Materials Science and Engineering C 72 (2017) 576–582

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Fabrication of hydroxyapatite thin films on polyetheretherketone substrates using a sputtering technique

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ARTICLE INFO

Article history:
Received 17 October 2016
Received in revised form 15 November 2016
Accepted 24 November 2016
Available online 5 December 2016

Keywords:
Sputtering
Hydroxyapatite
Polyetheretherketone
Titanium

ABSTRACT

Hydroxyapatite (HA) thin films were coated on a polyetheretherketone (PEEK) substrate using a sputtering technique. A thin titanium (Ti) intermediate layer was formed between the HA and the PEEK surface to improve adhesion of the HA film to the PEEK substrate. The coated films were recrystallized using a hydrothermal treatment to reduce the dissolution of the HA film. The films were then characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM), and a UV-Vis spectrophotometer. A pull-out test was performed to measure the film-to-substrate adhesion strength, and an immersion test was performed in ultra-pure water.

In the XRD patterns of the sputtered film with the Ti intermediate layer on the PEEK substrate, small HA peaks and large Ti peaks were observed. After the hydrothermal treatment, the intensity of the HA peaks increased. The transmittance of the HA films with 5 and 10 nm Ti intermediate layers was >79% and 68%, respectively, in the visible light wavelength region (400–700 nm) after the hydrothermal treatment. The adhesion strength of the hydrothermally treated HA films increased with decreasing thickness of the Ti intermediate layer, and the strength reached 2.7 MPa with the 5-nm-thick Ti intermediate layer. In the immersion test, the HA film with a 5-nm-thick Ti intermediate layer without hydrothermal treatment exhibited a released Ti concentration of 42.0 ± 2.4 ppb. After hydrothermal treatment, the released Ti concentration decreased to 17.3 ± 1.1 ppb.

1. Introduction

Dental implants increase the quality of life for many patients with tooth loss. The material of choice for dental implants is titanium (Ti), which was first introduced by Brånemark because Ti osseointegrates into bone [1]. However, Ti implants have some problems. One problem is a potential allergy to Ti [2]. Some studies have reported the possibility of hypersensitivity to titanium implants [3–5]. According to Müller et al., 56 patients had developed severe health problems after receiving Ti implants, and 37.5% of the patients were positive to Ti, tested with memory lymphocyte immunostimulation assay (MELISA) method. Removal of the Ti implants led to remarkable recovery within six to nine months [4]. Another problem is the higher stiffness of Ti, which has a higher Young's modulus (110 GPa) than bone (10 GPa) [6]. This higher stiffness induces high stress peaks during load transfer at the bone-implant interface, which may lead to a damage of the bone [7–8]. In addition, Ti can cause aesthetic problems due to its metal colour, which can present as a greyish colour in the peri-implant soft tissue in the case of mucosal recession around a Ti implant. An increasing number of patients are demanding dental implants made of metal-free materials [9].

Currently, ceramic dental implants made of zirconia have attracted attention because of their tooth-like colour, biocompatibility, and high fracture toughness [10]. However, zirconia implants may have a problem in regard to the stress distribution around the implant because zirconia has a high Young's modulus of 210 GPa compared to that of the Ti (110 GPa) [11]. The zirconia implants can also cause a high stress peak at bone-implant interface as is the case with the Ti implants [12–13].

Another biocompatible material with a Young's modulus of 3–5 GPa, which is closer to that of bone, is polyetheretherketone (PEEK) [14]. This low stiffness should prevent the generation of the high stress peak at the bone-implant interface. Regarding mechanical durability, Schwitalla et al. reported that static pressure tests with PEEK materials under maximum biting force. They concluded that PEEK materials were suitable for the use as dental implants though a cyclic fatigue loading tests had to be performed to prove the long-term stability of PEEK as a further step [15]. Since PEEK also showed resistance to degradation in vivo, the several orthopaedic and spinal devices manufactured from PEEK have been approved by the U.S. Food and Drug Administration (FDA) in the late 1990s [16]. PEEK was offered commercially in 1998 as a biomaterial for long-term implants [17]. Since then, PEEK has been shown to be a high performance thermoplastic polymer to replace metallic implants in the field of orthopaedics [18]. These developments suggest that PEEK could be a substitute for Ti in dental implants. However,

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http://dx.doi.org/10.1016/j.msec.2016.11.111
0928-4931/

PEEK has a low energy surface due to a relatively hydrophobic surface, which limits cellular adhesion. In terms of biocompatibility and osseointegration, PEEK is a biologically inert material [19]. Surface properties are important for tissue responses. Modification of the PEEK surface can make it more attractive for osteoblast growth, leading to improved bone integration.

Hydroxyapatite (HA) coating is a good potential alternative for surface modification of PEEK for the improvement of osseointegration because of the excellent osteocompatibility of HA. Many HA coating techniques have been reported, such as plasma spraying, sol-gel, sputtering, laser ablation, and biomimetic and electro deposition [20]. Among these techniques, the radio frequency (RF) sputtering technique is a particularly attractive method because it results in a homogeneous thin film <1-μm-thick that exhibits strong adhesion to the substrate [21]. Sputter-coated HA thin films have shown superior bone bonding strength and have been used clinically for dental implants [22–23].

However, HA cannot be coated onto PEEK by the sputtering technique because the adhesion strength of the HA film to PEEK is very poor. Chemically, PEEK is intrinsically inert and has a different thermal expansion coefficient (4.7×10^{-5}/°C) than HA (1.4×10^{-5}/°C) [24–25].

Ti can be coated onto PEEK by the sputtering method, and the adhesion strength of the Ti film to PEEK satisfies the required level for coating PEEK dental implants [6,26]. The adhesion strength of the sputtered HA film to Ti is also high [22]. Taking the preceding point into consideration, fabrication of a Ti intermediate layer between an HA film and a PEEK surface can be expected to improve the adhesion strength of the HA film to PEEK. The Ti intermediate layer should also be thin because the greyish colour of the Ti has to be minimized as much as possible.

In the present study, we prepared HA films on a PEEK substrate by forming a Ti intermediate layer between the HA film and PEEK using a sputtering technique. The thickness of the Ti intermediate layer was varied to investigate the influence of the Ti layer thickness on the transparency of the film and the adhesion of the HA film to the PEEK substrate.

2. Materials and methods

2.1. Materials

The substrates used were PEEK plates ($10 \times 10 \times 2$ mm^3). In addition, quartz substrates ($10 \times 10 \times 1$ mm^3) were used for analysis of the visible light transmittance of the films. A Ti plate (50 mm diameter × 5 mm thick, Kojundo Chemical Corp., Japan) and powdered HA (Taihei Corp., Japan) were used as sputtering targets.

2.2. Methods

2.2.1. Deposition

RF magnetron sputter coating was performed using an Anelva Model L-210HS-D magnetron sputtering system (Anelva Corp., Japan). An RF generator operating at 13.56 MHz was coupled to the target electrode through an impedance matching network. The sputtering chamber was evacuated to a pressure below 1×10^{-5} Pa using an oil-diffusion pump equipped with a liquid nitrogen trap. Argon gas (99.999%) was then introduced into the chamber using a mass flow controller at a constant flow rate of 1.5 sccm. Before deposition occurred, the target was covered with a shield and pre-sputtered using Ar ions for 15 min. The Ti deposition was performed on the PEEK substrate using an Ar gas pressure of 0.5 Pa and a discharge power of 100 W to fabricate 5, 10, 50, or 100 nm thick intermediate layers. Then, the HA was coated using an Ar gas pressure of 0.5 Pa and a discharge power of 60 W to obtain a 1-μm-thick film. The HA films with the Ti intermediate layers was fabricated as seen in Fig. 1. The HA films with 5-, 10-, 50- and 100-nm-thick Ti intermediate layers were labelled as Ti5nm-HA, Ti10nm-HA, Ti50nm-HA and Ti100nm-HA. In addition, the 1-μm-thick HA film with 1000-nm-thick Ti intermediate layer was also fabricated for analysis with X-ray diffractometry (XRD) to obtain enough diffraction intensity from the Ti intermediate layer. The diffraction intensity from a Ti intermediate layer that was <100 nm thick was too weak to detect. The HA film with the 1000-nm-thick Ti intermediate layer was labelled as Ti1000nm-HA.

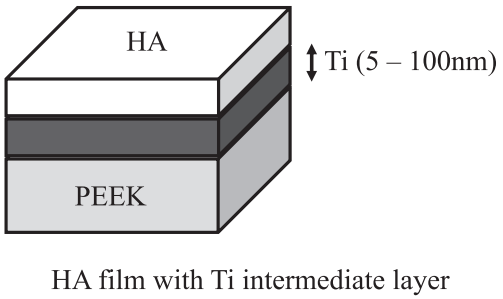

Fig. 1. Schematic drawing of the HA film with the Ti intermediate layer.

The hydrothermal treatment was performed at 120 °C and 0.2 MPa in a NaOH solution in a stainless steel vessel for 24 h to recrystallize the HA film. The NaOH solution (pH = 9.5) was used to reduce film dissolution during the treatment [16]. The sputtered films were placed in 400 mL of the NaOH solution during the hydrothermal treatment. After the treatment, the films were washed in distilled water to remove any residual NaOH solution. The hydrothermally treated HA films with 5-, 10-, 50-, 100- and 1000-nm-thick Ti intermediate layers were labelled as Ti5nm-HA(hyd), Ti10nm-HA(hyd), Ti50nm-HA(hyd), Ti100nm-HA(hyd) and Ti1000nm-HA(hyd).

The prepared films were evaluated using X-ray diffractometry (XRD) (Ultima IV, Rigaku Corp., Japan) with a CuKα radiation source operating at 40 kV and 30 mA excitation current. The surfaces of the films were examined by scanning electron microscopy (SEM) (S-4300, Hitachi, Japan) with an accelerating voltage of 5 kV. The visible light transmission of the films was measured using a UV-Vis spectrophotometer (U-3010; Hitachi, Japan).

2.2.2. Pull-out tests to determine the adhesion strength of the films to the substrate

Six-millimetre diameter aluminium rods were glued onto the films using an epoxy resin adhesive (SW2214, Sumitomo 3 M Corp., Japan). The rods were pulled from each film at a crosshead speed of 0.5 mm/min using a precise tensile tester (LCS-1, Tokyo Testing Machine Corp., Japan). After the tests, the substrates were examined with an optical microscope to determine the location of the failure, and chemical analysis of the surface of the substrate was performed by X-ray photoelectron spectroscopy (XPS: JPS-9010TR, JEOL) to evaluate residual layers. The adhesion strength was calculated by dividing the pull-out force by the observed contact area. The strength was determined from an average of eight tests.

2.2.3. Immersion tests

The Ti5nm-HA and the 5-nm-thick Ti film without the HA film (Ti5nm) coated on the PEEK substrates were immersed in ultra-pure water to evaluate the dissolution of Ti ions. The ultra-pure water was prepared using a Millipore Elix Essential apparatus (MD, U.S.). Each sample was placed in 10 mL of the water and maintained at 37 °C. The Ti plates ($10 \times 10 \times 1$ mm^3) and the PEEK plates were also immersed for the control. After a period of a week, the water was sampled, and the Ti concentration of the water was analysed using inductively coupled plasma mass spectrometry (ICP-Mass; 7500CX, Agilent Technologies, US). The final values were determined from an average of the three samples.