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Biocompatible Nanostructured High-Velocity Oxyfuel Sprayed Titania Coating: Deposition, Characterization, and Mechanical Properties

R.S. Lima, H. Li, K.A. Khor, and B.R. Marple

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Nanostructured titania (TiO_2) coatings were produced by high-velocity oxyfuel (HVOF) spraying. They were engineered as a possible candidate to replace hydroxyapatite (HA) coatings produced by thermal spray on implants. The HVOF sprayed nanostructured titania coatings exhibited mechanical properties, such as hardness and bond strength, much superior to those of HA thermal spray coatings. In addition to these characteristics, the surface of the nanostructured coatings exhibited regions with nanotextured features originating from the semimolten nanostructured feedstock particles. It is hypothesized that these regions may enhance osteoblast adhesion on the coating by creating a better interaction with adhesion proteins, such as fibronectin, which exhibit dimensions in the order of nanometers. Preliminary osteoblast cell culture demonstrated that this type of HVOF sprayed nanostructured titania coating supported osteoblast cell growth and did not negatively affect cell viability.

Keywords biomedical coating, bond strength, hardness, hydroxyapatite, nanostructured TiO_2

1. Introduction

1.1 Current Concerns Regarding the Long-Term Performance of Hydroxyapatite Coatings

Hydroxyapatite (HA) coatings deposited by air plasma spray (APS) are routinely applied on metallic hip-joint implants to promote the fixation of the implant to the bone (Ref 1). This is one of the most common methods to promote this fixation. APS HA coatings are a success, and they may be considered the state-of-the-art for the current standards. Despite this success, there are still concerns regarding the long-term performance of the APS HA coatings, that is, the stability of the HA in the human body. Hydroxyapatite is a material that exhibits low values of mechanical strength and toughness. In addition to that, it is widely known that HA coatings exhibit dissolution and are affected by osteolysis in vivo (Ref 2). This dissolution and/or osteolysis may lead to a weakening of the coating. In fact, reports in the medical literature show that the rate of aseptic loosening and/or osteolysis of HA-coated implants can be high, mainly for the acetabular cup. According to Reikeras and Gunderson (Ref 3), after 10 years postoperation 20% of the HA-coated acetabular cups in patients in their study were revised due to aseptic loosening and/or osteolysis. Blacha (Ref 4) observed a failure rate of 23% of the HA-coated acetabular cups, caused by aseptic loosening and/or osteolysis, after an average of six years post-implantation. In a study by Lai et al. (Ref 5), 18% of the HA-coated acetabular cups exhibited aseptic loosening and/or osteolysis after an average of 10 years postimplantation. Lai et al. (Ref 5) demonstrated that there is a strong correlation between aseptic loosening and/or osteolysis and the residual amount of HA coating covering the implant. Other factors contribute to the concerns toward the long-term performance of HA coatings. The resorption/dissolution of HA is significantly accelerated during loading (Ref 6), which is not a desirable characteristic if a hip joint is implanted in young and active patients. Due to these factors it is thought that the introduction of a nonabsorbable coating, with excellent mechanical performance and nanostructural characteristics may be an interesting alternative to replace APS HA coatings in implants for young and active patients, as is discussed in the next section.

1.2 Enhanced Mechanical Properties and Biocompatibility of Nanostructured Materials

It has been demonstrated that the mechanical performance of titania thermal spray coatings made from nanostructured powders is superior to that of conventional titania thermal spray coatings (Ref 7, 8). Nanostructured and conventional titania powders were thermally sprayed via APS, vacuum plasma spray (VPS), and high-velocity oxyfuel (HVOF). The HVOF sprayed titania coatings made from the nanostructured feedstock exhibited (a) the highest abrasion resistance, (b) the highest slurry-wear resistance at 30° impact angle, (c) the highest slurry-wear resistance at 90° impact angle, (d) the highest bond strength, (e) the highest ductility, and (f) the highest relative toughness when compared with all other nanostructured and conventional titania thermal spray coatings (Ref 8). Therefore because of (a) the superior

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mechanical performance of the HVOF sprayed titania coating made from the nanostructured feedstock, (b) the nontoxicity and nondissolution of the titania by the human body, and (c) the possibility of producing nanotextures on the surface of the coatings, it is thought that this type of coating could be a good candidate to replace APS HA coatings on implants, mainly for younger patients. These characteristics could lead to engineering a coating with a successful long-term performance and stability.

It has been demonstrated that nanostructured ceramics, such as, alumina, titania, and HA exhibit higher osteoblast cell proliferation and adhesion (in vitro) when compared with their conventional counterparts (Ref 9). Webster et al. (Ref 9) explained this better performance of the nanostructured material as the effect of the nanotexture or nanoroughness of these materials on the adsorption of the adhesion proteins such as vitronectin and fibronectin. These types of proteins mediate the adhesion of anchorage-dependent cells (such as osteoblasts) on substrates and coatings (Ref 9). These adhesion proteins are initially adsorbed on the surface of an implant almost immediately upon its implantation in the human body. When the osteoblast cells arrive at the implant surface they "see" a protein-covered surface that will connect with the transmembrane proteins (integrins) of the osteoblast cells. It is important to point out that these proteins, such as vitronectin and fibronectin, exhibit nanosized lengths and structures. It is interesting to note that the surface of a nanostructured material (nanosized grains) will exhibit nanocharacteristics, such as nanoroughness, whereas the surface of a conventional material (microsized grains) will exhibit microcharacteristics. It was proven that the interaction or the adsorption of a nanosized protein (e.g., vitronectin and fibronectin) to a nanotextured surface will be more effective than that provided by a microtextured one (Ref 9). Therefore, the use of a nanostructured coating, containing regions on its surface exhibiting nanotexture (nanoroughness), seems to be an interesting method to improve the adhesion of the osteoblast cells on the coating, contributing for a better long-term performance of the implant.

The objective of this work was to engineer a biomedical coating to exhibit high mechanical and biological performances. This study deals primarily with coating deposition, microstructural characterization, and mechanical property evaluation in comparison to that of HA coatings. Detailed information about in vitro testing in which the biocompatibility of this HVOF sprayed nanostructured titania coating was evaluated using a cell culture with osteoblast cells and compared with that of an APS HA coating can be found in a companion paper contained in this volume (Ref 10).

2. Experimental Procedure

2.1 Nanostructured Titania Feedstock and HVOF Spraying

The nanostructured titania feedstock used in this work (VHP-DCS, 5 to 20 μm), (Altair Nanomaterials Inc., Reno, NV) exhibited a nominal particle size range from 5 to 20 μm. The feedstock powder was thermally sprayed via the HVOF technique using an oxypropylene based torch (Diamond Jet 2700-hybrid, Sulzer Metco, Westbury, NY). The coatings were deposited on Ti-6Al-4V substrates that had been grit blasted to roughen the surface before spraying. Initially during HVOF spraying (before coating deposition), the velocities and temperatures of the titania particles in the spray jet were measured using a diagnostic tool (DPV 2000, Tecnar Automation, Saint Bruno, QC, Canada). The diagnostic tool is based on optical pyrometry and time-of-flight measurements to measure the distribution of particle temperature and velocity in the thermal spray jet. A total of 5000 particles were measured at the centerline of the thermal spray jet, where the particle flow density was the highest. The particle detector was placed at the same spray distance as used when depositing the coatings, that is, 20 cm from the torch nozzle. During the spraying process on the Ti-6Al-4V substrates, a cooling system (air jets) was applied to reduce the coating temperature, which was monitored using a pyrometer. The maximum surface temperature was approximately 240 °C.

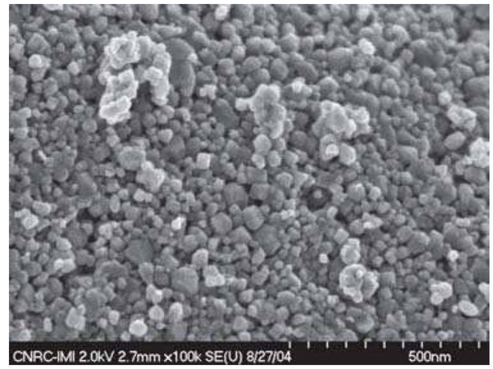


Fig. 1 Individual nanostructured titania particles agglomerated via spray drying

2.2 Nano- and Microstructural Characterizations

The nanostructural and microstructural features of the feedstock and HVOF sprayed coating were evaluated via scanning electron microscopy (SEM). X-ray diffraction (XRD) (Cu-Kα radiation) was used to determine the phases present in the titania feedstock and coating. A 2θ diffraction angle ranging from 20 to 60° (using a step size of 0.05° and step time of 2.5 s) was used.

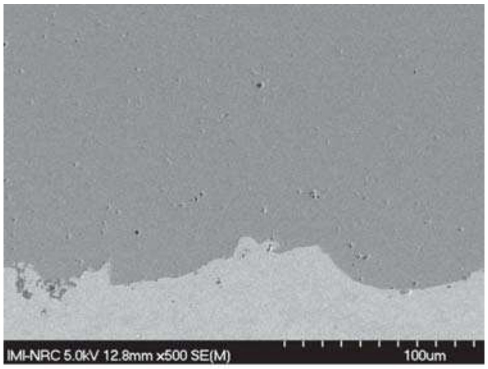
2.3 Mechanical Properties

Vickers microhardness measurements were performed under a 100 and 300 g indentation load for 15 s on the cross section of the coating. A total of 10 microhardness measurements were performed for each indentation load. The bond strength of the coating was tested using the ASTM standard C 633-01 (Ref 11) for determining the adhesion or cohesion strength of thermal spray coatings. A total of five coatings were bond strength tested.

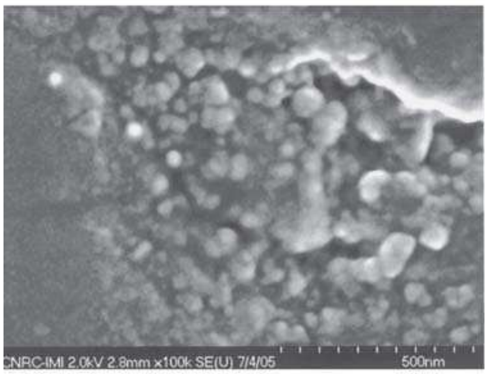
3. Results and Discussion

3.1 Nanostructure of the Feedstock

When analyzed at high magnification it is possible to observe the nanostructured features of the feedstock (Fig. 1). Each microscopic feedstock particle is formed by agglomeration via spray drying of innumerous individual nanosized particles of ti-



(a)



(b)

Fig. 2 (a) Cross section of the HVOF sprayed titania coating made from the nanostructured feedstock on the Ti-6Al-4V substrate. (b) Higher magnification view of (a) showing a nanostructured zone (formed by a nanostructured agglomerate that was semimolten in the spray jet)

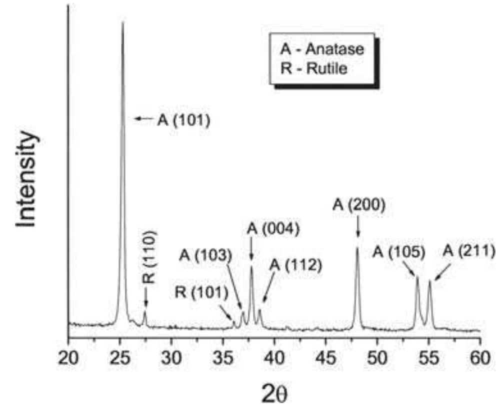


Fig. 3 XRD pattern of the nanostructured titania feedstock powder

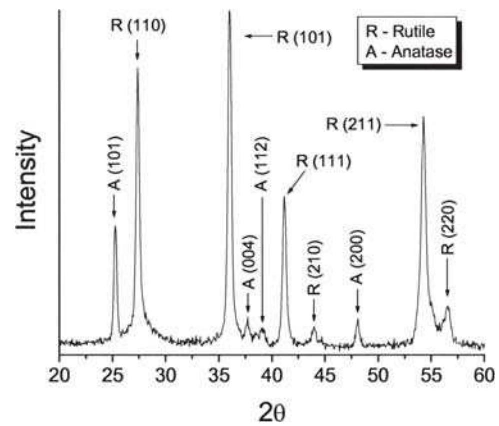


Fig. 4 XRD pattern of the HVOF sprayed nanostructured titania coating

tania. All individual nanosized particles of titania exhibit a diameter not larger than 100 nm. Therefore, it is confirmed that this feedstock is nanostructured.

3.2 Particle Temperature and Velocity

The average values of particle surface temperature and velocity in the spray jet were 1874 ± 136 °C and 635 ± 89 m/s, respectively. As the melting point of titania is 1855 °C, it is considered that not all particles were fully melted during spraying; that is, semimolten particles were also deposited in addition to the fully molten ones. Therefore part of the original nanostructure of the feedstock is embedded in the coating microstructure, as is shown in the next section.

3.3 Bimodal Structure of the Coating

Figure 2(a) shows the cross section of the titania coating made from the nanostructured feedstock on the Ti-6Al-4V substrate. It is possible to observe that the coating microstructure is very uniform, not exhibiting the typical layered or lamellar structure of thermal spray coatings. It may be stated that this coating has an isotropic microstructure. By looking at the microstructure of an HVOF sprayed coating made from a nanostructured titania feedstock, such as that of Fig. 2(a) at high magnification, nanostructured zones are observed (Fig. 2b).

The nanostructured zone is formed by a feedstock particle, such as that of Fig. 1, that was partially molten in the thermal spray jet. The nanostructured zone is embedded in the conventional matrix formed by the feedstock particles that were fully molten in the thermal spray jet. The particles that were fully molten in the thermal spray jet lost their nanostructural character, and therefore it is assumed that when they resolidify they will exhibit the same behavior as conventional thermally sprayed ceramic particles. It is important to point out that the nanostructured zones such as that of Fig. 2(b) are uniformly dispersed throughout the coating microstructure. Therefore, it can be stated that the titania coatings made from the nanostructured feedstock exhibited a bimodal structure.

The XRD analysis also confirms the bimodal character of the nanostructured coating. The XRD pattern of the nanostructured titania feedstock is found in Fig. 3. This powder has anatase as the predominant phase, with a minor content of rutile. The XRD pattern of the nanostructured coating shows two phases, rutile and anatase (Fig. 4). Anatase transforms irreversibly to rutile at temperatures from 400 to 1000 °C; therefore, the anatase phase found in the coating probably represents the semimolten particles embedded in the coating microstructure. The particles that were fully molten probably represent the rutile phase in the coating microstructure.

Table 1 Vickers microhardness values, porosity, and thickness of the HVOF sprayed nanostructured titania coating, plasma sprayed HA, and bulk (sintered) HA

Material	Indentation load, g	Porosity, %	Thickness, μm	Vickers hardness
HVOF nano TiO_2	300	<1	~150	824 ± 40 (*n* = 10)
Bulk (sintered) HA	300	5.0	Not applicable	513 ± 52 (Ref 11)
HVOF nano TiO_2	100	<1	~150	851 ± 30 (*n* = 10)
Plasma spray HA	100	Not available	Not available	275 ± 40 (Ref 12)

Table 2 Comparison of bond strength values (ASTM C 633-01), porosity and thickness for the nanostructured titania coating and various HA coatings available in the literature (substrate: Ti-6Al-4V)

Material	Feedstock	Process	Porosity, %	Thickness, μm	Bond strength, MPa
TiO_2	Nanostructured	HVOF	<1	~150	>77 (*n* = 5)
HA	Conventional	APS	Not available	Not available	23 ± 4 (Ref 13)
HA	Nanostructured	HVOF	1.4 ± 0.1	~150	24 ± 8 (Ref 14)
HA	Conventional	APS	Not available	~ 200	13 ± 1 (Ref 15)
HA	Conventional	APS	8.6	~400	7 ± 1 (Ref 16)
HA	Conventional	HVOF	Not available	Not available	31 ± 2 (Ref 17)
HA	Conventional	APS	7.3 ± 0.8	~180	27 ± 2 (Ref 18)

3.4 Hardness and Bond Strength

The Vickers hardness of the HVOF sprayed nanostructured titania coating is 61% higher than that of the bulk (sintered) HA and more than three times that of a plasma sprayed HA (Table 1) (Ref 12, 13). This shows that the nanostructured titania coating exhibits higher cohesive strength, which is an important property for a long-term performance implant.

The bond strength values of the HVOF sprayed nanostructured titania coating and various HA thermal spray coatings found in the literature (Ref 14-19) are listed in Table 2. The mechanical strength of the nanostructured titania coating is higher than the mechanical strength of the epoxy glue used during the bond strength test of the ASTM standard C 633-01. Therefore, during the tensile test for bond strength, the epoxy glue breaks (fails) before the coating at 77 MPa. As the mechanical strength of the epoxy glue is 77 MPa, the bond strength value of the nanostructured titania coating is higher than 77 MPa. Consequently, the bond strength value of the nanostructured titania coating is at least 2.5 times that of the highest bond strength value found in the literature for an HA coating.

3.5 Nanotexture of the Nanostructured Coating

As previously stated, the nanotexture or nanoroughness of nanostructured materials helps to improve osteoblast cell adhesion on biomaterials by enhancing the adsorption strength (interaction) of adhesion proteins such as vitronectin and fibronectin with the surface of the biomaterial (Ref 10). It was previously stated that the HVOF sprayed titania coating made from the nanostructured feedstock exhibited a bimodal structure and the nanostructured zones such as that of Fig. 2(b) were uniformly dispersed throughout the coating microstructure. Therefore, it should be possible to find these nanozones not only in the inner part of the coating microstructure, but also on its surface. When the surface of the HVOF sprayed nanostructured titania coating was observed at high magnifications, it was possible to observe (a) smooth regions, corresponding to fully molten particles and

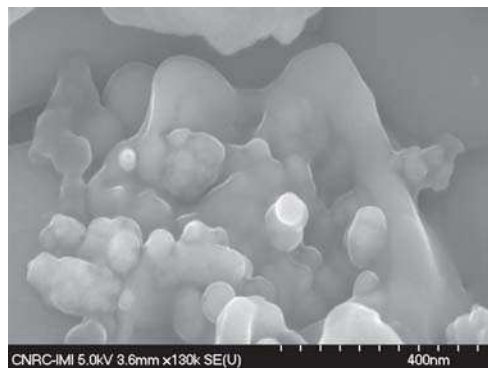


Fig. 5 A nanotextured region on the surface of the HVOF sprayed nanostructured titania coating

(b) nanozones corresponding to semimolten particles. A typical nanozone is shown in Fig. 5. This zone resembles the particle of Fig. 1; that is, this is a semimolten nanostructured titania particle. It is hypothesized that these nanozones (exhibiting nanotexture) on the surface of the nanostructured titania coating may help to increase the adhesion strength of the osteoblast cells on its surface. If it is proven true, this is another very desirable characteristic for engineering a coating for long-term performance on a hip-joint implant.

4. Conclusions

- The HVOF sprayed titania coating made from a nanostructured feedstock exhibited an isotropic and bimodal microstructure formed by particles that were (a) fully molten and (b) semimolten in the spray jet.
- The Vickers hardness of the nanostructured titania coating is 61% higher than that of a bulk (sintered) HA and more than three times that of a plasma sprayed HA coating. This is considered an advantage because it shows that the nanostructured titania coating has a higher cohesive strength.

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- The bond strength of the nanostructured titania coating is at least 2.5 times higher that of the bond strength values for HA thermal spray coatings reported in the literature.
- The nanostructured titania coating exhibited regions showing nanotexture on its surface. These regions are created by the semimolten nanostructured particles that were deposited on the coating surface during spraying. It is hypothesized that these regions may enhance osteoblast adhesion on the coating by creating a better interaction with adhesion proteins, such as fibronectin (Ref 10).
- A preliminary osteoblast cell culture, analyzed via SEM analysis and alkaline phosphatase activity, can be found in the companion paper included in this volume (Ref 10). It indicated that the HVOF sprayed nanostructured titania coating exhibited a degree of cell proliferation equivalent to or higher than that of APS HA coatings.
- It is important to point out that in contrast to HA, titania does not dissolve in the human body; therefore, this titania coating should be totally stable and conserve its properties once implanted.
- Different tests will have to be performed to determine if this HVOF sprayed nanostructured titania coating can be used as a biomedical coating; however, the initial results indicate that it may represent an alternative to APS HA coatings in the future.

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