

# Abstract

Total hip arthroplasty (THA) is a widespread treatment for diseases of hip joint. The ever increasing number of THA and young patients who need this kind of surgical treatment has led to the need to improve the lifespan of the hip implants, that is 10-15 years nowadays.

Generally speaking, a THA is composed of a stem and a head that joints with an acetabular cup through an insert. Depending on the used materials the hip implants are classified in metal on polyethylene (MoP), metal on metal (MoM), ceramic on ceramic (CoC) and ceramic on polyethylene (CoP). The first material refers to the one of the head while second to the one of the insert. Both CoC/CoP and MoM couplings allow to reduce the wear rate of the implant, nevertheless other issues are related to these couplings. On one side, ceramic materials are brittle, need a strict proper positioning, have high costs and squeaking can occur under motion. On the other side, MoM coupling is associated to adverse reaction to metal debris and ions release.

Gold standard for THA is MoP coupling, where CoCrMo alloy (or stainless steel) are used for the femoral head and ultrahigh molecular weight polyethylene is employed for the insert. The stem, instead, can be made of Ti6Al4V alloy (cementless prostheses) or stainless steel (cemented prostheses).

Ti6Al4V alloy has high biocompatibility, good mechanical properties and corrosion resistance, nevertheless it has low wear and fretting resistance. For these reasons, it is used for orthopaedic implants in contact with bone, but it is not used where wear and fretting occur (femoral head or cemented stem) and it can be damaged at the head–neck junction (self-interlocking taper connection).

Taking into account all these aspects, the aim of this PhD thesis is to focus on improving the bio-tribological properties of Ti6Al4V by means of a surface modification treatment.

A low cost process of surface ceramic conversion was performed; it consists of a solid pack diffusion process by thermal treatment in a mixture of boriding powders.

The aim is to obtain a titanium borided coating on Ti6Al4V alloy substrate, in order to combine the good lubricant and tribological properties of a ceramic coating with the good mechanical properties of the metallic substrate.

Five different mixtures of boriding powders were compared, but only one allowed to develop an effective coating. Once selected the mixture of boriding powder, the process was performed following several strategies: without any pre/post treatment of the substrate, with a pre-treatment of surface deoxidation, with a pre-treatment of surface oxidation and with a post thermal treatment. Moreover, the effect of temperature and time of treatment was also evaluated.

All the treated samples were characterised in terms of chemical composition, microstructure, structure, coating thickness, hardness, roughness, wettability, coating adhesion and friction coefficient. From this analyses, it was assessed that time and temperature of treatment have mainly effect on thickness, hardness and adhesion of the coating, because of the different boron diffusion rate, and on the microstructure of the substrate, because of the occurrence of different phase transformations. While chemical composition, wettability and friction coefficient are approximately the same for all the conditions tested according to similarity of composition of the external layer of the coating.

According to these results, the samples treated at the highest temperature and for the longest time, without any pre/post treatment, were selected to evaluate wear and fretting behaviour, as well as interaction with physiological fluids.

In both cases, pin on disk/palate tests showed an enhanced tribological behaviour in comparison to reference material such as untreated Ti6Al4V and CoCrMo alloys. It is of relevance the change of wear mechanism of UHMWPE from adhesion (in current used couplings) to abrasion (in contact with the treated Ti6Al4V alloy), the high resistance to wear of the coating when tested on itself (as it could occur at the head-neck junction) and the ability of the treated Ti6Al4V surface to chemically bind PMMA (as it could occur at the stem-cement interface).

Moreover, the treated material would be used in contact with biological fluids, thus the treated samples were analysed by means of zeta potential measurement and XPS analyses before and after protein adsorption. The titanium borided coating shows attitude to chemically bind proteins at physiological pH.

This PhD thesis, even if it is not an exhaustive analysis of all the properties of the titanium borided coating, gives good results based on which it is possible to think to a future application of it as biomaterial.