श्री चित्रा तिरुनाल आयुर्विज्ञान और प्रौद्योगिकी संस्थान, त्रिवेंद्रम, तिरुवनन्तपुरम - 695 011, केरल, भारत
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PROJECT COMPLETION REPORT

1. **Project Number** : 6047
2. **Title of the Project** : TITANIUM NITRIDE COATINGS FOR MEDICAL DEVICES
3. **Funding Agency Name** : Technology Development Fund, SCTIMST.
4. **Project Reference Number provided by the Funding Agency**:

   No. TDF/2011-12/6047
5. **Principal Investigator (Name & Address) :**

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7. **Implementing Institution** : SCTIMST, Trivandrum
8. **Collaborating Institutions** : None
9. **Date of Commencement** : 01 Jan 2012
10. **Duration** : 2 years, 7 months.
11. **Date of Completion** : 31 July 2014.
12. **Objectives as approved :**
    1. Develop Titanium Nitride (TiN) coatings for medical devices using a physical vapour deposition (PVD) coating system

2. Apply this coating to various medical devices such as coronary stents, and in Phase 2 on CBP spindle and LVAD casing.

13. Deviation made from original objectives if any, while implementing the project and reasons thereof :

Objectives 1 completed fully and 2 completed partly.

TiN coating was applied only to coronary stents as part of Objective 2.

The Phase 2 of the project could not be completed due to frequent breakdown of the turbomolecular pump used to develop high vacuum in the coating chamber.

14. Field/Experimental work giving full details of summary of methods adopted, data collected supported by necessary tables, charts, diagrams and photographs :

For each application the coating process for TiN using the PVD system needs to be established. The following important factors are considered for developing the coating process:

(i) Process time
(ii) Process Vacuum
(iii) Partial pressures for both Ar and N_2
(iv) High tension cleaning time
(v) TiN coating time
(vi) Bias for magnetrons and cathode
(vii) Magnetron field current and
(viii) Process temperature.

Further cleaning, vapour degreasing and handling procedures, and device specific fixtures for coating were developed.

a. SAMPLE PREPARATION

Samples were cut from rods in either plate form or circular disc form.

For titanium alloy (Ti6Al4V) the samples were cut from rods of 25mm dia and into plates of 5mm W x 25mm L and thickness of 3mm. These samples were then polished as per procedure in Appendix A.1.

For Haynes 25 (Cobalt chromium alloy) the samples were cut from rods of 25mm dia using wire cut EDM, into plates of size 5mm W x 25mm L and thickness of 3mm. These samples were then polished as per procedure in Appendix A.2.

For stainless steel (SS 316L) the samples were cut in disc form from 15mm rods and polished using a set of abrasive discs and suitable polishing suspension in a Buehler polisher.

b. SAMPLE CLEANING

The polished samples were then ultrasonicated in soap solution and distilled water, and then vapour degreased in isopropyl alcohol. The cleaning procedure is described in Appendix B.1. A fixture for vapour degreasing up to 12 samples was developed using a glass apparatus.

c. SAMPLE LOADING

The samples are loaded into the coating chamber after cleaning. The samples are hung or fixed as appropriate on the planetary work holder at a height so that the full length is exposed to the sputtering targets. Care is taken to ensure that all faces of the sample get exposed so that a uniform coating is generated as the planetary system rotates. The rotation is at a speed of about 5 - 10 RPM.

The chamber door is closed and vacuum pumps are switched ON. The rotary and roots pump achieve a vacuum of about 5E-2 mBar following which the high vacuum valve is switched ON. At this stage the molecular turbo pump takes over and a high vacuum of 5E-5 to 5E-6mBar is achieved and then the radiant heaters are switched ON to raise the chamber temperature to about 180˚C and remove absorbed gases in the chamber walls. Once the vacuum reaches 5E-5mBar after heating the process steps below are carried out.

d. PROCESS

i. *IN-SITU* PRE-CLEANING

For good adhesion of the coating it is necessary that the sample surface is clean and free of oxide layers. To remove any residual material on the sample and also remove the oxide layers an *in situ* ion bombardment based cleaning is performed at a high bias voltage of 800V and a low sputter current of 500mA. The Ar and sputtered Ti ions in the plasma impinge with a high velocity and strike the sample removing a thin layer from the surface. This is done for about 10 to 15 minutes.

ii. TITANIUM INTERLAYER COATING

An interlayer of titanium is sputtered first on to the sample surface. Only Argon gas is allowed into the chamber at about 180sccm to achieve a process vacuum of 3E-3 mBar. The magnetron current is maintained at high value of 3 – 5 A and sample bias voltage at 150V. This is run for about 10 to 15 minutes to generate a 0.1 to 0.2 micron thick coating.

iii. TITANIUM NITRIDE COATING

Finally Nitrogen is also introduced into the chamber at about 15 to 25 sccm and the plasma changes colour to reddish brown at the centre of the chamber. A golden coating of TiN is observed as the samples turn golden with time. Other process parameters are usually kept the same and coating is run for 1 to 3 hours depending on the coating thickness required. A coating of 1 micron thickness is generated for a run of 3 hours at a sputter current of 3A.

15. Detailed analysis of results :

2. COATING CHARACTERIZATION

a. Microhardness test

Microhardness measurement is performed using a Microhardness test (MHT) system from M/s CSM Instruments, Switzerland. A Vickers diamond indenter tip is driven into the material by applying a gradually increasing normal load. When the load reaches a preset maximum value, the normal load is reduced until partial or complete relaxation occurs. The position of the indenter relative to the sample surface is continuously monitored with a differential capacitive sensor. For each loading / unloading cycle, the applied load value is plotted with respect to the corresponding position of the indenter. The resulting load / displacement curves provide information specific to the mechanical behavior of the material under examination. Since the coating thickness obtained was for the most part sub micron, the MHT was performed only on a limited number of cases.

Parameter	**Details**
Indenter geometry	**Triangular pyramid (α = 136° ± 0.2°)**
Maximum load	**50mN**
Loading cycle	**100 mN/min loading, 10s hold, 100 mN/min unloading**
Measurement type	**3 x 3 matrix with 250 µm gap between measurements**

Table 3: Microhardness Test parameters

b. Microscratch test for Coating adhesion

The coating adhesion studies were carried out using a micro scratch test system (Micro – Combi Tester, M/s. CSM Instruiments, USA). Scratch testing is a comprehensive method of quantifying the adhesion properties of coatings. The technique involves generating a controlled scratch with a diamond tip on the sample under test. The tip, either a Rockwell C diamond or a sharp metal tip, is drawn across the coated surface under either a constant or progressive load. At a certain critical load the coating will start to fail.

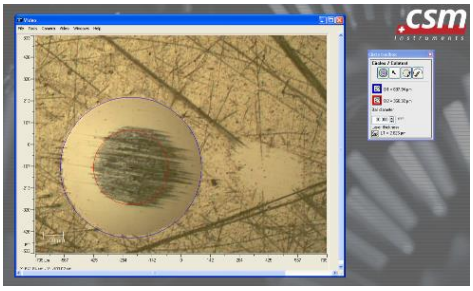
Parameter	**Details**
Indenter	Rockwell (Diamond) 100µm radius
Type of test	Linear scratch (progressive)
Loading rate	30 N / min
Start load	0.05 N
End Load	20 N
Scratch length	4 mm
Scratch speed	6 mm / min

Table 4: Scratch Test parameters

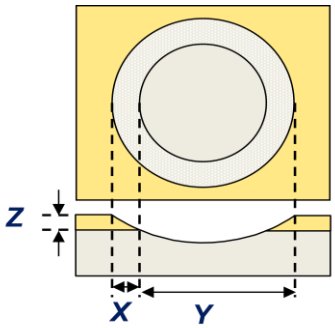
The critical loads are used to quantify the adhesive properties of different film - substrate combinations. These parameters constitute a unique signature of the coating system under test. The test conditions are chosen to ensure that reproducible scratch

maps are obtained for the coating under investigation [Table 6]. The critical loads are detected precisely by means of an acoustic sensor attached to the indenter holder. The same could be cross checked and verified using the frictional force observed on the indenter, sudden changes in the penetration depth profile as well as with the help of optical microscopy, by examining the scratch profile.

c. Crater Test (Calotest) for Coating thickness



This test is used to determine the coating thickness. A spherical ball of known diameter is made to rub against the coated surface in the presence of an abrasive suspension such as diamond or silicon carbide particles for a set time at a set speed. This action removes a spherical layer from the coated surface abrasively exposing the base material and a ring of coating. From the diameters of the rings and inner circle the coating thickness can be measured. This instrument can easily measure the thickness of coatings in the range 100 nm – 50 µm in a short time of few minutes.



$$Thickness = Z = \frac{X \cdot Y}{\phi ball}$$

16. Summary sheet of not more than 2 pages under following heads : (Title, Introduction, Rationale, Objectives, Methodology, Results, Translational Potential)

- Coating process to obtain a yellow golden colour with an adhesion of 3N (Lc1) for a 1 micron coating has been established.
- A presentation titled 'TiN coatings for Medical Devices' has been made at the International Workshop on Coatings, Surfaces and Biomaterials in Feb 2014 at IIT Madras.

17. Contributions made towards increasing the state of knowledge in the subject :

- Sujesh S. Titanium Nitride Coatings for Medical Devices. *International Workshop on Coatings and Surfaces for Biomedical Engineering, 2014*, IIT Madras, India.

18. Conclusions summarising the achievements and indication of scope for future work :

The coating was deposited on flat rectangular samples as already mentioned in Section 3 (a,b,c). The coated samples were evaluated using Scratch test and Calotest as mentioned earlier.

A total of more than 100 coating trials were performed during the project period and results analyzed. The process parameters (i, iii, vi, and vii) were varied during the study.

The process repeatability was poor as the PVD equipment did not have a servo valve to control the process vacuum. The vacuum control was achieved by controlling the inflow of the process gases which is not ideal. A butterfly valve would be necessary to improve the process repeatability.

Future work:
The project objectives included TiN coating of other medical device components as well. However, these objectives were not pursued due to time constraints. These could be taken up in a subsequent project.

19. Science and Technology benefits accrued :

a. List of research publications with complete details :

- Sujesh S. Titanium Nitride Coatings for Medical Devices. *International Workshop on Coatings and Surfaces for Biomedical Engineering, 2014*, IIT Madras, India.

b. Manpower trained on the project :

i.	**Research Scientists or Research Fellows :**	2 Project Assistants trained.
ii.	**No. of PhD's produced :**	NIL
iii.	**Other Technical Personnel trained :**	NIL

c. Patents taken, if any : NIL

d. Products developed, if any : A process for coating TiN on devices such as coronary stent.

20. Abstract: (In 300 words for possible publication in ..... Bulletin)

Titanium Nitride (TiN) coatings are widely used in medical devices to improve their mechanical and physiological properties. They are highly wear resistant and have a low coefficient of friction making them suitable for use in articulating surfaces. They are biocompatible as well as blood compatible allowing use in medical implants as well as blood contacting surfaces. These properties are significantly better for TiN coated surface than the bare surface of biocompatible metals such as stainless steel (SS316L), CP-Titanium or Ti6Al4V alloys. TiN is a hard ceramic material. It has a low corrosion rate and hence is used in applications were friction, wear and erosion are important design considerations especially in orthopedic and dental applications.

TiN coatings have been found suitable for the new tilting disc heart valve being developed at SCTIMST. They have been validated in preclinical studies for the new model of Chitra heart valve which is under development. TiN coatings can be generated using physical vapour deposition (PVD) techniques under high vacuum of the order of 0.001 to 0.1 millibars by sputtering a pure titanium target with the substrate as cathode in an atmosphere of Argon and Nitrogen. Such a PVD unit is being operated at SCTIMST.

TiN is being investigated as a blood compatible, low friction and corrosion free coating for several medical devices including a coronary stent, blood pump pivot bearing and left ventricular assist device. Coatings were generated of up to 1 micron for the applications mentioned above. Coating characterization includes (i) coating thickness, (ii) coating adhesion, (iii) coating hardness, (iv) surface smoothness, (v) abrasive wear and (vi) corrosion studies. Device specific characterization need to be performed to validate the coating for intended use. Coating performance during fatigue cycling and plastic deformation, as seen in coronary stents during expansion, need to be validated.

In vivo experiments include haemocompatibility, tissue compatibility and toxicological studies as per ISO 10993 series of standards. Coatings generated for the artificial heart valve were characterized and they indicate the superior physical and biological properties of TiN coated Ti6Al4V over the bare substrate. A large animal pre-clinical experiment was performed for the TiN coated heart valves in adult sheep animal model. The analysis of the explanted valves showed that the tissue in growth into the valve orifice area was much less in the case of TiN coated model.

Very good blood and biocompatibility coupled with resistance to wear and inherent stability make TiN ideal an ideal surface for a wide range of cardiovascular applications. Artificial heart valves, bearings for blood pumps, left ventricular assist devices and stents are potential areas of application. TiN coatings with their excellent friction and wear properties make them ideal candidates for articulating orthopedic implantations. The reduction in friction and wear leads to formation of less debris. There can be a substantial improvement over the current metallic biomaterials as one of the most prominent failure modes of articulating orthopedic implants is aseptic loosening due to continuous inflammation caused by wear debris. There is however a concern regarding susceptibility to fretting corrosion for articulating surfaces.

21. Procurement/Usage of Equipment:

a. Details of Equipment: None

Sl. No.	Name of Equipment	Make/ Model	Cost (Rs.)	Date of Installation	Utilisation	Remarks regarding maintenance breakdown
	NIL					

b. Suggestions for disposal of equipment(s):

No Equipment was procured as part of this project.

01.12.23

(Name and Signature of PIs with date)

Routing: *Signed copy of "Project completion Report" by PI →* root@sctimst.ac.in, rpc@sctimst.ac.in