In vitro Behaviour of Alumina-Hydroxiapatite Composites Coatings

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Hydroxyapatite (HA) is a very common material used for biomedical applications. Usually, in order to improve its poor mechanical properties is combined or coated with other high-strength materials.The present paper reports the manufacturing and the biocompatibility behaviour of two different biocomposite coatings consisting of alumina (Al_2O_3) and hydroxyapatite (HA) using the high velocity oxygen fuel (HVOF) spraying method which were deposited onto the surface of a commercially pure titanium substrate. The biological properties of the Al_2O_3-HA materials were evaluated by in vitro studies. The morphology of the coatings before and after their immersing in the simulated body fluid (SBF) solution was characterized by scanning electron microscopy (SEM). The results showed an important germination of the biologic hydroxyapatite crystallite on the surface of both coatings.

Keywords: alumina, hydroxyapatite, HVOF spraying method, microstructure, microscopy, biocompatibility

Degenerative diseases mainly require surgery to replace one or both damaged hip surfaces using prosthetic components (replacement of a half of the hip prosthesis - hemiarthroplasty, and replacement of both components - total hip arthroplasty). Following this idea the medical implants should have good surface properties in order to provide the biocompatibility and osteointegration with the human body.

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) has been widely used as coating for metallic implants because of their compatibility and to improve their stability and osteoconductivity. However its poor mechanical properties made necessary the combination with high-strength materials [1, 2].

The mechanical properties of hydroxiapatite (HA) are ussual improved by using reinforcement materials obtaining a ceramic-matrix composite material. For efectiveness the strength and the elastic modulus of the ceramic phase must be higher than those of the matrix [3, 4]. It is very important that the reinforcement agent does not react with the HA in oder to reduce its compatibility. Based on these, alumina, which is classified as a bioinert material, can used as reinforcement for many ceramics because of its high strength and fracture toughness [5].

Alumina (Al_2O_3) has been used in orthopedic applications due to its excellent wear resistance, high hardness and high abrasion resistance [6]. Also, the protective effect of Al_2O_3 helps with corrosia and at the same time is capable of reducing the friction on articular surfaces [7].

In our previous study it has been demonstrated that the HVOF spraying of Al_2O_3-HA coatings deposited onto the surface of a titanium substrate had a positive effect onto the tribological properties in terms of coefficient of friction and wear rate [5, 8].

The aim of this study is to evaluate the biological properties of two different Al_2O_3-HA coatings exposed in a simulated body solution for 21 days.

Experimental part

Materials and methods

The Al_2O_3-HA coatings were deposited by HVOF spraying method [8, 9] onto the surface of a commercially pure titanium bar. Before deposition, the specimens (60 mm diameter) were sand blasted and cleaned with acetone. The powder mixture ratio of Al_2O_3-HA used for experiments consisted of two chemical composition: 50%Al_2O_3 +50%HA and 80 %Al_2O_3+20%HA.

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 bioactivity of the coatings was realized by *in vitro* tests by immersion the samples in liquids which simulate the biologic fluids (SBF). A simulated body fluid (SBF) is a solution with an ion concentration close to that of human blood plasma, kept under mild conditions of *p*H and identical physiological temperature [10]. SBF was first introduced by Kokubo et al. in order to evaluate the changes on a surface of a bioactive glass ceramic [11].

The SBF can be used as an in vitro testing method to study the formation of apatite layer on the surface of implants so as to predict their in vivo bone bioactivity [12]. So that for an artificial material to bond to living bone, the formation of bonelike apatite layer on the surface of an implant is of significant importance [13].The consumption of calcium and phosphate ions, present in the SBF solution, results in the spontaneous growth of bone-like apatite nuclei on the surface of biomaterials in vitro [6]. Herefore, the apatite formation on the surface of biomaterials, soaked in the SBF solution, is considered a successful development of novel bioactive materials [14]. The SBF technique for surface modification of metallic implants is usually a time consuming process and obtaining uniform apatite layers on substrates takes at least 7 days with daily refreshing of the SBF solution [15].

These media consist of 142.0 mM Na^+, 5.0 mM Mg^{2+}, 2.5 M Ca^+, 147.8 mM Cl^-, 4.2 mM HCO_3^-, 1.0 mM HPO_4^{2-} and 0.5mM SO_4^{2-} [6,7]. The specimens were dipped in glass recipients filled with SBF solution at a constant temperature of 37 °C for 21 days.

The morphology of the coatings before and after their immersion in the simulated body fluid (SBF) solution was characterized by scanning electron microscopy (SEM: Philips XL-30 scanning electron microscope equipped with EDAX analyser) [16].

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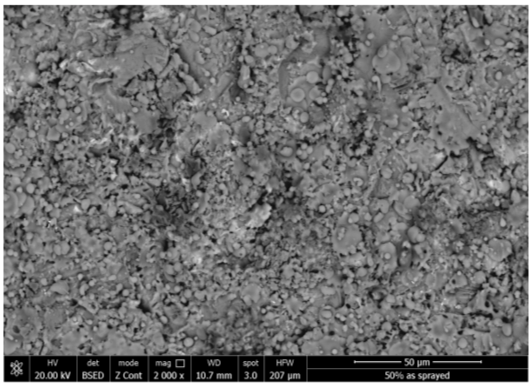

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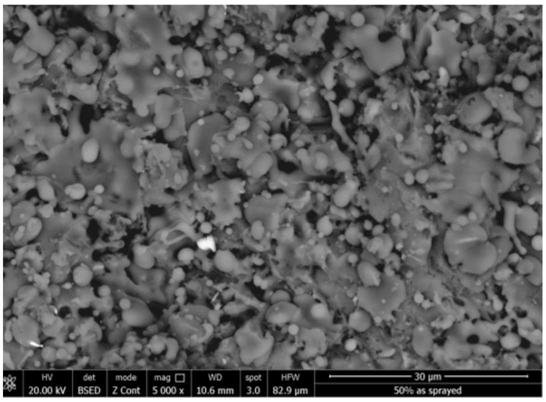

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Fig. 1. Topographic image of the HVOF sprayed 50% Al_2O_3 + 50% HA coating

Results and discussions

Coatings morphology

Figure 1 and 2 presents the surface morphology (at different magnifications) of the HVOF sprayed coatings using the two Al_2O_3-HA powders compositions. As it can be seen no specific thermal spraying defects (cracks, exfoliations, etc) were revealed. The EDAX analysis and the associated elements quantification from Figure 3 and 4 confirms the chemical composition differences between the deposited coatings, in the latter spectrum a higher alumina content was recorded.

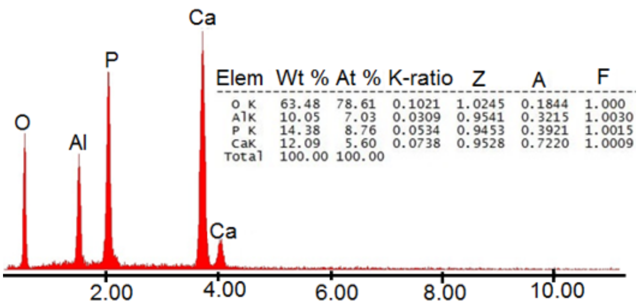


Fig.3. EDAX spectrum of the of the HVOF sprayed 50%Al_2O_3 + 50%HA coatings

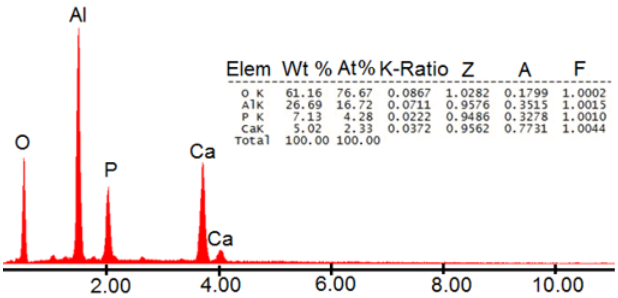
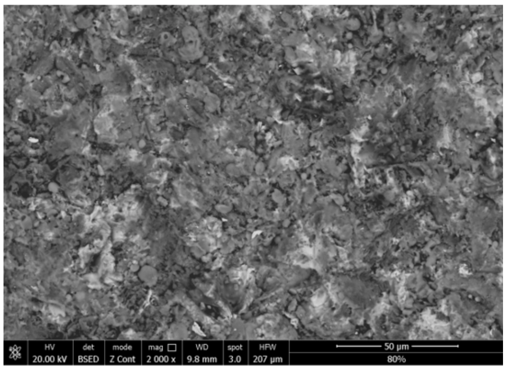


Fig.4 EDAX spectrum of the of the HVOF sprayed 50%Al_2O_3 + 50%HA coatings



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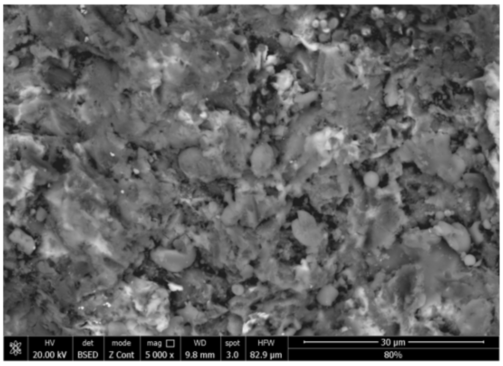

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Fig. 2. Topographic image of the HVOF sprayed 80% Al_2O_3 + 20% HA coating

In vitro mineralization behaviour of the coatings

The in vitro mineralization behaviour of the both 50 %Al_2O_3+50%HA and 80 %Al_2O_3+20%HAsprayed coatings was evaluated by immersing them in SBF solution for 3 weeks. The SEM images from figures 5 and 7 shows the morphology of the exposed samples after their cleaning in distiller water.

Analysing the images it can be noticed that in both cases an important germination of the biologic hydroxyapatite

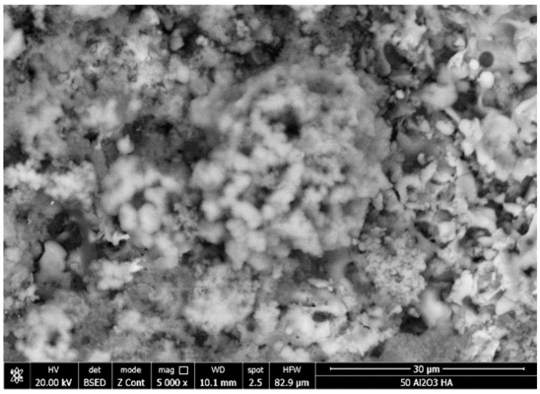

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Fig.5 SEM micrographs of the coating surface composed from 50%Al_2O_3 + 50%HA after *in vitro* mineralisation

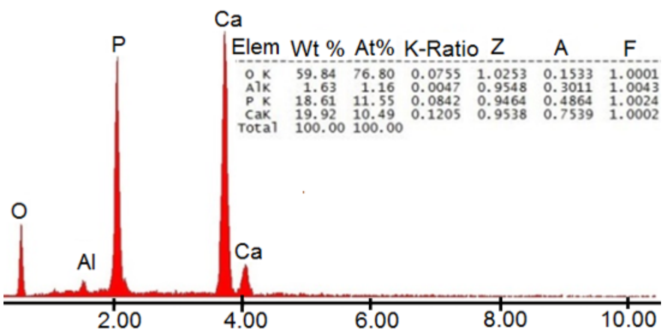

Fig.6 EDAX spectrum of the coating surface composed from 50%Al_2O_3 + 50%HA after in vitro mineralisation

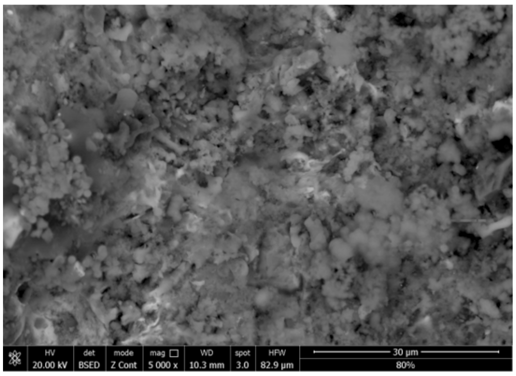

Fig.7 SEM micrographs of the coating surface composed from $80\%Al_2O_3$ +20%HA after *in vitro* mineralisation

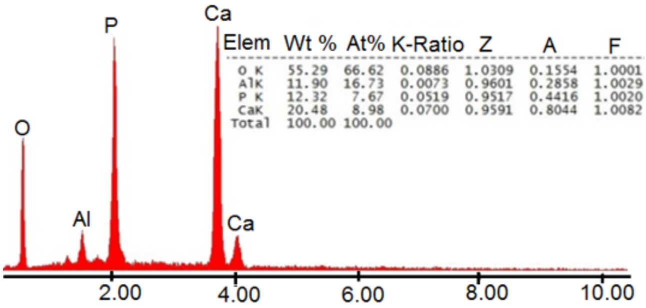

Fig.8. EDAX spectrum nof the coating surface composed from n$80\%Al_2O_3$+ 20%HA after *in vitro* mineralisation

onto the surface of the coatings. The sample with 50 % HA seems to have a higher concentration on the hydroxy-apatite crystallite compared with the other specimen. This observation is also confirmed by the EDAX analyses from figure 6 and 8 where by the latter spectrum a higher concentration of aluminium was quantify onto the surface of the coating.

The development and growing of the biologic hydroxyapatite shows a good bioactivity of the deposited coating using the HVOF spraying method. This is a necessary condition for medical implants covered with bioactive materials in order to provide a good bonding with the human tissue. Moreover, onto the surface of the formed hydroxyapatite layer the presence of interconnected pores is observed. Theyhave a positive effect regarding the anchoring of the tissue and prevent the detachment of the implant.

Conclusions

The immersion of the Al_2O_3-HA coatings, deposited by high velocity oxygen fuel method onto the surface of commercially pure titanium, in SBF solution has revealed positive results regarding their biocompatibility. Onto the surface of the exposed samples developed and growth biologic hydroxyapatite showing a good bioactivity of the deposited coating.

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