Titanium Coating of Scaffold Carbon Foam by ECR Sputtering

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Titanium films, of 5 µm in thickness were deposited uniformly on three-dimensional structures of scaffold carbon foam substrates using a hybrid electron cyclotron resonance-direct current (ECR-DC) sputtering system. A cylindrical hollow cathode with internal diameter of 80 mm and external diameter of 90 mm and length of 60 mm, negatively biased, was used as titanium atoms supplier. The DC sputtering voltage applied to the target controlled the feeding with excited titanium atoms. The Vickers micro-hardness of the films was found to be in the range of 250–300 HV. The film surfaces were smooth and showing pure titanium, preferentially grown on the Ti (100) crystallographic phase. Flexural strength and elastic modulus of the carbon foam were improved by a factor of 1.5 and 2.6 respectively.

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1. Introduction

In recent years, scaffold carbon foams are widely used for tissue engineering. Carbon foam consists of a honeycomb three-dimensional structure, obtained mainly by pyrolyzing a polymer at high temperature in an inert gas atmosphere. The number of pores per mm varying from 0.2 to 4 characterizes the carbon foams. These cellular materials are thermally stable, low in weight and density, chemically pure, resistant to thermal stress and shock, and are relatively inexpensive.

Materials for tissue engineering should be biocompatible and corrosion resistant.1 These materials should also have appropriate mechanical properties.2 A current method for increasing mechanical properties and biocompatibility of the scaffold carbon foam is the chemical vapor deposition (CVD).3 During CVD, a continuous thin film of metals such as rhenium, tantalum, titanium or compounds such as silicon carbide can be distributed throughout the interior of a 3-dimensional structure. The films confer certain thermal or tensile properties to a carbon foam substrate and to the structure as a whole. Low cost, low density, high chemical purity, controlled thermal expansion and high thermal stability characterize the resulting product.

In the present study we aim to develop a method for uniform coating–isotropic deposition from titanium (known as a biocompatible material4, 5) outside and inside the foam structure by using a hybrid ECR-DC sputtering system. The low working pressure (10^{-2}–10^{-1} Pa) affects the properties of the film surface in terms of cleanliness and adhesion. Titanium and TiN films can be prepared with high deposition rate also by magnetron sputtering6) or electron beam sustained Ti arc plating6) but in these methods a strong directional mode of deposition–anisotropic deposition-occur. The effects of the sputtering potential on the excited Ti atom intensities, the film composition and the mechanical properties as flexural strengths and elastic modulus of the coated scaffold carbon foam have been investigated.

2. Experimental Procedures

In our experiment we used carbon foam sized of 50 mm × 25 mm × 5 mm having pores of 200–500 µm in diameter. The carbon foam substrates were introduced inside the cylindrical shaped target of the ECR-DC sputtering system shown schematically in Fig. 1.

Microwave power with 2.45 GHz frequency was introduced in the cylindrical plasma chamber of 300 mm in diameter and 300 mm in height through a quartz window. The argon gas was introduced into the plasma chamber via mass flow controller near by the quartz window. A magnetic coil surrounding the plasma chamber produced the magnetic field with 0.0875 T strength necessary to fulfil the ECR condition. The electrons having high energy in circular motion produced the positive Ar ions. A negative potential was applied to the target with respect to the ground in order to accelerate the Ar ions toward the target and induce sputtering. Due to the cylindrical symmetry of the target titanium atoms were isotropically directed toward the carbon foam substrate settled inside the target (See Fig. 1). The deposition chamber 280 mm × 320 mm × 300 mm in dimensions (Anelva ECR 300 S System) was evacuated by an oil diffusion pump and a mechanical rotary pump. The target was of cylindrical form.

Fig. 1 Schematic drawing of the arrangement of a carbon foam specimen inside the cylindrical target of the ECR-DC sputtering system.
(internal diameter: 80 mm, external diameter: 90 mm, length: 60 mm) and consists of a stack of 5 mm length titanium rings. In order to find optimum processing parameters the plasma stream was diagnosed optically and electrically. The emission light produced by expanding plasma has been imaged onto the entrance slit of a SM-240 CCD Spectrometer (CVI Laser Optics) using an UV type optical fiber.

Surface appearance and the thickness of the deposited film were observed and measured by an optical microscope (OM) connected to a CCD camera. Vickers micro-hardness (HV) was measured using an AKASHI MVK-G3 hardness tester (applied load; 9.8 and 49 mN, loading time; 15 s) and the phase composition of the films was analyzed by X-ray diffractometry (XRD) using monochromatic Cu–Kα radiation at 40 kV and 80 mA. Flexural strength and the elastic modulus of the carbon foam samples before and after deposition were measured using an AUOTGRAPH SHIMADZU DCS5000 (sample span 15 mm at 17 μm/s speed). The typical operation conditions are listed in Table 1. Films with thickness of 5–8 μm were formed in the conditions given in the table.

3. Results and Discussion

3.1 Plasma diagnosis

In situ plasma diagnostics was performed by monitoring the emission lines of the working gas and of the titanium that was used as target. The DC bias voltage, named further the sputtering potential applied on the target controlled the feeding with excited Ti atoms.

Figure 2 shows the optical emission spectra acquired during the plasma process. Among the characteristic emission lines of argon atoms and titanium ions named in Table 1, films with thickness of 5–8 μm were formed in the conditions given in the table.

Table 1  Typical operation conditions of the ECR-DC sputtering deposition process.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microwave frequency, v/GHz</td>
<td>2.45 GHz</td>
</tr>
<tr>
<td>Microwave power, W/W</td>
<td>500 kW</td>
</tr>
<tr>
<td>Sputtering potential, U/V</td>
<td>−900 V</td>
</tr>
<tr>
<td>Argon gas pressure, P/Pa</td>
<td>9 × 10^{-2} Pa</td>
</tr>
<tr>
<td>Heater temperature, T/K</td>
<td>623 K</td>
</tr>
<tr>
<td>Pre-sputtering time, t/ks</td>
<td>1.8 ks</td>
</tr>
<tr>
<td>Deposition time, t/ks</td>
<td>14.4 ks</td>
</tr>
</tbody>
</table>

Figure 3 Discharge current and the intensity of the Ti I (400 nm) optical emission line as function of the sputtering potential.

3.2 Film composition and scaffold carbon foam appearance

XRD analysis of the films showed a preferential growth in the Ti (100) phase, as can be seen in Fig. 4. Titanium films prepared at 500 W microwave power, −900 V sputtering potential, 9 × 10^{-2} Pa gas pressure were identified as pure 

![Fig. 2 Optical emission spectrum of argon plasma containing excited titanium atoms provided by ECR-DC sputtering.](image-url)

![Fig. 4 XRD pattern of the titanium film.](image-url)
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3.3 Mechanical properties

Vickers micro-hardness of the films measured by using 9.8 mN and 49 mN indentation loads were in the range of 250–300 HV, typically values for the titanium films prepared by sputtering.

Flexural strength and elastic modulus of the carbon foam of 25 mm × 5 mm × 5 mm (cutting a test sample of 25 mm × 5 mm × 5 mm from a test piece of 50 mm × 25 mm × 5 mm) before deposition; (a) and after deposition; (b) are both shown in Fig. 6. On can observe an increasing by a factors of 1.5 and 2.6 of the flexural strength and the elastic modulus, respectively. These mechanical properties are crucial in tissue engineering applications as bone restoration for dental implants. The porous structure and mechanical properties similar to bone allow the scaffold carbon foam to be formed or machined into complex shapes. The bone can gradually infiltrate into and through the scaffold carbon foam in a process similar to natural healing. The natural and artificial materials combine and can reconstruct the maxillofacial bone.

4. Conclusions

Titanium film was deposited uniformly by using a hybrid ECR-DC sputtering system on a three-dimensional structure of scaffold carbon foam in order to increase their biocompatibility and mechanical properties. Films with 5 µm thickness were deposited in the center of the carbon foam of 5 mm thickness. The DC sputtering voltage applied to the target controlled the feeding with excited titanium atoms. The Vickers micro-hardness of the films was found to be in the range of 250–300 HV. The film surfaces were found to be smooth and composition of the films analyzed by XRD showed pure titanium grown preferentially in the Ti (100) phase.

The flexural strength and the elastic modulus of the scaffold carbon foam were increased by factors of 1.5 and 2.6, respectively, allowing them to be used in bone restoration for dental implants.

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REFERENCES