Microstructure and Wear Behaviour of Ti Reinforced HVOF Coating

A Szabo*, I D Utu, I Hulka, I Bordeasu and I Mitelea

„Politehnica“ University of Timisoara, Timisoara, Romania, EU

*Corresponding author: alexandru.szabo@upt.ro

Abstract. In order to improve the wear resistance and biocompatibility of titanium, which is well known as a common orthopaedic and dental implants material, aluminium oxide (Al2O3)-hydroxyapatite (HA) composite coatings were deposited onto titanium substrate using high velocity oxygen fuel (HVOF) thermal spraying process. The microstructure of the Ti reinforced HVOF coating was investigated by scanning electron microscopy (SEM) and phase identification was performed using X-Ray diffraction techniques (XRD). The surface properties of the titanium substrate before and after Al2O3-HA coating deposition in terms of roughness and wear resistance, using pin on disk method, were determined. The obtained results showed that Al2O3-HA coatings can extremely improve the wear resistance of the titanium substrate. A higher roughness of the coating evidently has a positive effect onto the adhesion of the implant osseointegration.

1. Introduction
Titanium and its alloys are the most used materials in the biomedical domain gradually replacing other metallic biomaterials like stainless steel and cobalt-chromium alloys in applications where high mechanical strength requirements [1]. They have been successfully used in the field of orthopaedic and dental implants due to their excellent mechanical properties, corrosion resistance, and biocompatibility [2]. Usually these characteristics of the implants in terms of surface texture, bioadhesion, non-toxicity, wear resistance, etc can be enhanced by depositing materials [1].

Coating deposition of aluminium oxide (Al2O3) and hydroxyapatite (HA, Ca10(PO4)6(OH)2) mixtures may improve the bioactivity and corrosion resistance of the originally bio-inert material [3,4]. Hydroxyapatite coated implants are being widely used to improve osteoconductivity of metallic implants, its structure being close to that of the human bone mineral component, while alumina is a ceramic material which possesses high values for hardness and good wear resistance properties in physiological environment [5].

Many studies are also focused in recent years on the manufacturing of composite coatings, using different deposition methods (thermal spraying, laser, sol-gel, etc), consisting of metallic biocompatible materials and bioactive ceramic materials based on biodegradable calcium phosphates [6].

The paper is focus on manufacturing of different Al2O3-HA coatings using the high velocity oxygen fuel (HVOF) spraying method onto the surface of a titanium substrate in order to improve its wear resistance and biocompatibility.
2. Materials and experimental procedure

As substrate material a commercially titanium bar was used which was cut in specimens of 60 mm diameter. Before depositions the surface of the substrate was sand blasted and cleaned with acetone (Fig.1a). The coatings were obtained by HVOF spraying method using a powder mixture of Al₂O₃-HA (Fig.1b). The powders were mixed by ball milling with agate balls with a Al₂O₃/HA (wt%) ratio of two chemical composition: 80 %Al₂O₃+20%HA and 50 %Al₂O₃+50%HA.

![Figure 1](image1)

Figure 1. Macroscopic image of the titanium surface substrate: a) - sand blasted, b) - coated by HVOF sprayed Al₂O₃-HA powder.

For deposition, a 2700 DJM HVOF gun from Sulzer Metco was used. The spraying parameters were: 430 l/min oxygen, 60 l/min propane and 470 l/min air, the spraying distance being kept by 170 mm.

The morphology of the sprayed coating has been characterized by scanning electron microscopy (SEM: Philips XL-30 scanning electron microscope equipped with EDAX analyzer) and the phase composition has been investigated by X-ray diffraction analysis using a Cu Kα radiation (Philips X’Pert Diffractometer).

The roughness, \(R_a [\mu m]\), of the deposited materials was measured using a SJ-201 equipment from Mitutoyo.

In order to determine the sliding wear resistance of the coating and of the titanium substrate a pin-on disk tribometer (Tr-20 Micro from DUCOM-Material Characterization System) was used. The wear rate of the materials was calculate according to the variation of the wear track depth with applied load. The testing conditions were: normal load 20 N, the relative velocity between the ball (WC) and surface \(v=20 \text{ cm/s}\), and the testing distance 2000 m (the trajectory was a circle with a radius of 15 mm).

3. Results and discussion

3.1 Coatings morphology and phase composition

Figure 2 presents the surface morphology of the sprayed coating using the Al₂O₃/HA powder compositions. Analysing the SEM images from Fig. 1b and Fig.2 it can be seen that no specific thermal spraying defects (cracks, exfoliations, etc) were noticed. The EDAX analysis from Figure 3 confirms the differences between the chemical compositions of the coatings.

In Figure 4 and 5 are shown the XRD patterns of the deposited coatings. In both cases the identified phases were Ca₅(PO₄)₃(OH), Ca₃(PO)₄, Al₂O₃ and CaAl₂O₄. Beside the commonly phases hydroxyapatite and tricalcium phosphate which are usually identified, the presence of alumina and monocalcium aluminate can be noticed. CaAl₂O₄ is the main constituent of calcium aluminate cements.
Figure 2. SEM micrographs of the deposited coatings:

a) 50% Al₂O₃+50% HA, b) 80% Al₂O₃+20% HA.
Figure 3. EDAX analyses of the deposited coatings:
   a) 50%Al₂O₃+50%HA, b) 80%Al₂O₃+20%HA.
Figure 4. XRD pattern of the 50% Al₂O₃ + 50% HA coating.

Figure 5. XRD pattern of the 80% Al₂O₃ + 20% HA coating.
3.2 Roughness measurements of the coatings

The roughness of a surface is an important parameter that characterizes the quality of the coatings. In most biomedical applications, where hydroxyapatite coating are used a rough surface is required. This enhances the initial attachment of osteoblast cells and mineralization phenomena.

In the experiments the surface of the Al₂O₃-HA coatings was measured in five different areas, the value, Ra, being taken as an arithmetic mean between the five measured values of the roughness. The values obtained are shown in Table 1.

| Coating                  | Ra, µm |
|--------------------------|--------|
| 50%Al₂O₃+50%HA          | 5.64   |
| 80%Al₂O₃+20%HA          | 5.48   |

In both cases the average roughness value was about Ra=5.5 µm.

3.3 Sliding wear behavior of the coatings

In order to evaluate the tribological behaviour of the materials the wear resistance of titanium substrate before and after coating deposition was tested. The evolution of the coefficient of friction for the tested materials is presented in Fig. 6 and the average values are shown in Table 2.

| Material                  | µmed  |
|---------------------------|-------|
| Titanium                  | 0.42  |
| 50%Al₂O₃+50%HA coating    | 0.52  |
| 80%Al₂O₃+20%HA coating    | 0.67  |

In case of the Al₂O₃-HA coatings higher values for the friction coefficient were recorded compared with the Ti substrate. The different tribological behaviour of the tested materials was influenced by the wear of the counterpart. For titanium there was quite no wear trace on the surface of the counterpart compared with the Al₂O₃-HA coatings where the wear of the worn WC ball was higher, so that the contact surface between the wear partners was greater and the friction coefficient increased.
The wear resistance of the materials was determined according with the volume of the lost material (Fig. 8). As it was expected the deposition of Al₂O₃-HA coatings had a positive effect onto the sliding wear behaviour, the wear rate of the coated titanium exhibited the lower degree. The 80%Al₂O₃+20%HA coating had the best wear resistance because of the higher amount of the alumina phase.
4. Conclusions
High velocity oxygen fuel (HVOF) spraying method can be used for obtaining of Al2O3-HA coatings deposited onto the surface of a titanium substrate in order to improve its wear resistance and biocompatibility.

The XRD patterns showed that the hydroxyapatite structure has suffered no important modifications, which could decrease the restauration of the bone tissue. Moreover the measured surface roughness revealed high values (Ra≈5.5 μm) which provide a good osteointegration of the implant in the human body because of a greater contact surface.

The presence of alumina in the deposited coatings improved the wear resistance of coated titanium by approximatively 2-3 times.

5. References
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