Presidential Letter

Friends,

It is often said that in today's world the only certainty is change. For any organisation to succeed in such an environment a clear vision of the future and of the way it will evolve is crucial. The T.I.C.'s strategy as an association is to help its members become better informed by a strong vision of the nature and of the changing nature of the business enterprise in which we are all engaged. To this end we look to our membership to contribute toward that vision through technical papers for presentation at the forthcoming Symposium. This will be the opportunity for all of us to actively contribute to its success and developing an even stronger association. I would call upon all of our members to actively consider providing a paper. Such papers can be submitted to the Technical Promotion Officer, the Secretary General or a member of the Executive Committee including the President. We of course would also be delighted if you can persuade your customers to attend and better still provide a paper for the Symposium. This is our chance to inform the world as well as ourselves.

We have many knowledgeable, professional and expert members who can make a clear contribution to our enterprise and a Symposium is the ideal time. Please actively participate and contribute so we may continue to reflect the interests, aspirations and concerns of our members as well as to inform.

William A. Millman
President

General Assembly and Symposium, October 2005

The Forty-sixth General Assembly will be held on October 17th 2005 as part of the next International Symposium.

Tantalum and Niobium World will present technical papers covering a wide range of aspects of tantalum and niobium production, processing and uses. This will be the next in the series of international Symposia organised by the T.I.C. The previous events were in 1978, 1988, 1995 and 2000, and all were well attended and successful. The broad scope of the presentations makes this an essential conference for everyone involved with tantalum and niobium.

Following registration and a welcome reception on Sunday October 16th, the technical programme will be presented on October 17th, 18th and 19th. A complementary social programme will also be arranged, including a gala dinner for all participants and sightseeing tours for accompanying persons.

On Thursday October 20th a field trip to the processing plant of H.C. Starck (Thailand) will be offered, with an alternative tour for competitors.

The general sessions and social events will be held in the delightful setting of the Royal Cliff Grand Hotel, near Pattaya, in Thailand, where delegates will also stay (see photograph above). Set in its own tropical parkland, the hotel offers several restaurants - not only Thai food but other styles as well - and swimming pools. It has a fitness room, with a jogging track and tennis courts in the hotel grounds, and a large number of golf courses in the region, for any spare time delegates may find.

Invitations will be sent to the delegates of member companies. Others interested in attending should contact the T.I.C. secretariat soon.

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Tantalum and Niobium World

International Symposium
October 16th to 20th 2005
Pattaya, Thailand

Offers of papers will be welcomed

ADVERTISE IN THE BROCHURE!
Deadline March - apply to T.I.C. now
TRANSPORT

The Transport Committee of the T.I.C. continues its efforts to make the IAEA and the Competent Authorities of a number of countries aware of the difficulties encountered by many companies in the transport of tantalum raw materials. The Transport Committee is engaging expert consultants in the field of environmental sciences to carry out a survey of tantalum raw materials in respect of uranium and thorium content and the level of radiation in the vicinity of containers packed for transport and to write a report.

In March 2005 the Transport Safety Standards Committee (TRANSSC) of the International Atomic Energy Agency will hold a meeting in Vienna. According to the provisional agenda, TRANSCC will consider whether to arrange a Co-ordinated Research Project on naturally-occurring radioactive materials, a category which includes tantalum raw materials. The T.I.C. has expressed its wish to take part in such a project, if it is initiated, by contributing a report on its survey. The Transport Committee will also use any other opportunities it can identify to counter over-regulation of raw materials.

TECHNICAL PROMOTION OFFICER

Applications are invited for the post of Technical Promotion Officer to the T.I.C. Candidates may contact the T.I.C. for more information.

TANTALUM COATED MATERIALS FOR SURGICAL IMPLANTS

This article is based on the paper presented by Dr Bo Gillesberg, Danfoss A/S, at the Philadelphia meeting of the T.I.C. on October 11th 2004

ABSTRACT

Tantalum coating on metal substrates such as stainless steel and CoCrMo alloy makes (heavy) load bearing tantalum implants available by combining a high strength core with a diffusion barrier of tantalum. Further tantalum coating improves the fatigue strength of the substrates by up to 60% compared to uncoated material. Implantation of tantalum coated implants shows a bone integration rate significantly better than titanium.

Tantalum coated carbon-carbon composite cages for spinal fusion offer excellent bone integration and inherent X-ray marking while the desirable properties of the C-C substrate are preserved. Implantation confirms adequate strength, biocompatibility, bone integration and compatibility with radiology and CT-scanning, both producing clear images of the implant and the bone inside.

INTRODUCTION

In comparison to materials such as titanium, stainless steel and cobalt chrome alloys, tantalum has, today, only a limited use within the medical device area. Many surgeons consider titanium and titanium alloys to be state-of-the-art materials. Tantalum is, in contrast, relatively unknown, despite the fact that tantalum has been used for implantation for decades with no critical bio response. In addition several studies suggest that tantalum has even better bio response than titanium. Tantalum materials may therefore be better candidates than titanium for implantation.

More than 60% of today’s tantalum market is taken up with capacitor production. In order to stabilise future business, penetration of new markets for tantalum will be important, hence medical device markets are obviously interesting. The market for joint replacement implants (hip and knee implants) currently has a value of approximately $US6 billion and is still growing. The spinal implant market is also of interest.

Although parts made of solid tantalum are not candidates for such implants, Danfoss has developed coating technologies with a potential of entering these markets. This paper reviews the performance of tantalum coating and its suitability for medical devices.

HISTORICAL USE OF TANTALUM FOR SURGERY

For more than 50 years, tantalum has been widely used in clinical applications:
- as a radiographic marker for diagnostic purposes, due to its high density
- as the material of choice for permanent implantation in bone, as osteomigration prevents migration
- as vascular clips, with the particular advantage that since tantalum is not ferromagnetic it is highly suited to MRI scanning
- in the repair of cranial defects - a United States of America medical material standard exists for tantalum in this application
- as a flexible stent to prevent arterial collapse
- as a stent to treat biliary and arteriovenous (haemodialyzer) fistular stenosis
- in fracture repair
- in dental applications
- in various other applications

In several studies tantalum has been acknowledged as being bio-inert and as such has been selected as a negative control in certain experimental situations. For example, Miller et al. utilised tantalum as a negative control in a study where rats with tantalum implants were sampled for urine and plasma, and the samples tested for mutagenic activity using the Ames test: all results were negative. Chronically implanted stimulating electrodes for neural prostheses are being developed to alleviate neural deficits. In comparative work by Johnson et al. the use of tantalum-tantalum oxide electrodes was investigated in brain implantation studies with cats. The study concluded that the tantalum-tantalum oxide electrodes resulted in less tissue damage than electrodes made from rhodium, platinum or carbon, and tantalum-tantalum oxide electrodes did not result in neurotoxic effects.

When tantalum is implanted as a foil, wire or mesh in soft tissues in either animals or humans, the main local tissue response is the formation of a thin, glistening membrane without any evidence of inflammation. In work by Crochet et al. an understanding of the pathological processes following implantation of tantalum stents into the femoral artery of sheep provided further evidence of the good biocompatibility displayed by tantalum based products. In a specific biocompatibility study Matsumo et al. studied tantalum after implantation in the subcutaneous tissue of the abdominal region, and in the femoral bone marrow of rats for either two or four weeks. No inflammatory response was observed around the implants and all were encapsulated with thin fibrous connective tissue. The study concluded that tantalum has sufficient biocompatibility for use as a biomaterial.

There are few published data relative to in vitro studies to predict in vivo degradation. An oxide film with very low solubility covers tantalum over a wide range of pH and pO2 combinations, which are reflective of biological situations. The tantalum-tantalum oxide equilibrium reaction is impossible to characterise directly due to the protective power of the oxide. In vivo corrosion release is very slight, there are no reports indicating local, systemic or remote site concentrations related to corrosion release. The most usual observation in both animals and clinical reports is the absence of visible corrosion or corrosion products.
POTENTIAL USE OF TANTALUM COATING FOR LOAD BEARING IMPLANTS

Although the biological performance of commercially pure (c.p.) tantalum has been shown to be outstanding, tantalum is still quite rarely used, and only a limited number of tantalum designs are available. Major problems are tantalum's high density (16.6 g/cm³) and poor strength, which limit the use of solid tantalum for (heavy) load bearing implants such as joint implants. One solution is to apply tantalum as a coating, thereby combining the high strength of a substrate such as stainless steel or CoCrMo alloy with the biocompatible surface of tantalum.

Further, tantalum as a coating on non metallic substrates such as carbon fibre reinforced materials would be an interesting technology. A potential use could be for a spinal fusion cage, where it may be possible to combine good radiographic (X-ray evaluation) properties with improved bone integration. Carbon fibre reinforced carbon-polymer composite spinal fusion cage implants have been used widely in clinical practice, having the advantages of radio transluency and low stiffness. Good biocompatibility has been reported, but the bone integration has been inconsistent and unsatisfactory when using these implants. The formation of fibrous tissue is less pronounced for certain metallic materials. Metallic implants, however, are not radio translucent and thus impair radiographic evaluation.

EVALUATION OF TANTALUM COATED STAINLESS STEEL AND CoCrMo ALLOYS

In order to evaluate the potential of tantalum coated stainless steel and CoCrMo alloys for load bearing implants, a series of laboratory tests has been made. Critical issues are coating integrity (i.e. ‘corrosion resistance’), tensile and fatigue strength. Further implantation tests have been made. The evaluated tantalum coating for the studies was electrochemical deposited coatings supplied by Danfoss Tantalum Technologies, Lyngby, Denmark.

Metallurgical evaluation

Figure 1 shows a micrograph of a standard tantalum coating on a threaded stainless steel rod. The coating is even with no cracks or pinholes and the thickness is around 20 microns. The roughness of the tantalum surface is similar to the roughness of the steel surface.

![Micrograph of standard tantalum coating on stainless steel 316VM](Ref. 13)

Evaluation of coating integrity

To verify that the coating was free of pinholes, a hydrochloric acid vapour/liquid test was used. The coated specimens were lowered halfway down into a 35% HCl solution at 75°C in a tight container. Uncoated reference pieces of stainless steel showed pronounced corrosion after a few minutes and would be completely dissolved within four days. Tantalum coated 316 LVM stainless steel and CoCrMo alloy were able to withstand the hydrochloric acid vapour/liquid for four days without any signs of corrosion on their surface and no coloration of the liquid. The coating integrity was further confirmed by extraction experiments according to ISO 10993-12 (a medical device standard for biocompatibility). Extract in saline and peanut oil showed no dissolution of metals from the substrates. From a chemical point of view the coating can be considered as 'safe'.

Mechanical testing

Two methods were used for determination of changes in the strength of the implant material as a consequence of the surface modification process: Tension test and Four-point bending fatigue test.

The tension test concluded that the tensile strength for stainless steel (316LVM) and CoCrMo alloy were not changed by the tantalum coating.

Fatigue testing showed a quite interesting result as shown in the Whöler curves in Figure 2. A significant change was demonstrated in the maximum fatigue strength for CoCrMo after tantalum coating. The fatigue limit in the untreated material has been tested up to 550 N/mm² and in the tantalum surface modified material up to 875 N/mm², which is an increase in the fatigue strength of approximately 60%. A likely explanation of this phenomenon can be the soft and very ductile nature of the tantalum surface. Together with compression stress in the tantalum layer this will reduce notch effects in the CoCrMo material.

![Whöler fatigue curves from results of fatigue tests of tantalum coated and uncoated stainless steel, CoCrMo. Titanium and Ti6Al4V are included as reference (Ref. 13)](Ref. 14)

The fracture sites of test specimens from the fatigue test were subjected to a metallographic investigation. A micrograph of a cross section of such a specimen in stainless steel is shown in Figure 3. It can be seen that no cracks appear in the surface layer or in the substrate-tantalum interface. It can therefore be concluded that there is no detachment of the tantalum layer prior to the fatigue failure, and that the fatigue tested parts show mechanics corresponding to a homogenous material (a substrate/tantalum composite). Evaluation of a series of fractured parts indicates the following fracture mechanism: fractures tend to initiate in the substrate below the tantalum surface, and the tantalum surface being fully intact until final fracture.
Implantation

To investigate the biological properties of the tantalum coating, an in vivo study [canine model] has been made at Aarhus University Hospital, Denmark (Sindet-Pedersen et al.18). In a part of this study, screws were inserted into the tibia of 12 one-year-old beagle dogs. Commercially designed c.p. titanium screws (Nobel Biocare system, 7 mm long and 3 mm in diameter) were used as controls. An unloaded model with operation in tibia according to standard (dental) Bränemark operating procedure has been used. The removal torque of the screws was registered at the time of sacrifice.

![Figure 3: Micrograph of fracture site of tantalum coated 316 LVM (Ref. 13)](image)

The results of removal torque measurements are summarised in Figure 4. The data obtained are in the Figure divided into four groups based on ranges of removal torque values: less than 45 Ncm is insufficient fixation for implant load; 45-75 Ncm is low fixation; 75-99 Ncm is high fixation; and 100+ Ncm is very high fixation (it was impossible to remove the screws by the tool applied). A statistical evaluation of the data shows a significantly higher removal force after 12 weeks for the tantalum coated screws (5 good / 4 less good) compared to the titanium reference (1 good / 5 less good).

The results of the present study thus suggest a faster fixation [due to better integration] of tantalum coated parts compared to implants made from titanium. From a clinical point of view, this is important since tantalum implants may therefore be subjected to a load earlier than implants made from titanium. A faster integration may further reduce the chance of implants' failure and reduce patient suffering.

EVALUATION OF TANTALUM COATED CARBON MATERIALS FOR SPINAL IMPLANTS

Using carbon materials coated with a thin layer of tantalum may be a way to combine a good bio response [integration] with the possibility of X-ray evaluation. X-ray evaluation is not possible on metallic spinal cages, since metal absorbs the X-rays. Carbon is however light and thus radio transparent. Since carbon is not sensitive to corrosion a dense (pinhole free) layer is not demanded in this application. More important is a well distributed tantalum layer in order to improve diagnostics.

![Figure 5: Human CFC Cage from Acromed-Dupuy, model Brantigan PUF (PLF = Posterior Lumbar Interbody Fusion) was used for the study. (Ruler in foreground shows centimeters)](image)

A cage design as shown in Figure 5 was fabricated from carbon-reinforced carbon and tested for strength, bio response and diagnostics19. A 0.5+/-.3 micron tantalum layer was deposited on the cage by a CVD procedure by Danfoss Tantalum Technologies, Lyngby, Denmark.

Mechanical evaluation

![Figure 6: Spinal cage implant between tapered polyethylene blocks during compressive strength test (Ref. 14)](image)

The compressive strength was determined using the set up pictured in Figure 6. The fixtures of the test machine were lined with tapered polyethylene blocks to imitate the bone structure. The compressive strength of the tantalum coated C-C cages was determined to 4.9±0.2 kN (5 samples) which was considered to be sufficient for animal implantation (porcine). Slight design changes (removing the holes from the side walls) were further shown to increase the compressive strength to 12 kN (an approximately 140% increase). This large increase was confirmed theoretically by FEM modelling (Figure 7), where it can be seen that the stress limits reduce drastically when the side holes are removed. From the test it could be concluded that tantalum coated CFC is mechanically suitable for spinal surgery. The strength of the CFC implants is however very sensitive to specific geometrical design.
**CONCLUSIONS**

Based on the performed studies, it can be concluded that:

- Tantalum coating can be applied pinhole free to stainless steel and CoCrMo alloys with no delaminating risk.
- Tantalum coating on stainless steel and CoCrMo alloy improves the fatigue strength by up to 60%.
- Tantalum coated stainless steel and CoCrMo offer significant better bone integration than c.p. titanium.
- Tantalum coated CFC materials offer excellent bone integration, significantly better than uncoated carbon materials.
- Thin layers of tantalum have been proven to work well together with X-ray and CT scanning.

An overall conclusion is that tantalum coated stainless steel and CoCrMo alloy offer a good opportunity as materials for load-bearing implants such as hip and knee prostheses. Tantalum coated carbon materials are interesting materials for spinal surgery, since it is possible to combine good biocompatibility of the tantalum surface with good diagnostic possibilities.

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**References**

2. The Economist 19th June 2003: "Joint effort!".
13. Sandel-Pedersen S., Christensen J, Strandgaard E.A., Dano N.; Overgaard...
DLA/DNOSC

On January 5th 2005, the Defense National Stockpile Center announced the following awards in December 2004 under the BCA system:

- Tantalum metal powder (capacitor grade) 8000 lbs Ta
- Tantalum metal powder (vacuum grade) 11 000 lbs Ta
- Tantalum oxide 20 000 lbs Ta
- Tantalum minerals 108 000 lbs Ta₂O₅
- Columbium metal (vacuum grade) 11 000 lbs Cb

Companies which bought materials, which generated approximately $6.1 million in revenues, were DM Chemi-Met, H.C. Starck Inc, ABS Alloys, Sovereign Recycling and Umicore USA.

These sales exhausted the tantalum oxide included in Annual Materials Plan for fiscal year 2005.

The DNOSC solicited offers for 2250 lbs tantalum carbide and 6624 lbs metal powder (capacitor grade) on January 13th 2005. Awards of 6000 lbs metal powder (capacitor grade) worth approximately $350 000 were announced on February 7th: DM Chemi-Met and H.C. Starck Inc were the purchasers.

The results of offers in February for awards of tantalum minerals with 180 000 lbs Ta were announced on March 7th: Mitsui Mining and Smelting, Ubara Metallurgical and Umicore USA were the purchasers, and the sales generated approximately $8.6 million in revenues, reported the DLA.

MEMBER COMPANY CONTACTS

Please note the following charges for member companies:

Nichicon Tantalum Corp
Change of address:
Karasumadori Oike-ogaru, Nakagyo-ku, Kyoto 604-0845, Japan.
Telephone and fax numbers unchanged.

Rittenhouse International Resources
Change of e-mail address:
dhanderson@rittenhouseir.com

Reference Metals/CBMM
New contact details for Tadeu Carneiro, member company delegate and member of the Executive Committee:
Tadeu Carneiro, Superintendent of Technology
CBMM
Rua Pequenino 111, Sao Paulo – SP – 04552-902, Brazil.

MEMBER COMPANY NEWS

Angus & Ross
Angus & Ross announced on February 10th 2005 that it had concluded the first part of a corporate re-organisation of its Australian subsidiary Queensland Tantalum Pty Ltd. This subsidiary ‘owns a variety of mining and exploration licences’ for gold deposits in northern Queensland. A public listing on the Australian Stock Exchange is planned, to raise new capital.

Cabot Supermetals
On January 4th Cabot Corporation announced that Ms Carol Flack would return to the Strategic Planning Group of the Corporation, and Mr Eduardo E. Cordeiro was named General Manager of Cabot Supermetals.

At the end of January Cabot announced net income of $35 million for the quarter ended December 31st 2004, compared with $29 million for the December quarter of 2003. Cabot Supermetals reported a decrease of $5 million in operating profits compared to the equivalent quarter a year earlier. Kennett Burnes, Chairman and CEO of Cabot Corporation commented that the ‘Supermetals Business was negatively impacted by the timing of contracted volumes and lower prices’, which were partially offset by higher non-contracted volumes.

Cambior
A drilling campaign during 2004 increased the proven and probable mineral reserves of Cambior to 24.3 million tonnes at 0.66% Nb₂O₅ at the end of the year. The value of sales of niobium from the Niobec mine increased in the year to US$36.6 million, as the mine was wholly owned by Cambior since July 2nd 2004 when the merger with Sequoia Minerals was completed. Production will be expanded and mill optimisation is planned in the second half of 2005.

Commerce Resources
Commerce Resources announced in February that it had acquired a 100% interest in the Mud Lake property, with carbonatite occurrences, in the Blue River area.

Sons of Gwalia
The metals press reported in January that the company, in voluntary administration, had accepted the resignation of the non-executive directors. John Leewers remains as Managing Director. In February it was reported that the administrators were suing the auditors for their poor work.

Sons of Gwalia continues to produce and to supply tantalum raw materials to its contracted customers.

Kemet
Dr Jeffrey Graves resigned as CEO on January 26th. While the Board of Directors sought candidates for the post, the responsibilities of CEO would be assumed by James McClintock and David Gable, reported Kemet.

A net loss (before special charges) of US$18.6 million was posted for the December quarter 2004, compared with a net loss of US$16.7 million for the September quarter and a net loss of US$7.3 million for the December quarter 2003. A ‘challenging demand environment’ and negative impact of the inventory cycle were reasons given for the results.

Tertiary Minerals
Executive Chairman Patrick Cheetham expressed his hopes of a positive outcome to the company’s efforts to secure alternative funding for the Ghurayyah tantalum project in Egypt after a last-minute breakdown of negotiations with a potential partner. Inventories had been depleted and the tantalum market was growing again, led by a resurgence in consumer spending on electronics, he commented. A loss was reported for the year ended September 2004, although the company had ‘an excellent portfolio of exploration assets’, said Mr Cheetham.