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Biomimetic Ceramic Surfaces Produced by Thermal Spraying Nanostructured Titania: A Coating Alternative to Hydroxyapatite on Orthopedic Implants?

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Abstract. There is an ongoing effort to improve the quality and performance of orthopedic implants. Part of this work involves the development of coatings suitable for use in the human body and having properties and bio-performance characteristics better than those of existing materials. The present study focused on developing thermal spray titania coatings engineered to have a bimodal structure consisting of a major fraction of micron scale dimensions within which were dispersed zones of nanostructured material. The coatings were found to exhibit much stronger adhesion to Ti-6Al-4V substrates than conventional hydroxyapatite coatings and to possess excellent crack propagation resistance characteristics. Cell culture studies indicated that human osteoblasts attached and proliferated well on the coating surface. The surface nano-features and nanostructured zones in the coating are believed to play an important role in the improved bonding, mechanical properties and bio-performance.

Introduction

Plasma sprayed hydroxyapatite (HA) coatings are widely used on certain orthopedic implant components to promote bone in-growth and bonding between the implant and surrounding bone and tissue. Despite the success of this approach, some studies of retrieved implants have raised questions concerning the long-term survival of these HA coatings. Specifically, dissolution and reabsorption can lead to a deterioration of the bond due to inadequate contact (weaker adhesion) in zones where the HA has been lost [1]. The mechanical performance of plasma sprayed HA coatings is also a concern; in particular, the properties are often variable and inconsistent and bonding of the as-sprayed coating to the metal substrate is relatively weak [2].

These questions concerning the long-term performance of HA are becoming increasingly relevant as changes in age demographics and life styles transform the age profile of patients requiring implants and increase the demands placed on orthopedic devices following implantation. In many developed countries there is an aging population, resulting from the "greying" of the baby boomer generation [3]. As well, improved access to medical treatment and health care is leading to increases in life expectancy. There also have been improvements in the level of education and standard of living, raising the expectations of senior citizens that they will remain active and have a good quality of life well into their later years. As a result, the medical community and biomaterials researchers are being challenged to find longer term solutions for replacing or repairing diseased, injured or worm-out joints in post-middle age patients. In younger patients, there is a need for similar solutions for treating orthopedic problems. These problems arise for a number of reasons, including a more sedentary life style and increased levels of obesity in some populations and injuries from sports-related activities and a more active life style in others. The present study focused on two aspects of coatings for orthopedic implant applications: (i) replacing HA with a biocompatible, non-absorbable material and (ii) engineering a coating with biomimetic features in the structure to improve the mechanical properties and help foster osteo-integration.

Materials and Methods

A nanostructured agglomerated titania (TiO_2) powder (Altair Nanomaterials, Nevada, USA) was used as the primary material for synthesizing coatings. Each agglomerate in the powder was comprised of nanosized particles having a size in the order of 30-50 nm. The coatings were deposited on Ti-6Al-4V substrates using high velocity oxy-fuel (HVOF) spraying (DJ2700, Sulzer Metco, New York, USA), a lower temperature and higher velocity thermal spray process than the air plasma spray technique normally used for producing bioceramic coatings. The coating structure was studied using a field emission scanning electron microscope (SEM) (Model S4700, Hitachi Instruments Inc., Tokyo, Japan) at high magnification. Bonding between the coating and substrate (adhesion) was assessed using a standard tensile test [4]. Resistance to crack propagation was investigated by indentation techniques using a Vickers pyramid indenter under a load of 5 kg. A stylus profilometer was employed for measuring the roughness of the coating in the as-deposited state. The bio-performance of the coating was evaluated by incubating human osteoblasts on the coating and using the MTT test to study cell proliferation. An air plasma sprayed hydroxyapatite coating was employed as the control. Briefly, the cell culture work involved using human osteoblasts produced from spontaneous miscarriage. These were cultured for three days in Dulbecco’s modified Eagle medium supplemented with 10% fetal bovine serum and 0.5% antibiotics under a humidified, 5% CO_2-95% air environment at 37ºC. These tests were run in triplicate and repeated at three different times per coating.

Results and Discussion

Micrographs showing the titania feedstock powder and a polished cross section of the resulting coating produced by HVOF spraying are presented in Figs. 1 and 2. The titania coatings were uniform, dense, near pore-free and exhibited a bimodal structure comprised of nanostructured zones distributed throughout a larger scale microstructure. This results from a portion of the internal nanostructure of the powder agglomerates being retained during thermal spraying and becoming embedded in the structure formed by the resolidifying molten particles. Such features in these titania coatings are quite different from the more porous, lamellar-type structure of typical APS-sprayed HA coatings, which are more microstructurally and compositionally heterogeneous. The lower temperature of the HVOF process (in contrast to the relatively high temperature characteristic of APS) plays a key role in engineering the bimodal structure using this nanostructured powder.

Comparison of the level of bonding of the HVOF-sprayed titania coating to the metal substrate with that of a HA coating produced by APS indicated superior adhesion for titania. The tensile tests showed the bimodal coating to have a bond strength of >77 MPa, more than twice the value found for the conventional HA coating produced by plasma spraying (Table 1). This value for the titania coating far exceeds the minimum recommended level required by some standards for coatings used on implants [10]. Because titania is stable in the body, it is not expected to exhibit the decrease in bond strength that can arise from reabsorption and dissolution of phases present in HA coatings.

The titania coatings had a roughness (R_a) of 2.22 ± 0.33 μm in the as-sprayed state. This is significantly lower than the typical value of 6-10 μm reported for APS-sprayed HA coatings [6, 11]. This outer coating surface is very important because it is the material in immediate contact with the bone and tissue following implantation. It is on this surface where bonding between the implant and the body will initially occur. High magnification images of regions of the as-sprayed titania coating surface are presented in Fig. 3. These SEM micrographs reveal a nano-topography and nano-proturberances. Research by others has identified the potential advantage of using nanostructured surfaces to foster strong bonding between the coating and bone [12].

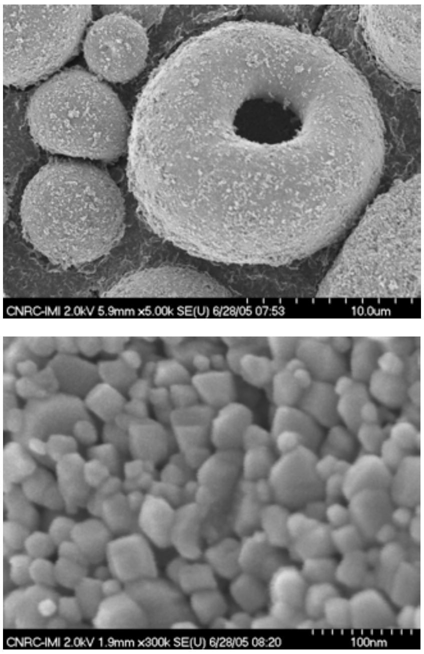

Fig. 1. SEM micrographs of the starting titania powder showing agglomerate morphology and nanostructure.

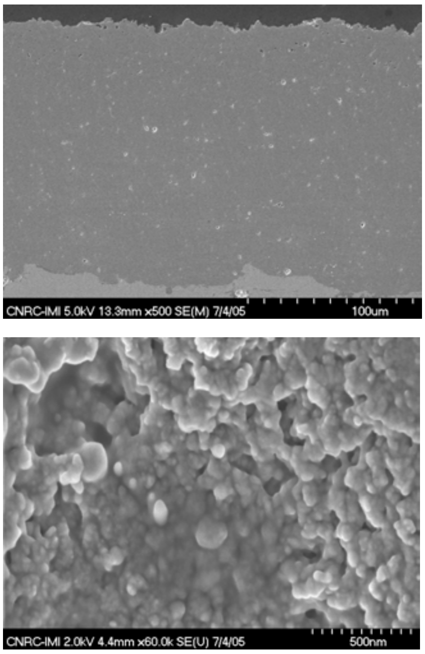

Fig. 2. Microstructure and nanostructure of a polished cross-section of the bimodal titania coating.

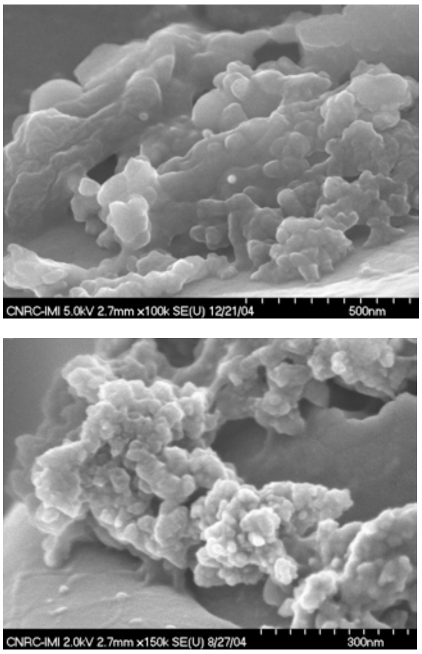

Fig. 3. Images of the as-deposited titania coating surface showing nanograins, nanoparticles and nanopores.

Table 1. Bonding strength of coatings on Ti-6Al-4V.

Coating	Feedstock*	Process	Bond strength (MPa)
TiO_2	N	HVOF	>77
HA	C	APS	13-31 [2, 5-7]
HA	C	HVOF	31 [8]
HA	N	HVOF	24 [9]

*N - nanostructured; C – conventional

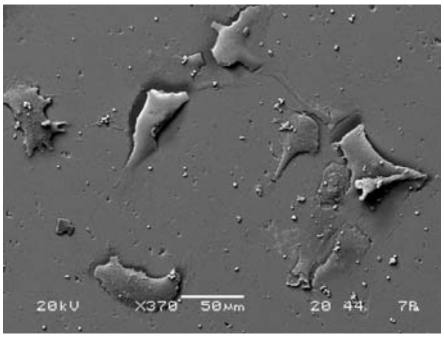

Fig. 4. Micrograph of human osteoblast cells proliferated on a bimodal titania coating after a three-day incubation.

The indentation studies in which the bimodal titania coating was compared to a conventional titania coating produced by APS revealed differences in performance. The indentation loads used in this work resulted in cracks forming at the four corners of the indents. As reported elsewhere [13], there were differences in the relative lengths of the four cracks emanating from the corners of the indent for the two coatings. It was found that the ratio of the length of the crack parallel to the substrate to that of the perpendicular crack was much closer to 1 for the bimodal coating than for the conventional APS coating. This type of performance is more typical of that observed in bulk materials and indicates that the properties of the biomodal coating are probably more isotropic. A second aspect to note was the length of the cracks running parallel to the substrate surface in the two coatings. The crack in the bimodal coating was substantially shorter than in the APS titania coating, suggesting a greater crack propagation resistance. Calculations indicated a crack propagation resistance parameter for the bimodal coating more than 1.5 greater than for the conventional coating. This result has been discussed in earlier work where it was suggested that the nanostructured zones in the coating play a role in contributing to the increase in crack propagation resistance [13]. Such behavior is attractive since it provides a mechanically robust, tough coating less prone to delamination, a feature important for coatings on implants.

The cell culture studies revealed that human osteoblasts attached and proliferated well on the surface of the titania coating. An example of this is shown in Fig. 4. Preliminary results from the MTT test indicated a cell growth rate after three days that compared favorably with that on conventional HA. This result is important because it is an indicator of the short-term performance of a coated implant and the rate of patient recovery following surgery. More extensive evaluation, including tests using animal models, is required to further assess the performance of these coatings.

A key feature of these coatings is the nano-topography and nano-features at the surface (Fig. 3). It is believed that these serve as anchors for proteins such as vitronectin and fibronectin and promote protein adhesion and cell bonding. Work by others has reported increased osteoblast function and bonding on nanostructured titania and attributed such behaviour to the nanoscale of the structure, which mimics that of actual human bone [14]. Increased protein adhesion and cell bonding should lead to stronger bonding between the coating and the surrounding bone, which, when combined with the long-term stability of titania, superior mechanical performance and increased bonding to the substrate, should provide for a better performing system for orthopedic implants.

Conclusion

The titania coating developed in this work possessed several attributes that make it attractive as a candidate for replacing HA on orthopedic implants. A biomimetic surface structure, superior bonding to the substrate, and crack propagation characteristics that suggest improved toughness are all attractive features. Growth and proliferation of human cells on the coating indicated that bonding with bone and tissue would be expected. The bimodal structure of the coating is considered to play an important role in improving the mechanical properties and fostering cell growth. The nanostructured regions and nano-topographical features that mimic those found in bone are believed to promote protein adhesion and bonding of the cells to the coating. The combination of improved mechanical properties, excellent potential for strong bonding with bone and expected long-term survival in the body make this coating a very promising candidate for use on orthopedic implants.

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