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Thibodeau, Michel; Lima, Rogerio; Marple, Basil

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## Structural Study of Titania/Hydroxyapatite Biocompatible Coatings for Implants

Michel Thibodeau, Rogerio Lima and Basil Marple

National Research Council Canada, 75 de Mortagne Blvd., Boucherville, QC J4B 6Y4

Coatings on implants are a way of improving the mechanical strength and chemical stability of human prostheses and of providing surfaces that favour the formation of a strong bond between the prosthesis and the bone. Hydroxyapatite (HA) is widely employed as a material for coatings on orthopaedic implants and there are ongoing research activities focused on improving its performance for this application. To that end, titania ( $\text{TiO}_2$ ) and  $\text{TiO}_2$ -HA composite coatings were investigated. Three powders were sprayed on Ti-6Al-4V substrates using an HVOF (high velocity oxy-fuel) thermal spray system. The studied powders were  $\text{TiO}_2$  and  $\text{TiO}_2$ -based blends with 10% (by weight) and 20% HA added. The same deposition conditions, (i.e., similar in-flight particle temperature and velocity values) were used in order to focus the study on the nature of the coatings.

Titania and HA powders of similar size were used to prepare the blends. The morphology of the powders was observed with a field emission scanning electron microscope. The  $\text{TiO}_2$  powder (Fig. 1a) has a spherical shape, typical of that produced in the spray dried process. A higher magnification (Fig. 1b) shows the nanosize aspect of the primary particles, with an average diameter of 100 nm. The HA powder (Fig. 1c) also has a spherical shape and a closer look (Fig. 1d) shows the dense bond between primary particles (grain boundaries), confirming a sintering treatment after spray drying. A laser diffraction particle size analyser showed a diameter size range of 5 to 22  $\mu\text{m}$  for the three powders.

Cross-sections of the coatings produced by cutting, mounting, and polishing were observed with a field emission scanning electron microscope. Each of the three coatings had an average thickness of 200  $\mu\text{m}$ . The pure  $\text{TiO}_2$  coating (Fig. 2a) exhibits a uniform non-lamellar structure and is relatively dense. Blends of  $\text{TiO}_2$ -10 wt% HA (not shown) and 20 wt% HA (Fig. 2b) show that most of the HA phase (darker-coloured regions) is present in a lamellar form; however, there are also some spherically shaped zones arising from the incorporation of partially or non-molten particles. Porosity measurements, performed by image analysis using backscattered electron images, yielded an average value of 3% for the titania coating and less than 1% for both  $\text{TiO}_2$ -HA composite coatings. The as-sprayed top surfaces of the three coatings were also observed. Images of the composite coating of  $\text{TiO}_2$ -10 wt% HA (Fig. 3) clearly show the texture difference between titania and hydroxyapatite. An EDS Ca Ka map confirms the location of HA. The HA splats have a flat texture and a size of 20-30  $\mu\text{m}$ , whereas the  $\text{TiO}_2$  tends to be much finer. The characteristics of these surfaces could be very interesting for implants because of the well known stability of  $\text{TiO}_2$  in the human body, combined with the bioactivity of HA.

XRD measurements, performed using a theta-theta configuration diffractometer, indicated the presence of anatase and rutile phases in the  $\text{TiO}_2$  initial powder and as-sprayed coated sample. It was observed that exposure to the high temperature thermal spray environment caused a phase transformation resulting in an increased intensity in rutile peaks and a decrease in anatase peaks.

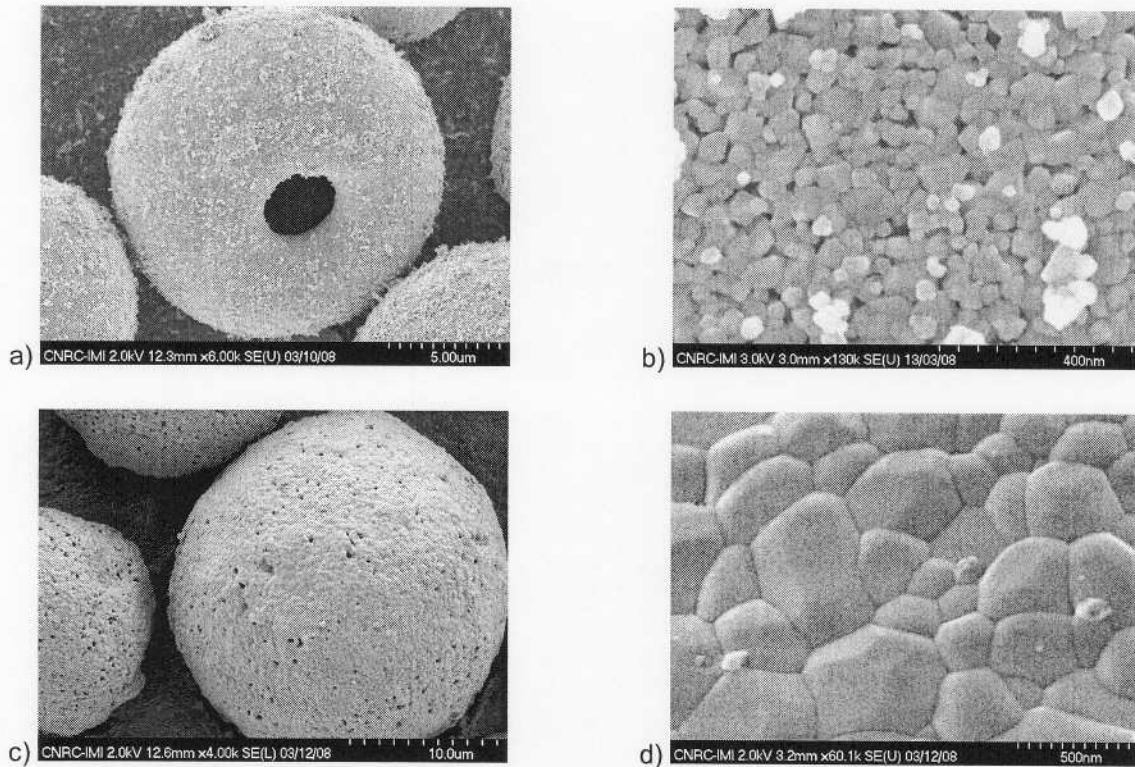


Fig. 1 SEM micrographs showing typical morphologies of starting powders: (a) and (b)  $\text{TiO}_2$ , (c) and (d) HA.

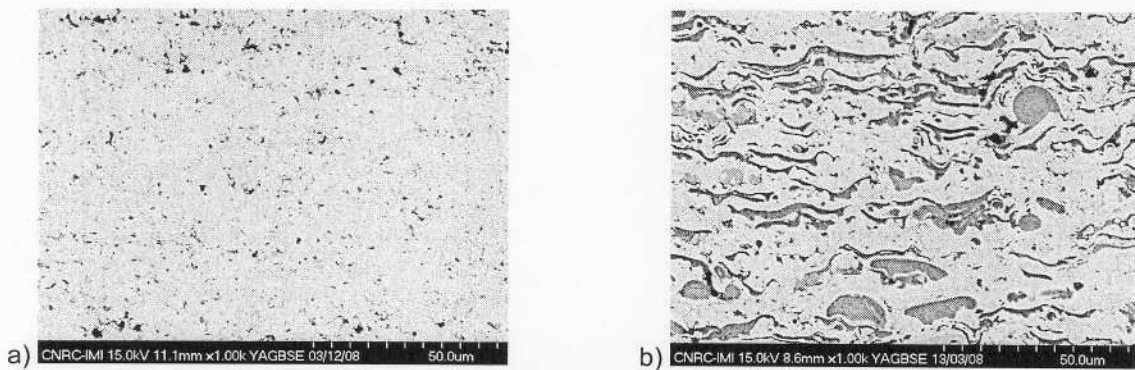


Fig. 2 Cross-section SEM micrographs of  $\text{TiO}_2$  (a) and  $\text{TiO}_2$ -20% HA (b) coatings.

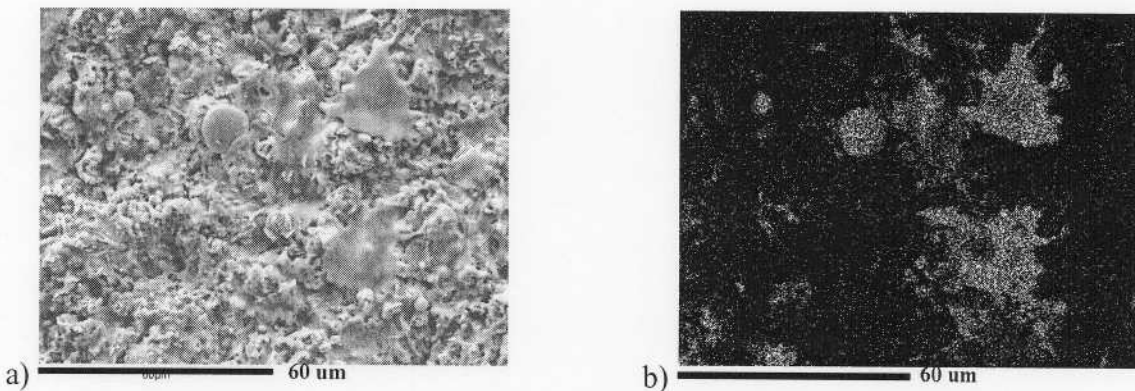


Fig. 3 Top surface SEM micrograph (a) and Ca Ka map (b) showing HA splats.