BULLETIN N° 147
ISSN 1019-2026

TIC

TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

PRESIDENT'S LETTER

Dear Members and Friends,

Welcome to our very first electronic Bulletin! I hope that those of you who have accessed it via our website found the process straightforward, and that it has saved you time in obtaining your copy.

There are just four weeks remaining before we meet in Almaty, Kazakhstan, for the Fifty-second General Assembly of the T.I.C. The level of interest, as indicated from the pre-registration activity, certainly suggests that once again we will have a lively and relevant meeting, with what promises to be an informative technical programme. To those of you who have not yet pre-registered, we urge you to do so as soon as possible, so that we can finalise the numbers with the hotel. It will also be important for you to assure yourselves there are seats remaining on the relatively few flights to and from Almaty.

We would like to extend our gratitude to NAC Kazatomprom and Ulba Metallurgical Plant for supporting the event and especially for hosting the Monday evening banquet. Also, many thanks to Ulba for organizing the site visit to their property in Ust-Kamenogorsk. This will be a long day for delegates but I am sure we will all agree that it was well worth it! Thanks especially to Emma Wickens who is, as always, tireless in her efforts in assisting delegates with travel arrangements, and in sorting out the details that make all the difference to delegates' enjoyment.

Your various Working Groups continue to work hard behind the scenes. Our Technical Promotion Officer is ably representing the T.I.C. at several international forums related to Transportation of Raw Materials, while several members are pursuing various initiatives regarding the mining and trading of minerals in Central Africa. This has been a difficult issue, but I truly believe that, finally, we are beginning to see real progress.

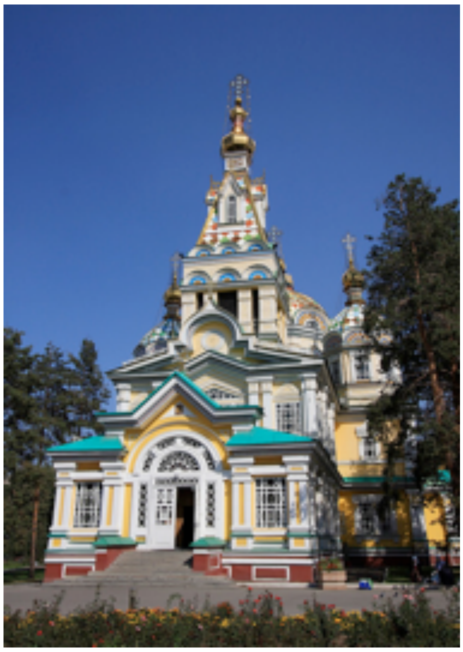
My second consecutive year as your President is fast coming to an end. They have both been challenging years, and I wish to thank you all for your support, without which it would have been a truly daunting task. Nobody ever said the tantalum industry is dull!

Looking forward to seeing you in Almaty.

Richard Burt
President

CONTENTS

FIFTY-SECOND GENERAL ASSEMBLY AND TECHNICAL MEETING



© Yodod@flickr/CC

Zenkov Cathedral, Panfilov Park

The Fifty-second General Assembly meeting of the Tantalum-Niobium International Study Center will be held in Almaty, Kazakhstan, from October 16th to 19th 2011. The event will take place at the Rahat Palace hotel, where delegates will also stay.

On Sunday October 16th, all participants are invited to a Welcome Reception from 6 to 8 p.m.

The formal General Assembly of the association will be held on Monday October 17th and will be followed by technical presentations for the rest of the morning, then a buffet lunch.

On Monday evening, all participants are invited by our hosts, NAC Kazatomprom and Ulba Metallurgical Plant, to a Gala Dinner in the Bakhchisaray restaurant.

A second technical session will be held on the morning of Tuesday October 18th, followed by lunch.

On Wednesday October 19th, there will be a plant tour to the facility of Ulba Metallurgical Plant. A chartered plane will take participants to Ust-Kamenogorsk.

Sightseeing tours for those accompanying the delegates are also being arranged.

TECHNICAL PROGRAMME - ABSTRACTS

The following papers are expected (not in running order):

Current trends in the development of production technology for tantalum powders with capacitance of up to 8 kCV

L.M. Frolova, A.E. Kaynazarova
NAC Kazatomprom, Ulba Metallurgical Plant

The main object of this report is the development of technology to modify tantalum powders with splintered particles, focusing on the stabilisation of the capacitor dielectric characteristics over a wide range of temperatures and at high voltage. These capacitors belong to a high reliability class that can be used in military equipment, aircraft components, space complexes and other units that operate in extreme conditions.

An assessment of the electronic component and capacitor powder markets has been performed. The world demand for tantalum powders made of purified compact tantalum, together with the rheological features and electrical characteristics desired by modern capacitor producers have also been considered.

The research focused on the determination of agglomeration conditions and the deoxidation technology which allows the oxygen content in powders with a capacitance of 2.5-8 kCV to be adjusted to a level securing a dynamic balance of oxygen content in the oxide layer. This allowed a decrease in the crystallization effect in the amorphous film on anodes, as well as increasing its breakdown voltage accordingly.

Tantalum powder with a capacitance of 6.5-8 kCV was preliminarily tested at a customer's production facility (Meson JSC, Russia), the result of this testing was positive and beginning in 2009 this powder was put into production. Also since 2009 tantalum powders with a capacitance of 2.5-6 kCV have been qualified at the companies Vishay and Stainless.

NbZr1 alloy used for superconductive joints for radiofrequency superconducting (RFSC) cavities

Bernd Spaniol (presenter), Andreas Uhlendorf, Joachim Rutz, Xenia Singer, Jacek Sekutowicz, Peter Kneisel
W.C. Heraeus

The connection of RFSC cavities is done with cone-flat flanges. The material used has to have a hardness of more than 200 DPH in order to be able to use the cone-flat flanges several times without destroying the sealing nozzle of the flange.

The state of the art is to use NbTi alloy. Unfortunately NbTi does not become superconductive at the operating temperature of the cavities at 4.2 K.

High purity Nb that has an excellent superconductivity cannot be used as the hardness is only about 40 DPH. In cooperation between Heraeus, DESY and the Jefferson Lab, we have developed a process for a controlled implementation of oxygen into NbZr1% to increase the surface hardness up to 400 DPH.

Flanges treated in this manner have been tested by closing and opening ten times. The vacuum tightness reached after the tenth closing was < 1.5 x 1E-10 torr l/sec. A first cavity using these flanges will be built next.

New operating developments at Mibra mine

Itamar Resende (presenter)
Companhia Industrial Fluminense

CIF MINERAÇÃO S.A., a subsidiary of Advanced Metallurgical Group (AMG), owns and operates the Volta Grande mine (MIBRA) located near the city of Nazareno in the state of Minas Gerais, Brazil.

Today CIF is believed to be one of the largest and most cost effective tantalum mining companies in the world through its unique mining model, which has supported the business for the last 10 years.

The presentation will focus on the next stage of development which will include its future expansion plans and the recovery of Ta_2O_5 to raise tantalum concentrate production to over 500 000 lb per annum by 2013.

The paper will also present how CIF will develop new co-products and utilise new technology to improve its mineral recovery, further reduce production costs and reduce the mine's overall environmental impact, paving the way for an exciting and sustainable future.

Current situation and prospects for high capacitance tantalum powder

Zhang Xueqing, Ma Yuezhong, Cheng Yuewei, Wang Zhidao, Luo Guoqing, Lin Fukun, Chen Xueqing
Presented by Guo Hong
CNMC Ningxia Orient Group

This presentation reviews the developments, at the R&D level, large-scale production, and highest application level of high capacitance tantalum powder over the last 20 years. It introduces the conventional processing method to produce high capacitance tantalum powder by sodium reduction from K_2TaF_7, as well as presenting the powder properties obtained by the above method, and explores the advancement and current status of the conventional method of production. It analyses the technical problems and difficulties in refining reduced powder, higher level of detrimental impurities and worse electrical properties during the development of higher capacitance tantalum powder. It introduces new techniques and new methods of producing this powder after recent years of R&D in this industry, nano tantalum powder induction plasma method by using conventional tantalum powder as the material and adopting RF Plasma in combination with DC Plasma. It also introduces the Homogeneous Method with a liquid ammonia homogeneous medium, reducing $TaCl_5$ by sodium to produce nano tantalum powder, the electrochemical process to make Ta_2O_5 powder into solid cathode, then using graphite or noble electrode as the anode to perform constant potential electrolysis at high temperature in a mixed molten salt with $CaCl_2$, and the Flame Synthesis, inserting sodium and $TaCl_5$ precursor into a burning part by injection technique, to get nano tantalum powder by reduction of sodium and $TaCl_5$ in a co-flow furnace. It summarizes the advantages and disadvantages of different powder particles, topography, properties of powder using different instruments, technologies and methods. Considering the technical complexity and critical problems facing conventionally produced high capacitance tantalum powder, it presents the thoughts from high capacitance tantalum powder to much higher capacitance development - to accelerate the progress of the engineering, the industrialization, and the scale-up, to promote the continuous and healthy development of high capacitance tantalum powder.

As it was and in our time

K. A. Stewart (presenter), G. T. Ibbs
A.S. Metallurgy (Liverpool)

A historical review of the analytical methods employed for the determination of tantalum and niobium throughout the years 1801 to the present time.

Historically tantalum and niobium arrived on the scene at the start of the nineteenth century with the discovery by the English chemist Hatchett of an elemental species in the form of an oxide that he called columbium. The following year in Sweden the chemist Ekberg discovered an elemental species in the form of an oxide that he called tantalum. The mineral species in each instance was related to the oxide, thus columbium was from columbite and tantalum was from tantalite. Wollaston suggested that the two metals were in actual fact from the same element and opted for the single name 'tantalum' for the two metals. It took till 1844 when the German chemist Rose concluded that in fact the oxide species of columbite was a mixture of two oxides, tantalum as per Ekberg and another species which he designated niobium. Around 1866 Marignac, a Frenchman, decided that Hatchett's columbium was in fact niobium. The duplicity in names columbium and niobium lasted until 1951 when IUPAC opted for niobium for the elementary species, despite some considerable resistance to this clarification.

At the beginning of the 20th century the metals' individual characteristics defined their emergence into the 'commercial' world, production started and analysis became less academic and more a real necessity. The similarity of the metals and their chemical properties, together with the other elements in co-occurrence, made for difficult analysis by classical means. Many clever chemists produced separations and determinant steps. With the evolution of instrumental methods of analysis, some colorimetric, spectro-photometric, X-ray and ICP-OES, the analysis has in some areas struggled to keep up with the demands of an industry that is now very significant. These methods are reviewed.

Development of electron beam melting technology at Ulba Metallurgical Plant JSC

S.J. Dobrussin, D.V. Popov
NAC Kazatomprom, Ulba Metallurgical Plant

The electron beam refining in vacuum plays a key role in the production of high purity tantalum. Refining by remelting of tantalum and niobium ingots at UMP JSC is carried out in two types of furnaces:

1. EMO-200, 250 - dynamic heating method (with a Pierce Gun). With this method, heating is carried out with the help of an electron beam with a defined cross section and power density, moving at the surface of the liquid bath in the crystallizer and operated by a processing machine operator.
2. Beam control systems installed on EBM-800 and EMO-1200 furnaces allowed to transfer from dynamic electron beam melting to quasi-stationary. Similar to stationary, quasi-stationary heating conditions are evidenced under equal heat distribution, added by electron beam at whole bath surface.

This installed system of electron beam scanning according to set position allows to move closer to stationary heating conditions.
The characteristic difference of EBM-800 melting is a vertical feed of the remelting ingot. Along with the quasi-stationary heating method, vertical feed allows to reach the following positive changes in electron beam treating of metal:
- Increased refining of the base metal from low-melting and gas admixtures expense more developed heating surface of melting ingot.
- Improve the quality of produced ingots by means of total exclusion of the shadow effect in melting.
- Decrease vaporisation of base metal in melting with consequent increase of 'yield point'.
- Decrease of admixture incorporation rate of high-melting elements.
- Improve homogeneity of melting ingots by means of automation of the melting process.

Nowadays the EBM-800 furnace includes melting processes of tantalum achieving chemical purity of 4N5 and higher. The maximum size of the ingot is a diameter of 235 mm and a length of 1800 mm. The main application of ingots is as the semi-product feed material for the production of sputtering targets.
The installed furnace shows good efficiency in high-purity niobium production. All the above advantages allow a reduction in the number of re-melts during the production of RRR purity niobium according to ASTM B393-02. The maximum size of the niobium ingot is a diameter of 300 mm and a length of 1800 mm.

Tantalum market trend in the Far East

Hiroaki Yoshinaga (presenter), Shigeo Nakamura
Advanced Material Japan

We would like to summarize the latest situation of supply/demand and market trend in China and Japan, following on from our presentation on this topic in Rio de Janeiro in 2007.

Though we can still not anticipate how Japan will recover from the disaster which hit the country in March this year, unfortunately there will be a significant impact on the Japanese economy due to the radiation problems, electricity power cuts, and many manufacturers being damaged by the massive earthquake and the huge tsunami. We will summarize what impact has been caused and how the Japanese economy will have recovered by the time of the T.I.C. meeting.

As far as raw material is concerned, the Japanese tantalum industry needs to diversify sources of tantalum minerals including DRC and adjoining countries. We will consider what the impact will be on demand if the tantalum market continues to experience a high price level.

Development of a new generation pilot plant for production of tantalum powders utilizing FFC Cambridge process principles

Ian Margerison (presenter)
Metalysis

Metalysis is an intellectual property company that is scaling up the FFC process for the production of titanium, tantalum and other high value metals. The current status and recent advancements in the use of the FFC Cambridge process for the production of tantalum powders is presented with reference to the new generation pilot plant. The pilot plant turns Ta_2O_5 pre-forms into a loosely agglomerated metal sponge. Typically immersing the oxide(s) to be reduced in a bath of electrolyte, in this case molten calcium chloride, at temperatures between 800 and 1000°C and applying a cathodic potential to the oxide via a suitable immersed anode. During the washing process the tantalum sponge loses its mechanical integrity and turns into tantalum powder. Lastly Metalysis will give an overview of the process and the advantages that the new generation pilot plant has over past FFC cell designs, and show that the pilot plant is of a sufficient scale to produce tantalum commercially.

Technology for production of niobium master alloy and high-purity niobium at Ulba Metallurgical Plant JSC

D.V. Popov, A.B. Savichev, G.A. Gaintsev
NAC Kazatomprom, Ulba Metallurgical Plant

At the present time UMP JSC has developed the technology to produce its own niobium metal, in particular niobium of superconductive grade that has special properties. To a great extent, these properties are defined by metal purity, therefore the content of some impurities in the metal should be at a minimum.

Among all possible methods of producing niobium metal, UMP JSC has preferred aluminothermy due to the high reducing ability of aluminium, the ability to reach a lower content of harmful impurities, especially carbon, in comparison with other metallurgical processes, and also due to the relatively inexpensive use of aluminium powder in comparison with magnesium powder or calcium powder.

A special water-cooled copper crucible was developed for conducting reduction melts that allow the production of niobium-aluminium master alloy with very high productivity due to the use of forced cooling of the reaction products.

Compact feed billets are manufactured from the reduced niobium, by way of welding together the niobium-aluminium master alloy on electron-beam apparatus OMA-250.

The compact feed billets further go through refining re-melts in electron-beam furnaces under special modes that allow more efficiently to remove easily fusible elements and gas impurities.

The major problem with refining niobium from gas impurities is removing nitrogen. Decontamination of niobium from gas impurities should preferably be conducted under quasi-stationary heating conditions that can be created with equilibrium heat distribution supplied by electron beam, along the whole surface of the liquid pool.

Using special modes of quasi-stationary method for heat supply allows a decrease in the number of re-melts to produce niobium of RRR purity according to ASTM B393-02.

T.I.C. Statistics and Transport update

Ulric Schwela (presenter)
Tantalum-Niobium International Study Center

Memory of the global economic downturn is fading, the impact on the niobium and tantalum industries in 2008 and 2009 being replaced with renewed demand in 2010, followed by production resumption at major mines. Events related to conflict minerals have seen production boycotted in some areas, while efforts to set up traceable supplies have proved fruitful for other areas. The statistics review will cover all the T.I.C. statistics categories for niobium and tantalum.

This transport update focuses on an in-depth description of denial of shipment. Firstly there is a definition of what constitutes denial of shipment, secondly an overview of what has been done to address this over the years and thirdly a detailed look at each of the separate ways forward being taken by the various stakeholders, including the International Atomic Energy Agency, national regulators, modal transport authorities and industry, and their collaboration through the International Steering Committee on the Denial of Shipments of Radioactive Material where the T.I.C. is the current Chair.

Tantalum market prospects

Anatoly Bosonogov, Alexey Tsorayev
NAC Kazatomprom, Ulba Metallurgical Plant

The current and predictable future situation on the tantalum raw materials market appears to be critical not only for UMP JSC but also for the whole tantalum industry. During the period of world financial crisis, three among nine legally operating tantalum mines were suspended. Also in December 2008 the biggest source of mineral raw materials, the Wodgina mine owned by Global Advanced Metals (formerly Talison Tantalum) in Australia was closed.

During 2009 industry did not incur any deficit of raw materials due to the fact that artisanal mining in the Democratic Republic of Congo (DRC) fully covered drop-out capacities. However, in the second half of 2009, sanctions pointing to illegal tantalite mining in DRC were made more rigorous by the United Nations Security Council. Moreover, implementation by the United States Government of the S.891 Congo Conflict Minerals Act in 2009 and the Dodd-Frank Wall Street Reform and Consumer Protection Act (Section 1502 fully corresponds to provisions of S.891 Act) resulted in considerable changes in the tantalum raw materials market.

Owing to the restrictions imposed by UN and USA on trading of tantalite from DRC and nine other neighbouring countries, tantalum raw materials spot market was exposed to a huge shortage followed by a threefold price increase for tantalite. The situation became even more aggravated when, in September 2010, mining in Eastern provinces of Congo (North, South Kivu and Maniema) was banned by the President of the DRC.

Trial restart of the Marropino mine owned by Noventa in Mozambique and the start-up of the Wodgina mine in Australia announced by Global Advanced Metals (GAM) will not have a strong impact on market shortage in 2011.

Successful implementation of the iTSCi initiative for transparent supply of cassiterite, tantalite and wolframite from the DRC pushed forward by the Tin Institute (ITRI) and the Tantalum-Niobium International Study Center (T.I.C.) is likely to increase supply on the tantalum raw materials market.

High prices for raw materials result in price increases for main tantalum products which in turn lead to demand slowdown for tantalum capacitors (due to strong substitutes being available) and demand slowdown for tantalum super-alloys (alternatives available). Tantalum products for sputtering targets are less sensitive to the evolution of raw material prices.

On the other side high prices for raw materials create more incentives to start up the projects whose activity was economically unprofitable at the price levels observed in 2002-2009.

Research on large grain Nb sheet process used in superconducting accelerating cavity

Xie Weiping
Presented by Jiang Bin
CNMC Ningxia Orient Group

This article studies the processing of large grain Nb sheet used in producing superconducting RF cavities. The studied production process for large grain Nb sheet is simple and easy to control, can not stain the Nb material and so makes it easier to meet the technical requirements of the superconducting RF cavity. The result shows that the RRR value and physical properties of the large grain Nb sheet are similar to ingot and meet the technical requirements of the superconducting RF cavity, because the production process of the large grain Nb sheet does not need forging, annealing, and rolling processes that can increase interstitial element (C, N, H, O) contents and would reduce the RRR value of the Nb material.

Update on conflict free Supply Chain management issues

William Millman, AVX, and Richard Burt, GraviTa

This paper will review the status of the various industry led initiatives including those of the T.I.C., the regulatory environment, and the involvement of Advocacy Groups, that have had an impact on the conflict free supply chain of tantalum over the previous twelve months.

Overview of the artisanal mining sector in eastern DRC: current initiatives on the ground

John Kanyoni
Mining Chamber, Fédération des Entreprises du Congo

Before 2006, artisanal mining in eastern DRC was not formalized as such - there were fewer than 15 comptoirs in North and South Kivu. The exploitation was not significant due to smuggling and the informal nature of the sector, while there were still sufficient quantities produced by artisanal miners.

We decided after 2006 to set up 'the association of comptoirs in North and South Kivu', the main objective being to formalize the trade and make sure that the entire supply chain (diggers, négociants and comptoirs) is responding to the mining code of the DRC.

The impact of mining is huge as it covers also many other businesses (transport, insurance…) and gives jobs to many thousands of Congolese. The mining sector also provides to the government of eastern DRC more than 35% of its income in taxes.

Challenges of initiatives of the ground:

Due to the pressure of advocacy groups, the mining sector in eastern DRC was labelled as the main one fuelling the armed groups and creating abuse of human rights, while everyone knows that the problems of DRC did not start through mining in eastern DRC. With the support of international partners, we decided to make the sector more transparent based on three elements: traceability, due diligence and certification.

A lot has been achieved so far, starting with traceability, with the support of ITRI and T.I.C. We can say today that the iTSCi programme has proved in Katanga and Rwanda that it is the way to make material more traceable from the mine up to the point of export.

The second tool is the due diligence guidelines from OECD and UN. The guide was endorsed by stakeholders in DRC and most of the comptoirs have decided to join the implementation phase of the guide.

The last tool is certification. The ICGLR, which is a regional body, has endorsed tools which will help all the eleven countries to fight against illegal exploitation of natural resources in the Great Lakes region.

Finally our message to the end consumers is to support the various initiatives in the region. This is the message we conveyed several times to the SEC. It is important that the rules support all the efforts made so far to save the local industry, to comply with the initiatives on the ground and save the livelihoods of thousands of Congolese who are facing a 'de facto embargo' due to poor interpretation of the Dodd-Frank Act.

NEW CORROSION RESISTANT MATERIALS MAKE CUTTING EDGE ENERGY PROCESSES POSSIBLE

This article was prepared from a paper presented by Bo Gillesberg from Tantaline at the Fifty-first General Assembly of the T.I.C. held in Nevada, U.S.A., in October 2010.

INTRODUCTION

The sulfur-iodine thermochemical process, developed by General Atomics, is a process that allows for the production of hydrogen gas without the use of fossil fuels. The sulfur-iodine thermochemical process has extreme operating environments and therefore a variety of significant material challenges. As conventional materials are pushed to their limits in order to achieve the next generation of chemical processes, new materials are required to meet those challenges.

This paper will discuss the process conditions and the challenges faced in the sulfur-iodine thermochemical process and how Tantaline's materials were used to meet the mechanical, chemical and economic challenges where virtually all other specialty materials like nickel-based alloys, fluoropolymers, glass and tantalum metal have failed.

BACKGROUND

Combustion of fossil fuels currently provides about 86% of the world's energy. [1],[2] In an effort to reduce our dependence on fossil fuels and lessen the environmental impact, hydrogen fuel presents an attractive alternative. However, the problem with hydrogen as fuel is that it is produced from fossil fuels, negating any benefits that could be seen with hydrogen. An alternative is hydrogen production by thermochemical water-splitting, which is a process that enables the decomposition of water into hydrogen and oxygen without the need for fossil fuels.

The sulfur-iodine thermochemical process requires heat and water as the only inputs and oxygen and hydrogen are the only outputs or products. All of the reagents are self-contained within the process and recycled, creating no waste. When combining this technology with solar or nuclear power as a heat source, it becomes a very attractive process for hydrogen production and a viable alternative to fossil fuels.

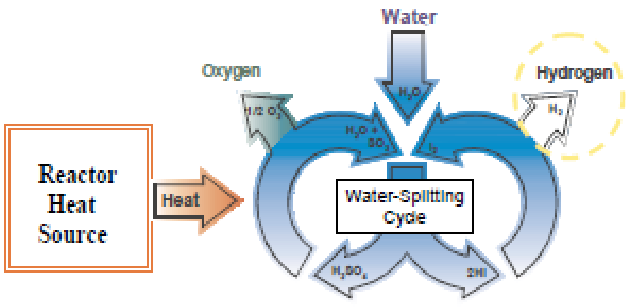


Figure 1: water-splitting cycle [4]

The sulfur-iodine water-splitting cycle represents a leading candidate for thermochemical hydrogen production and it consists of three chemical reactions that sum to the dissociation of water. [3]

II: $H_2SO_4 \rightarrow SO_2 + H_2O + \frac{1}{2}O_2$
I: $xI_2 + SO_2 + 2H_2O \rightarrow 2HI_x + H_2SO_4$
III: $2HI_x \rightarrow xI_2 + H_2$

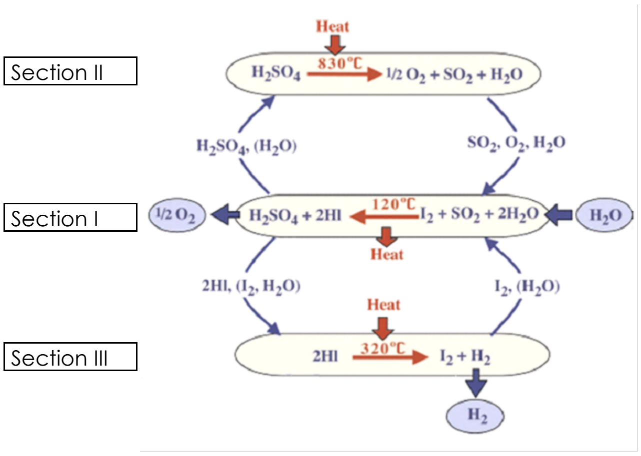


Figure 2:
Section I: Recycling and acid (HI and H_2SO_4) generation
Section II: Sulfuric acid concentration and decomposition
Section III: Hydrogen iodide concentration and decomposition

The sulfur-iodine thermochemical process is an aggressive process mechanically and chemically. It is a hot process where the hydrogen efficiency is a function of the process temperature. When the process is pushed to 900°C, efficiencies as high as 55% could be achieved. Utilizing high temperatures, pressures and concentrated acids, the materials of construction for the process (which include valves, fittings, vessels and instrumentation) are pushed beyond their typical limits. Unfortunately, this leads to corrosive failures, creating an unsafe and unstable process environment, which can often lead to higher operating costs and make this process economically unfeasible.

For this process to become efficient, economical, safe and reliable, new materials are needed to meet the challenges of the sulfur-iodine thermochemical process.

The material challenges facing the sulfur-iodine thermochemical process are extreme. It is the combination of the corrosive chemicals, high pressures and high temperatures that makes this process environment so aggressive and the material choices limited.

With regards to corrosion, the process contains mixtures of sulfuric acid (H_2SO_4), hydroiodic acid (HI) and phosphoric acid (H_3PO_4) at temperatures of more than 300°C and pressures between 20 and 30 atmospheres. It is important to note that while hydroiodic acid is not a common acid, it is one of the strongest acids in the halide group when compared to HCl and HBr. This makes containing the hydroiodic solution (HIx - Hydroiodic acid + water) very difficult.

Some of the most corrosive conditions that the materials face consist of a solution of phosphoric acid, hydroiodic acid and water with the following chemistry:

80 wt% H_3PO_4, 8 wt% HI, 12 wt% H_2O up to 280°C at 150 psi

This environment is so corrosive that common materials and even specialty materials struggle to survive a few days. [5]

Because of the high temperatures and pressures, polymeric materials are not a suitable option. Although glass would fare well corrosively, because of the pressures and the brittle nature of glass, glass is not a feasible option in a production environment. This leaves metals as the only real practical option.

When considering metal options, a variety of specialty metals were considered which included nickel alloys like Monel® alloys, Hastelloy® alloy B and C grades, zirconium, titanium, tantalum and gold. Of these materials, only tantalum demonstrated the corrosion resistance needed to survive in this corrosive environment and was therefore selected as the only material of choice for dealing with the HIx solutions.

While tantalum metal is known as the most corrosion resistant material commercially available, there are many problems associated with the practical use of tantalum metal. First and foremost is the cost of tantalum. Tantalum metal is an extremely expensive exotic metal costing around 50 times more than stainless steel. The second problem with tantalum is its availability in the form of usable products. While one can easily purchase ingots, rods, tubes and sheets of tantalum metal, getting tantalum in the form of common process equipment is extremely difficult. For example, to simply find a variety of valves, fittings, pumps and instrumentation in solid tantalum to assemble a chemical processing system could prove to be very difficult - if not impossible - due to the cost of the metal and difficulty of machining and welding. Furthermore, custom fabrication of solid tantalum is not easily performed and is typically carried out by specialized and highly skilled fabricators.

In any case, designing a process out of solid tantalum metal has some serious practical limitations, engineering difficulties and economical flaws. Since tantalum metal was the ideal material for the process environment, the feasibility of designing a sulfur-iodine thermochemical system was dependent on finding an alternative to solid tantalum metal without sacrificing the performance.

SOLUTION

Having the ability to utilize commercially available products with a corrosion resistance similar to that of solid tantalum at an affordable price were the main drivers for deciding on a particular material solution. With this in mind, General Atomics decided that the material best suited to meet the challenges of the sulfur-iodine process is the tantalum surface alloy produced by Tantaline.

What makes tantalum metal extremely corrosion resistant and more corrosion resistant than other specialty metals is the tenacious oxide layer which is only a few angstroms thick. Tantalum metal forms this oxide layer instantaneously even in very low oxygen containing solutions. Since the protective oxide layer is on the exterior of the tantalum metal surface, having more mass of tantalum does not provide any extra corrosion protection in environments that show a nil corrosion rate. Since tantalum metal is extremely expensive, a thin, rugged and durable surface of tantalum metal is ideally all that is needed for unmatched corrosion performance.

A tantalum metal surface alloy approaches this ideal by creating a 50 µm thick commercially pure tantalum surface that is metallurgically alloyed to steel parts. Based on a chemical vapor deposition process, tantalum metal is chemically reacted and vaporized at high temperatures. With this reaction, a gaseous atmosphere of tantalum is created, where the tantalum metal diffuses into and continues to grow on top of the substrate. Because the process occurs at an atomic level and is at high temperatures, an alloy zone approximately a half micron thick is created in the substrate (see Figures 3 and 4), which is typically stainless steel. Since this is a chemical/metallurgical bond as opposed to a mechanical bond, the tantalum surface is extremely rugged and durable withstanding thermal shock, mechanical bending and impacts.

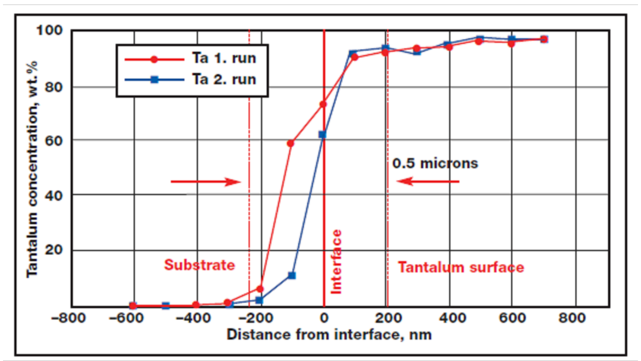


Figure 3: creation of an 0.5 µm thick alloy zone

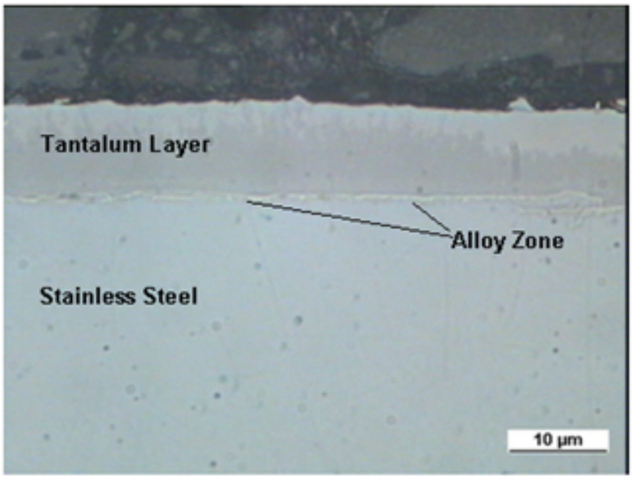


Figure 4

Once the alloy zone is formed, the process continues to produce a pure tantalum metal surface having all the chemical properties of commercially pure tantalum metal as specified by ASTM B364. This tantalum surface is typically 50 µm (0.002") thick as this has shown to be the optimal thickness for most applications (though it could be made as thick as 0.008" if needed).

Compared to typical coatings like thermal sprays, the tantalum surface alloy is extremely rugged and durable. Since the tantalum atoms are actually being grown into and on top of all surfaces as opposed to projecting line of sight globules at a surface, voids are virtually eliminated. Furthermore, because the process occurs in a vacuum, brittle oxide inclusions do not exist, making the tantalum surface alloy extremely ductile.

Unlike thermal sprays, the Tantaline process is a gas phase process making it geometry independent and not constrained by line of sight (see Figures 5 and 6). As a result, both internal and external steel surfaces could easily be treated as long as there are no mass transfer constraints that could be imposed (for example a long and small diameter tube could constrain adequate mass transfer of the gasses).

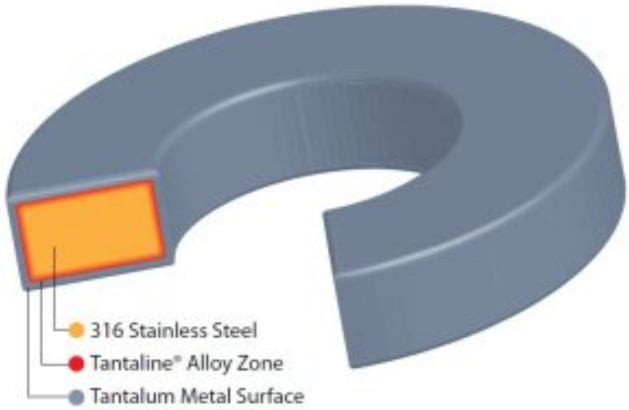


Figure 5

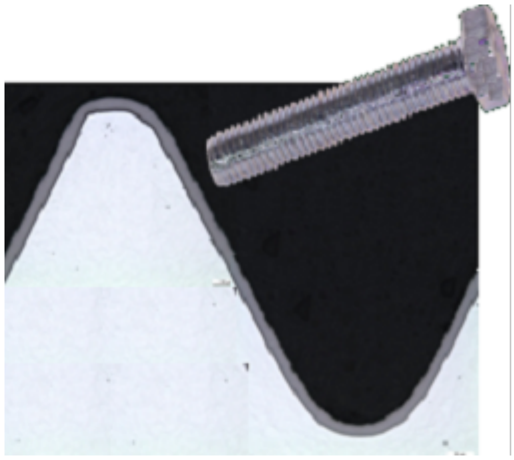


Figure 6

Finally, the ability to utilize standard commercially available parts is primarily due to Tantaline's tolerance etching capabilities. Tolerance etching allows the original part's dimensions to be maintained by first removing, for example, 50 µm of steel before growing 50 µm of tantalum onto the substrate surface. As a result, the net change in the dimensions of the part is zero. By having the ability to use commercially available parts without the need for custom fabrication was a key benefit in keeping the costs down, lead-times short and ultimately to the success of this project.

ECONOMICS

Material choices for corrosion solutions are always guided by the economics of implementing those materials. While not always true, the costs of corrosion resistant metals typically increase with higher corrosion performance. In the case of tantalum metal, it is very expensive. A simple ½" Swagelok® tube fitting fabricated in solid tantalum will cost in the range $1500 - $2500 and for more complex parts like valves, a half ball valve costs tens of thousands of dollars. With several hundred components needed to build a system which includes valves, fittings and instrumentation, it becomes quickly clear that utilizing a solid tantalum system is cost prohibitive and impractical.

With tantalum surface alloys, since tantalum metal is utilized so efficiently and there is no fabrication needed with a gas phase process, the costs of components are typically ten times less than with solid tantalum. Being competitively priced to nickel alloys like Hastelloy® C276, a tantalum surface alloy could not only be used to replace solid tantalum metal but it is economically feasible to replace nickel alloys, titanium, and zirconium metals as well.

RESULTS

With the extremely corrosive conditions created in the sulfur-iodine thermochemical process, gold, titanium, Monel® and Hastelloy® C276 could only survive at most 50 hours. As a result, the Tantaline solution was adopted for all corrosive areas of the system covering more than 90% of the process valves, fittings, instrumentation and custom products.

Between 2007 and August 2009, more than 1200 Tantaline parts have been installed in the General Atomics system. With more than two years of history and thousands of hours of operation, temperature cycling, mechanical abuse and process spikes, the Tantaline products have proven to be an excellent solution and have met General Atomics' needs for high performing, readily available and economic products.

ADDITIONAL FINDINGS

A surprising result delivered by installing Tantaline parts in the thermochemical process was that Tantaline parts were actually outperforming solid tantalum parts. Because the General Atomics process is actually generating hydrogen, there are relatively high concentrations of free hydrogen in the environment which have led to hydrogen embrittlement and premature failure of solid tantalum components. In the same environment, it was observed that Tantaline parts were actually surviving many times longer than solid tantalum. This has also been the case in high temperature vacuum furnaces where Tantaline has outlasted solid tantalum for support racks in the bottom of the vacuum furnace. While the exact mechanism is still being evaluated, there are two theories being considered as to why this is the case. The first theory is that Tantaline surface hydrogen embrittles too; however, it does not matter since the mechanical load is taken by the stainless steel substrate. The second theory is that the hydrogen attacks the grain boundaries of typical tantalum that is formed from ingot. In the case of Tantaline, traditional grain boundaries do not exist, therefore it is resistant to embrittlement. Whatever the reason, the fact remains that Tantaline has outperformed solid tantalum in this environment and appears to be hydrogen embrittlement resistant.

CONCLUSION

Tantaline has helped General Atomics significantly reduce maintenance costs and also drastically improve the safety of their process, as no other material could adequately contain their process reliably.

Overall, Tantaline's technology allowed General Atomics to have the performance of tantalum they demanded with the availability of commercially available stainless steel products, at a price similar to that of nickel alloys. This not only made their process feasible both technically and economically, but also provided a level of safety that could not be reached with other materials.

Since the General Atomics application, KIER (Korean Institute of Energy Research) is also building a similar sulfur-iodine thermochemical process. [6] For this process, KIER has chosen Tantaline as the material of choice for its corrosion resistant needs.

REFERENCES

1. *International Energy Outlook 2000: DOE/EIA-0484 (2000)*
2. *Annual Energy Outlook 2000 with projections to 2020: DOE/EIA-0383 (2000)*
3. *Paul M. Mathias and Lloyd C. Brown, Thermodynamics of the Sulfur-Iodine Cycle for Thermochemical Hydrogen Production, March 2003, pages 1-3*
4. *Ken Schultz, Thermochemical Production of Hydrogen from Solar and Nuclear Energy, Presentation to Stanford Global Climate and Energy Project, April 2003*
5. *Ben Russ, Program Manager – Energy Process Group, General Atomics*
6. *KIER, Korean Institute of Energy Research*

MEMBER COMPANY NEWS

We would like to inform you that articles concerning T.I.C. members or the industry in general are posted regularly on the T.I.C. website in the recently created section entitled 'News'.

Changes in member contact details

Honeywell Specialty Chemicals Seelze GmbH

Honeywell Specialty Chemicals Seelze GmbH has nominated a new delegate to the T.I.C.: Dr Mattis Gosmann replaces Dr Harry Zumaqué. His e-mail address is: mattis.gosmann@honeywell.com.

NAC Kazatomprom

NAC Kazatomprom has moved its offices from Almaty to Astana. Please find below the new contact details.

Address: 10 D. Kunayev St., 010000 Astana, Republic of Kazakhstan.
Tel.: +7 717 2551398
Fax: +7 717 2551399

The delegate to the T.I.C. remains Dr Vladimir Shkolnik.

Tantaline

Mr Peter Lock is the new delegate to the T.I.C. for Tantaline, replacing Dr Bo Gillesberg. His e-mail address is: pl@tantaline.com.

www.tanb.org
e-mail to
info@tanb.org