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Optimizing lateral homogeneity of ion-induced surface modifications of non-planar dielectric polyethylene components employing ion fluence simulations and optical measurements of the sp2-dependent reflectivity

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ABSTRACT

An approach to enhance the durability of artificial joint replacements is to modify the surface of their polymeric bearing material to diamond-like carbon (DLC) by ion-induced polymer-to-DLC-transformation in a plasma-immersion ion implantation process. Due to the dielectric character of the polymer and thus the impossibility of direct application of high voltage pulses to the component, this process requires an additional accelerator electrode above the surface. We here present two useful tools to optimize the geometry of such electrodes. First, we simulate the ions' trajectories for various electrode geometries and receive the resulting fluence distribution across the surface of the treated part. Second, we introduce a novel optical method to determine non-destructively the local ratio of sp^2 hybridized carbon atoms and thus the locally implanted fluence utilizing changes in reflectivity. Combining both tools, we here optimize, by way of example, the geometry of a grid electrode to obtain a homogeneous DLC-modification of a typical hip replacement inlay.

1. Introduction

Representing the sixth most frequent surgery in Germany in 2016, the implantation of a hip total endoprosthesis was performed more than 230,000 times [1]. Considering the demographic change – the share of citizens of the overall population at the age of 65 and older will increase from 21% in 2013 to 33% in 2060 [2] - and the average age for primary total hip joint replacements (currently 69.7 years [3]), the interest in increasing the life span of an artificial joint replacement is clearly visible. The service life in today's joint replacement amounts to 15 to 20 years which explains the quantity of about 47,000 revision surgeries (hip + knee) in 2014 in Germany [4]. Aseptic loosening accounts for more than two thirds of all failing issues and is mainly caused by wear debris increasing the activity of macrophages and osteoclasts and ending up in enhanced osteolysis and thereby loosening of the implant [5].

Considering the amount of wear particles, a major step has been taken by using highly cross-linked polyethylene as inlay material in combination with a ceramic joint head [6–8]. Further progress could be possible with the application of diamond-like carbon (DLC); an amorphous modification with a significant portion of sp^3 hybridized carbon atoms (at least 10%) showing high hardness, excellent bio-compatibility and low surface roughness [9,10].

Therefore, DLC coatings are used in a broad range of industrial applications: Especially its outstanding tribological properties qualify it for bearings, sliding surfaces and protective coatings, e.g. in the automotive industry, for magnetic storage media or, as mentioned, in a medical context [11]. In principal, the metastable DLC is prepared under ion bombardment of the growing film [12]. The desired film composition and thus its properties strongly depend on the deposition method which can mainly be categorized in PVD (physical vapor deposition) and PECVD (plasma-enhanced chemical vapor deposition) techniques. Hydrogenated forms of DLC (a-C:H) can be produced in a PECVD process in which the vapour deposition occurs due to chemical reactions on the substrate. The required energy is provided by a plasma which thus allows much lower process temperatures compared to common CVD [12–14]. In contrast, hydrogen free amorphous carbon (a-C) and tetrahedral amorphous carbon (ta-C) films result from PVD where a carbon containing material is evaporated and the carbon ions are condensed to the substrate's surface. Common PVD processes are

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magnetron sputtering (often used in industrial applications), pulsed laser deposition or vacuum arc evaporation [10,15–18].

Another appropriate way of realizing diamond-like properties is the ion bombardment of a polymeric base material leading to densification, hydrogen loss and cross-linking of the carbon network and finally resulting in a DLC modification of the surface layer up to a depth of about 300 nm [19,20]. Compared to common coatings, the risk of delamination is strongly reduced due to the decreased layer tension as result of the range distribution of the ions and thus a gradient in hardness and density [21,22]. A further benefit is the easy integration of antibacterial properties by implanting metal nanoparticles [23].

Ion implantation in electrically conducting objects using Plasma Immersion Ion Implantation is easily possible [24]. On the contrary, surface modifications of an insulating polymer can either be performed by using an additional cathode above the surface or at the sample's backside. This can be realized in a simple way for planar samples. However, complex-shaped objects require greater effort, especially if the use of a back-side electrode is not possible due to a variation of the sample thicknesses resulting in a variation of the effective electrical field. Because of the dependence on the orientation of the surface according to the moving direction of the accelerated ions, DLC modification becomes inhomogeneous for non-planar components in the case of a flat grid cathode (see Fig. 1 a)). Therefore, the geometry of the electrode has to be optimized for each specific sample geometry.

To do so, we simulated the ions' trajectories using different geometries of the grid electrode to gain the implanted ion density on the surface of the implant. Using the developed simulation, we optimized the electrode shape for homogeneous surface modification of a hip inlay. As a second step, we introduced a novel optical method to determine non-destructively and space-resolved the ion fluence locally implanted into complex shaped surfaces. Based on the measurement of the local reflectivity which varies according to the local ratio of sp2 hybridized carbon atoms, this method allows to measure the implanted ion fluence and thus gives information about the homogeneity of the surface modification. Combining simulation and optical examination, it is possible to optimize the geometry of the grid electrode for homogeneous modification adapted to the shape of the component.

2. Materials and methods

2.1. DLC

As primary material we used a highly cross-linked Ultra High Molecular Weight Polyethylene (UHMWPE) which is vitamin E stabilized (Vitelene®, Aesculap AG, Germany) [25,26] and has a molecular mass of about 5000 kg/mol before irradiation [27].

We transformed the surface of the polymer to DLC by implanting ions in a plasma immersion ion implantation step. Due to cross-linking, densification and a rearrangement of bonds, this process leads to the formation of a diamond-like carbon surface. For this process, we used a gas mixture of 20% Argon and 80% Hydrogen at a pressure of $p = 5\ 10^{-3}$ mbar. We applied $P_m = 800$ W of microwave power ($f = 2.45$ GHz) to generate the plasma in an electron cyclotron resonance (ECR) plasma source. The ions of the plasma were accelerated towards the surface by applying a pulsed high voltage of $V_p = 20$ kV with a repetition rate of $f_R = 20$ Hz and a pulse width of $\tau = 5$ µs to the electrode grid. Due to the range distribution of the impinging ions, the result is an about 300 nm thick surface near region of DLC with a gradient in hardness, density and diamond-like properties. This gradient reduces the internal stress and could be of great advantage for the adhesion of the DLC-surface and could therefore improve the long-time stability of the surface.

2.2. Simulation

To evaluate space-resolved the implanted fluence on the sample surface, we simulated the trajectories of the ions which are extracted from the plasma boundary sheath and accelerated towards the grid electrode, passing it and finally hitting the target's surface, as illustrated in Fig. 2.

As first step, we modelled all components (inlay, grid electrode etc.) by using a common 3D computer-aided design software (Autodesk AutoCAD® 2017) which also makes it possible to integrate existing 3D models, for example a commercially available hip inlay. The plasma was simulated by an arrangement of positive charged particles with a median distance of 72 mm to the electrode. The median distance was estimated using Child's Law, which shows that the plasma sheet expands from 18 mm to 132 mm during a 5 µs lasting high voltage pulse. Because of the low impact of this distance on the ion trajectory, we simply assumed an intermediary distance of 72 mm. According to the experimental setup the mesh size of the grid cathode varied from 0.16 mm to 1.5 mm. However, above a distinct distance between electrode and sample, the grid characteristic of the anode can be neglected and the electrode can be replaced by a massive body which is penetrable by ions (see *3.2 Results: Grid shading*).

By utilizing a finite element tool (Comsol Multiphysics® 5.2.0.220 with AC/DC (electrostatics) and CAD Import module) we then simulated the electric field of the arrangement. To keep the computing time within an acceptable range, a physics-controlled mesh was used with higher point density on the sample to improve accuracy. The electric field as well as the geometries of the electrode and the sample were subsequently exported as a point cloud to a python script.

As first step of the script, a starting configuration was generated distributing the particles equally across the plasma boundary sheet

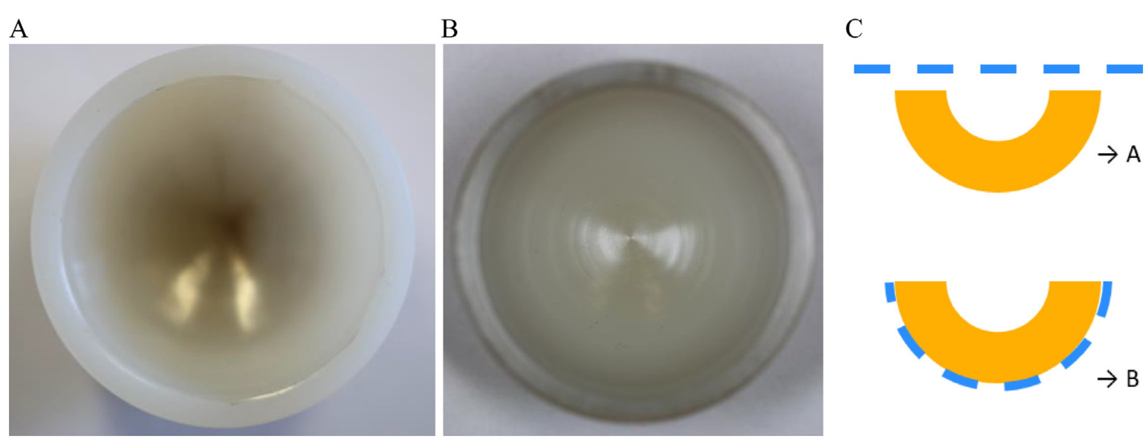

Fig. 1. Modification of non-planar samples A) Inhomogeneous surface modification using a flat top-side grid-electrode B) Homogeneous modification using a backside-electrode. C) Illustration of flat top and curved backside electrode.