

PUBLISHABLE SYNTHESIS REPORT

BRITE-EURAM CONTRACT 91-0477

**COMPARISON OF SURFACE MODIFICATIONS BY ION IMPLANTATION
AND COLD PLASMA ASSISTED TREATMENTS AS AN ALTERNATIVE
TO OTHER COATING TECHNIQUES**

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INTRODUCTION

The major problem associated with currently used metal implants has been identified as inadequate tissue-implant interface properties. For load-bearing orthopedic and dental implant systems, this is indicated by implant loosening, often necessitating revision surgery. To reduce corrosion and wear rates as well as to increase fatigue strength, surface treatments such as cold plasma coatings, and ion implantation have been investigated. Taking into account the increasing number of european programmed dealing with nitrogen implantation of classical orthopedic alloys (TAV, 316L SS, . ..). it appears very important to carefully evaluate and compare (that has not been done in the currently available litterature) ion implantation, low temperature diffusion and physical deposition processes (PVD, PACVD) for improvement of bearing surfaces in osteo-articular prostheses,

OBJECTIVES AND INDUSTRIAL APPLICATIONS

In this programme, 3 alloys (TiAlV, TiAlFe, 316L SS) were used as base materials and 3 methods of treatment were compared : glow discharge ion implantation (without mass separation), sputter deposited coatings of C doped SS, plasma diffusion and chemical deposition process (PDT + PACVD).

The project should lead to proposals for the development of the most appropriated surface modification techniques at an industrial-scale, depending on the prostheses biomechanical and economical requirements.

Therefore Deutsche Titan, Peter Brehm GmbH, and Eurorad decided to participate in the programme in an active manner, to develop the technology needed to respond the future market requirements in a satisfactory way.

DESCRIPTION OF THE RESEARCH WORK

The following methodology was used to reach the project goals :

Surface treatments

1) Ion implantation :

(Ion incrustation : unanalyzed accelerated glow discharge beam)

The glow-discharge, implantation method without mass separation, was chosen in the energy range of 30-60 KeV. It was decided to focus the work limit on nitrogen ions (other ions are also possible : C, B, O, . .) and on the solid solution concentrations (10^{16} - 10^{18} ions/cm²). Alloys like TiN are easy to be realized. This treatment was done for TAF, TAV and SS.

2) Sputter deposited coatings :

Two plasma assisted surface modification treatments were performed on biomedical grade SS, respectively consisting of carbon doped 316L SS coatings prepared below 200°C by reactive magnetron sputtering, and of low temperature plasma nitriding (below 400°C).

3) PDT, PDT + PACVD treatments :

Two methods were used : nitrogen plasma diffusion (PDT) and combined PDT with PACVD (Plasma Assisted Chemical Vapor Deposition).

Methods of evaluation

1) Corrosion was tested by electrochemical accelerated corrosion tests (ACT) in simulated bioenvironments.

2) Auger and XPS for surface analysis were done for all samples before and after corrosion tests and in vivo exposure. XRD was performed to determine the phase and thickness after treatment for implanted and cold plasma treated samples. SIMS, RBS, and nuclear reactions completed these measurements in order to visualise profiles, thickness and eventual impurities pollution during the treatment.

- 3) Fatigue tests were done for the 3 alloys and the 3 treatments by the stair-case method on 16 samples for each case using an electrohydraulic DARTEC machine
- 4) Biocompatibility studies were performed in vitro using cell cultures (human osteoblasts and fibroblasts) ; in vivo implantation on rabbits complete this evaluation.

ROLE OF THE PARTNERS

- 1) ULP/LEED Biomatériaux as the leader of the project, is responsible for the coordination of the joint research. It is also working on the surface characterization using ESCA, Auger, and related surface analyse techniques, in close cooperation with the IPCMS/GSI.
- 2) CNRS/Laboratoire PHASE performs ion implantation (N, C, B) on SS and Ti alloys, develops a biodevices implanter, and performs SIMS, RBS, N R analysis.
- 3) EMN/LSGS realizes coatings by sputtering (amorphous, microcrystalline), or low temperature plasma nitriding of SS.
- 4) TUB/IOPW uses plasma nitriding, and plasma nitriding + PACVD techniques on Ti alloys.
- 5) The INEB laboratory in Porto has specialized on corrosion study (Accelerated Corrosion Test, Mott-Schottky impedance test, . . .) in simulated bioenvironments.
- 6) The IEBM/IRC concentrates on biocompatibility (in vitro studies : cell cultures ; in vivo studies : surgical implantation in rabbits).
- 7) EURORAD (Strasbourg), PETER BREHM (Weisendorf), and DEUTSCHE TITAN (Essen) are the industrial endorsers of the project.

DESCRIPTION OF THE RESEARCH

The main deliverables of this project can be regrouped into the following categories with a technological objective from above :

Surface treatments optimization

1) Ion Implantation :

instead of classical implantation with mass separation an ion source (Kaufman) machine was built, without mass separation, the cost of implantation is reduced by **2-5** times. The profile of implanted species of this machine (N_2^0 , N^+ , N_2^+) is equivalent of that with few implantation energies ;

all compositions were possible : solid solution (like N in Ti alloys) or alloy formation (like TiN) with better adherence properties than the deposited one ($TiN \rightarrow Ti_xN \rightarrow Ti$) at the interface ;

this treatment was applied to 3 alloys (TiAlV, TiAlFe and SS316L), with electrical doses ranging from 10^5 - 10^8 on 500 samples ;

corrosion, fatigue and biocompatibility are improved as indicated hereafter ;

physical analysis (SIMS, RBS, nuclear reactions) are done for a better understanding of mechanisms.

2) Sputter deposited coatings and plasma nitriding :

The process of two plasma assisted modification treatments on biomedical grade 316L SS was optimized. Carbon doped 316L SS coatings (C) prepared below $200^\circ C$ by reactive magnetron sputtering and low temperature plasma nitriding (N) were used. The resulting surface layer is a carbon or nitrogen metastable supersaturated solid solution. Improvement of corrosion, wear and fatigue resistance were obtained for both (N) and (C), but the in vitro biocompatibility was satisfactory only for (C).

3) PDT, PVD + PACVD treatments :

Plasma nitriding treatments were performed by varying the substrate temperature, applied voltage, pressure, and the pulse Dwell time. Layers of TiN, Ti_2N and Ti_2AlN were formed, providing thus a continuous hardness profile and an excellent adhesion of the compound layer. The highest TiN layer thickness has been found to be $0.4 \mu m$, the highest Ti_2N layer thickness was about $2.3 \mu m$. The surface hardness depends only on the TiN layer thickness and has been found to be $2250 HK_{0.01}$ in the best case. The roughness R_a is lower than $1 \mu m$.

To increase the TiN layer thickness pulsed DC plasma CVD immediately after PDT were performed. The thickness of the TiN layer becomes (1.4 - $4.9 \mu m$). The surface hardness has found to be in the range from 2320 to $2611 HK_{0.01}$. The surface roughness for the optimized parameters is in both cases (PDT and PDT + PACVD) lower than $0.3 \mu m$.

Fatigue tests

For fatigue test, the stair case method was used, 16 samples were treated in the same way, the first sample is submitted to cyclic stress in the range of few hundred MPa ; if it sustains 10 M cycles the sample is considered as good and the stress is increased for the next one by 20 MPa ; if it breaks before, the loading is decreased by 20MPa for the next, and so on.

- before treatment, the average supported stress are as follow :480-500 MPa for Ti Al V and 316L SS (to be confirmed after annealing treatment) ; 520-540 MPa for Ti Al Fe
- after implantation in the optimized conditions, Ti Al V increase its supported pressure to 600-620 MPa, TiAlFe increase from 536 to 580 MPa, 316L SS increase from 465 to 480 MPa.
- PDT, as expected, decreases the fatigue properties owing to the high temperature treatment. Up to (300-320) MPa for TiAlV, TiAlFe and (360-380) for SS316L.

Corrosion tests

Surface roughness before WW tests is uniform for all samples. After WW tests a great increase in roughness is observed. WWT, SSE and MIT were performed.

1) Ion implanted samples :

For stainless steel system, the best performance is for the 10^{16} fluence. E_{corr} is the highest and i_{corr} is the lowest, hysteresis loop is absent during cyclic anodic polarisation. Ion implantation with 10^{15} does not change significantly the electrochemical characteristics. For Ti6Al V and Ti Al 2.5F systems, the results obtained are satisfactory for all three fluences.

2) Sputter deposited coating:

All surfaces are accepted.

3) Plasma nitriding (PDT, PACVD and PDT+ PACVD) :

Samples are listed in the improving order : P1(900°C) → P3 = P4 (800°C) → V2 (700°C)

P1 (900°C) coating is eliminated for pitting corrosion,

P1 5V (100 Pa) and P16V (350 Pa) are eliminated due to R_{tc} (charge transfer resistance) low values.

S14F (20 g/h $TiCl_4$) and S14V PDT + PACVD treated samples are accepted.

Low temperature plasma nitrided was accepted except for N3 treatment (pulsed plasma - T = 420°C).

Surface analyses

XPS surface analysis were performed on the all samples before and after corrosion tests.

1) Samples treated with PDT and PACVD :

Carbon and oxygen contamination could be found on all the samples, before and after corrosion tests. The main result is that the nitrogen peak disappears completely on the PI 5V (100 Pa) and P16V (350 Pa) samples after corrosion tests, in opposite to the P7V (350V) and P16V (350 Pa) samples. Also calcium and phosphorus contamination could be detected on all samples after corrosion tests. For samples PI 5V (100 Pa) and PI 3V (650V) the surface is covered with titanium oxide after corrosion tests.

2) Samples coated by sputtering.

There is more carbon on D3 (Amorphous) than D1 (microcrystalline) sample. Also a little nitrogen adsorption peak was found on both samples. After corrosion tests, P, Ca, Na and Zn contamination was observed on both samples. On the N2 sample the nitrogen peak was more important than on D1 and D3. The carbon and oxygen contamination were about the same before and after corrosion tests while the calcium and phosphorus were more important.

3) Samples ion-implanted :

The nitrogen peak heights are about proportional to the nitrogen fluences. On the TAV and TAF series, fluor contamination or implantation could be found proportionnal to the nitrogen fluences in some particular cases. Moreover, on the TAV series, one does not detect the Ti peak while there is an important simultaneous implantation of carbon, oxygen and silicium. On the TAF serie, besides the carbon and oxygen simultaneous implantation, there is a calcium contamination proportional to the nitrogen fluence. On the 316L SS samples, there is also fluor contamination. The main result is that the nitrogen implantation seems to be accompanied by simultaneous implantation of C and O due to vacuum residual partial pressure. This is a positive effect according to the results of the sputtered C coating task.

Biocompatibility tests

Cytocompatibility was assessed at the level of both the basic (attachment, proliferation, viability and cell protein content) and the specific features (intracellular alkaline phosphatase activity, osteocalcin content and scanning electron microscopy) of the cells. Indirect immunofluorescence staining of fibronectin and collagen I, two major proteins synthesized by fibroblasts, has also been performed. Glass and untreated material were used as controls.

According to the results obtained, the biomaterials and the surface treatments can be classified as follow :

- Biomaterials : TA6V4 = TA5Fe2,5 > stainless steel = glass
- Surface treatments
 - . for titanium alloys : N implantation = untreated material > PDT = glass
 - . for stainless steel : N implantation \geq C coating = untreated SS = glass > nitriding

The in vivo studies have shown that all treatments were well tolerated in spite of a little inflammatory reaction with PACVD treated sample (however no tissue necrosis was found).

EXPLOITATION PLAN

- 1) The main practical application is the increase of the long term performances of :
 - hip and knee prostheses,
 - dental implants,
 - surgical/dental cutting tools,
 - various related biomedical applications.
- 2) Three method of surface treatment are patentable:
 - ion implantation in (TAV, TAF, SS) alloys,
 - carbon doped sputter deposition of SS,
 - PDT, PDT + PACVD on (TAV, TAF) alloys.
- 3) Contact with potential users :
 - an exploitation plan has already been prepared by the industrial endorsers (Peter Brehm and Eurorad) ;
 - other advanced contacts are taken with implant manufacturers and dental suppliers.
- 4) Other aspects on results dissemination :
 - mechanical industry could benefit from the results of some surface treatments evaluated in this project, even if not clinically applicable (i.e. nitrided SS).

CONCLUSION

The project is successful in its investigations and subsequent development of surface treatment techniques (ion implantation, cold plasma diffusion, PVD, PDT + PACVD) performed on 3 materials (SS, TAV, TAF) for specific biomedical applications as well as in mechanical and corrosion properties improvement. Results are summarized in the enclosed table.

KEYWORDS

Ion implantation, low temperature plasma nitriding, reactive sputter deposition (PVD), Plasma Diffusion (PDT), Plasma Assisted Chemical Vapor Deposition (PACVD), fatigue resistance, wear, corrosion, biocompatibility, titanium alloys (TiAlV, TiAlFe), stainless steels(SS316L).

SUMMARIZING TABLE

PERFORMANCES (score from 1 = worst to 5 = best)										
Material	Surface treatment	Adhesion	Fatigue	Wear	Corrosion ACT	SSE	Bioc. in vitro	Thickness (μm)	Rec. clin. applic.	Cost
SS 316L	virgin nitrided carbon doped implanted N_2	-	3 ?	5	3	3-4	3	-	no fatigue rejected no fatigue multiple	5
		5	-	-	3	-	1	12		4
		5	3	5	5	4	3	13		2
TAV	virgin PDT PDT + PACVD implanted N_2	5	4	4-5	5	5	5	-	multiple + high fatigue level fatigue/common use ? multiple + high fatigue level	3
		(4) ?	2	4-5	5	(P_3)	3	105 (TAV)* 110 (TAF)*		2-3
		5	2	3-4	5	3	3	65 (TAV)* 70 (TAF)* 0.5		2
TAF	virgin PDT PDT + PACVD implanted N_2	-	4	5	5	5	5	-	multiple + high fatigue level no fatigue/com. use ? multiple	3
		5	2	4-5	5	3	3	65		2-3
		(4) ?	2	3-4	5	5	3	65 0.5		2 2-3

* Nitriding depth

PDT : Plasma Diffusion Treatment (plasma nitriding)

PACVD : Plasma Assisted Chemical Vapour Deposition

implanted : ion implantation using nitrogen

ACT : Accelerated Corrosion Test

SSE : Slow Strain Experiment