carbonate at the surface. HE experiments below 100 °C resulted in the deposition of calcium carbonate but no CaTiO_3 . The localized hydrothermal method [15] also failed to grow CaTiO_3 , producing only calcium carbonate. Therefore, and contrary to BaTiO_3 , CaTiO_3 cannot be prepared on titanium under mild hydrothermal conditions.

The microstructure in the films, particularly the plate-like regions, indicates a growth habit parallel to the surface. This is different to the microstructure found in BaTiO₃ [7] and SrTiO₃ coatings [16], which normally exhibit a granular structure. The microstructure is also different to that reported by Yoshimura *et al* [10], who found cubic-shaped CaTiO₃ crystals around 1 μm in size after hydrothermal–electrochemical treatment of TiAl alloys in Ca(OH)₂ + NaOH. We do not know if this difference is caused by different preparation conditions or is related to the substrates.

An important finding is that the magnesium concentration in the CaTiO₃ films was around 6%. This is twenty times larger than the magnesium content of the starting Ca(OH)₂. It is also larger than the magnesium content in animal bones and therefore there is room to tailor the magnesium content in the film to match a value closer to it.

5. Conclusions

We have shown that the hydrothermal–electrochemical process at 200 °C and high pH is able to coat titanium as well as Ti6Al4V with orthorhombic calcium titanate. The film is more homogeneous on pure titanium. The absence of the vanadium photoelectron peaks on the CaTiO₃ film grown on the Ti6Al4V substrate and the magnesium incorporation in all cases could be beneficial for prospective biomedical applications.

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