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Application of the Berreman effect to the characterization of TiO2 thin layers formed onto titanium substrates

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Abstract

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) with polarized radiation is employed to characterize TiO_2 thin films thermally grown on Ti substrates, which exhibit the so-called Berreman effect. The DRIFT analysis of thin films in the context of the Berreman effect is simple and fast, and allows the identification of the crystalline/amorphous structure of TiO_2 thin layers even in the presence of other coatings, such as hydroxyapatite deposits, on top of the titanium oxide films.

Keywords: Titanium; Titanium oxide; Apatitic coatings; Infrared spectroscopy; Berreman effect

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1. Introduction

Titanium and titanium alloys are widely used in implants submitted to high biomechanical loads. Because the bone aposition process might be slow on titatium, bioactive ceramic coatings are deposited onto the titanium surface in order to accelerate this process. Calcium phosphates coatings, especially hydroxyapatite ones, promote spontaneous bone growth and implant fixation [Kodama et al. 2009, Chen et al. 2009].

Chemical and thermochemical treatments on Ti are usually employed to produce an oxidized layer, which improve the bioactivity of titanium pieces and have beneficial effects on a subsequent deposition of apatitic layers [Boon Sing Ng et al. 2005]. The characterization of the TiO_2 thin films by X-ray diffraction can be impaired by the thinness (typically in the order of hundreds of nm) of the oxide layer and the presence of the apatitic coating.

Infrared reflection absorption spectroscopy has been widely applied to characterize the surface and interface of thin films on metallic substrates [Zoppi et al. 2002, Trasferetti et al. 2004, Scarel et al. 2008], especially in connection with the so-called Berreman effect [Berreman 1963].

In this work, we present an infrared spectroscopic characterization of TiO_2 thin films formed on Ti specimens, which were subsequently coated with apatitic thick layers. This technique takes advantage of the Berreman effect, i.e. a split between vibrations parallel and perpendicular to the surface which take place on thin films (< 1 μm) and can be analyzed with polarized infrared radiation. As far as the authors are aware, Berreman effect has never before been exploited for the phase characterization of biomaterials.

2. Experimental

Plates of commercially pure titanium were polished with silicon carbide emery paper and then were subjected to different chemical treatments and thermochemical treatments. Samples were placed in 1.38 M HF and 1.97 M HNO_3 solution during 2 min at room temperature followed by soaking in 4.4 M H_2O_2 and 0.05 M HCl solution at 80 ºC for 30 min. Temperatures of 400 ºC and 800 ºC were selected for growing the oxide layer. Samples were treated at 400 ºC for 5 h and at 800 ºC for 10 min in air. Following activation treatments, apatitic coatings were deposited employing a biomimetic method. This method has been employed because of its simplicity and because it allows obtaining coatings with elemental and phase composition similar to that of the inorganic component of bone [Faure et. al. 2009, Mihranyan et.al. 2009]. Supersaturated calcium solution

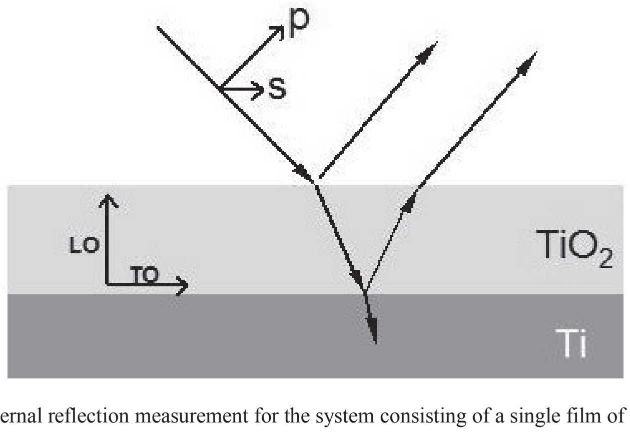

Figure 1. Schematics of the external reflection measurement for the system consisting of a single film of titanium dioxide on a semi-infinite substrate of titanium.

(SCS) was prepared dissolving 1110 mg of $CaCl_2$, 300 mg of NaH_2PO_4 and 126 mg of $NaHCO_3$ in 1 l of distilled water. Samples were immersed vertically into the solution at 37 ºC for 24 h.

The coatings were characterized by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) with *s*-polarized and *p*-polarized radiation. DRIFT spectra were collected using a Thermo 6700 spectrometer. A schematic representation of the reflection measurements is shown in Figure 1.

3. Results and discussion

The diffuse reflectance infrared Fourier transform spectra, obtained with *s*-polarized and *p*-polarized radiation, of Ti samples treated in an oxidizing atmosphere at 400 ºC and 800 °C are showed in Figure 2. A rather broad band at around 800-850 cm^{-1}, which can be attributed to TiO_2 vibration modes, is observed when *p*-polarized radiation is employed, but not when *s*-polarized radiation is employed. Additionally, a band around 480 cm^{-1} is observed for the Ti treated at 800 °C with *p*-polarized radiation. These facts can be explained in terms of the Berreman effect, and several important conclusions can be drawn from these spectra.

The Berreman effect is related to the occurrence of strong infrared absorption bands in thin flat films. They occur in transmission through films as well as when the films are deposited onto metallic substrates and appear at the frequencies characteristic of polar longitudinal optic modes of long wavelength in infinite crystals. The bands occur only when the incident radiation beam is not normal to the surface and only in the

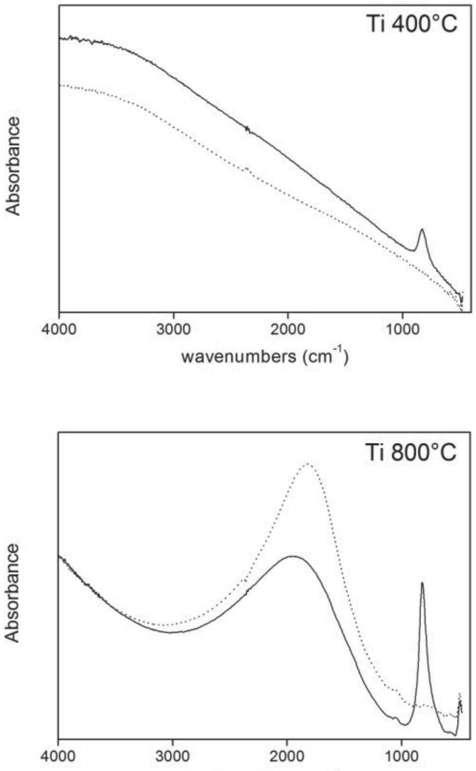

Figure 2. Diffuse reflectance infrared spectra obtained with *p*-polarized (full line) and *s*-polarized (dotted line) radiation of a Ti sample treated at 400 ºC (left) and 800 °C (right).

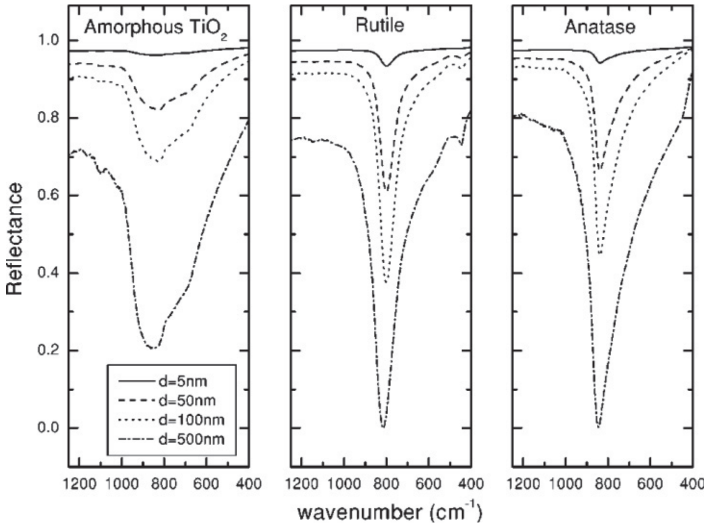

Figure 3. Simulated reflection-absorption spectra (*p*-polarization and an incidence angle of 70°) for a TiO_2/Pt system and four different film thickness. Taken from Trasferetti et al. 2001.

p-polarized component of the radiation. The Berreman effect can be employed to obtain information on the crystalline structure of the film, and in the next paragraphs we will summarize the main consequences of the Berreman effect for TiO_2 thin films [Trasferetti et al. 2001].

Two phonons can be distinguished in TiO_2 films thinner than 1000 nm: transverse optical (TO) and longitudinal optical (LO) modes. TO modes correspond to atomic vibrations parallel to the surface and LO modes correspond to atomic vibrations perpendicular to the surface. Polarized radiation interacts distinctly with these two modes. While normal-incidence radiation can only interact with TO vibrations, the *p*-polarized component of oblique incident radiation has subcomponents parallel and perpendicular to the film surface, which in addition to exciting the TO phonon, can also interact with LO vibrations (see Figure 1). The work carried by Trasferetti et al. is especially useful for the characterization of TiO_2 thin films taking advantage of this phenomenon, called the Berreman effect.

From materials characterization point of view, the results presented by Trasferetti et al. 2001 extracted from simulated and experimental spectra of TiO_2 thin films when *p*-polarized radiation is employed at a relative high incidence angle (typically 70º), can be summarized as follows:

α) For very thin films, only LO bands are observed in the infrared spectra, while TO band are not. For thicker films, both LO and TO bands are seen but LO bands continue to be predominant.

β) The position and the shape of LO bands with a maximum in the 800-900 cm^{-1} range depend on the crystalline structure of the TiO_2 thin films (Figure 3). Although there is a dependence of the absorbance maximum with the film thickness, the spectra still can be successfully used to identify the TiO_2 phases present in the film. Amorphous TiO_2 presents a broad and asymmetric band, which cannot be mistaken for the crystalline phases. Anatase and rutile bands are more symmetric and sharp.

χ) Only rutile presents a LO band at about 445 cm^{-1}. Since this band is absent in anatase and amorphous TiO_2, it can be employed as a way to confirm the presence of rutile in thin films.

- LO bands observed in the infrared spectra when *p*-polarized radiation is employed, disappear if *s*-polarized radiation is employed. Therefore, LO modes in TiO_2 thin films can be distinguished in a multilayer coating by acquiring infrared spectra with *p*-polarized and *s*-polarized radiation. This consequence of the Berreman effect will be exemplified later for Ti | TiO_2 | hydroxyapatite multilayers.

The infrared spectra shown in Figure 2 can be explained and analysed in the context of the Berreman effect, and several important conclusions can be drawn. Firstly, the film thickness must be less than 1000 nm for this effect to be observed. Secondly, the bandwidth and position is related to the crystalline structure; broad bands such as the one observed in the sample treated at 400 °C can only be attributed to amorphous TiO_2. On the other hand, the DRIFT spectrum of the sample treated at 800 °C presents two sharp bands at 821 and 480 cm^{-1}, that can be attributed to rutile LO vibration modes. DRIFT spectra analysed in the context of the Berreman effect revealed the presence of thin films of amorphous TiO_2 and rutile. It is worth noting that this information is not easily obtained by conventional X-ray diffraction because of the film thinness and the amorphous character of one of the coatings.

Figure 4 shows the diffuse reflectance infrared spectra obtained with *p*- and *s*-polarized radiation of a Ti sample treated at 400 ºC and 800 ºC followed by the deposition of hydroxyapatite. When *p*-polarized radiation is used, titanium oxide bands and hydoxyapatite bands can be seen in the spectra. However, when *s*-polarized radiation is employed, titanium oxide LO modes are no longer observed. This fact makes the identification of the TiO_2 crystalline/amorphous structure straightforward. Firstly, the bands corresponding to the LO modes of titanium oxide are recognized as the ones disappearing in the *s*-polarized radiation. Secondly, the amorphous structure can be distinguished because of its broad band. Otherwise, if the bands are sharp, they can be attributed to a crystalline structure. Finally, anatase and rutile can be distinguished because only rutile presents a LO band at about 445 cm^{-1}.

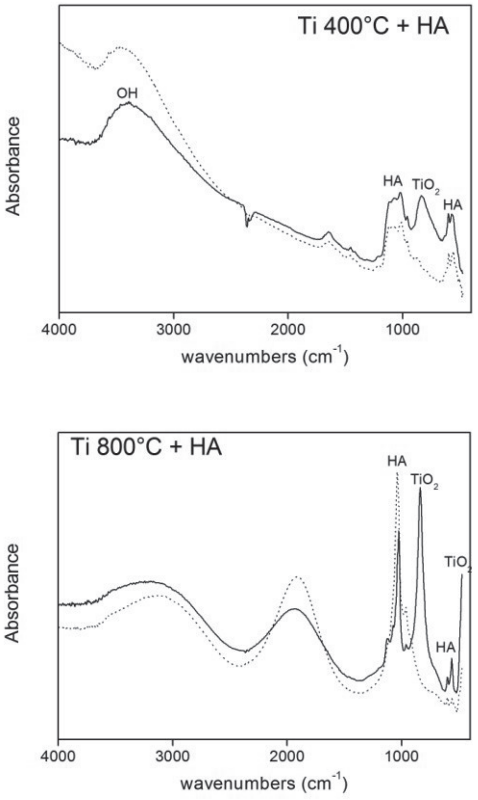

Figure 4. Diffuse reflectance infrared spectra obtained with *p*-polarized radiation of a Ti sample treated at 400 ºC (full line) and 800 ºC (dotted line), with a hydroxyapatite (HA) top coating.

4. Conclusions

The position and shape of the band provide information regarding the amorphous or crystalline structure of TiO_2 coatings. In particular, the presence of amorphous oxide (broad bands) and rutile (narrow bands at 825 and 425 cm^{-1}) are identified with a high degree of confidence. The DRIFT spectra are easy to obtain experimentally and the analysis of thin films in the context of the Berreman effect is also simple and fast, and can be exploited even in the presence of other films deposited on top of the titanium oxide films, as was shown with hydroxyapatite coatings. To our knowledge, this is the first attempt to characterize a multiplayer biomaterial such as Ti | TiO_2 | hydroxyapatite by exploiting the Berreman effect.

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