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#### **Applied Surface Science**

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# Wear of UHMWPE against nitrogen-ion-implanted and NbN-coated Co-Cr-Mo alloy formed by plasma immersion ion implantation and deposition for artificial joints

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#### ARTICLE INFO

## Article history: Received 27 February 2012 Received in revised form 4 May 2012 Accepted 4 May 2012 Available online 11 May 2012

Keywords:
Plasma immersion ion implantation and deposition (PIII&D)
Artificial joints
Total hip replacement
Pin-on-disk wear test
Niobium nitride (NbN)
Nitrogen ion implantation

#### ABSTRACT

NbN thin film was deposited on the Co–Cr–Mo alloy by plasma immersion ion implantation and deposition (PIII&D) to reduce the volume wear rate of UHMWPE. In addition, nitrogen ions were implanted on the surface of the Co–Cr–Mo alloy prior to the NbN film deposition in order to increase the hardness of the substrate. XPS analysis revealed that nitrogen ions were implanted into the surface of the Co–Cr–Mo alloy, leading to the formation of CrN and  $\text{Cr}_2\text{N}$ . The UHMWPE volume wear rate was measured using a pin-on-disk tribometer. The wear test result showed that the volume wear rate of UHMWPE against NbN-coated Co–Cr–Mo alloy declined by 20% as compared to that in the untreated Co–Cr–Mo alloy. In addition, the UHMWPE wear rate against the nitrogen-ion-implanted and NbN-coated Co–Cr–Mo alloy could be drastically reduced by up to 48%. It can be concluded that a combination of prior nitrogen ion implantation and NbN coating via PIII&D is a promising surface treatment tool for extending the lifetime of metal-on-polymer artificial joints.

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#### 1. Introduction

Owing to the increase in the average lifespan and the growth in accident and disease incidence rates, there has been a rapid increase in the demand for artificial replacements of body parts. When a natural joint wears out, either by accident, disease, or aging, an artificial joint is needed to replace the function of the natural joint. More than 200,000 people receive a hip prosthesis every year in the USA, and more than 500,000 people do so around the world [1,2]. However, many researchers report that the probability of failure or loosening for such prostheses increases sharply 15–20 years after implantation [3].

In the area of orthopedic hip implants, a metal–polymer material combination is most commonly used because of the high ductility and good wear performance of the components [4]. Stainless steel, Co–Cr–Mo alloy, and Ti-based alloy are some of the metallic materials used for fabricating the femoral head. Among these, Co–Cr–Mo alloy is most commonly used because of their high hardness and excellent wear properties [5–7]. Ultra-high-

molecular-weight polyethylene (UHMWPE) is extensively used to fabricate the polymeric acetabular cup owing to its superior properties such as high toughness and excellent wear properties [3,8,9].

However, the wear debris generated from the bearing-like motion of the UHMWPE cup causes a decrease in the lifetime of the orthopedic implant [8–10]. This UHMWPE debris is transported to hard and soft tissues, where it causes tissue necrosis and osteolysis. This is known to be the major cause of the loosening and failure of artificial joints, and it necessitates repeated replacement operations [10].

For this reason, numerous studies have been conducted to increase the lifetime of artificial joints, focusing on the metal–polymer bearing system. These studies can be divided into two different types. One kind looks at the modification of the UHMWPE liner material, and the other concerns the modification of the metallic femoral head, which is made of materials such as Ti-6Al-4V alloys, 316L stainless steel, and Co–Cr–Mo alloys. With the aim of improving the wear properties of UHMPWPE, many researchers have investigated approaches such as gaseous ion implantation on the surface of UHMWPE [11,12], cross-linking of UHMWPE by means of an electron beam [13,14], and coating hard materials on UHMWPE [15].

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As an alternative, research has been conducted on surface modification of the metallic femoral head, to reduce the volume wear rate of UHMWPE liner material, by implanting gaseous ions such as nitrogen, carbon, or oxygen ions on the metallic surface [7,9,16–20]. However, this kind of ion implantation has the limitation of a shallow implantation depth [19,21]; further, it is not possible to control the release of metal ions [22], which can interact with cell groups and thereby lead to apoptosis or necrosis [20,23].

For this reason, many researchers have studied the deposition of hard ceramic films such as TiN, CrN, or DLC films on the metallic femoral head to reduce the volume wear rate of UHMWPE and deter metal ion release [3,6,8,24,25]. However, the disadvantage of this technique is delamination of the ceramic film and consequent accelerated wear of UHMWPE, which can only be solved by precautious interface engineering.

Plasma immersion ion implantation and deposition (PIII&D) is a more advanced method for surface modification because it allows for simultaneous modification of the films being deposited and the underlying metallic substrate during the deposition process through ion implantation. Therefore, PIII&D is the most suitable method for surface modification of the materials used for artificial joints.

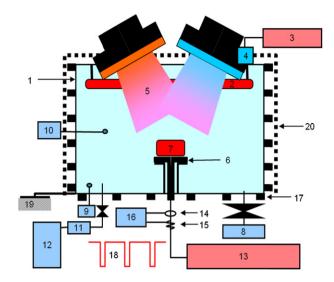
In our previous work, we deposited a TiN film on 316L stainless steel by using PIII&D to reduce the wear of UHMWPE in artificial joints. The volume wear rate of UHMWPE was reduced considerably by modifying the interface between the TiN layer and 316L stainless steel through PIII&D [6].

In this study, we introduce a niobium nitride (NbN) film, which has been investigated for application in various fields because of its high hardness, wear resistance, temperature stability, and chemical inertness [26]. Recently, it has been shown that NbN has outstanding biocompatibility [27]. Thus, it is anticipated that NbN films will find extensive applications in the biomaterials field. The aim of this study was to reduce the volume wear rate of UHMWPE against the Co–Cr–Mo alloy by depositing a NbN film on the surface modified Co–Cr–Mo alloy using PIII&D.

#### 2. Materials and methods

#### 2.1. Surface modification

In order to reinforce the substrate, nitrogen ions were implanted in the Co-Cr-Mo alloy prior to the deposition of the NbN film using PIII&D. Fig. 1 shows a schematic of the PIII&D instrument used, which is described in detail in our previous reports [6,28]. A Co-Cr-Mo substrate (Stellite® 21 alloy) was used as a disk. It consisted of a Co-Cr-Mo alloy matrix containing dispersed hard carbides that strengthen the alloy and give it a high degree of hardness. The surface of the Co-Cr-Mo substrate was polished using 1-µm diamond paste, and the substrate was placed inside the vacuum chamber. After the chamber was evacuated to a base pressure of  $0.67 \times 10^{-3}$  Pa, the substrate was sputtercleaned in Ar plasma to decontaminate the surface, by applying a pulsed DC bias of -500 V. Upon completion of the cleaning process, nitrogen plasma was generated by RF discharge using an inductively coupled plasma (ICP) antenna installed inside the vacuum chamber. The ICP was generated using a 13.56-MHz RF power supply. Nitrogen gas was introduced into the vacuum chamber to maintain a pressure of 0.09 Pa, and 200 W of RF power was applied to the ICP antenna. Subsequently, pulsed negative DC bias of -30 kV and -50 kV were applied to the substrate stage to perform nitrogen ion implantation. Details of the experimental conditions for the ion implantation are described in Table 1.



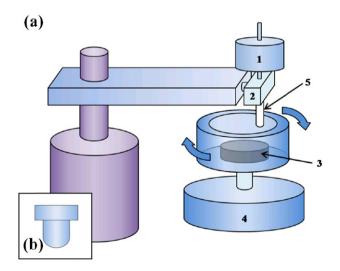
**Fig. 1.** A schematic view of PIII&D instrument: (1) vacuum chamber, (2) RF antenna, (3) RF generator, (4) matching network, (5) plasma, (6) substrate stage, (7) substrate, (8) vacuum pump, (9) high-vacuum gauge, (10) Langmuir probe, (11) MFC, (12) working gas, (13) high-voltage pulse generator, (14) pulse current transformer, (15) HV divider, (16) oscilloscope, (17) magnet, (18) HV pulsed DC, (19) ground, and (20) lead shield.

**Table 1**The experimental condition of nitrogen ion implantation.

Dose (#/cm <sup>2</sup> )	Time (min)
$5\times10^{16}$	16
$5 \times 10^{16}$	8
$1.5\times10^{17}$	8
	$5 \times 10^{16}$ $5 \times 10^{16}$

#### 2.2. NbN film deposition

A NbN film was deposited on the nitrogen-ion-implanted Co–Cr–Mo alloy using the PIII&D process. The Nb target (LTS Chemical, 99.95%) of 76.2 mm diameter was installed on the magnetron sputtering gun. The sputtering target was sputter-cleaned in Ar plasma by applying a pulsed DC bias of  $-450\,\mathrm{V}$ . The NbN film was then deposited by applying a DC power of  $600\,\mathrm{W}$  to the Nb target in a gas mixture of Ar and N<sub>2</sub>. In addition,  $200\,\mathrm{W}$  of RF power was consistently applied to the ICP antenna in order to



**Fig. 2.** (a) A schematic view of pin-on-disk wear tester: (1) normal load, (2) load cell, (3) Co-Cr-Mo disk, (4) motor, and (5) UHMWPE pin. (b) Shape of the UHMWPE pin.

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