BIOCOMPATIBILITY OF ION BEAM PROCESSED FILMS DEPOSITED ON SURGICAL Ti-6Al-4V

I-S. Lee, J-S. Song and I-J. Yu*

Korea Orthopaedics & Rehabilitation Engineering Center, WAMC, InChon 403-120, Korea
*Industrial Chemical Research Center, KISCO, TaeJon 305-380, Korea

ABSTRACT

Ion beam processing of materials for medical application has gained increasing interest in the last decade, and the implantation of nitrogen into Ti-6Al-4V to improve corrosive-wear performance is currently used for processing of total hip and knee joints. Oxides and nitrides of Ti, Zr, Al, Cr were deposited on Ti-6Al-4V substrates by DC magnetron sputtering, dual ion beam sputtering, and ion beam assisted deposition. The cytotoxicity of these films were investigated by MTT method, and showed comparable to untreated Ti-6Al-4V. Plasm-sprayed hydroxyapatite(HAp) coatings showed excellent cytotoxicity regardless of heat treatment. Intermediate layer coatings of nitrides and oxides increased the bond strength of HAp to substrate by introducing chemical bond at interface. Heat treatment of HAp coatings also improved the chemical bond at interfaces, and increased the bond strength of untreated Ti-6Al-4V to 16.4 kg/cm^2, but still lower than 33.1 kg/cm^2 of Ir oxide as a imtermediate layer caoting.

1. INTRODUCTION

The failure of fixation is the most common cause of failure of partial and total joint replacement arthroplasty and a major contributing element in fracture malunion and nonunion. The concept of fixing total hip prosthese by bony ingrowth rather than cement has evolved in an attempt to decrease the incidence of loosening.[1,2] Bioactive materials such as hydroxyapatite(HAp) is capable of interacting with the surrounding bone and produces direct attachment of the implant to bone without an interposed fibrous tissue layer because of the presence of free calcium and phosphate compounds at surfaces. Due to its poor mechanical properties of sintered body, HAp is commonly applied to metallic implants as a coating material. The application of plasma spray coating of HAp has increased significantly in recent years because of its advantages, i.e. increased tolerance of surgical inaccuracies,[3] fast fixation of the implants in bone[4] and firm

implant-bone attachment.[5] HAp coatings usually apply to T-6Al-4V for combining alloy's excellent properties such as a low elastic modulus, low density, high tensile strength, good corrosion resistance, good fatigue resistance: but clearly the most desirable property is its biocompatibility. The use of HAp coating to Ti-6Al-4V for fixation has been successfully applied and accepted clinically. However, concern has arisen recently about coating strength of HAp to implant.[6,7] Also, the wear resistance of Ti-6Al-4V bearing surfaces in contact with ultra high molecular weight polyethylene (UHMWPE) has been questioned for long-term reliability and performance in total joint replacement applications.[8,9]

The purpose of this research is to improve the biological performance of metallic implant with ion beam processed surface modification technique. Deposition processes of DC magnetron sputtering, dual ion beam sputtering, and ion beam assisted deposition were used to produce oxides and nitrides of Ti, Zr, Al, Cr on Ti-6Al-4V substrates. The wear properties and cytotoxicity of these films were investigated. For the cytotoxicity test, the lysis of cells, the inhibition of cell growth, and other effects on cells caused by these oxides and nitrides were determined with the use of cell culture techiques. Studies also describe whether these films including pure metallic element of Ti, Zr, Ag, and calcium phosphate deposited with ion beam asisted deposition as a intermediate layer have any beneficial effects to increase the bonding strength of plasma-sprayed hydroxyapatite coating to metallic implant.

2. EXPERIMENTAL PROCEDURES

Thin film Deposition

Samples of 1" in diameter of Ti-6Al-4V (ASTM F136) with thickness of 2 mm were cut from annealed rod. Since the bonding strength of plasma-sprayed HAp coating comes from mainly mechanical interocking of substrate, samples were sand blasted, and ultrosonically cleaned with ethanol. The 1 μm polished samples were also prepared for the measurement of wear and cytotoxicity.

Before the sputter deposition, samples were etched with the power of 450W for 30 mins. The working pressure was maintained around 6.3 x 10^{-3} torr, and the reactive gas of N_2 or O_2 was properly mixed with Ar for nitride and oxide deposition, respectively.

Dual ion beam sputter deposition was performed with RF filamentless ion source, high energy version of 500-1500 eV for depositon and low energy version of 100-500 eV for etching and asist. Prior to the deposition process, the 6" tragets sitting water cooled holder were sputter cleaned with Ar ion (RF = 100W, 300V) for 5 mins, and the parameters for deposition are shown in Table 1

Table 1. Deposition parameters for DIBS

MATERIAL	TARGET	GAS,SCCM	RF, W	GRID V	GRID I, A
Ti	Ti	Ar-10	100	60/6	0.04
Ti oxide	Ti	O-15	120	60/6	0.05
Zr oxide	Zr	O-15	120	60/6	0.05
Al oxide	Al	O-15	120	60/6	0.05
Ti nitride	Ti	N-10	90	60/6	0.02
Zr nitride	Zr	N-10	90	60/6	0.02
Al nitride	Al	N-15	200	60/6	0.05

The ion beam assisted deposition facility, with a electron beam evaporator (15Kw rated power supply) and end-hall type ion source, is shown in Figure 1. The evaporation rate was set at 1 Å/s and was controlled by a quartz crystal rate monitor while the ion flux was adjusted to 0.6 A at 150 V. The premixetured gas, $N_2(O_2)/Ar$ = 1, was supplied to ion source for the reactive depositpn of nitrides(oxides). The substrate was heated to 200°C if required for the reactive deposition. Substrates were Ar ion beam(120 V, 2A) etched for 20 mins befor each deposition

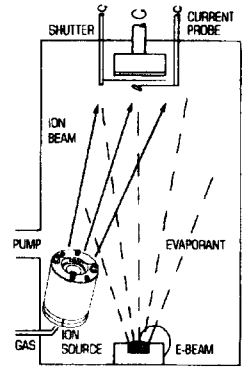


Fig 1. IBAD

Bond strength test

A Sebastian Five adhesion testing apparatus(Quad Group, Spokane, WA, USA) was used. For the tests, 5/32′ ϕ x1/2′ aluminium pull studs, pre-coated with a thermal curing epoxy, were vertically set to the center of each sample and cured in the oven for 1 h at 150°C. After curing, the samples were inserted into the machine platen of the Sebastian Five and gripped. When activated, the stud was pulled down against the platen support ridge until failure occurred either in the coating or the epoxy bond. The tensile force required to cause failure was registered by the machine. SEM or reflected light photomicrographs of all failed samples were taken to determine the location of the bond failure.

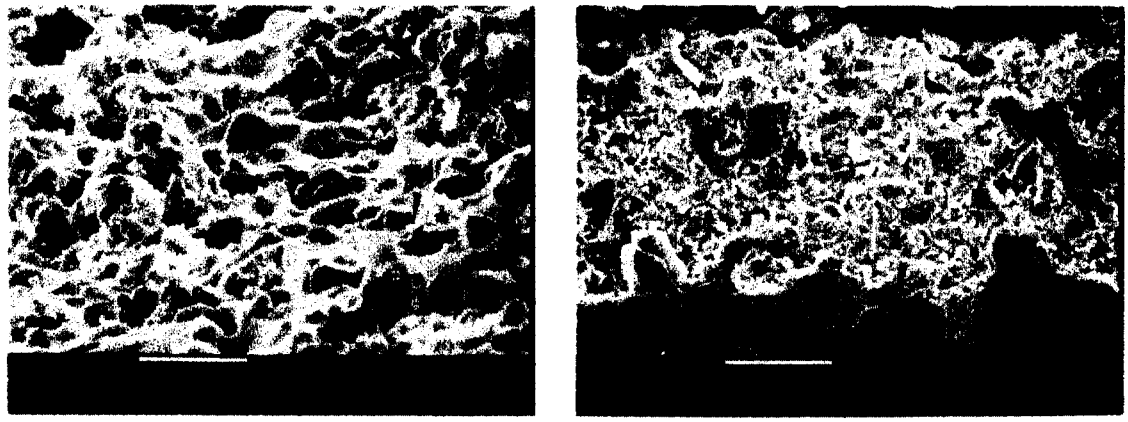
Cytotoxicity

Swiss 3T3 fibroblasts were grown in a 100 mm tissue culture dish with RPMI-FCS

(RPMI containing 100 units of penicillin and streptopmycine, and 10% fetal calf serum) at 37°C, 5% CO_2. To test cytotxicity, Swiss 3T3 fibroblasts were detached from the tissue culture plate by trypsinzation, and adjusted into 10^5/㎖ of RPMI. Each 1㎖ cell suspension was added into a 24 well culture dish containing sample. Incubated cell for overnight were tested by MTT method. MTT(1-4{4,5-dimethylthiazol-2yl}-3,5-diphenyl formazan) was purchased from Sigma. After 1 day culture, the metal sample on which Swiss 3T3 cells were cultured were transferred into wells of a new 24 well dish containing 500 ㎕ of RPMI-FCS in each well. Then 50 ㎕ of MTT (5 mg/㎖) were added into each well of the 24 well dish, and incubated for 2 hrs at 37°C, 5% CO_2. After 2 hr incubation, 0.5 ㎖ of 0.1 N HCl in 10% SDS were added into each well. The cell solutions were pipted up and down vigorously 3-4 times to dissolve the dark blue crystal. Then the plate were allowed to sit for 2 hrs at 37°C. The solutions were read in a spectrophotometer using a 570 nm filter.

3. RESULTS AND DISCUSSION

Figure 2 shows SEM micrographs of as-plasma spray coated sample for (a) surface morphology tilted to 75° and (b) cross section. The thickness of coating is near 100 ㎛ and the parmeters for plasma spray coating have been described in some detail elsewhere.[10] The HAp coatings consist of overlapping HAp particles with a melted shell and unmelted or partially melted cores. The completely melted shell of HAp particles wore off faster than the unmelted cores during polishing, so the unmelted cores were raised up higher than the melted shells in Figure 2(b). The coatings also exhibited



(a) (b)

Figure 2. SEM micrograph of as-plama coated Ti-6Al-4V (a) Surface morphology tilted 75°, (b) cross section (scale bar is 50 ㎛)

porosity of varing morphology either in the form of smooth pores circular in cross section and contained within the splats or lamellae, or elongated, channel-like pores between individual splats; these interlamella channels suggested strongly the possibility of interconnected porosity throughout the coathing thickness.

Figure 3 shows the bond strength data for the as-HAp coated and heat treated after plama spray coating. The interlayers were deposited with sputtering. Heat treatment was done in atmosphere at 850°C for 1 hr, and then furnace cooled. For the as-plasma sprayed samples, the bond strength was increased in the range of 6.8 times for Zr

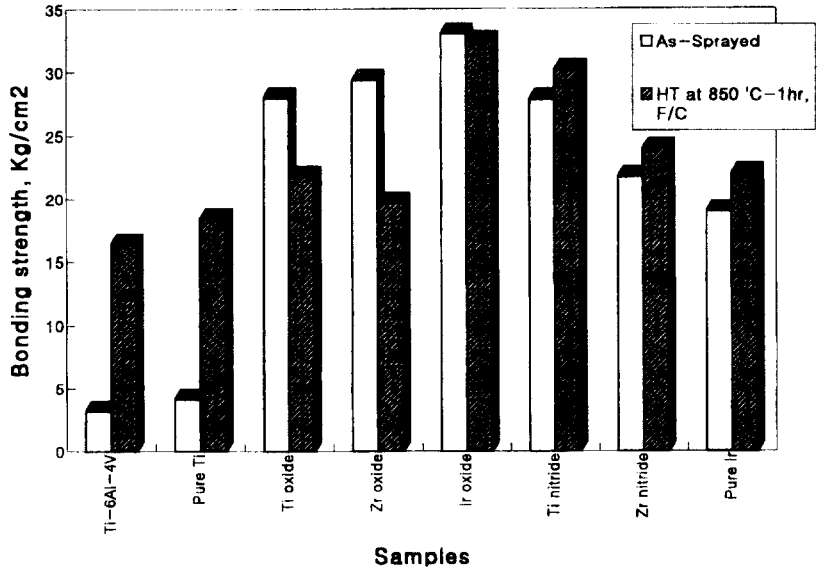


Figure 3. Bond strength of as-coated and heat treated sample

nitride to 10.3 times for Ir oxide relative to untreated T-6Al-4V. Although mechanical inerlocking is a major factor contributing to plasma -sprayed HAp to substrate bonding, Lacout et. al.,[11] observed some chemical bond with Ti-6Al-4V. This phenomenon is probably more easily occurred by interlayer coating of nitride and oxides, which changes the bonding of HAP-to-metal to HAp-to-ceramic. Heat treatment also increases interdiffusion at interfaces, thus, improved the bond strength of untreated Ti-6Al-4V from 3.2 Kg/cm^2 to 16.4 kg/cm^2. However, this effects are marginal or even detrimental to the interlayer coated samples. Difference in failure modes were observed between as-spray coated and heat treated coatings. Failure always occured at the substrate/coating interface for as-spray coated condition, but heat treated samples typically exhibited failure within the coatings. This is probably formation of microcracks due to differences in thermal expansion coefficient.[12] Heat treatment promotes chemical reactions at the interface but the weakening of coating is also occurred.

Figure 4 shows the results of cytotoxicity of nitrides or oxides deposited by IBAD on polished Ti-6Al-4V. The cytotoxicity was measured by MTT method. The principle of MTT is sililar to the 3H thymidine incorporation.

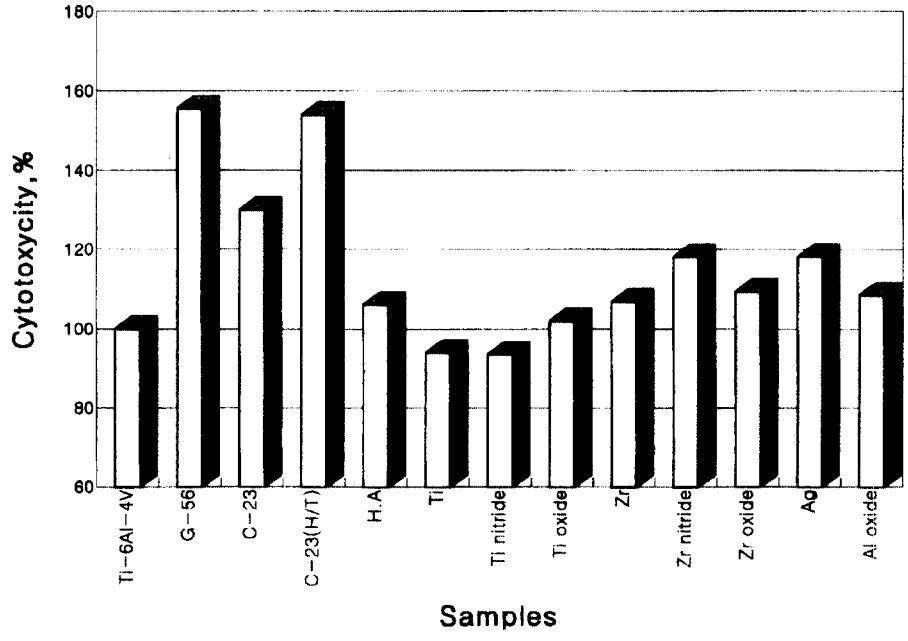
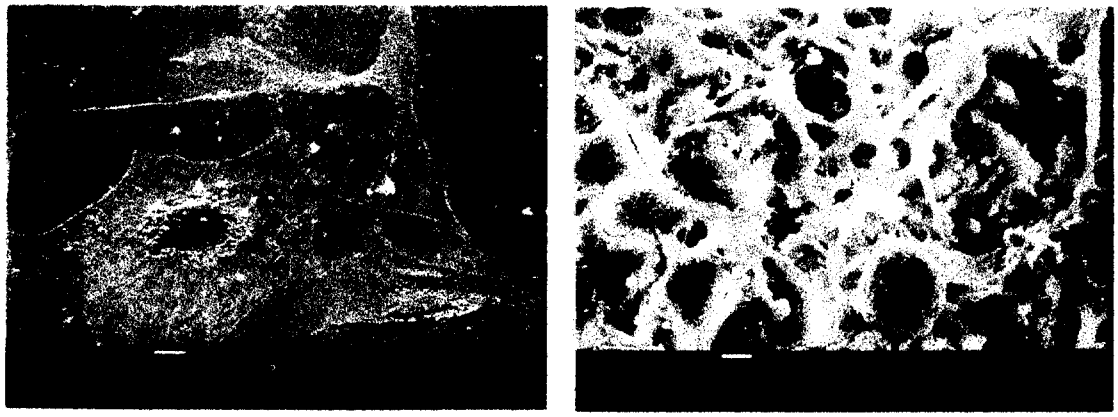


Figure 4. Cytotoxicity of tested samples

MTT assay was measuring MTT into a blue colored product of formazan by the mitochondrial enzyme succinate dehydrogenase. This assay was widely used for assaying cell survival and proliferation. This conversion takes place only in living cells and the amount of formazan produced is proportional to the number of cells present. The data were expressed as % of cell attached to the disk {(abs of sample/abs of cell without sample x 100}. The rate of cell growth was calculated by{(% of cell attached to the sample/% of cell attached to the control) x 100}. Under the consideration of typical 10% error, the cytotoxicity of treated samples is about same except HAp coating with and without heat treatment. HAp is classified to bioactive material, whereas the other tested samples are bioinert. This is probably why HAp is favorable for cell growth, and is confirmed by SEM photograph shown in Figure 5. This sample was prepared after cell grown in the sample for overnight at 37°C, 5% CO_2, Then, the cell was washed 3 times with phosphate buffered saline, and fixed with 2.5% glualdehyde in 0.1M sodium cacodylate buffered (pH=7.3) solution for overnight. The specimens were dehydrated with increasing ethanol for 5 mins. After dehydration, the specimens were immersed in aceton and critical point dried.



(a) (b)

Figure 5. SEM photographs of cell grown on (a) Ti-6Al-4V and (b) HAp ($10\overline{\mu m}$)

REFERENCES

1. R. Judet, M. Siguier, B. Brumpt, and T. JudetClin. Ortho, 137, 76-84, 1978.
2. G. A. Lord, J. R. Hardy, and F. J. Kummer, Clin Orthop, 141, 2-16, 1979
3. J. A. Jansen J. Van de Waerdan, J. G. C. Wolke, and K. de Groot, J. Biomed. Mater. Res., 25, 973-989, 1991.
4. S. D. Cook, K. A. Thomas, J. F. Kay, and M. Jarcho, Clin Orthop, 232, 225-243, 1988.
5. W. J. A. Dhert, C. Klein, J. G. C. Wolke, E. A. Van de Velde, K. de Groot, and P. M. Rozing, J. Biomed. Mater. Res., 25, 1183-1200, 1991.
6. I. M. O. Kangasneimi, C. C. P. M. Verheyen, E. A. van der Velde, K. de Groot, J. Biomed. Mater. Res., 27, 1315-1327, 1994.
7. R. Y. Whitehead, L. C. Lucas, and W. R. Lacefield, Clinical Materials, 12, 31-39, 1994.
8. H. J. Agins, N. W. Albock, M. Bansal, J. Bone Joint Surg., 70A, 347-352, 1988.
9. A. V. Lombardi, Jr., T. H. Mallory, B. K. Vaughn, P. Drouillard, J. Bone Joint Surg., 71A, 1337-1342, 1989.
10. I-S. Lee, J-S. Song, M. Mun, S-Y. Kim, G-H. Lee, and S-C. Kwon, will be presented at AEPSE'97, Oct. 5-9, Seoul, Korea, 1997.
11. J. L. Lacout, J. Assarance, and J. C. Trombe, Acad. Sci. [III], 29, 173-181, 1984.
12. J-W. Choi, Y-M. Kong, H-E. Kim, and I-S. Lee, accepted and will be published in J. Am. Ceram. Soc., 1997.