

# Multifunctional Ceramic Thin Films For High-Performance Orthopaedic Implants

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## ABSTRACT

Protective hard films on soft inorganic/organic substrates are appealing for several technological applications like solar cells, organic electronics, fuel cells, etc. The main concern is still related to the bad quality of the interface and to the weak mechanical properties of the film as a consequence of the low working temperatures mandatory to prevent substrate softening/melting. Our research activity at Rizzoli Orthopaedic Institute is mainly directed toward the deposition of functional ceramic thin films to improve the mechanical properties (and thus the clinical performances) of the load-bearing plastic component of the prosthetic implant. To this aim, we use a novel sputter-based electron deposition technique named Pulsed Plasma Deposition (PPD) able to provide nanostructured ceramic thin films highly adhered to the plastic substrate and with optimum mechanical performances even if working at room temperature and using very-soft substrates.

**Keywords:** Pulsed Plasma Deposition, anti-wear coatings, YSZ, ZTA, UHMWPE.

## 1 INTRODUCTION

### 1.1 Materials for Total Joint Replacement (TJA)

Total joint arthroplasty (TJA) is the most frequent treatment for a joint subjected to degenerative diseases, including osteoarthritis, rheumatoid arthritis, ankylosing spondylitis, and vascular necrosis. At present, standard orthopedic implants are based on a metallic (cobalt-chromium or titanium alloys, stainless steel) or ceramic (alumina or zirconia) component articulating against a polymeric material (ordinarily UHMWPE). Even if metal-on-metal, ceramic-on-ceramic and metal-on-ceramic articulations have been investigated, most of the joint replacements envisage UHMWPE, due to its toughness, durability and biological inertness [1]. TJA can be generally considered a successful treatment; however the mean life span of the implant is limited to 10-15 years depending on several factors. Recent literature on implant retrievals reported that the main reasons for failure include aseptic loosening and

osteolysis [2] that are directly related to the formation of UHMWPE wear debris [3, 4]. Failure of the implant implies a revision surgery, with a rising of the costs for the Regional Health Care System and additional perceivable troubles for the patient. In the latest years, several approaches have been pursued to reduce implant wear, including: the replacement of the plastic component with ceramic or metallic materials; the chemo/physical modification of the surface of the metallic component; the coating of the surface of the metallic part with low-friction and low-wear materials [5, 6]. However, despite the efforts, a common agreement on the best solution for the detrimental problematic of wear debris formation in TJA has been not reached yet, leaving the way open for completely new approaches.

### 1.2 Pulsed Plasma Deposition technique

Pulsed Plasma Deposition (PPD) has been emerging as a powerful physical vapor deposition technique able to stoichiometrically deposit thin films of a number of materials such as complex oxides, nitrides, carbides, carbon-based films, semiconductors for several applications like solar cells, fuel cells and microelectronics. [7, 8]. In PPD a high-power electron beam accelerated with a potential difference up to 25kV, is focused on the surface of a rotating target material. The electron beam vaporizes the first layers of the target material and generates a dense plasma plume perpendicular to the target surface and directed toward a rotating substrate properly located at a certain distance. A primary advantage of PPD is the ability to efficiently work even at room temperature, enabling the deposition on heat-sensitive substrates like plastics [9]. PPD is conceptually similar to the more widespread PLD, but when compared to the latter it presents several advantages, as a direct consequence of the different nature of the ablating source (electrons vs. photons): higher pulse energy, frequency and energy efficiency (> 30%); capability to ablate wide band-gap or highly reflective materials (Eg > 6 eV); easier scalability of the process for the deposition of large area films by relatively low-cost multiple systems. PPD exhibits high average deposition rates that result in the deposition of more continuous and smooth films when compared to those deposited with other techniques at lower deposition rates: the possibility to obtain crystalline films at room temperature, to ablate highly refractive (wide band-gap) materials and to deposit on plastic materials.

To overcome the above-mentioned detrimental issue of plastic deformation and debris formation, we investigated the deposition of hard, well-adhered and tough nanostructured yttria-stabilized zirconia (YSZ) and zirconia-toughened alumina (ZTA) thin films directly deposited onto the surface of UHMWPE by the PPD technique. We show here the results of the chemical, structural, mechanical and tribological characterizations of such coatings.

## 2 MATERIALS AND METHODS

3% yttria-stabilized zirconia (YSZ) and zirconia-toughened alumina (ZTA, 75% alumina, 25% zirconia) films were deposited by Pulsed Plasma Deposition (PPD) technique on medical-grade UHMWPE substrates [9]. The morphology, micro-structure and chemistry of deposited films were characterized by Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray Spectroscopy (EDS), X-ray diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS). Mechanical properties and coating-substrate interface quality were investigated by nanoindentation and scratch tests. Preliminary pin-on-disk tribological tests were carried out in air, water and physiological solution against an alumina ball counterpart to evaluate the efficacy of the proposed approach and the worn track analysed with SEM-EDX.

## 3 RESULTS

Deposited zirconia films exhibited a fully cubic structure and a smooth nanostructured surface. Coatings up to several microns thick have been deposited by PPD (Fig. 1).

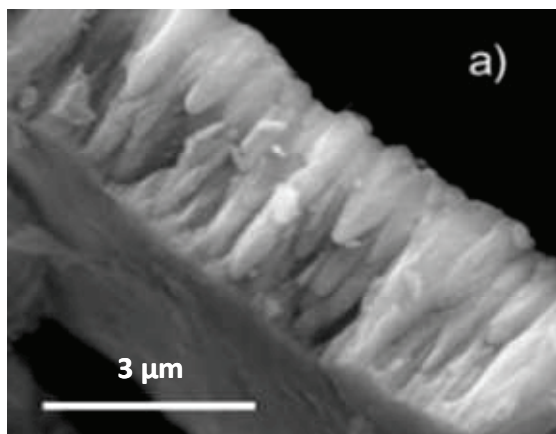


Figure 1: SEM image of the cross section of a thick YSZ film deposited on UHMWPE.

Mechanical tests showed that hard, tough and well-adherent films were deposited. In particular, nanoindentation tests revealed rather high hardness and Young's modulus values (17 GPa and 154 GPa respectively), while critical fracture tests revealed that, even under loads as high as 500 mN (equivalent to ~ 8 times the maximum pressure exercised on a femoral head during normal walking activity) no radial cracks, spalling or pile-up phenomena were observable, revealing a high fracture toughness and a very high adhesion degree of the ceramic film to the plastic substrate.

The very strong interface adhesion was also assessed by scratch tests.

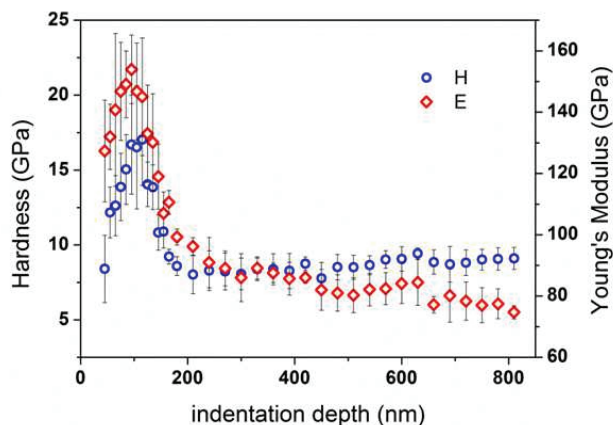


Figure 2: Nanoindentation curve reporting hardness and elastic modulus of YSZ film deposited on UHMWPE.

An indentation depth reduction of about 330% was registered when the UHMWPE substrate was covered by a ceramic film as thin as 1.5  $\mu\text{m}$ . Hence, the presence of the ceramic film was sufficient to greatly adsorb the applied stress, drastically decreasing the plastic deformation of the substrate.

Further, the viscoelastic behavior of the coated plastic insert under local load was measured: the material yielding under an applied constant load (creep) was larger for UHMWPE compared to coated UHMWPE, whose total creep being only the 19% of the total creep of UHMWPE, respectively.

Finally, preliminary tribological tests carried out in air against an alumina ball counterpart showed wear rate as low as  $3.2 \cdot 10^{-6} \text{mm}^3 \text{N}^{-1} \text{m}^{-1}$  after 500.000 cycles. Interestingly, the formation of a smooth tribolayer was observed in the area of the worn track, being very likely the responsible for the very low wear rate values.

## 4 CONCLUSIONS

An incontrovertible solution to the detrimental problematic of plastic wear debris formation in TJA has not been found up to the present, leaving the way open for novel routes. The proposed approach was able to directly coat the plastic insert of a commercial implant joint with hard ceramic materials as yttria-stabilized zirconia and zirconia-toughened alumina, thus providing specific additional mechanical and superficial properties, while preserving the well established mechanical properties of UHMWPE. The results of this study expanded the knowledge about the tribo-mechanical behavior of the ceramic-plastic combination, thought to be an alternative and promising approach to improve UHMWPE mechanical properties in TJA.

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