3.7 Ceramic Coatings in Metal-PE Joints: Where Are We Now?

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Abstract

Several types of hard coatings were applied onto metallic components in arthroprostheses' bearings to reduce UHMWPE wear and the consequent wear debris-induced periprosthetic osteolysis, that is still the main problem in arthroplasty. This approach was aimed to obtain in the surface of metal components finish and scratch resistance similar to the ones of alumina ceramic components. Many attempts were made to improve the surface properties of stainless steel, of cobalt-chromium, of titanium alloys and of zirconium alloys. Arthroprostheses' bearing components coated by titanium nitride (TiN) or diamond-like carbon (DLC), and more recently zirconium-2,5 Nb alloy with a surface layer of monoclinic zirconium dioxide were introduced on the market. This paper briefly reviews the literature on ceramic coatings in prosthetic bearings to assess the today's status of this technology in arthroplasty.

Introduction

Metal-on-polyethylene bearings are still the most used in arthroplasty [1], performing with satisfactory outcomes especially in older, less active patients [2]. From a long time polyethylene was identified as the main source of debris-induced periprosthetic osteolysis that is still among the main causes of implants failure. Many attempts made to reduce the wear of metal-on-polyethylene bearings, focussed on both components of the joint. Research was addressed both to improve the tribological properties of polyethylene e.g. by introduction of second phases or by enhancing the polymeric chains cross-linking, both to improve by a ceramic coating the hardness and the finish stability of metallic THR ball heads and femural TKR components. The results achieved on the latter topic are briefly reviewed in the following.

Physical Vapor Deposition (PVD) Coatings

Plasma spray coatings are not of help in bearings, due to their limits in adhesion to the substrate and to their residual porosity. The most commonly used processes Physical Vapor Deposition (PVD) technologies, e.g. Arc Vapor Deposition, Sputtering (Magnetron Sputtering) and Electron Beam evaporation. Briefly, PVD process consists in the generation of a plasma of metal ions that are "transported" by an electric field to the surface to be coated. Depending on the process, the behaviour of the plasma may be different, obtaining in turn coatings with different properties notwithstanding the same name. The common characteristics of these processes is that the parts to be coated must be exposed to the plasma, and are then referred as "line of sight" processes. This fact may have significant implication when complex shapes are to be coated, like e.g. in the case of the femoral component of knee replacements.

Titanium Nitride Coatings

TiN is a popular wear protective coating so far, and is used also for its brilliant golden colour to improve the aspect of objects like e.g. door handles. Being biocompatible [3], TiN coatings are used also in several biomedical applications, including dental instruments, dentures, orthodontic archwires, endovascular stents and catheters.

TiN coatings may show very high internal stresses due to differences in coating properties at local level depending on the deposition process parameters (e.g. reaction environment, presence of impurities, rate of formation, angle of deposition), that joined to the relatively low adhesion may lead to the spallation of the coating from the substrate. The use of higher coating temperatures, that lead to some diffusion bonding, or of an interlayer may improve the coating characteristics. TiN coatings were applied in hip, knee, ankle and shoulder replacements, but little exists in the literature concerning their clinical outcomes. Positive clinical results after ten years of a series of 50 TiN coated total ankle replacements was recently reported [4], but other reports are raising concerns about the ability of TiN coatings to withstand wear damage in clinical applications [5] and the analysis of THR heads retrieved after clinical use [6] put in evidence extensive abrasion of the coating, that reached about 70% of the articulating surface in the case of an high-demand heavy patient.

Diamond-Like Carbon Coatings

The name of Diamond-Like Carbon (DLC) identifies a class of carbon-based materials, characterised by the simultaneous presence of sp^3 and sp^2 C-C chemical bonds giving them structure and properties intermediate between diamond and graphite. The characteristics of these materials are often described by the ratio sp^3/sp^2, e.g. the concentration of diamond-type bonds vs. the graphite ones, which value is depending on deposition conditions of the film. The structure of DLC films, that may be described as a dispersion of diamond "nodules" in a graphite matrix, is inherently metastable, and may transform to graphite at high temperatures or under irradiation. Also in DLC coatings the main problem is the adhesion to the substrate, as the interfacial residual stresses may reach very high values within the 1-2 μm thick coating layer.

The biocompatibility of DLC coatings is a well documented behaviour [7,8] and was confirmed also by recent studies [9]. Notwithstanding the fact that it is known at least DLC coated ball heads are in clinical use the literature is concerning only laboratory tests, that gave controversial results. Wear tests aimed to evaluate DLC as a coating for tibial trays of knee prostheses [10] measured 3.5 increase in wear of UHMWPE pins sliding against DLC-coated Vs. cast CoCr alloy plates, leading the Authors to remark the unsuitability of DLC coating for the intended application. Also the results of biaxial hip simulator tests were controversial: similar wear of UHMWPE cups against CoCr DLC-coated and uncoated heads was reported [11], both values higher than the wear of the same cups against alumina heads, while other Authors [12] measured wear rates of UHMWPE cups similar for Alumina and DLC coated heads, both higher than CoCr coupled to the same cups. In pin-on-disk tests against PMMA pins [13] DLC coated Ti6Al4V disks performed worse than wrought CoCrMo alloy raising doubts about coating resistance to third body wear.

An original bearing couple DLC-on-DLC was tested in a simplified hip simulator and in pin-on-disk wear tests with satisfactory results [14], but this bearing couple was not transferred to clinic up to now.

In-Situ Zirconia Coating

The formation of hard zirconium dioxide (ZrO_2) layer on zirconium alloys to protect them from corrosion is a very well known process, used in the past to protect the claddings of Zircalloy-2 nuclear fuel pins from fretting corrosion on spacer grids in Light Water Reactors [15]. Black or blue-black zirconium dioxide layers may be obtained on zirconium alloys in air, in steam or in water at temperature between 350 and 600°C [16], or in molten salts like chlorides, nitrates, cyanides at temperatures in the range 700-800°C [17].

Composition		**Mechanical Properties**	
Zr	Min 95,5	Density (g/cm^3)	6,44
Fe+Cr	0,2	Yeld Strength (MPa)	380
Hf	Max 4,5	U.T.S. (MPa)	552
Nb	2,5	Fracture Strain (%)	16
O	0,18	Young Modulus (GPa)	98

Microindentation tests [18] put in evidence that the oxide layer formed in-situ increase the hardness to about 14 GPa for a depth some 5 µm beneath the surface, then in 3-4 µm the hardness drops to the value of the underlying zirconium alloy (about 3 GPa).

Oxidised zirconium gave positive results in laboratory tests. Pin-on-disk wear tests against cartilage pins allowed to assess its suitability for emiarthroplasty [19], and tests against PMMA pins assessed the effectiveness of the treatment in protecting the soft metallic zirconium alloy against scratching due to third bodies in the joint [13]. Similar positive results were reported in knee simulator tests performed on femoral components in comparison with CoCr [20]. Further knee simulator tests showed a remarkable reduction in wear rate of UHMWPE tibial inserts running against oxidized zirconium alloy in comparison with CoCr alloy, the reported wear rates were 4,68 mm^3/Million cycles against and 0,69 mm^3/Million cycles, respectively [21]. The treatment proven its effectiveness also in THR ball heads: UHMWPE-oxidized zirconium alloy couple showed in hip simulator tests a significant reduction in wear in comparison to UHMWPE -CoCr alloy couple both in clean, both in abrasive wear conditions [22].

Discussion and Conclusions

Ceramic coating perform very well in reducing wear and friction in engineering applications, and then their application on metallic components of arthroprostheses to reduce UHMWPE wear appeared a attractive to solve the problem of debris-induced periprosthetic osteolysis. The analysis of the literature shows that the significant research effort devoted to develop TiN and DCL coatings for artroprostheses' bearings by many research groups worldwide has not led to widespread clinical applications up to now. On the other hand, oxidised zirconium layers formed by in-situ reaction on zirconium alloy looks very promising.

Laboratory wear tests of UHMWPE coupled to TiN coated metals are rather controversial, and joined to the reports of cases of TiN coating delamination [5,6] may have decreased the interest for the use this coating in arthroprostheses. Also the laboratory tests on DLC coatings show controversial results on the improvements in wear achieved by this treatment in comparison to CoCr alloy. Research aimed to control by optimised deposition conditions the high internal stresses of these extremely thin coatings to avoid coating spallation and detachment are still in progress.

Oxidised zirconium layers were reported to reduce PE wear with respect to CoCr alloy both in simulated hip and knee bearing conditions [21,22], and on these basis positive clinical outcomes may be expected. The recent voluntary withdrawal from the market of uncemented oxidised zirconium knees due to some early loosening [23] seems unrelated to the wear behaviour of the coating. While a significant mass of data about laboratory tests on ceramic coatings is present in the literature, at the best of author's knowledge only one report concerning the clinical outcomes of ceramic coatings on metallic bearing surfaces of arthroprostheses was published up to now, concerning TiN-coated ankle replacements [4]. The lack of reports of clinical results on ceramic coatings applied on arthroprosthes bearings was on already remarked by Sauer and Antony [1] in their 1998 review, and the same situation may be remarked today: notwithstanding the time elapsed and the progresses made the literature is still concerning laboratory tests only.

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