XXI ENMC
ENCONTRO NACIONAL DE MODELAGEM COMPUTACIONAL
IX ECTM
ENCONTRO DE CIÊNCIA E TECNOLOGIA DE MATERIAIS

08 a 11 de Outubro de 2018
Instituto Federal Fluminense
Búzios - RJ

ENABLE THE POSSIBILITY OF DEPOSITION ON SS SUBSTRATE COATING POWDER MIXTURE COMPOSED OF TITANIUM (TI CP) AND PTFE THROUGH FLAME THERMAL SPRAY PROCESS

Thiago Leite dos Santos[1] – thiago-leite@outlook.com.br
Ramón Sigifredo Cortés Paredes[1] – ramon@demec.ufpr.br
[1] Universidade Federal do Paraná (UFPR) – Curitiba, PR, Brazil

Abstract. *Improving prosthesis performance used as orthopedic implants has been a trend in recent years. Though there is still space for improvements, due to the implant loss and high failure rate. An alternative to accomplish such refinement is the surface modification in the form of coating. Stainless steel (SS) biomaterial may have potential to be used in implants for consolidating bone fractures if their bioactivity is improved. Thus, samples of SS were coated with a coating powder mixture composed of titanium (Ti cp) and polytetrafluoroethylene (PTFE) through the flame thermal spray process, using nitrogen as carrier gas. All coatings were coated 68 μm thicknesses. The coatings were characterized by scanning electronic microscope (SEM) and energy dispersive x-ray detector (EDS). Ultimately, the results of the analysis confirm the created of composite coating (PTFE-Ti) on SS and It will may reveal the potential this material.*

Keywords: *Thermal spray process, Titanium coating, SS substrate, Bioactivity, Implants*

1. INTRODUCTION

The highlights of this work are the feasibility of use Flame Thermal Spray process (FS) on a Stainless steel (SS) substrate for powder mixture (Ti+PTFE) composed of titanium (Ti cp) and PTFE. The tests results obtained suggest that the material can been potentially good materials for static orthopedic implants.

2. LITERATURE REVIEW

ThIn the late 1940s and early 1950s, when the first medical devices based on scientific principles were applied to humans, there was an accelerated growth in the field of biomaterials. This increase has been intensified by the aging of the elderly population, increased life expectancy in developing countries, current health problems such as cancer and osteoporosis, and the evolution of treatment of previously untreatable medical conditions (RATNER et al., 2013).

The development of new materials is essential for permanent implants to have a longer lifespan, and the temporary ones do not need to be removed due to complications from the material (PERIAGO, 2007; WOLNER et al., 2006; BAGNO et al., 2004)

Biocompatible materials are not necessarily inert or innocuous, biocompatibility occurs when the material receives adequate tissue responses, that is, when the responses induced by the implant are controlled (HALLAB; JACOBS, 2013).

The use of polymeric materials in medicine has intensified with the discovery of synthetic polymers. Making way for studies in surgical experiments, using materials such as polytetrafluoroethylene, high density polypropylene and polyurethanes. The polymers are used in the most diverse applications in biomaterials, due to the variety of compositions, properties and forms (solid, fiber, fabric, film and gel) and the ease of being manufactured and processed (RODRIGUES, 2013)

Polytetrafluoroethylene is among the most widely used materials in biomedical applications. Medical devices such as surgical sutures and vascular prostheses are made from fluoropolymers, due to low surface energy, low coefficient of friction, good chemical resistance and biocompatibility (EBNESAJJAD, 2017).

In the context of this work, when addressing the interactions between an implantable device and the biological tissue, one must consider, besides the implant properties that ensure overall performance, the immediate response that the body gives to the surface of the invasive material. In many cases, in which invasive medical devices are included, it is in the best interest of the material chosen to have mechanical and biological properties that will reduce the negative effects of this interaction. The design of a medical device is conditioned by the appropriate choice of the material used for its manufacture, which must be governed by biocompatibility, bioadhesion, biofunctionality and resistance to corrosion. In addition, understanding the interactions through the liquid-solid interface behavior is critical for biomedical implants (OSHIDA, 2013).

According to Bramowicz et al. (2016) and Vranceanu et al. (2016), the most used metallic materials for applications in orthopedics are: 316L stainless steel, chromium-cobalt alloys and titanium alloys. However, the moduli of elasticity of these materials are considerably different from natural bones, which may increase the risk of failure or fracture due to load transmissions.

In general and according to Ribeiro (2009), the material chosen for the manufacture of the device does not present the properties / characteristics necessary for its functionality. Despite efforts, few systems have the features necessary for optimal use in medical implants. Then, there is a need to modify the surface of the base material in order to improve the response in the biotic / abiotic material interaction so that, after implantation, the surface promotes biological action and accelerates osseointegration, reducing the time required for the bony apposition.

In this work, the modification of surfaces is defined as a "way of adapting the surface properties to the utilization requests". In this way, the modification process aims to improve the surface properties of the implants, given the fundamental role they play in the response of the organisms. Among several technologies, surface coating of biomaterials has been extensively studied for the purpose of: improving tribological behavior, resistance to corrosion and promoting biological action, such as osseointegration (OSHIDA, 2013).

It is intended to experimentally study the modification of the SS surface, depositing a mixture of titanium powders and PTFE powders with the aid of the coating technique, Thermal Spray (AT) Flame Powder process. This study aims to make possible the deposition of a composite coating, metal + polymer, by AT on metal substrate. PTFE was chosen because of its good properties, such as thermal and chemical stability, high melting point and low coefficient of friction. It was believed that with these properties the polymer material will not degrade during the deposition process and will allow the coating, besides allowing application as biomaterial for orthopedics.

After the deposition tests, the SS surface is expected to exhibit a satisfactory adhesion coating.

3. MATERIAL AND METHODS

SS substrate were grit blasted with alumina with a CMV equipment followed by powder Ti+PTFE deposition through flame thermal spray process with a Sultzer equipment and a gun model 6P-II.

Coating raw material is divided by mass percentage (70% Ti and 30% PTFE) and composed of commercially pure titanium grade 4, ASTM standard F67-13 and PTFE powder. The size of the powder granules is shown in table 1.

Table 1. Coating raw material

	METALLIC POWDER	POLYMERIC POWDER
Name	Titanium	PTFE
Granulometry (μm)	-106 +63	-106 +63

The parameters and process gases were estimated with initial tests, can be observed in table 2 and 3, respectively.

Table 2. Process parameters
All sample was deposited by four completed passes.

FATOR	LEVEL I (A)	LEVEL II (B)
Stand-off distance (SOD)	300 mm	450 mm
Powder feed rate	45 g/min	60 g/min
Substrate temperature	TA*	60

Table 3. Process gases
SCFH = Standard cubic feet per minute.

	COMBUSTION GAS		CARRIER GAS	PROTECTION GAS
Name	C_2H_2	O_2	Ar	Air comp.
Flow (SCFH)	60	100	15	80

Sample surfaces were characterized by Scanning electronic microscopy (SEM) and energy dispersive x-ray detector (EDS). Coating adherence was tested by analyze of interface.

4. RESULTS AND DISCUSSION

Figure 1 present Scanning electronic microscopy image of the titanium material used as metallic powder, revealing standard geometry and size of the powder granules. It can observe in Figure 2, because there is demonstrate some important details as particle surface, geometry and imperfections.

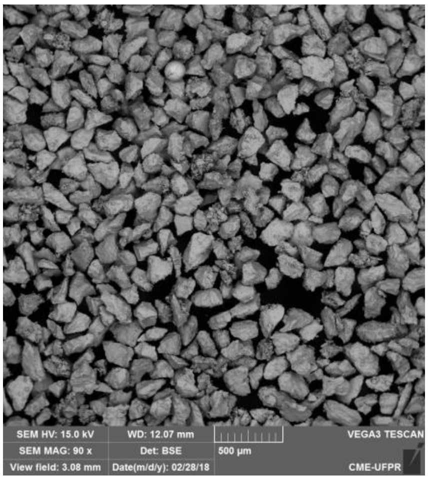


Figure 1. SEM image of the titanium material used as metallic powder

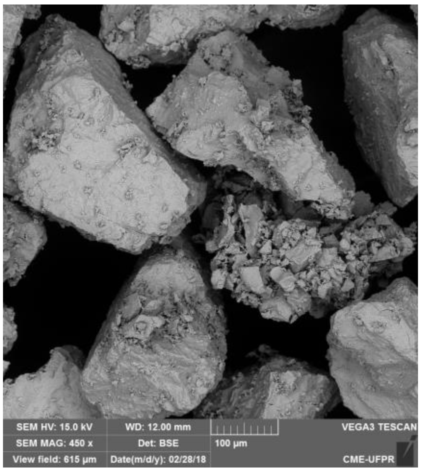


Figure 2. Detailed image of the titanium material used as metallic powder

Similarly, polymeric powder geometry was evaluated by SEM image. It shows irregularities, impurities and several geometry variations, according Figure 3 and 4. However, different geometrical patterns can be deposited by Flame Spray, although it is not having information about the effects of these geometric variations on the process, but it is desirable that the raw material has a continuous flow during the process.

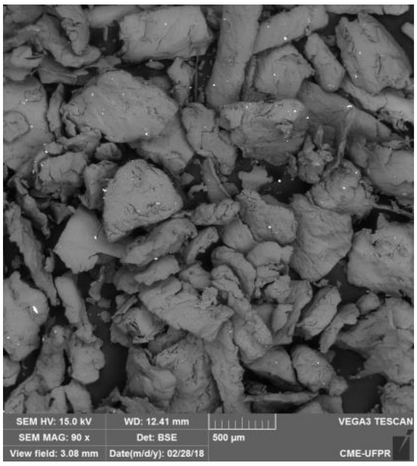


Figure 3. SEM image of the PTFE material used as polymeric powder

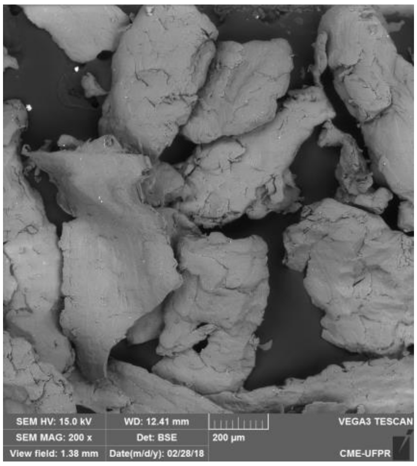


Figure 4. Detailed image of the PTFE material used as polymeric powder

The coating raw material is consisting of powder mixture divided by mass percentage (70% Ti and 30% PTFE). Therefore, both materials were grouped and mixed to obtain the coating raw material, see Figure 5 and 6. SEM causes color difference to illustrate the materials, the lightness is Ti and darkness is PTFE.

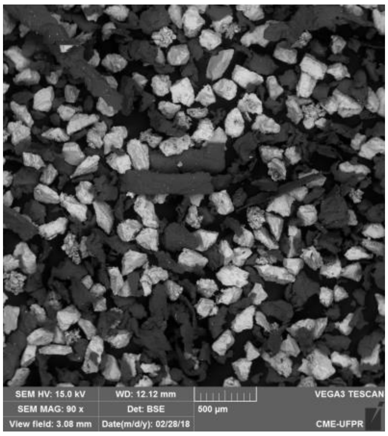


Figure 4. SEM image of powder mixture

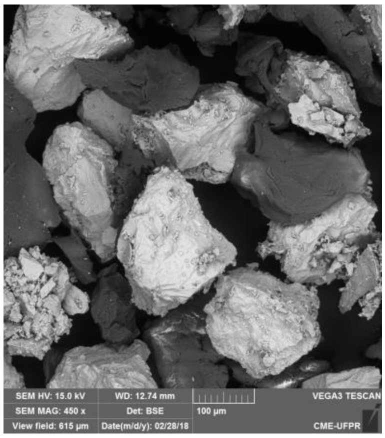


Figure 5. Detailed image of powder mixture

Material composition also needed to be analyze, besides that the composition is important to confirm what materials were presents after deposition. Thus, the powder mixture was analyzed by EDS and It can be verified in Figure 6 and 7.

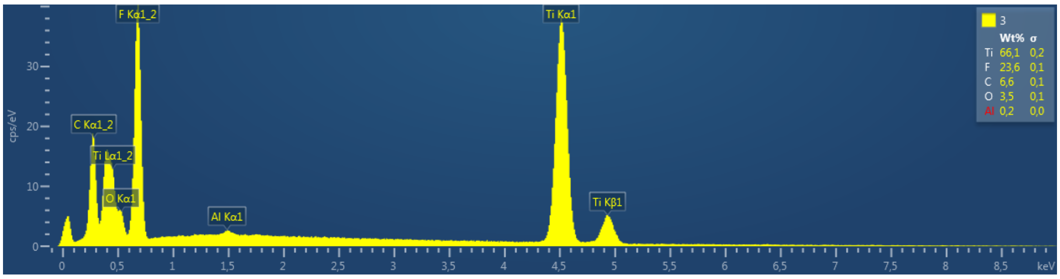


Figure 6. Analyze of powder mixture by EDS on point 3 (see Figure 7).

Figure 7 shows point 3, which was randomly chosen to indicate the composition. Note that there is a large weight percent of Ti (66.1%) and Fluorine (F) (23.6%), even though there are also other materials. Symbol “C”representing Carbon is, exactly as fluorine, from the PTFE polymer chain. The chemical element Oxygen, represented by the symbol “O”, is included in the Flame Spray process. Nevertheless, symbol “Al” has not been considered, because Aluminum (Al) is from sample base.

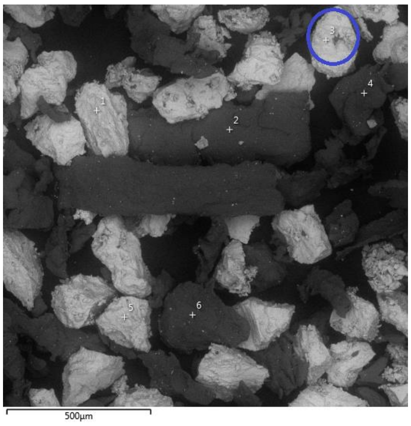


Figure 7. Mapping of point 3.

Using process parameters was possible created samples with only four completed passes by deposition. Two samples were selected, it named conforming to parameter level. So, the first one corresponds “Sample A” and second “Sample B”, according Table 2.

Figure 8 and 9 presents SEM images of Sample A and B, there can be seen visually the appearance and distribution of coating. Likewise, respectively it can been observing more details in Figure 10 and 11.

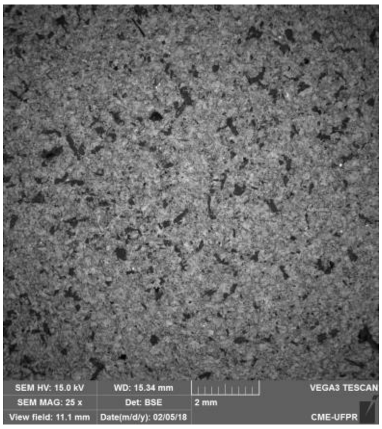


Figure 8. SEM image of Sample A

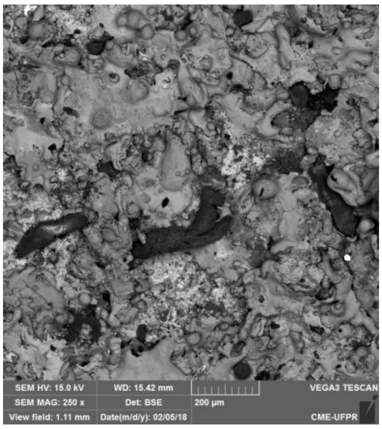


Figure 10. Detailed image of Sample A

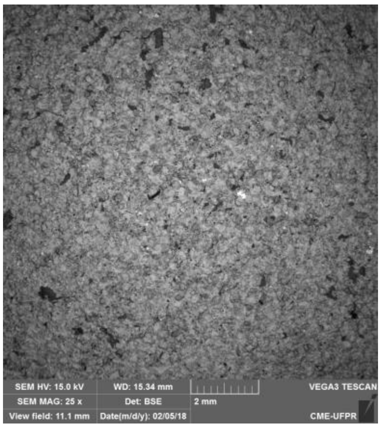


Figure 9. SEM image of Sample B

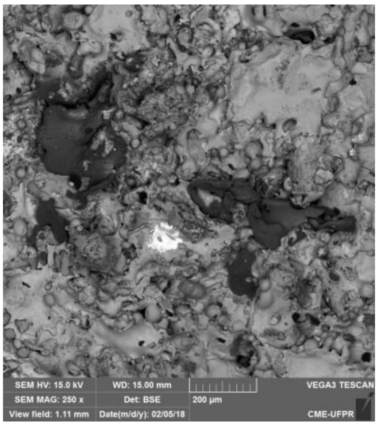


Figure 11. Detailed image of Sample B

Aiming to prove the presence of titanium and fluorine on the surface, EDS analyze was evaluated. In Figure 12 is possible to observe some agglomerated of fluorine on the surface of Sample A. However, the agglomerated geometry may be meaning non-degradation of PTFE, nonetheless many fluorine points are separated on all surfaces. On the other hand, titanium was dispersed on the surface suggesting a uniform distribution of powders and their bonding.

Figure 12a is representing a surface elemental mapping, their colors demonstrate elements different indicating elemental composition of the sample. Red represents the fluorine as show in Figure 12b. Titanium can be identified in Figure 12c by yellow.

In the flame spray process the Ti particles oxidize, in despite of carrier gas is neutral, mainly by the contact with the oxygen contained in the air used to transfer the molten particles to the substrate and later with the air of the environment.

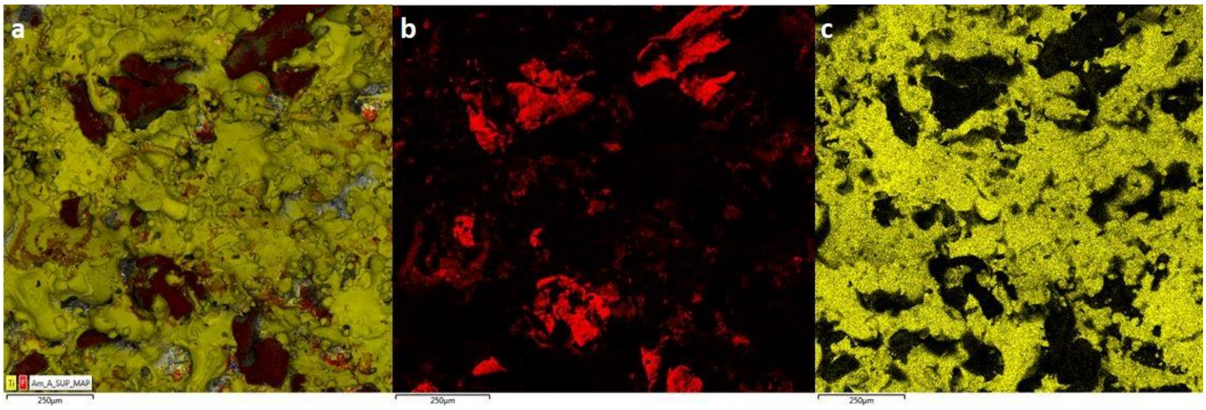


Figure 12. EDS analyze Sample A.

In the same way, Figure 13 shows the EDS analysis Sample B. The Sample B has the similar features than Sample A, both sample was not completely coated. The little points gray confirms this.

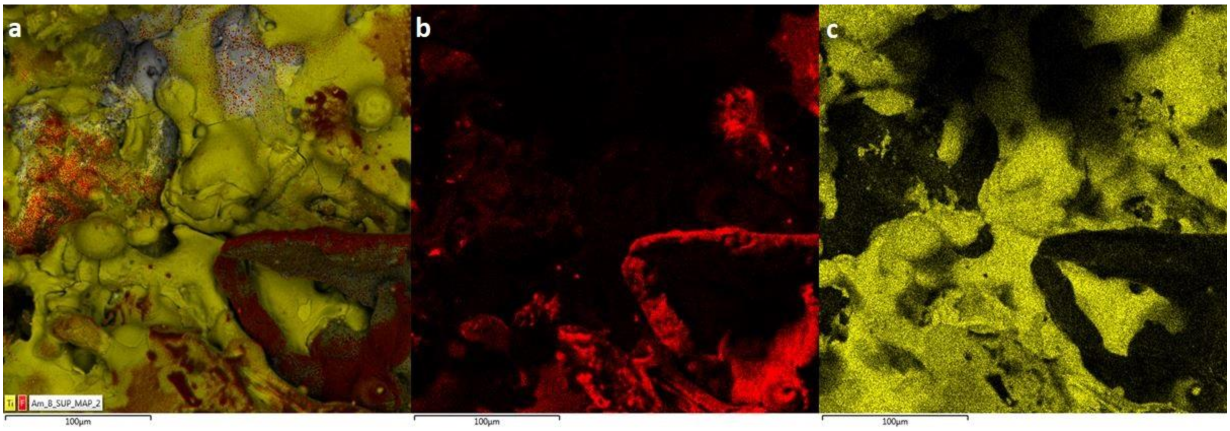


Figure 13. EDS analyze Sample B.

Ultimately, the sample/coating interface was evaluated to estimate coating adherence. A cross-sectional analysis of the coating of Sample A and B was analyzed in Figure 14 and 16, more details are represented in Figure 15 and 17.

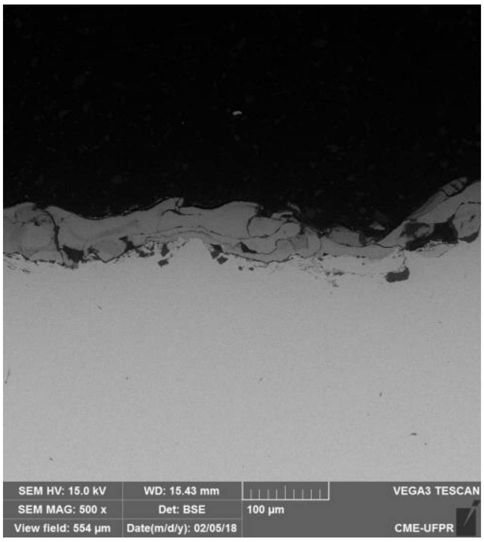


Figure 14. Cross-sectional analysis of Sample A

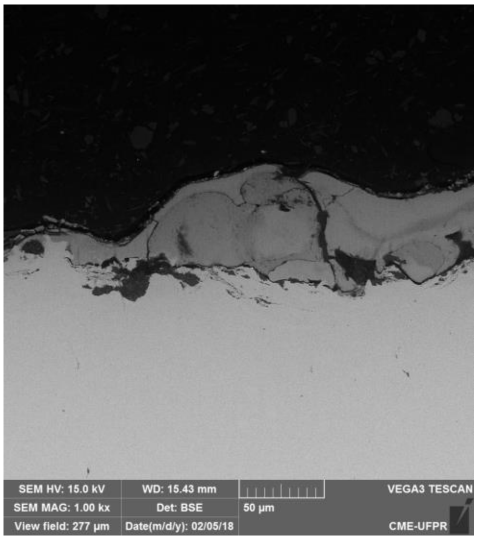


Figure 15. Detailed Cross-sectional analysis of Sample A

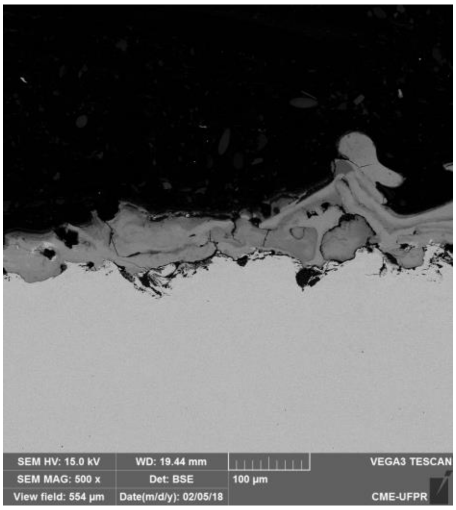


Figure 16. Cross-sectional analysis of Sample B

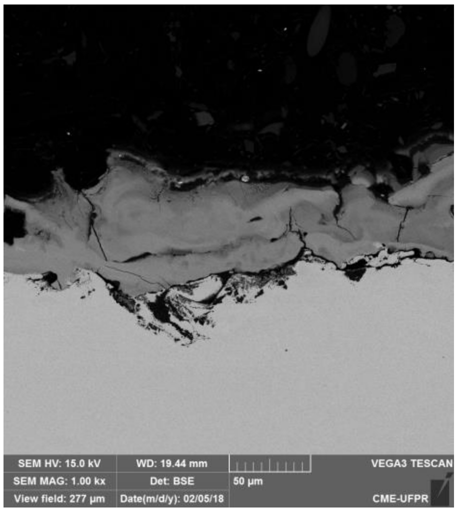


Figure 17. Detailed Cross-sectional of Sample B.

A process characterization has been therefore initialized, showing the relationship between properties of feedstock powders against deposition behavior. Cross-sectional analysis enables thickness measurement of the coating, both samples had coatings of similar thickness, approximately 68 microns (μm). However, the initial preparation of the sample surface impairs the measurement of the thickness due to the variable surface profile caused by the peaks and valleys. Remembering that this roughness creates anchor points providing better adhesion of the coating to the substrate.

Process parameters are essential to performing good coating interface without pores, stresses and unfused particles. Figures 14, 15, 16 and 17 disclose important characteristics of the coating / substrate system as anchoring points, molten and semi-molten particles and suitable stacking of the particles. Although, the coating showed some cracks and occasional anchorage failures. This suggests that the thickness of the coating has been insufficient and that it can be increased to uniformize the coating. Changes in the parameters can also be performed as another alternative to smooth the coating by reducing the cracks.

Note, according Chalker, Bull e Rickerby (1991), the development of a reliable, quantitative, non-destructive technique is still some way off, thus the test selected only represent a single supposition about adhesion and cohesion of coating. It is necessary to make the best use of the currently available techniques if reliable conclusions about coating-substrate adhesion are to be drawn.

The 3D mapping of the entire surface may illustrate the coating roughness and topography. After analyzing the surface, it can be measuring some parameters of the coating. The coating has the average height of the selected area is 67.83 µm, maximum peak height of the selected area is 184.07 µm and maximum peak to valley height of primary profile is 101.22 µm. Both samples have values similar, it can see in Figure 19 and 20.

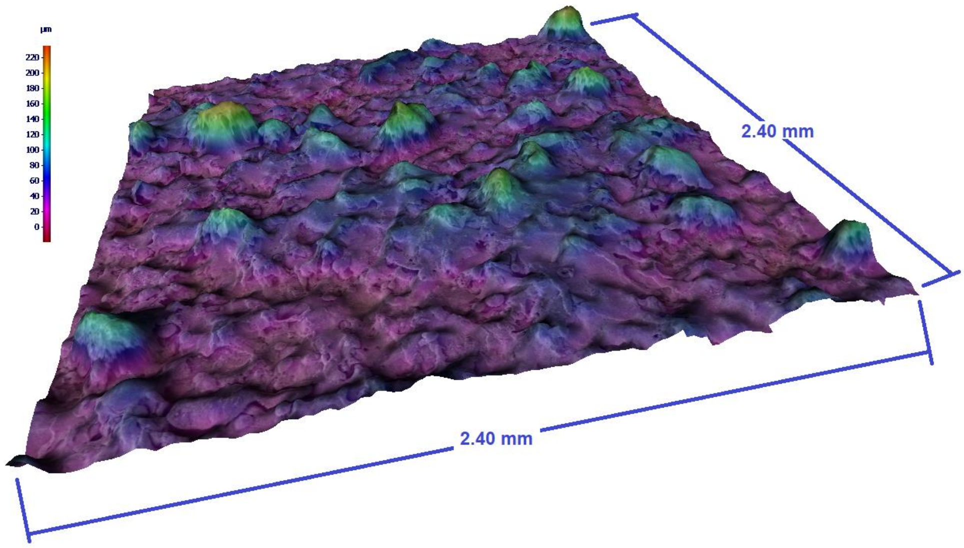
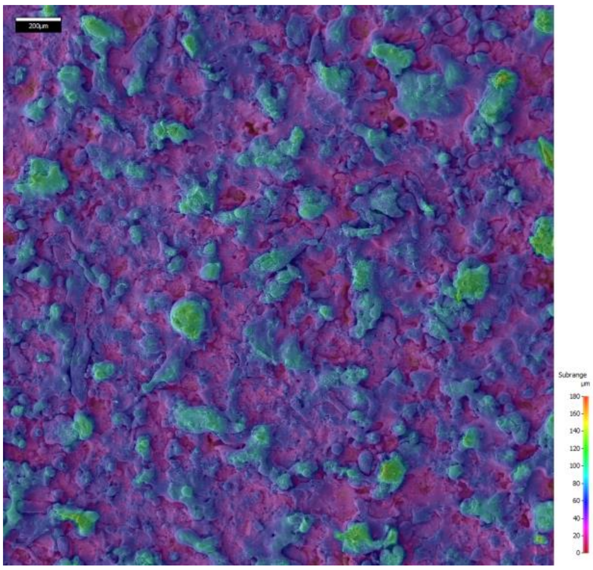


Figure 18. 3D mapping for surface roughness.



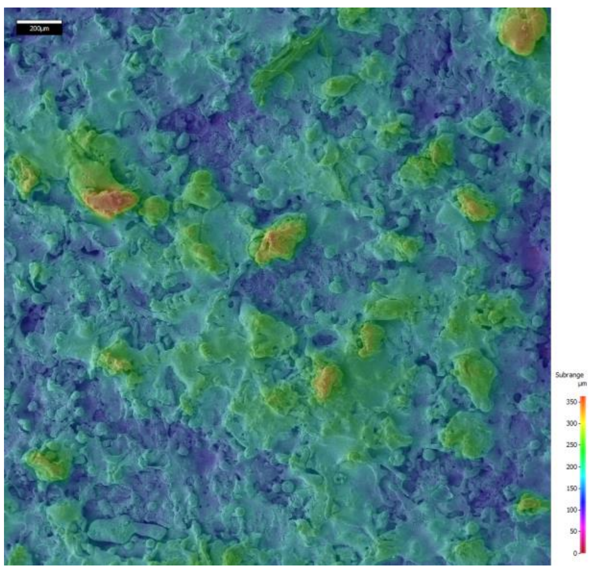


Figure 19. Topography of Sample A.

Figure 20. Topography of Sample B

5. CONCLUSIONS

It was possible to prepare deposition on a SS substrate coating powder mixture Ti-PTFE through the flame thermal spray process. EDS analysis detected the presence of Ti and F in the coating and Ti on the entire surface. It can be concluded that there were differences between the coatings caused by the parameter difference, however, the variation of the parameters did not bring conclusive results. A statistical method is recommended to evaluate the effect of each parameter and to find a coating with fewer cracks and pores.

Acknowledgements

The authors wish to thank the Coordination of Improvement of Level Staff (CAPES) and Graduate Program in Mechanical Engineering (PGMEC UFPR) for fellowship given.

REFERENCES

BAGNO, Andrea et al. *Contact profilometry and correspondence analysis to correlate surface properties and cell adhesion in vitro of uncoated and coated Ti and Ti6Al4V disks*. Biomaterials, [s.l.], v. 25, n. 12, p.2437-2445, May 2004. Elsevier BV. http://dx.doi.org/10.1016/j.biomaterials.2003.09.018.

BRAMOWICZ, Miroslaw et al. *Mechanical properties and fractal analysis of the surface texture of sputtered hydroxyapatite coatings*. Applied Surface Science, [s.l.], v. 379, p.338-346, ago. 2016. Elsevier BV. Available in: <http://dx.doi.org/10.1016/j.apsusc.2016.04.077>. Access in: 12 out. 2016.

CHALKER, P.r.; BULL, S.j.; RICKERBY, D.s.. *A review of the methods for the evaluation of coating-substrate adhesion*. Materials Science And Engineering: A, [s.l.], v. 140, p.583-592, jul. 1991. Elsevier BV. http://dx.doi.org/10.1016/0921-5093(91)90482-3.

EBNESAJJAD, Sina, *7 - Properties, Characteristics, and Applications of Expanded PTFE (ePTFE) Products*, In Plastics Design Library, William Andrew Publishing, Oxford, 2017, Pages 163-170, Expanded PTFE Applications Handbook, ISBN 9781437778557, https://doi.org/10.1016/B978-1-4377-7855-7.00007-9.

OSHIDA, Yoshiki. Bioscience and Bioengineering of Titanium Materials. 2. ed. Indianapolis: Elsevier, 2013. 500 p.

PERIAGO, R. Z. *Osteointegración en amputados de miembros*. Rehabilitación (Madr), v. 41, n. 4, p. 180-184, 2007.

RATNER, Ed. R. D. et al. *Biomaterials Science: An Introduction to Materials in Medicine*. 3. ed. Oxford: Elsevier, 2013. 1555 p.

RIBEIRO, Carla de Oliveira. *Comportamento de proteínas em stents vasculares modificados por pulverização catódica*. 2009. 78 f. Dissertation (Master degree) - Integrated Master's Degree in Biomedical Engineering, Center for Mechanical Engineering, University of Coimbra, University of Coimbra, Coimbra, 2009.

RODRIGUES, Luciano Brito. *Aplicações de biomateriais em ortopedia*. Estudos Tecnológicos em Engenharia, [s.l.], v. 9, n. 2, p.63-76, 4 out. 2013. UNISINOS - University of Vale do Rio Dos Sinos. http://dx.doi.org/10.4013/ete.2013.92.02.

SULZER METCO. *An Introduction to Thermal Spray*. Manufacturer's Information Notebook. V.4, 2013.

VRANCEANU, D.m. et al. *Osseointegration of sputtered SiC-added hydroxyapatite for orthopaedic applications*. Ceramics International, [s.l.], v. 42, n. 8, p.10085-10093, jun. 2016. Elsevier BV. Available in: <http://dx.doi.org/10.1016/j.ceramint.2016.03.114>. Access in: 12 out. 2016.

WOLNER, C; et. al. *Possible reasons for the unexpected bad biocompatibility of metal-on-metal hip implants*. Materials Science and Engineering C; v. 26, p. 34-40, 2006.