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Research Paper

Silicon nitride films for the protective functional coating: Blood compatibility and biomechanical property study

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ABSTRACT

Behaviors of silicon nitride films and their relation to blood compatibility and biomechanical have been interesting subjects to researchers. A systematic blood compatibility and biomechanical property investigation on the deposition of silicon-nitride films under varying N_2 and CF_4 flows was carried out by direct current unbalanced magnetron sputtering techniques. Significant role of surface property, chemical bonding state of silicon nitride film and blood compatibility, mechanical properties for the films were observed. The chemical bonding configurations, surface topography, contact angle and mechanical properties were characterized by means of X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and nano-indentation technique and CSEM pin-on-disk tribometer. Blood compatibility of the films was evaluated by platelet adhesion investigation. The results of the platelet adhesion tests shown that the effect of fluorine and nitrogen-doped revealed an intimate relationship between the ratio of polar component and dispersion component of the surface energy and its hemocompatibility. Si–N–O coating can be a great candidate for developing antithrombogenic surfaces in blood contacting materials. The chemical bonding state made an adjustment in microstructured surfaces, once in the totally wettable configuration, may improve the initial contact between platelet and biomedical materials, due to the appropriate ratio of dispersion component and polar component. To resist wear, biomedical components require coatings that are tough and hard, have low friction, and are bio-inert. The study suggests that by Si–N coating the metal surfaces could be a choice to prolong the life of the sliding pair Co–Cr–Mo alloy/UHMWPE implants.

1. Introduction

Biomedical implants such as vascular grafts, artificial heart valves or interventional devices and artificial hip and knee joints have been gaining widespread use with development of medical engineering. Thrombus generation on the surface of the blood-contacting biomedical devices remains as one of the particularly major problems that trigger the life-threatening device failure. The artificial hip and knee joints are implanted in the human body to fulfill biological and

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mechanical functions. The implants should withstand dynamical mechanical contact pressures and avoid formation of debris over a desired long-term biological interaction with the surrounding biological tissue (Loir et al., 2004; Jacobs et al., 1996). With time, mechanical wear and stress, corrosion and tissue reactions lead either to a mechanical failure or to aseptic loosening of the implant, the lifetime of the artificial joint implant is limited (Peters et al., 2002; Tiainen, 2001).

Surface modification techniques are indispensable for improving both the mechanical and physical properties of biomaterial implants in direct contact with the blood and tissue (Saito et al., 2005). Some of protective functional films materials being considered for biomedical materials applications may prevent or alleviate production of wear debris, and inhibits platelet adhesion and activation (Thomson et al., 1991; Tran et al., 1999; Shi et al., 2003). The films coated the artificial joints can reduce corrosion and wear and therefore extend the service lifetime to the benefit of the patients (Loir et al., 2004; Hauert, 2003.; Sheeja et al., 2005; Ge et al., 2003; Daisaku et al., 2002). Silicon nitride (Si-N) thin films are of special interest in both scientific research and industrial applications due to their remarkable properties such as high thermal stability, chemical inertness, high hardness and high-corrosion resistance. These properties make the films good candidate as biocompatible and biomechanical coatings for biomedical devices and tools. Silicon nitride films on Co–Cr–Mo alloy as biomechanical coating was put forward in this paper, and it is worthwhile to study this matter further in order to point out its practical benefits, advantages, and limitations.

However, the blood coagulation mechanism on silicon nitride films in biological environment has not been well understood so far (Okpalugo et al., 2004; Nurdin et al., 2003). There have been several research that platelet adhesion on the surface of film modification is related to surface energy and wettability (Li et al., 2010; Yang et al., 2003; Wan et al., 2007).These reports indicate that hydrophobic surface tends to inhibit blood cell adsorption. As for hydrophobic property, it is well known that fluorocarbon structure provide great water-shedding characteristics (Saito et al., 2005). Thus, we propose that fluorine–carbon modified silicon nitride films process to research hemo-compatibility of materials.

Fluorinated silicon nitride films have been deposited from fluorinated ammonia (NF_3) or silicon halides (SiF_4, SiF_2) mixtures in order to avoid the incorporation of hydrogen (Fainer et al., 1997), those films were demonstrated to have some advantages, such as the complete elimination of Si–H bonds from the films and an improvement in their chemical and electrical stability (Jun et al., 1999; Fujita et al., 1985).

Diamond-like carbon (DLC) (Wan et al., 2007; Wang et al., 2004), carbon nitride film (Wang and Jiang, 2009), fluorine-doped and silicon-incorporated DLC films (Saito et al., 2005; Su et al., 2010; Roy et al., 2009) are widely used in many kinds of blood contacting medical devices. However, the limited understanding to-date of the role of deposition technique, coating composition, and coating surface properties on the biological performance of the coatings has been a barrier to their optimization for a given biomedical application.

The silicon nitride with the same chemical bond C–C, C–N, C–F, and Si–C bonds coating on Co–Cr–Mo alloy as biomechanical coating was put forward. There is no information in the available literature about Si–N films coatings orthopedic materials or their comprehensive investigations.

In the present work, silicon nitride (Si–N–O and F:Si–C–N) films have been deposited by DC unbalanced magnetron sputtering physical vapor deposition using mixtures of N_2/Ar (and CF_4) in different deposition parameters. The relationship between the surface property (surface energy or wettability), chemical bonding state of silicon nitride film and blood compatibility, mechanical properties were investigated, to clarify the dominant factor determining the compatibility. The objective of the present work is to explore the potential of Si–N (Si–N–O and F:Si–C–N) films being able to fulfill the demand of protective coatings in the biomedical field.

2. Materials and methods

2.1. *Coating preparation*

The films were deposited on commercially Co–Cr–Mo alloy ($\Phi 14 \times 1.5\ mm^2$) using our newly designed unbalanced sputtering apparatus at different deposition conditions. The base pressure was 1×10^{-3} Pa; Ultra high purity crystal silicon (99.9999%) was used as sputtering target; high purity argon (99.99%) was used as the sputtering gas, and high purity nitrogen and CF_4 (99.99%) was used as the reactive gas for the film deposition. The working pressures and sputtering time were held at 0.5–0.6 Pa and 7 min throughout the experiments. The target-to-substrate distance was 85 mm; the substrates negative biasing voltage is 150 V and the substrate ion current density is 150–160 mA. In order to investigate the influence of the deposition conditions on the film properties, F:Si–C–N films were deposited under various the CF_4 flows: 3 sccm, 6 sccm, 9 sccm, the N_2 flow was maintained in 20 sccm; The other films (Si–N–O) were also deposited under the different N_2 flows: 0 sccm, 10 sccm, 15 sccm, 20 sccm.

2.2. *Structural and compositional characterizations*

The film thickness was measured by the step profiler (AMBIOS XP-2, USA). The XPS analysis was performed with Thermo VG Scientific Multitech 2000 XPS system, UK. The peak shift due to charging was calibrated with the shift of C1s peak. The peaks were deconvoluted after background corrections using shirley method and the curves were best fitted with the Gaussian fitting.

2.3. *Surface characterization*

The atomic force microscope was used to study the surface topography of the deposited films. AFM imaging was conducted using a MFP-3D (Asylum Research, USA) under AC mode in air using Olympus AC 240 TS probe (Si_3N_4 cantilevers), with nominal spring constants of 3.91 nN/nm. Different locations on the coatings were investigated in random position. The average particle sizes and roughness values of the deposited films were calculated using image processing software.