INDO SWISS JOINT RESEARCH PROGRAMME (ISJRP)

RESEARCH FELLOWSHIPS

EXCHANGE GRANT REPORT

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Part 1 - General Information

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<th>Tribological behaviour of Ti based biomaterials in physiological solution</th>
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Part 2 - Exchange Participant(s) Details

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Part 3 - Scientific & Technical Information

3.1 Purpose of visit

Titanium and titanium alloys are widely used for many biomedical applications due to their low density, excellent biocompatibility, corrosion resistance and mechanical properties. Ti-6Al-4V is most popular alloy used in biomedical application. The release of Ti and other alloying elements into the surrounding tissue has been reported due to either passive corrosion or accelerating process such as wear. The release of aluminum and vanadium ions was found to be toxic and their accumulation in the surrounding body was of great concern. Further α+β alloys have elastic moduli significantly higher than the elastic modulus of bone. This can lead to early loosening of implants because of large fretting-corrosion damage at the alloy/tissue interface. In order to overcome this drawback, β Ti alloys were developed with the aid of β stabilizing elements such as Nb, Mo, Zr and Ta. β Ti alloys were found to have higher elasticity and thus enhanced biocompatibility and increased compatibility with the mechanical properties of bone.

The aim of the present research work was to evaluate and compare the fretting corrosion and sliding wear behaviour of established and newly developed biomedical grade β titanium alloys in physiological solution like Hank’s solution in presence of various additives and lubricants found in-vivo. Visvesvaraya National Institute of Technology, Nagpur planned to work in collaboration with Defence Metallurgical Research Lab, Hyderabad who has developed a series of new titanium alloys that were characterized with respect to mechanical and corrosion properties. In order to characterize their tribological behaviors in physiological solution under controlled mechanical and chemical conditions a special tribometer equipped with an electrochemical cell is needed. In India there is no such tribometer while at the EPFL there exist excellent facility for carrying our investigation. Both Institutes have decided to join their competences with the aim to collaborate in an attempt to enhance the performance level of titanium based biomaterials for total joint replacement. Continued progress in biomaterials research is increasing dependent upon collaborative efforts among several different disciplines, as well as closer coordination among funding agencies and effective partnerships involving universities, industry and national laboratories.

3.2 Short description of work carried out during the visit

Fretting Corrosion: Fretting corrosion is a degradation process resulting from the combined action of corrosion and small movements between contacting parts. Fretting wear occur at neck/head and at the stem/bone interface of human joints. Fretting corrosion causes early failure of metallic implants. Fretting corrosion tests carried out on tribometer of EPFL which is equipped with electrochemical test facility. Open circuit potential, applied potential tests were done to test tribo-corrosion behavior of β titanium alloys in Hank’s balanced salt solution against alumina ball. In order to better investigate the degradation mechanism of the metal, an Al₂O₃ sphere served as a counterpiece because of its chemical and mechanical inertness.

The contact configuration consisted in a stationary alumina ball rubbing against an underlying Ti alloys disc samples. The titanium specimens were of cylindrical shape 10 mm in radius and the alumina counter piece of spherical shape (5mm in radius). The contact was immersed in a HBSS electrolyte and its potential was controlled using a three-electrode set-up including a platinum coil (inert counter electrode), a reference electrode (commercial Mercurous sulphate) and the working electrode (Ti alloy). Experiments were performed for open circuit potential and applied potential of +2V for all the alloys in concentrated ions HBSS electrolyte corresponding to the passive state of titanium alloy.
For OCP experiments fretting start at constant open circuit potential. Potential was +2V with respect to the Mercurous sulphate electrode for all experiments of applied potential (all potentials given here are referred to this reference electrode). The motion of the flat sample was achieved through a piezoelectric actuator driven by a triangular waveform signal with an oscillation frequency of 1 Hz. After mounting the specimen and the counterpart on the fretting apparatus, the selected solution was poured into the electrochemical cell and the temperature was set and maintained at 37°C. The load was applied and after 5 min immersion time, the selected potential was applied.

After 0.5 h polarisation, the fretting oscillation with a displacement of 100µm and a frequency of 1 Hz was applied for 1h. The applied load was 10 N. During the fretting tests the normal force, tangential force, electric current and vertical position of the Al2O3 counterbody was monitored. The average values of friction coefficient and current over the whole test were determined by averaging the mean values over the fretting time. Each experiment was repeated once to check reproducibility. Fretting log diagrams were also plotted to determine slip regime. The degradation of the passive surface layer can be observed through changes in the corrosion potential or through changes in the corrosion current. Few tribological tests were also carried out in synovial constituents like bovine serum albumin (BSA), DPPC and hyaluronic acid (HA) found in vivo. Secondary electron spectroscopy, optical microscopy and laser profilometry were used to characterize the wear morphology for different experimental conditions. After each experiment the samples were extracted from the cell and rinsed with distilled water. The wear volume was determined with non-contact profilometry.

**Sliding Wear:** Sliding wear takes place between acetabular cup and femoral head of human joints. Titanium alloys for femoral head and UHMWPE for acetabular cup are most recommended materials for total joint replacement. Therefore, sliding wear test also carried out for all titanium alloys against technical grade UHMWPE to mimic in-vitro sliding wear behavior of titanium alloys with tribometer of EPFL. Titanium discs of 20 mm diameter and UHMWPE pins of 12 mm diameter and 38 mm overall length with one hemispherical end was used as specimens for sliding wear test tribometer. All samples were cleaned in acetone and ethanol for 10 minutes prior to test. The applied load was 6.5 N with stroke length of 5 mm and temperature was 37°C for all tests.

Experiments were performed for open circuit potential and applied potential at +2V (all potentials given here are in reference mercurous sulphate reference electrode and platinum electrode as counter-electrode) in Hank’s balanced salt solution (HBSS) like fretting corrosion for 3600 S. For OCP experiments sliding start at constant open circuit potential. Few tests were also performed in lubricants like DPPC, BSA and HA at +2V applied potential in HBSS found in vivo. Wear of UHMWPE specimen was determined by taking optical micrographs of worn hemispherical end and volume of material removed measured.

### 3.3 Outcomes

**Fretting corrosion:** Figures 1 and 2 shows set of mean values for an experiments performed at a displacement amplitude of 100 µm, 1 Hz oscillation frequency and normal force of 10 N for an open circuit potential and applied potential of +2V. Figures shows change of open circuit potential, anodic current. Potential changes during fretting in open circuit potential tests. Current decreases during application of potential showing the progressive passivation of the metallic sample. Before fretting, the whole surface is passive and the anodic current is low.

The current increases at the onset of rubbing because abrasion removes the passive film. The current exhibits peaks during rubbing at regular intervals corresponding to the formation of wear particles and
their ejection from the contact. Few tests were also carried out in synovial constituents like BSA, DPPC and HA under applied potential of +2 V to mimic in vitro behavior of titanium alloy. Figure 3 shows SEM micrographs of worn surfaces after 3600 cycles of fretting for open circuit potential and applied potential of +2 V.

![Figure 3: SEM micrographs of worn surfaces after 3600 cycles of fretting for open circuit potential and applied potential of +2 V.](image)

**Fig. 1:** Evolution of (a) Variation of open circuit potential (b) friction coefficient. Test conditions are normal force 10 N, displacement amplitude 100 µm, duration 3600 S, oscillation frequency 1Hz in Hank’s balanced salt solution.

![Figure 2: Evolution of (a) anodic current (b) friction coefficient. Test conditions are Normal force 10 N, displacement amplitude 100 µm, applied potential duration 3600 S, oscillation frequency 1Hz in Hank’s balanced salt solution.](image)
Fig. 3: SEM micrographs showing wear morphology after 3600 s fretting at displacement amplitude of 100 µm and 10 N normal force in Hank’s balanced salt solution (a) open circuit potential (b) applied potential of +2V (mercurous sulphate electrode).

Sliding Test: Figure 4 and 5 shows variation of open circuit potential, anodic current and friction coefficient for sliding test. The degradation of the passive surface layer can be observed through changes in the corrosion potential or through changes in the corrosion current. The enhancement of anodic current and variation of potential can be described by depassivation of oxide layer for both fretting and sliding tests. The enhancement of anodic current and variation of potential can be described by depassivation of oxide layer for both fretting and sliding tests. The achievement in reducing the modulus of elasticity is very good to reduce clinical problem like osteointegration and bone resorption. This project will generate a lot of experimental and scientific background on the degradation of biomaterials under corrosion-wear in physiological solution.

Fig. 4: Evolution of (a) Variation of open circuit potential (b) friction coefficient. Test conditions are normal force 6.5 N, stroke length 5mm, sliding duration 3600 S and oscillation frequency 1Hz in Hank’s balanced salt solution.
This information of fretting corrosion and sliding wear performance is very helpful to compare biotribological behavior and will help in selection of titanium alloy with better corrosion resistance, biocompatibility and mechanical properties. This will help in technology transfer between universities, national laboratories and industries.

This research is most relevant for getting inside in new cutting edge technologies for titanium based biomaterials manufacturing industries. A thorough understanding of mechanisms governing in-vivo degradation of biomedical alloys by combined wear and friction should allow easier, more rational and more rapid design and selection of suitable materials.

### 3.4 Future collaboration with host institution

Future research on fretting corrosion tests of titanium alloys with PMMA would be interesting study for biomedical applications with host institution. This will help in titanium alloy selection with better biocompatibility, corrosion resistance and alloy development for commercial production with industry-institute interaction. After thorough evaluation of the obtained data both institutes intend to continue collaboration in order to further exploit their complementary competences. Collaboration in the scientific domain will be focussed first in the evaluation (and publication) of the acquired data and later on the development of scientific criteria for the design of new biocompatible, high elasticity alloys for biomedical implants. In parallel, technological exploitation of the developed alloys and competences is sought possibly by involving potentially interested industrial partners in India and Switzerland.

### 3.5 Various comments

Thanks to Switzerland Govt for wonderful bilateral Indo-Swiss Joint Research Programme with Department of Science and Technology (DST), India for giving me best opportunity of my life to work at EPFL for excellent facilities in the area of tribo-corrosion which is emerging area in material science. I am very thankful to ‘Tribocorrosion symposium 2006’ held at Hyderabad in India which was hosted by my guide Dr Manish Roy to nucleate idea to work in area of tribo-corrosion of biomaterials.
I am very thankful to Prof Stefano Mischler for his valuable guidance for preparation of proposal, concepts of electrochemistry and tribology and to give me permission to work in his lab. Scientific discussions with Prof Stefano Mischler were very helpful. I would like to thanks to Postdoc fellows Dr Nikitas Diomidis and Dr Sebastian Equey for their help for use of equipments and scientific discussion. I am also very grateful to Mr Nicolas Xanthopoulos and Mr Pierre Mettraux for XPS and SEM measurements. It really gave me very good research education experience and more for integrating research in international environment. It will help me for my personal development and career.

3.6 Projected publications/articles resulting or to result from the exchange

We plan to publish in international journals two articles. On one side the fretting corrosion investigation has nicely shown the beneficial effect of the newly developed high elasticity alloys and new criteria for future developments. Such information is relevant and timely with respect to the state of the art. On the other hand, the sliding experiments against PE clearly illustrate the crucial role played by alloy and surface chemistry on PE transfer and thus on wear. This is open new ways for reducing the wear of polyethylene implants that determines the lifetime of most the art artificial joints presently implanted.