

# Formation and adhesion of biomimetic hydroxyapatite deposited on titanium substrates

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## Abstract

This study has been carried out to investigate the bioactivity of rutile and to deposit hydroxyapatite (HA) on heat-treated titanium through a biomimetic method. Biomimetic deposition of HA has gained large interest because of its low deposition temperature and good step coverage; however, it demands a substrate with bioactive properties. Commercially pure titanium is not bioactive but it can acquire bioactive properties through various surface treatments. In the present study, titanium plates were heat-treated at 800 °C to achieve rutile TiO<sub>2</sub> surfaces. These samples were immersed in a phosphate-buffered saline solution for seven days in order to deposit a HA layer on the surface. The rutile TiO<sub>2</sub> surfaces were found to be highly bioactive: after seven days of immersion, a layer of HA several micrometers thick covered the plates. The HA surfaces were confirmed by electron microscopy and X-ray diffraction. A scratch test was used to assess the adhesion of the HA coatings. This is a standard method to provide a measure of the coating-to-substrate adhesion and was found to be a useful method to test the thin HA coatings deposited on the bioactive surfaces. The critical pressure of the layer was estimated to be  $2.4 \pm 0.1$  GPa.

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*Keywords:* Hydroxyapatite; Bioactivity; Biomimetic deposition; Rutile; Adhesion

## 1. Introduction

It has been reported that titanium oxidized to the rutile phase is bioactive [1–3]. This is a property first discovered for certain ceramics such as Bioglass<sup>®</sup> and sintered hydroxyapatite (HA). Bioactivity is a desirable property for implants that are to be integrated into bone. A layer of bone-like apatite forms on a bioactive surface when it is implanted in vivo. This apatite layer chemically bonds to the bioactive surface and acts as an intermediate layer between new bone and the implant. Unprocessed titanium is not bioactive but is used as a material for implants because of its biocompatibility and its mechanical properties. The native oxide that spontaneously forms on the titanium surface in ambient air is amorphous, very thin (2–6 nm) and works as a passivating layer [4]. Crystalline

phases of TiO<sub>2</sub> occur naturally as rutile, anatase and brookite. Rutile is the thermodynamically stable phase of crystalline TiO<sub>2</sub> and can be formed on titanium by heat treatment. When rutile surfaces are exposed to body fluids, OH-groups adsorb to the titanium ions in the oxide [5]. The isoelectric point (IEP) of rutile is about 5.9 [6], which is lower than the pH of body fluids (~7.4). This leads to a deprotonation of the rutile surface and negative Ti–O<sup>−</sup> groups are formed over it. These negative sites attract Ca<sup>2+</sup> ions from the body fluid that bond to the surface [5]. A layer of amorphous calcium titanate is hence formed and the surface becomes slightly positively charged as the layer grows due to the Ca<sup>2+</sup> ions. It will then attract negatively charged phosphate ions, which bond to the surface, and a metastable phase of calcium phosphate is formed. This layer is then crystallized into bone-like apatite because it is thermodynamically more favourable for the amorphous calcium phosphate to adopt a crystalline structure in a wet environment [7,8]. Osteoblasts adhere to the

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apatite and produce a network of collagen fibres, which constitutes the organic phase of bone. This collagen network is mineralized by apatite and new bone is formed.

It is not fully understood why rutile is bioactive. The dissociation of water on rutile could explain the adsorption of OH-groups. However, this mechanism is controversial, and experimental and theoretical studies contradict each other [9]. Dissociation is a surface structure-dependent phenomenon and is often more regulated by the crystal structure than by the type of metal ions that are present at the surface [10].

To examine the bioactivity in this study, a biomimetic method was used. The bioactive substrate is exposed to an acellular solution with pH and ion concentrations similar to those of human blood plasma and HA is deposited on the surface due to differences in pH and IEP. The biomimetic method is a way to predict and to study how a layer of HA will form in vivo [11]. The method is also suitable for deposition of a HA coating on titanium oxide before implantation. Plasma spraying is currently the most common method for deposition of HA on orthopaedic implants; this has some disadvantages, such as poor step coverage and high deposition temperature, that may affect the substrate. The biomimetic method is an interesting alternative to plasma-spraying because it is a low-temperature process that reduces the risk of the coating flake off; it forms bone-like HA crystals with good bioactivity; it has good step coverage on implants; and it can incorporate bone-growth-stimulating factors.

Adhesion tests between biomedical coatings and substrates are normally performed using standard ASTM methods [12,13]. These methods can be briefly described as follows: a specific glue (FM 1000) with strength properties equal to 34.5 MPa is used to bond two coated plates to each other and then the breakage strength is measured. The method can determine a coating adhesion value, as long as this is below 34.5 MPa. Within the surface and coating community, scratch testing of coatings is a widely used method to determine coating adhesion and failure modes [14–16]. Scratch testing is normally performed under controlled conditions (increasing load and constant speed or vice versa, or both constant) via scratching of a coated surface with a specified indenter. A diamond-shaped indenter is usually used and from an exact knowledge of all test parameters and by a measurement of the critical load when the coating fails, the adhesion can be estimated. In this study, a spherical indenter was used to better mimic the actual strain that a coating deposited on an implant is exposed to when inserted into bone.

The objective of the present paper is twofold: (i) to study the formation of biomimetic apatite on rutile surfaces; and (ii) to measure the adhesion of the coating using a scratch test.

## 2. Materials and methods

Plates of commercially pure titanium  $25 \times 25 \times 0.5$  mm were oxidized in a furnace at 800 °C for 1 h in order to

Table 1  
Ion concentrations in blood plasma and Dulbecco's PBS [17] ( $10^{-3}$  M)

Ion	Blood plasma	PBS
Na <sup>+</sup>	142.0	145.0
K <sup>+</sup>	5.0	4.2
Mg <sup>2+</sup>	1.5	0.5
Ca <sup>2+</sup>	2.5	0.5
Cl <sup>-</sup>	103.0	143.0
HCO <sub>3</sub> <sup>-</sup>	27.0	–
HPO <sub>4</sub> <sup>2-</sup>	1.0	9.6
SO <sub>4</sub> <sup>2-</sup>	0.5	–
pH	7.2–7.4	7.1–7.5

transform the surfaces into rutile. Before the heat treatment, the plates were cleaned in an ultrasonic bath with acetone and ethanol. The furnace temperature was increased at 5 °C min<sup>-1</sup> until it reached 800 °C. Subsequently the temperature was held constant for 1 h before the furnace was turned off with the plates left in the furnace to cool slowly. Afterwards the plates were cleaned with an alkaline cleaning agent (Upon, pH 11.6) and ethanol in an ultrasonic bath before they were exposed to Dulbecco's 1 × /phosphate-buffered saline (PBS) [17], which was used to deposit HA. PBS is an acellular solution with a pH and ion concentrations similar to those of human blood plasma (Table 1). The plates were placed standing in plastic tubes with 40 ml preheated PBS in an incubator at 37 °C for seven days; the PBS was exchanged after three and five days, so that a lack of ions would not inhibit the coating process. Afterwards, the plates were gently rinsed in deionized water. Plates of untreated titanium were also exposed to the PBS for seven days for reference.

### 2.1. Analysis equipment

The surfaces and coatings were analysed using an X-ray diffractometer (Siemens Diffractometer D5000, Cu K $\alpha$ ) with a grazing incidence set-up, a scanning electron microscope (Leo 440) and a transmission electron microscope (FEI Tecnai F30 ST for imaging). Cross-section transmission electron microscopy (TEM) samples were produced using focused ion beam (FIB) microscopy (Strata DB235). Preparation of TEM foils using FIB microscopy has been described in detail elsewhere [18]. In brief, FIB microscopy uses Ga<sup>+</sup> ions either to image or mill samples; using the milling functions, thin foils can be fabricated to a very site-specific accuracy (of the order of microns). The foils are normally of the order of 10 × 20  $\mu$ m in size and about 100 nm thick.

A scratch test was used to estimate the adhesion of the coating/substrate composite (CSEM). The configuration used in this study was an Al<sub>2</sub>O<sub>3</sub> (alumina) ball that was drawn against the coating with an increasing load (from 0 to 100 N). The scratch velocity was 10 mm min<sup>-1</sup> and the load rate was 100 N min<sup>-1</sup>; thus, each millimeter equals a 10 N increase in load. The created scratch was studied in an optical microscope to obtain the critical load (length

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