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# Characterization of titanium coatings on substrate of Poly (Ether-Ether-Ketone) - PEEK applied through thermal spray process for implant applications

## Caracterização de revestimentos de titânio sobre substrato de Poli (Éter- Éter-Cetona) - PEEK, aplicados através do processo de aspersão térmica para aplicações em implantes

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### ABSTRACT

Samples of PEEK - poly(ether-ether-ketone) were coated with titanium through flame thermal spray process, using nitrogen or argon as carrier gas. The coatings were characterized by optical and scanning electronic microscope (SEM), energy dispersive x-ray detector (EDS) and diffraction x-ray (DRX). Tribological tests were performed on the Titanium (Ti) coatings and an abrasive wear was identified for both samples. The bioactivity of the as-prepared coating surface samples was evaluated in *in vitro* tests by immersion of the samples in simulated body fluid (SBF) for different periods of time, up to 23 days. The coated specimens were analyzed by SEM and EDS and revealed that a layer containing Calcium (Ca) and Phosphorus (P) was deposited upon immersing the samples in SBF, suggesting that compounds similar to bones (apatite) were formed and therefore, the materials have a potential use in implants for consolidating bone fractures.

**Keywords:** Thermal spray process; Titanium coating; PEEK substrate; Bioactivity; Implants; Wear strength.

### RESUMO

Amostras de PEEK - poli (éter-éter-cetona) foram revestidas com titânio através do processo de pulverização térmica por chama utilizando o gás nitrogênio ou argônio como gás de transporte. Os revestimentos foram caracterizados por microscopia óptica electrônica de varredura, espectroscopia de raios X por dispersão em energia (EDS) e difração de raios-X (DRX). Ensaios de tribologia foram realizados sobre os revestimentos de Titânio (Ti) e um desgaste abrasivo foi identificado em ambas as amostras. A bioatividade da superfície de revestimento das amostras preparadas foi avaliada por testes *in vitro* por imersão das amostras em fluido corporal simulado (SBF) durante diferentes períodos de tempo, até um total de 23 dias. Os revestimentos foram analisados por SEM e EDS após a imersão em SBF, e revelou uma camada contendo Cálcio (Ca) e Fósforo (P) depositado em cima das amostras, o que sugere que compostos similares aos ossos (apatita) foi formado e, por conseguinte, os materiais têm uma potencial utilização em implantes para a consolidação de fraturas ósseas.

**Palavras-chave:** Processo de pulverização térmica; Revestimentos de Titânio; Amostras de PEEK; Implantes; Resistência ao desgaste.

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## INTRODUCTION

The highlights of this work are the use of flame thermal spray process on a poly(ether-ether-ketone) - PEEK substrate for Ti coating, the wear tests performed on the materials thus obtained to evaluate its potential use on non-static implants and the in vitro tests results obtained that suggest that the materials are potentially good performance materials for static orthopedic implants.

## LITERATURE REVIEW

Ti-alloys present high compatibility for implant applications but its elastic modulus is much higher than that of bones, causing atrophy in an attempt of the body to protect the bone from the tension generated(1). The strength of legs and arms bones are in the range of 100 – 200 MPa, the strength of the skull is about 97 MPa and that of vertebras are in the range of 1 – 10 MPa(2). When there is a mismatch in modulus of elasticity between the bone and the implant, implant failure occurs because the stress required by cells adjacent to the implant is shielded and thus, cells do not survive(3). Also, implants are submitted to the action of complex mechanical loadings in salty medium (blood and interstitial fluid) requiring implant materials to have a good corrosion resistance. The pH of normal blood and interstitial fluid is 7.35 – 7.45 but it decreases to about 5.2 in the hard tissue due to implantation and recovers to 7.4 in approximately two weeks. Body fluids contain amino acids and proteins that may accelerate corrosion(4). Therefore, polymers coated with Ti unite the high compatibility of Ti with the corrosion resistance and elastic modulus of macromolecules and so, these materials are potentially high performance materials for implants applications.

From results obtained by several authors, it was proposed that bone bioactivity of a material could be assessed by examining apatite formation in SBF preliminary to animal experiments(5-9). The SBF solution is supersaturated with respect to calcium phosphate and carbonate, and ion concentration nearly equals to those of human blood plasma without organic components, and so, apatite thus formed is very similar to the bone mineral in its composition and structure(8).

## EXPERIMENTAL

PEEK substrate were grit blasted with alumina mesh size 36 with a CMV equipment followed by powder Ti deposition through flame thermal spray process with a Sultzer equipment and a gun model 6P-II. As a carrier gas, nitrogen (15 SCFH, sample 1) or argon (15 SCFH, sample 2) were used else than 100 SCFH of $O_2$ and 60 SCFH of acetylene. Ti deposition was slow, with cooling (130-138°C) using compressed air between each pass (24 for sample 1 and 30 for sample 2). The distance gun-substrate varied in the range of 30-50 cm. Sample surfaces were characterized by diffraction X-ray (DRX Empyrian), scanning electronic microscopy (SEM Tescan Vega 3XMU), optical microscopy model Olympus BX 51M, energy dispersive x-ray detector (EDS Oxford XACT), Rockwell hardness (Versitron Newage Instruments) and tribology (Tribometer CSM). The static partner used in friction with the coated materials was a $100Cr_6$ sphere, with diameter of 6mm. The applied force in the tribological tests was of 3N in 150.000 cycles(10-11). The evaluation of apatite forming ability was made through *in vitro* tests and then the formed coating was characterized by EDS. Simulated body fluid (SBF) was prepared by dissolving reagent grade chemicals of NaCl, $NaHCO_3$, KCl, $K_2HPO_4$, $MgCl_2{\cdot}6H_2O$, $CaCl_2.2H_2O$, and $Na_2SO_4$ in deionized water and buffered at pH 7.4 with tris-hydroxymethyl aminomethane ($(CH_2OH)_3CNH_2$) and hydrochloric acid (1 mol/L) at 36,5 ± 0.5°C according to ISO / FDIS 23317. Samples were soaked in 15 mL of SBF (filtered through a 0,45 µm membrane (Sartorius®, Spain) in a Falcon tube and stored in a water bath at 37°C (±1°C) up to 23 days. After immersion for a pre-determined period of time (9, 18 or 23 days), the samples were removed from the SBF, gently rinsed with deionized water and then dried in ambient temperature. The samples were stored in a desiccator.

## RESULTS AND DISCUSSION

Figures 1(A) and 1(B) and Figures 2(A) and 2(B) present optical images of the Ti coated PEEK when nitrogen (sample 1) or argon (sample 2), respectively, was used as the carrier gas in the flame thermal spray process. It can be seen visually that samples 1 and 2 presented a yellowish colour because of the formation of TiN that has a golden colour. The coating layer in sample 2 was in the range of 214-304 µm, thicker than the one of sample 1 because instead of 30 passes, sample 1 was submitted to 24 passes in the flame

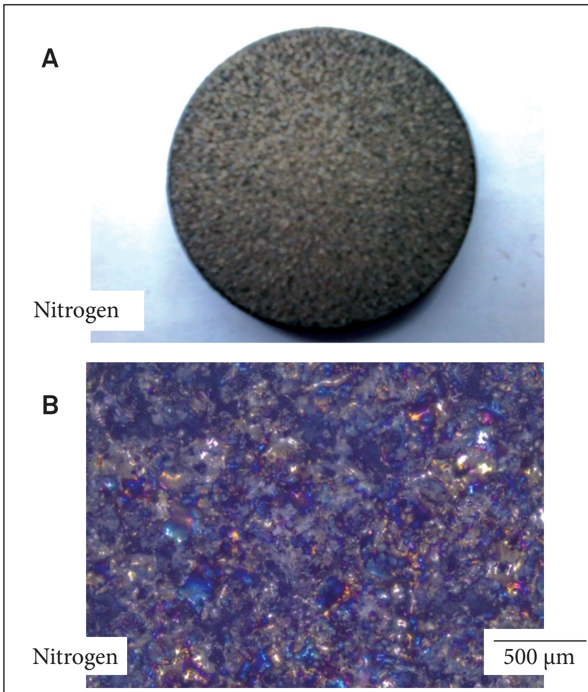


**Figure 1:** Sample 1 optical microscope (Ti coating on PEEK).

thermal spray process. Hardness of the Ti coatings were of 24.7 RHA and 20.0 RHA for samples 1 and 2, respectively.

Figures 3 and 4 show the diffraction patterns of both samples and the compounds identified. DRX results showed that in both samples osbornite (TiN), hongquilite (Ti) and titanium (Ti) were found. Aluminium was used as the sample uphold.

Figures 5(A) and 5(C) show that the formation of worn tracks characteristic of the abrasive wear, with grooves coincidental to the movement direction were formed. It was also observed the occurrence of the same abrasive wear in the static partners (spheres) as Figures 5(B) and 5(D) shows.

The coefficient of friction of the Ti coating of samples 1 and 2 presented an average value of 0.75 and 0.60 respectively as shown in Fig. 6. TiN presents a friction coefficient of 0.65. The wear tests show that after 120.000 cycles on sample 2, there is a tendency to

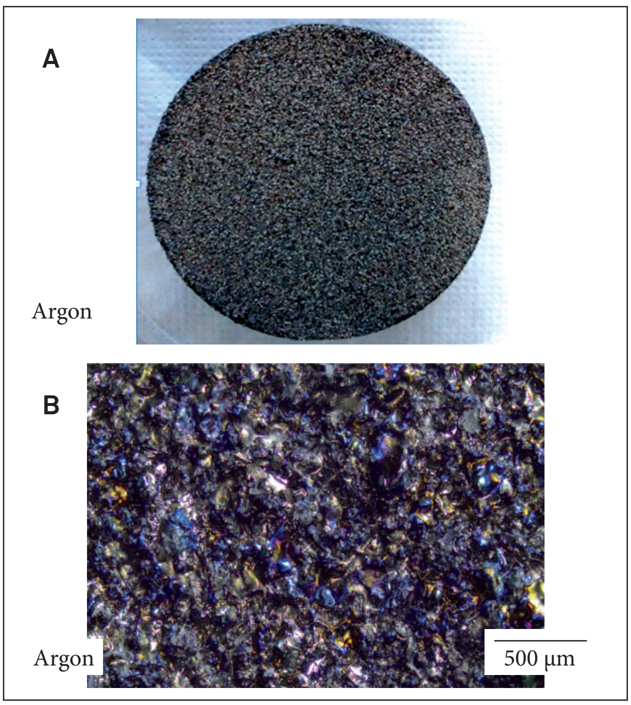


**Figure 2:** Sample 2 optical microscope (Ti coating on PEEK).

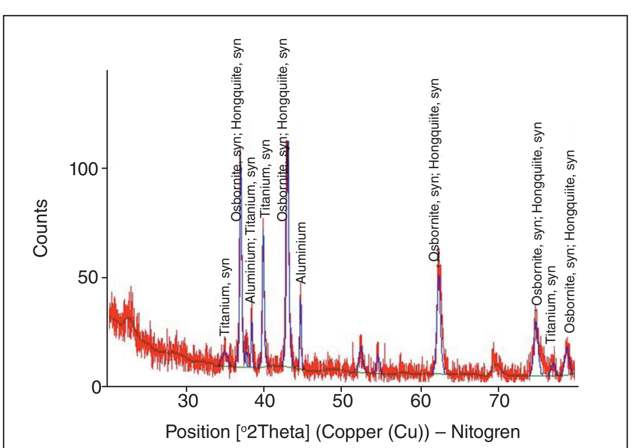


**Figure 3:** DRX of sample 1.

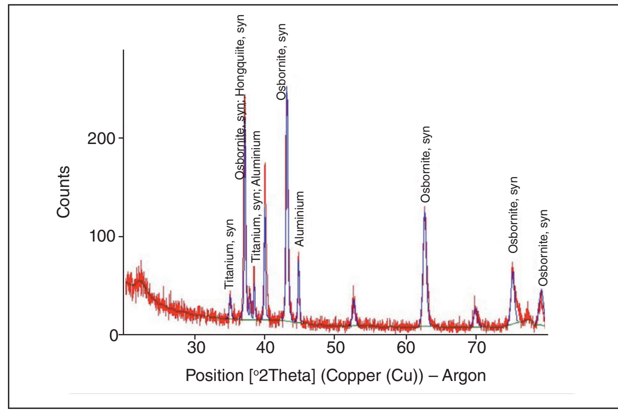


**Figure 4:** DRX of sample 2.

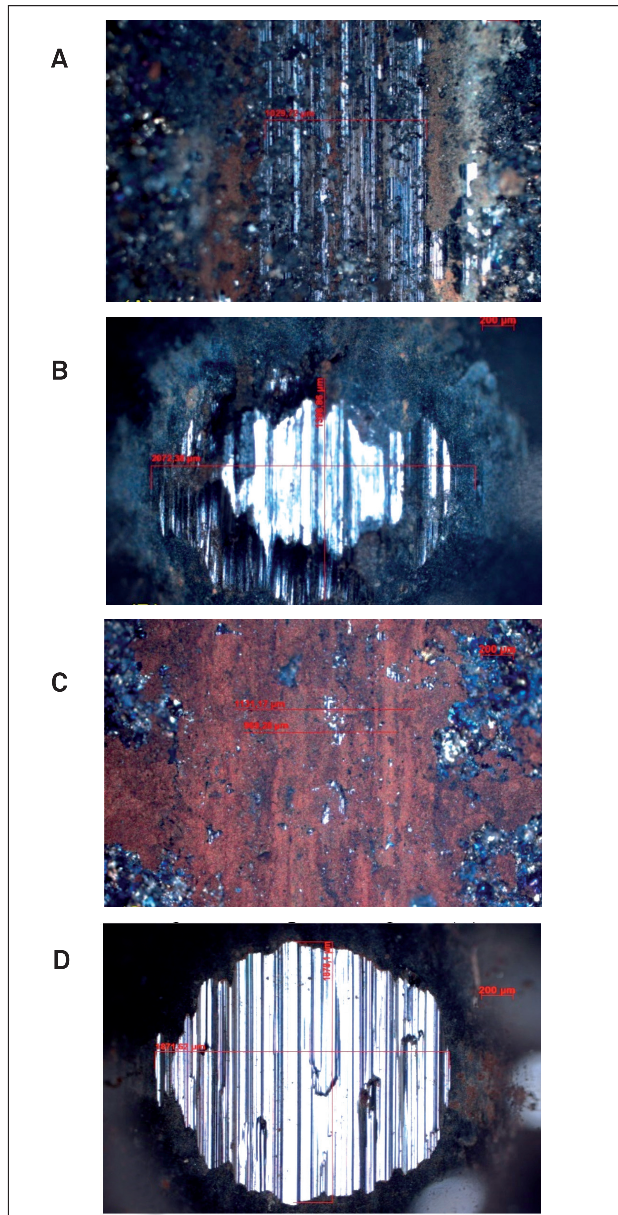


**Figure 5:** Images of wear tests. Track, nitrogen atmosphere (A); Sphere, nitrogen atmosphere (B); Track, argon atmosphere (C); Sphere, argon atmosphere (D).

the stabilization while after 40.000 cycles a stabilization is already registered for sample 1 that also presents high dispersion of values (extremes of 0.55 and 0.90).

Both curves show an evolution of the coefficient of friction in relation to the number of cycles. Sample 1, obtained using nitrogen as a carrier gas in the thermal spray process presented higher values of coefficient of friction than sample 2. This result may indicate that sample 1 presented a higher TiN content than sample 2 as this compound is very hard (Rockwell C hardness of 85). For both samples, a lot amount of material in the form of particles was obtained along and externally to the wear tracks. Also, optical microscopy showed that with the number of cycles tested (150.000), none of the Ti coating on the PEEK substrate fractured. Figure 7 present particles obtained in sample 1 and 2 wear test and they may be characterized morphologically according to ASTM F 1877 – 05 Standard Practice for Characterization of Particles as shown in Figure X2.6 – granular, irregular-rough and to Figure X2.5 – Granular, irregular-smooth, respectively[12].

Based on the images of particles obtained in the wear tests, it can be inferred that particles with dimension higher than 50 μm are probably derived from the thermal spray process and were removed during the test. On the other hand, particles with dimension lower than 5 μm may have been generated by the mechanical action of wear.

The hydroxyapatite formation in the surface of samples during immersion in the SBF was investigated by SEM and EDS. No alkaline treatment was performed on the samples trying to avoid a possible inflammatory reaction when used in vivo, which could be exacerbated by the release of sodium ions[13]. The beginning of the formation of the hydroxyapatite compound was observed after 18 days of immersion in SBF. The morphological appearance of the coating was observed by SEM.

SEM images of the PEEK sample coated with titanium using nitrogen as carrier gas (sample 1) followed by immersion in the SBF at 37ºC (±1ºC) for 23 days. SEM image showed a darker side of the micrograph corresponding to the coating formed in the *in vitro* tests and the lighter side of the micrograph corresponding to the titanium coating. It is believed that the apatite nuclei were formed after approximately 18 days of immersion and

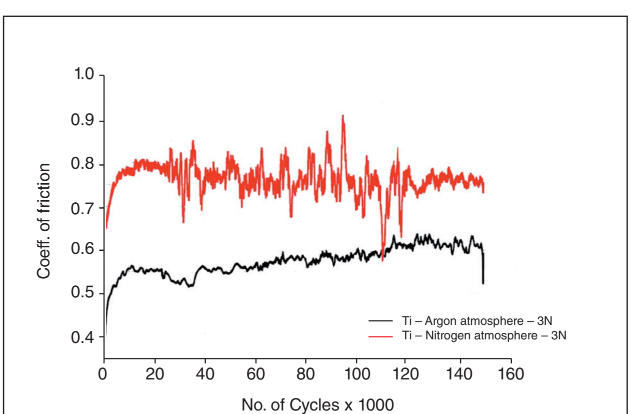


**Figure 6:** Coefficient of friction of samples 1 and 2.

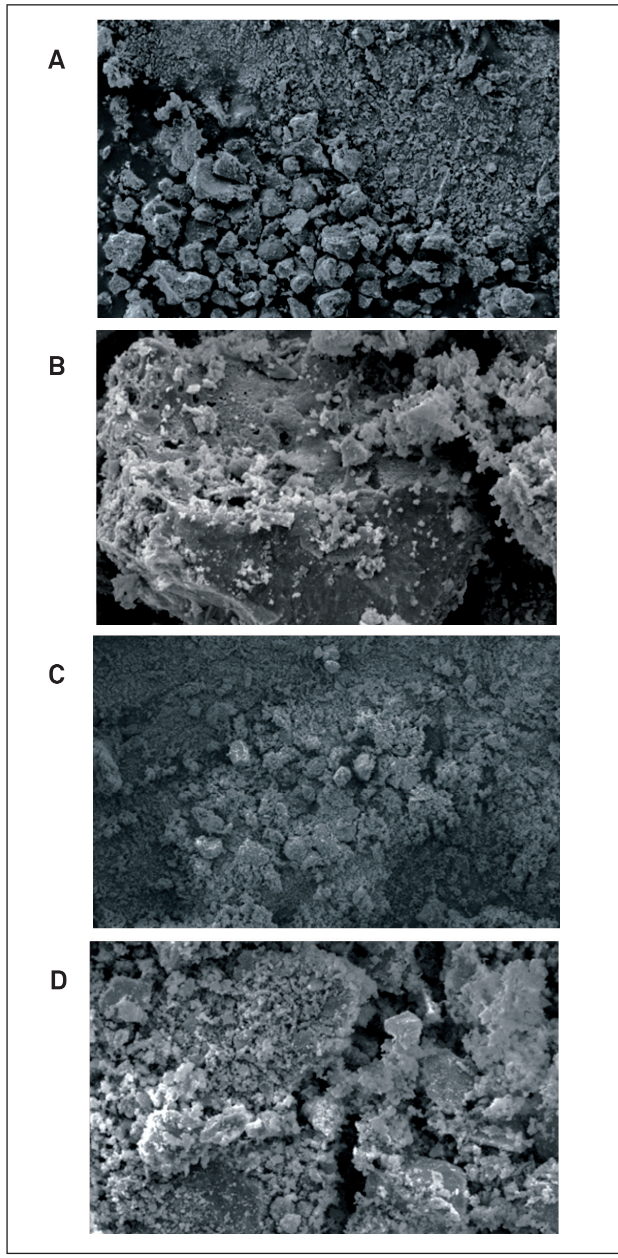


**Figure 7:** SEM of particles of wear tests of samples 1 and 2 nitrogen atmosphere (A - 100μm, and B, 10μm) – argon atmosphere (C-100μm, and D, 10μm).

continued to grow, spreading over the entire analyzed surface. EDS detected the presence of Ca and P in the coating surface of the samples and the relation Ca/P of the compounds found were to be 1.02, consistent to the formation of $CaHPO_4$, $Ca_2P_2O_7$, $Ca_2P_2O_7.2H_2O$ or $CaHPO_4.2H_2O$), 0.47, consistent to the formation of $Ca(H_2PO_4)2.H_2O$ and 1.7, consistent to the formation of hydroxyapatite - $Ca_{10}(PO_4)_6(OH)_2$[14].

## CONCLUSIONS

It was possible to prepare good Ti coatings on PEEK substrate using flame thermal spray process and when argon was used as a carrier gas, the formation of TiN was lower than when nitrogen was used as a carrier gas and thus, the coating presented a lower coefficient of friction. Although in wear tests a significant amount of particles were generated for both samples, none of the coatings was fractured within 150.000 cycles. The formation of hydroxyapatite and other precursors were detected by EDS on samples 1 and 2 after the *in vitro* tests. It can be concluded that PEEK coated by Ti may be potentially used as static orthopedic implants because the materials present bioactivity and when not submitted to wear, the coatings seem stable.

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