

- [54] **SPUTTERING OF BONE ON PROSTHESES**
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- [58] **Field of Search** 204/192, 298; 3/1.9, 1.911, 3/1.912, 1.913; 32/10 A; 128/92 C, 92 G

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[57] **ABSTRACT**

A system of coating prostheses with ground bone particles is presented. Prostheses made of various metals and other substances are coated using *rf* sputtering techniques to form a film which adheres to the device, stimulates living bone attachment thereto and which is ultimately replaced by new bone. Beef cattle bone material, some ground to 125 mesh and the remainder in chunks, has been successfully used in one embodiment as the coating applied by the *rf* sputtering process.

12 Claims, No Drawings

1 SPUTTERING OF BONE ON PROSTHESES

The present invention concerns improvements in bone replacement prostheses and, more particularly, the sputtering of bone onto such prostheses to form a covering which stimulates bone growth and attachment to natural bone.

Despite recent advances in the field of prosthetic replacement of bone, effective prosthetic replacement has not been achieved. Where total bone replacement is necessary, as in hip prostheses, present methods and devices are not adequate. The stresses in this area can be very large as indicated by estimated forces of up to four times the weight of the body and, consequently, the prosthesis to be inserted has to be very strong as well as resistant to corrosion, stress corrosion, and fatigue. Some advances in bone replacement in this area include the use of cobalt-chromium-molybdenum alloy, Vitallium, which has proved to be generally satisfactory and has an apparent advantage of case-hardening with use. This alloy provides a structurally sound answer to the mechanical wearing problem between the acetabulum, or hip-cup, and the femoral head prosthesis. In addition, high density polyethylene has been found to be suitable as a lubricant between these working parts since it has a low wearing rate, is resistant to creep, and has no toxic effects. Thus, some of the elements for forming a highly satisfactory metallic prosthesis exist. However, the overall problem is not completely solved since it is believed that both 316 stainless steel and cobalt-chromium-molybdenum implants may be carcinogenic in rats.

In addition to the suspected deficiencies in stainless steel and the cobalt-chromium-molybdenum alloy, the bone and pin inserts occasionally lose intimate contact due to the large forces acting on the femur around the intramedullary pin of the hip bone prosthesis. This loss of contact leads to failure of the prosthetic device and presents a need for a method and/or means for encouraging bone attachment to the implant.

The deficiencies associated with hip bone replacement also exist in relation to replacement of bone in repairing the damage sustained in such instances as gunshot wounds and vehicle accidents. Here there has been less success since the bone does not appear to always grow along the prosthesis filling the gap. This effect may be due to the prosthesis itself, but could also be due to the traumatized tissue in the injured area. This kind of wound is of particular concern to the armed services. Necrosis, i.e. failure of bone to grow and unite around the break therein, is not uncommon in these accidents. The present invention provides a method whereby bone may be deposited on any prosthesis and, by virtue of the presence of the deposited bone, living bone is encouraged to grow around the prosthetic implant and to reunite about the implant.

According to the present invention, prostheses may be formed by coating metallic substrates with bone particles by means of rf sputtering in a vacuum. One rf sputtering process may be that of ionized inert gas bombardment of an electrode to emit atoms of the

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electrode at high energy levels for deposit on a prosthesis. Bone material from beef cattle has been successfully adhered by this method to prostheses of polished stainless steel and aluminum, and to Pyrex test tubes and microscope slides.

Accordingly, it is an object of the present invention to provide a system for forming prostheses having a film which adheres to the prosthesis base and to which living bone may adhere.

Another object of this invention is to provide a system for forming hip joint prostheses wherein a metallic form provides the necessary structural strength and a film of adhered bone particles provides a base for joining the form to the living bone.

A further object of this invention is to provide a prosthesis for use in areas of large stresses and to which is adhered a coating of bone particles to promote bone growth and attachment to living bone.

Other objects, advantages and novel features of the invention will become apparent from the following detailed description thereof.

Bone material has been successfully deposited on microscope slides and pieces of aluminum and stainless steel by rf sputtering. The rf sputtering process used involved the ionized gas bombardment of an electrode to emit atoms or molecules of that electrode at high energy levels for deposit on a substrate. Sputtering was conducted at low power densities to the target, 0.19 watts/cm² to 0.81 watts/cm², to prevent thermal decomposition of the bone. Spark source mass spectrometric analysis and X-ray analysis verify that the sputtered films have the same atomic composition as pure bone target material. Scanning electron micrographs indicate that the films are amorphous in character. Details of the procedures are now presented.

EXPERIMENTS

Bone chips obtained from steer bone were used as the target, or cathode, in the sputtering system. The bone was first boiled in lye to remove muscle and fatty tissues and then cleaned in boiling water. Next, small bone chips were machined for use as a powder-type target and then heated at 120°C for 60 hours to remove moisture and to outgas the target material. The dried bone chips were placed on an aluminum backing plate and held by an aluminum oxide retaining ring, the target size being 12.2 cm dia × 0.4 cm height. Further outgassing was accomplished by pumping under high vacuum for approximately 15 hours, and the target was presputtered for a minimum of 40 minutes at 1.63 watts/cm².

The substrates used for bone deposition were either actual implant materials such as 316 L stainless steel, impervious Al₂O₃, porous Al₂O₃ and a composite porous-impervious Al₂O₃, or glass microscope slides for rate determination runs, procedure limitation experiments and thickness measurements. All substrates were cleaned with methyl alcohol and air dried in an environmental hood prior to insertion into the vacuum chamber.

Sputtering parameters were as follows:

Pump Down:

Most of the runs were left under a high vacuum overnight (~15 hours) to remove moisture and outgas the target. Some low power level runs could be sufficiently outgassed in as little as three hours.

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Blank Off Pressure:	1.0×10^{-5} mm Hg to 6.5×10^{-5} mm Hg (as measured on a Bayard-Alpert Type ionization gauge).
Operating Pressure:	3.4×10^{-3} mm Hg (as measured with a Pirani-type gauge).
Argon Flow Rate:	45 cc/min of gettered argon
Cathode-Anode Distance:	~2 inches
Presputter:	40 minutes at 1.63 watts/cm ² typically
Sputtering Power Densities:	0.54 watts/cm ² to 3.85 watts/cm ²
Substrate Temperatures:	210°C at 1.08 watts/cm ² 375°C at 3.26 watts/cm ²
Sputtering Run Times:	1-11 hours
Procedure Limitations:	The upper power level was determined by the temperature limitation of the rubber boot gaskets and O-ring used as vacuum seals on the sputtering chamber. If the target material is sufficiently outgassed, the bone target may be run at power densities exceeding 3.85 watts/cm ² provided the vacuum system has metal seals, water-cooled chamber, and end plates.

The color of the sputtered films obtained from the experiments ranged from a transparent light brown on glass and stainless steel, and beige, to almost black on Al₂O₃. The films on Al₂O₃ tended to be darker in color as thickness increased.

All of the sputtered coatings exhibited excellent adherence to each of the substrate materials. All samples passed the "Scotch tape" adherence test performed by ripping a piece of pressed-on Scotch tape from the coated substrate. The films could hardly be removed by scraping with a knife.

Sputtering rates and corresponding substrate temperatures were determined for rf power input to the target ranging from 1.08 watts/cm² to 3.26 watts/cm². Deposition rates were determined on masked glass substrates in a four hour sputtering run. Film thickness was measured on a Rank, Taylor, Hobson Talystep I machine and deposition temperatures were monitored using a PT/PT 10% RH thermocouple located in good thermal contact on the substrate holder. Deposition rates ranged from 375A/hr at 1.08 watts/cm² to 2370A/hr at 3.26 watts/cm². Substrate temperatures ranged from 210°C at 1.08 watts/cm² to 375°C at 3.26 watts/cm².

Specular reflectance analysis and transmission spectrums were performed on coated glass, stainless steel, and Al₂O₃ substrates. Although no definite identification of the coatings on the glass substrates could be made at power densities up to 3.85 watts/cm², the films sputtered onto Al₂O₃ and stainless steel at power densities up to 1.63 watts/cm² were shown by spectrographic analysis to have the same molecular composition as the original bone material. In addition, it was shown that material taken from the target was identical to the original bone.

The following materials were covered with bone for in vivo evaluation.

1. Impervious Al₂O₃
2. Porous Al₂O₃
3. Al₂O₃ composite having an impervious inner core and a porous skin.

The substrates were cleaned in methyl alcohol and air dried in an environmental hood. They were then mounted, i.e. wire held, on a substrate holder along

with a sample for analysis, a masked glass slide for thickness measurements, and a PT/PT 10% RH thermocouple. The specimens were coated on two side, requiring two runs. The sputtering power density was 2.17 watts/cm² and deposition temperatures were 374°C and 362°C. Resulting film thickness were 8500A and 9000A, i.e. an average deposition rate of 1250A/hr.

Although the results do not conclusively show that the material transferred on sputtering is identical to actual bone, spectrographic analysis shows that the chemical composition is virtually identical to the original bone, and other analysis shows that the same molecular bonding is present. The primary difference between the two is that the sputtered material is amorphous as opposed to the original crystalline structure.

Films applied by the system of the present invention have been subjected to spark source mass spectrometric analysis and scanning electron microscope analysis with X-ray analysis. Results of the spark source mass spectrometric analysis indicate that not only are the major components of the film the same as original bone, but also some characteristic lines of the structure are reproduced in the spectra of the deposit.

There is thus provided a system for coating prosthetic devices with material which will enhance healing at a bone implant as well as promote bone growth and attachment to the implant. Prosthetic devices made according to the present invention are structurally capable of withstanding even the very large forces which act on the femur in hip bone replacement. In contrast with prior methods and devices, prostheses may now be coated with a bone substance which has been found to adhere to structural forms by impingement through the rf sputtering process. Such a coating formed in such a manner assures that virtually any shape of the structural form will receive a uniform coating over its entire surface. Where necessary, the structural form or prosthesis may be rotated during the sputtering process to assure uniform distribution of bone particles over the entire exterior surface of the prosthesis.

The present invention demonstrates that bone particles as well as phosphosilicate glass, dielectric material,

etc. may be rf sputtered on a target. Not only may such a natural substance be deposited on a target, but under proper conditions of temperature and voltage the bone particles may be made to impinge upon and adhere to the target. The prostheses particularly adapted to the present system are ones which require substantial strength such as those for use in hip joint repair. However, the bone material may be made to adhere on forms having less strength, i.e. those made of substances such as metallic ceramics, glass and similar materials.

This adaptability of bone particles to adhere to metal surfaces leads to the formation of prosthetic devices in which the coating performs two important functions, one being that of covering the metallic base with a medium that is both non-toxic and will also induce bone growth, and the other being to provide a coating of a natural bone material. Even though this bone material coating is a foreign substance, it should not be rejected by the body in which the device is implanted since ivory which is also a foreign body is not rejected and, in fact, has been used successfully as an implant. Sputtered bone, therefore, when implanted in a human should behave the same as ivory implants have, i.e. be adaptable to being built upon by bone formed by body processes.

It has been determined that a coating thickness of substantially 1 micron is preferable to induce new bone growth and enhance the healing of a simple fracture or other bone damage. Such a thickness is also compatible with the present procedure for impinging bone particles on a metallic prosthesis in that appreciably thicker coatings tend to crack and break off when the prosthesis cools down. That is, the metallic prosthesis is raised to temperatures on the order of 350°C to 400°C by the impinging particles. In cooling down thereafter, a metallic substrate contracts more than the bone coating and partial separation can occur if the coating is too thick.

Sputtered-bone-coated prostheses made according to the present invention first induce living bone to grow on the implant and then to absorb and replace the implant coating over an extended period of time. This bone replacement process occurs on a non-toxic substrate or structural material which is implicitly in contact with the bone part of the body. The new bone growth promoted by the sputtered bone coating also results in the elimination of secondary grafting operations wherein bone is removed from the host and reintroduced in the area where bone is missing, e.g. in gunshot wounds. Two important areas for strengthening by prostheses coated according to the present invention thus are along the intramedullary pin of a hip-prostheses and in and around prostheses used for bone replacement in gunshot wounds where necrosis is particularly prevalent.

Obviously many modifications and variations of the present invention are possible in the light of the above teachings.

What is claimed is:

1. A prosthesis for use as a bone implant comprising:

a metallic base conforming to the shape of the bone to be replaced; and

a coating of bone material impinged upon and adhered to said prosthesis by rf sputtering,

whereby said bone material will induce living bone growth around the implant and, additionally, will eliminate the necessity for bone grafting.

2. The prosthesis as defined in claim 1 wherein the material of said metallic base is selected from the non-toxic group consisting of stainless steel, cobalt-chromium-molybdenum alloy, titanium and titanium alloys and said coating is formed by an rf sputtering process.

3. The prosthesis as defined in claim 2 wherein the bone implant is presputtered for substantially 40 minutes at a power density on the order of 1.63 watts per cm².

4. The prosthesis as defined in claim 3 wherein sputtering is conducted at power densities to the target in the range of from 0.19 watts per cm² to 0.81 watts per cm² to avoid thermal decomposition of the bone particles.

5. The prosthesis as defined in claim 4 wherein said bone material forming said coating is animal bone ground in part to a 125 mesh and in part in pieces of substantially greater size,

said bone material baked at substantially 125°C for substantially 18 hours prior to presputtering to evaporate moisture from the bone,

said coating having a thickness of substantially 1 micron.

6. A method of forming a bone replacement or bone repair prosthesis comprising adhering bone particles to a prosthetic form by rf sputtering.

7. The method of claim 6 wherein the prosthetic form is positioned at the cathode of the rf sputtering means at a distance of substantially 2 inches from the anode thereof.

8. The method of claim 7 wherein the sputtering is conducted at power densities to the target in the range of from 0.19 watts per cm² to 0.81 watts per cm² to avoid thermal decomposition of the bone particles.

9. The method of claim 8 wherein the prosthetic form is presputtered for substantially 40 minutes at a power density of substantially 1.63 watts per cm².

10. The method of claim 9 wherein sputtering is performed at an operating pressure of substantially 3.5×10^{-3} mm Hg and said bone particles are applied to a coating thickness of substantially 1 micron.

11. The method of claim 10 wherein the bone particles are derived from ground animal bone having a consistency in part of substantially 125 mesh and in part of substantially larger pieces,

said bone particles baked at substantially 125°C for substantially 18 hours to evaporate moisture therefrom.

12. The method of claim 10 wherein the bone particles are obtained by machining bone chips to a powder form and heating the powder to substantially 120°C for substantially 60 hours to remove moisture and gases therefrom.

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