BULLETIN N° 142
ISSN 1019-2026

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TANTALUM-NIOBIUM INTERNATIONAL STUDY CENTER

PRESIDENT'S LETTER

Friends,
June - and as I write this, in Central Canada at least, the long hot days of summer are already with us!

In April, the members of the Executive Committee (at least those who could dodge the ash clouds and get to Brussels) met, along with our Technical Promotion Officer and Secretary General, to review plans for the Fifty-first General Assembly to be held at Lake Tahoe, Nevada, U.S.A., on Monday October 4th. The T.I.C. meeting, technical programme and visits will extend from Sunday October 3rd to Wednesday October 6th. The technical programme is taking shape, and as you will see from the list of papers elsewhere in this Bulletin, it promises to be engaging and informative for both the niobium and tantalum industries. Complete details and registration forms will be sent to members in early July, and we ask that you register as soon as possible, as the meeting is a couple of weeks earlier than normal, to ensure that an early autumn does not hinder travel plans.

We wish to thank Niotan for hosting the event and for opening their plant for the Wednesday visit, which will be in conjunction with a tour of the nearby historic mining town, Virginia City.

The Committee has also started work on future Assemblies, with plans already well in hand for 2011 in Kazakhstan.

I would like to take the opportunity of thanking Mr He Ji-Lin for his many years of service to the Committee and wishing him a long and happy retirement.

Several members, in addition to the Working Group, have been active with the 'Supply Chain Initiative', working for the good of the industry by contributing to forums and discussions with the electronics industry EICC/GeSI initiative, as well as with the OECD deliberations on Due Diligence guidelines, and the various Bills before the U.S. Legislatures. Thanks to everybody for their contribution to these initiatives.

The Industry continues to rebound from the 2008/9 downturn, and the coming months could be challenging. In such times, it is even more important to be informed, involved, and that we contribute to associations such as ours. We look forward to seeing you in Lake Tahoe!

Richard Burt, President

CONTENTS

FIFTY-FIRST GENERAL ASSEMBLY AND TECHNICAL MEETING

Scott Schrantz @Flickr/CC

MS Dixie II paddleboat

The Fifty-first General Assembly meeting of the Tantalum-Niobium International Study Center will be held on the shores of Lake Tahoe, Nevada, U.S.A., from October 3rd to 6th 2010. The technical sessions and social events will take place at the Hyatt Regency, Incline Village, where delegates will also stay.

On Sunday October 3rd, the registration desk will be open from 10a.m. to 1p.m. and 2p.m. to 5p.m. All participants are invited to a Welcome Reception from 6p.m. to 8p.m.

The formal General Assembly of the association will be held on Monday October 4th and will be followed by technical presentations for the rest of the morning, then a buffet lunch.

Companies wishing to apply for membership at this General Assembly are reminded that their completed application forms should be returned to the T.I.C. by August 4th 2010. For any further information on becoming a member, please contact the Secretary General on info@tanb.org.

On Monday evening, all participants are invited to a Gala Dinner, to be held at the hotel.

A second technical session will be held on the morning of Tuesday October 5th, followed by lunch. The full technical programme is published on page 7 of this Bulletin.

On Wednesday October 6th, there will be a sightseeing tour to the historic mining town of Virginia City, located around one hour away from the hotel. Delegates will enjoy a narrated trolley ride through the historic city, and will discover the

Opera House and the Chollar mine, before taking lunch at the Gold Hill hotel. In conjunction with this tour, a group will also visit the facility of Niotan Inc. It must be noted that Niotan reserves the right of admission.

Sightseeing tours for accompanying persons are also being arranged. On Monday, participants will take a guided bus tour around the lake, with various stops at points of interest: the Thunderbird Lodge Estate (guided tour), the Visitors Center in South Lake Tahoe, Emerald Bay, Squaw Valley for lunch and shopping, and an artist's studio. On Tuesday, the group will continue to explore the beauty of Lake Tahoe on board the MS Dixie II paddle boat. Transfer from the hotel to the departure point at Zephyr Cove will be made by bus. A buffet lunch will be served on the boat. On Wednesday, the accompanying persons are invited to join the delegates for the sightseeing tour to Virginia City.

An invitation will be sent to the nominated delegate of each member company in early July. Others who would like to attend should contact the T.I.C. as soon as possible.

A NEW TANTALUM ALLOY WITH SIGNIFICANTLY IMPROVED CORROSION AND HYDROGEN EMBRITTLEMENT RESISTANCE

This article is based on the paper given by Mr Paul Aimone of H.C. Starck Inc., on October 19th 2009, as part of the Fiftieth General Assembly held in Tallinn, Estonia.

ABSTRACT

Tantalum and tantalum alloys have been extensively used in electronic, chemical processing, and other industries for many years. Alloying tantalum with tungsten improves mechanical strength as well as increasing corrosion and hydrogen embrittlement resistance without degrading the other physical properties of pure tantalum. The outstanding corrosion resistance of tantalum and tantalum alloys is attributed to a very thin, protective tantalum pentoxide (Ta_2O_5) film that forms upon exposure of the metal to oxidizing conditions. Only when the oxide film reacts with or is penetrated by a chemical reagent does corrosive attack occur on the underlying metal. Industrial experience has repeatedly shown that even when this attack occurs, hydrogen embrittlement rather than corrosion is the predominant failure mechanism for tantalum materials. H.C. Starck undertook development of a new tantalum alloy with improved corrosion and hydrogen embrittlement resistance. Test results have shown this derivative of the NRC®76 (Ta-3W) alloy has corrosion and hydrogen embrittlement rates that are significantly lower than conventional Ta-3W alloy in both hydrochloric and sulfuric acids with comparable mechanical properties.

INTRODUCTION

A significant amount of research and development was carried out in the latter half of the 1950s to determine the suitability of pure tantalum (UNS #R05200) for handling hot concentrated chemical compounds where most other metals and non-metallic materials were not suitable[1]. Improvements were made in the early 1960s by alloying tantalum with tungsten to improve mechanical strength by 30% as well as increasing corrosion resistance without degrading the other physical properties of pure tantalum. After several years of chemical plant performance and production of the tantalum-tungsten mill products, the tantalum-tungsten alloy Ta-3W (UNS #R05252) was established. However, since its introduction and commercialization, there has been little development of new tantalum alloys to improve upon the corrosion resistance and mechanical properties achieved with the Ta-3W composition.

Tantalum and tantalum alloys owe their excellent corrosion resistance in hot, concentrated acids to the formation of the extremely stable protective oxide layer, Ta_2O_5[2]. This oxide layer bonds to the metal, is essentially free of defects, and reforms spontaneously in case of damage. However, in the temperature range of 190°C to 250°C, the protective Ta_2O_5 oxide changes depending on the environment involved. Consequently, the corrosion resistance and inertness of tantalum begins to degrade and chemical attack can become rapid. Table 1 lists the temperature and concentration limits for tantalum in various acids. In the presence of hydrogen containing acids and/or in contact with metals that are more electronegative, tantalum can become hydrogen embrittled as a result of diffusion of atomic hydrogen along tantalum grain boundaries[1]. Consequently, the primary failure mechanism when dealing with tantalum in hot, concentrated acid service is hydrogen embrittlement rather than corrosion leading to metal loss.

Acid	Concentration	Temperature
HCl	<25%	230°C (446°F)
HCl	25% to 30%	200°C (392°F)
H2SO4	<98%	170°C (308°F)
H2SO4	>98%	100°C (212°F)
HNO3	0% to 100%	>150°C (272°F)

Table 1: Long term corrosion limits (5 mpy)

For tantalum and tantalum alloys, significant hydrogen embrittlement begins to occur at concentrations greater than 100 ppm. At the present time, the most prevalent method for slowing hydrogen embrittlement in tantalum alloys is through cathodic protection using small platinum spots on the surface of the tantalum exposed to the acid. Over time, these spots dissolve and need to be replaced otherwise rapid hydrogen embrittlement can occur. Previously[3] platinum spotting improved the corrosion and hydrogen (enrichment) embrittlement resistance of pure tantalum and the NRC®76 alloy although the effect was almost insignificant for the NRC®76 alloy. Therefore, the goal of this effort was to develop a new tantalum alloy with significantly improved corrosion and hydrogen embrittlement resistance with the same physical, mechanical, and fabrication properties as the widely utilized NRC®76 (Ta-3W) alloy.

EXPERIMENTAL PROCEDURE

H.C. Starck supplied all tantalum materials for this development effort. Platinum powders were purchased from Alfa Aesar. The starting NRC®76 ingot was formulated using conventional vacuum arc remelt (VAR) techniques. After light machining, a section of the ingot was forged to one inch diameter rod for further melt trials. Table 2 lists the target platinum concentrations for each small melt. Tantalum and platinum powders were blended to the desired composition and then pressed into powder bars. These bars were attached to the side of each one inch diameter rod. A single VAR melt cycle was performed to alloy the platinum into the NRC®76 alloy. After the melt cycle was completed each alloy ingot was allowed to cool under vacuum before being removed from the VAR furnace.

Target Pt Concentration (ppm)	Retained Pt Concentration (ppm) Top	Middle	Bottom
0	1	0	0
500		535	
680	710	850	670
900	870	1100	1100
1100	1100	900	1300
1360	1300	1400	1300
1500	1800	1400	1200
1750	1400	1200	2200
2030	2200	2000	2000
2700	2800	3200	2700
5000	5500	4300	4500
9600	9200	9900	9000

Table 2: VAR melting results

Each of the small ingots was lightly machined to remove the surface layer prior to thermomechanical processing. Conventional cold rolling on H.C. Starck's developmental rolling mill was used to bring each ingot down to approximately 0.020" thick sheet. After cleaning and pickling, each sheet sample was vacuum annealed using a standard heat treat cycle for the NRC®76 alloy.

Samples were cut from each 0.5 mm (0.020") thick sheet sample for characterization. Metallographic evaluations were performed to characterize the sheet microstructure. Room temperature tensile testing was performed according to ASTM E8 at Dirat's Laboratories using three samples per compositional variation. Corrosion Testing Laboratories (CTL) performed all the corrosion tests. The test specimens, measuring approximately 25 mm x 37 mm x 0.5 mm (1" x 1.5" x 0.020"), were cleaned, weighed, and measured prior to testing. Individual test specimens were fully immersed in each solution (environment). The samples were separated from each other using Teflon spacers.

All of the tests, except for the tests in HCl acid, were performed in conventional plastic labware. The HCl acid tests were performed in specialized, Teflon-lined pressure vessels. After the corrosion test was completed, each sample was rinsed and dried. Corrosion rate evaluations were performed based on weight change. The corrosion rate (mils/yr) was calculated based on the weigh change data.

RESULTS & DISCUSSION

Vacuum Arc Melting

Table 2 and Figure 1 show the chemistry results from the vacuum arc melt trials. Because of the small heat size, samples taken for this evaluation were cut from top, middle, and bottom of the ingot after rolling to strip on H.C. Starck's developmental rolling mill. These results show there was almost 100% platinum retention after melting. This is surprising since platinum has a vapor pressure of approximately 15 torr at tantalum's melt point (3014°C) (Figure 2). The relatively small size and short duration the alloy was in the molten state may account for this high platinum retention. In spite of this small heat size, the hydrogen content of the strip after all processing was 1 ppm.

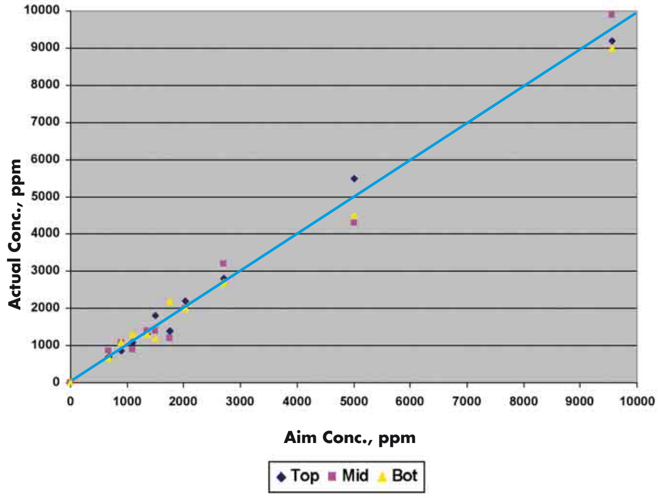


Figure 1: Platinum Retention after Vacuum Arc Melting

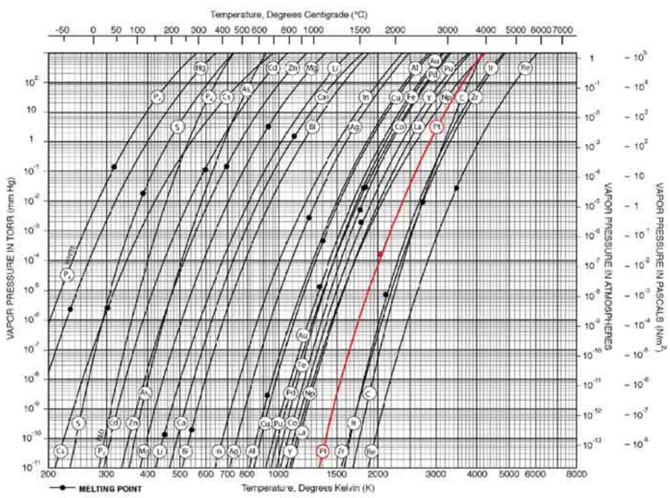


Figure 2: Vapor Pressures of Selected Elements (Pt in red)

Physical and Mechanical Tests

The results show that the platinum containing materials are at least as strong as the conventional NRC®76 alloy (Figure 3) and readily met ASTM B708 requirements for strength (UTS > 40 ksi and YS > 30 ksi) and ductility (elongation > 20%). These results suggest there may be a slight strengthening effect from the platinum addition with an almost negligible effect on ductility. Figure 4 shows that the platinum containing alloys have a fine, equiaxed microstructure with some very fine grains on the surface. These fine surface grains may be the result of the pass schedule used on the developmental rolling mill. In addition, there was no evidence of platinum particles within the microstructure of any of the alloys.

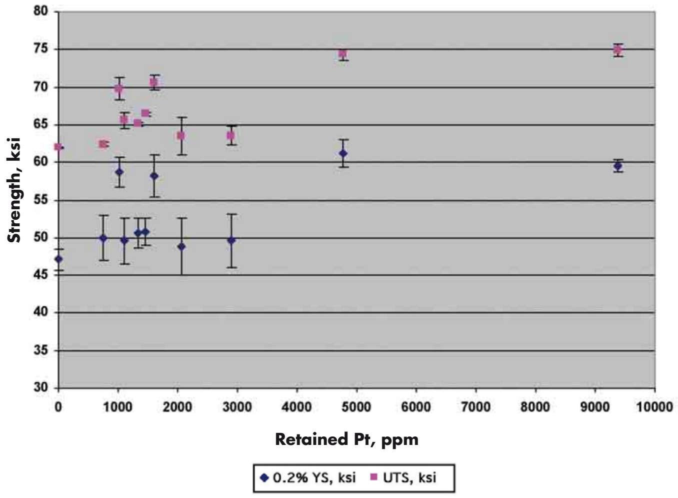


Figure 3a: Room Temperature Tensile Results: strength

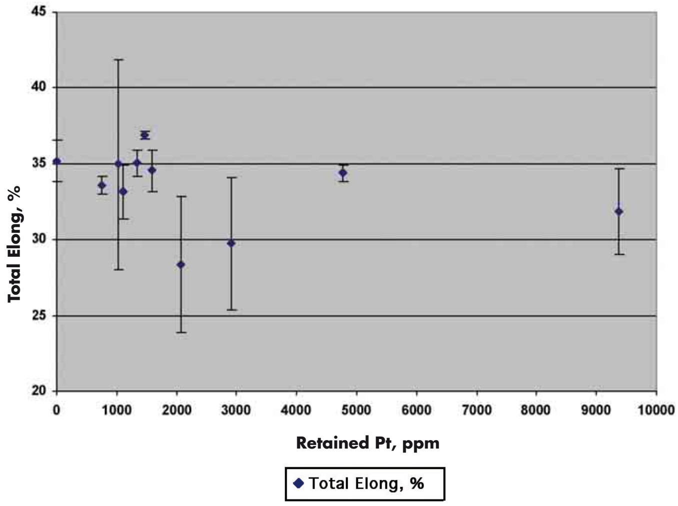


Figure 3b: Room Temperature Tensile Results: ductility

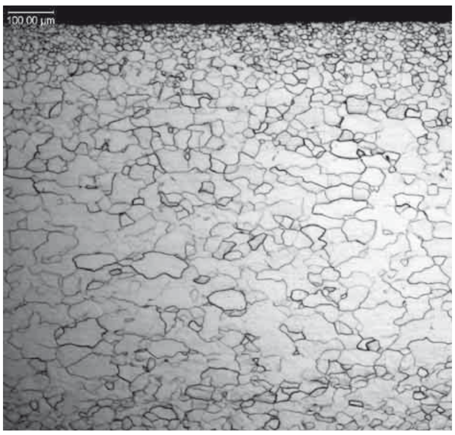
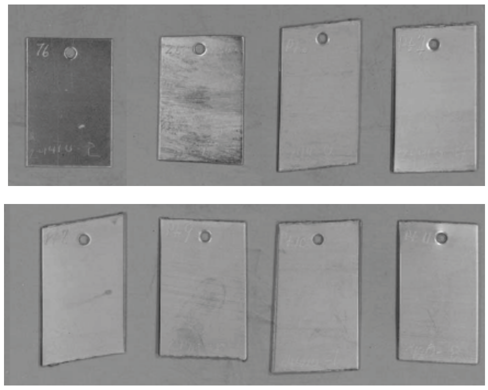


Figure 4: Typical Microstructure for Platinum Modified NRC76 Alloys

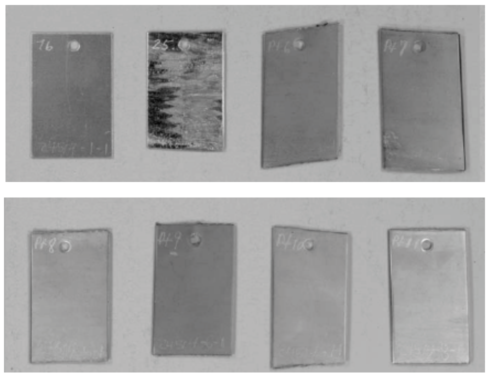
HCl Environments

Figures 5 to 8 illustrate the results of the corrosion tests in HCl acid. For the accelerated corrosion test in a 36% HCl acid solution, all samples showed no visible signs of corrosive attack except for some very light general uniform corrosive attack (Figure 5a). It is clear from Figure 6a that the addition of platinum to the NRC®76 material has reduced the corrosion rate from 16 mpy to as low as 2.5 mpy. As a result, hydrogen enrichment due to corrosion dropped from approximately 300 ppm for the conventional NRC®76 sample to as low as 1 ppm for the platinum containing samples (Figure 6b).

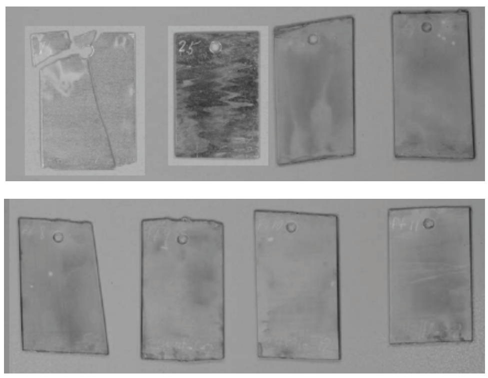
Samples tested in the 30% HCl acid solutions at either 200°C or 220°C showed some very light general uniform corrosive attack (Figures 5b and 5c, respectively). The only exception to this was the visible cracking of the conventional NRC®76 sample (Figure 5c) after testing at 220°C. Figures 7a and 8a show platinum additions reduce the corrosion rate of the NRC®76 material although these rates are already low and there is scatter in the results. On the other hand, hydrogen enrichment due to corrosion dropped by over two orders of magnitude compared to the conventional NRC®76 sample (Figures 7b and 8b).



(a)



(b)



(c)

Figure 5: HCl Corrosion Samples (a) 36%HCl @ 190°C for 6 days, (b) 30%HCl @ 200°C for 15 weeks, and (c) 30%HCl @ 220°C for 15 weeks. Conventional NRC76 on top left, increasing Pt content from left to right and top to bottom (500 ppm minimum)

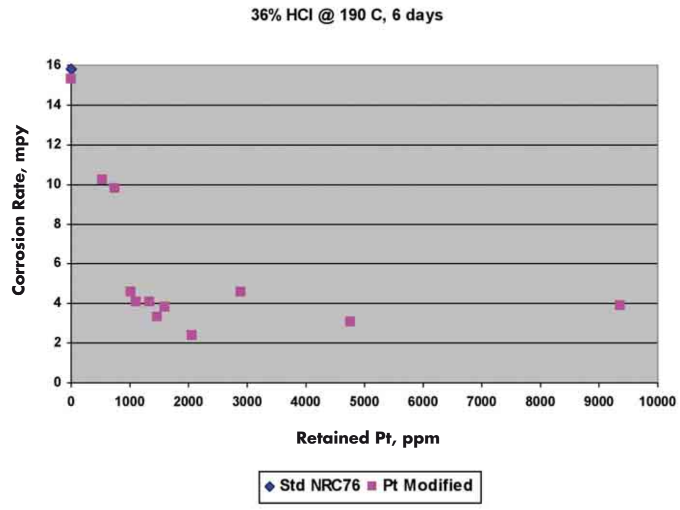


Figure 6a: Accelerated HCl Acid: Corrosion Rate

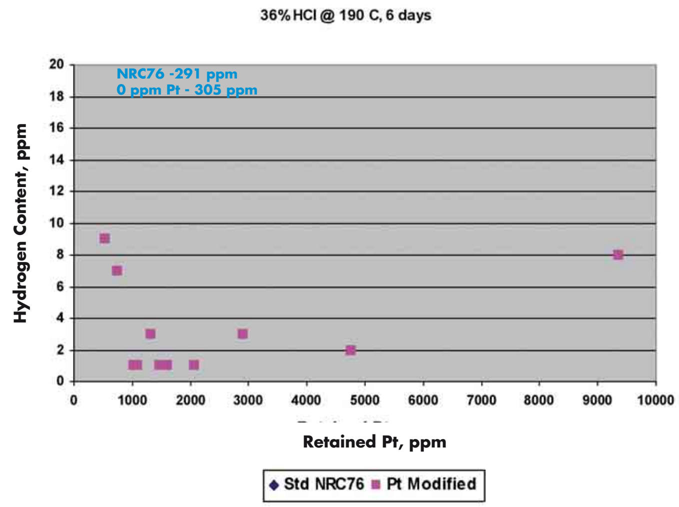


Figure 6b: Accelerated HCl Acid: Hydrogen Content

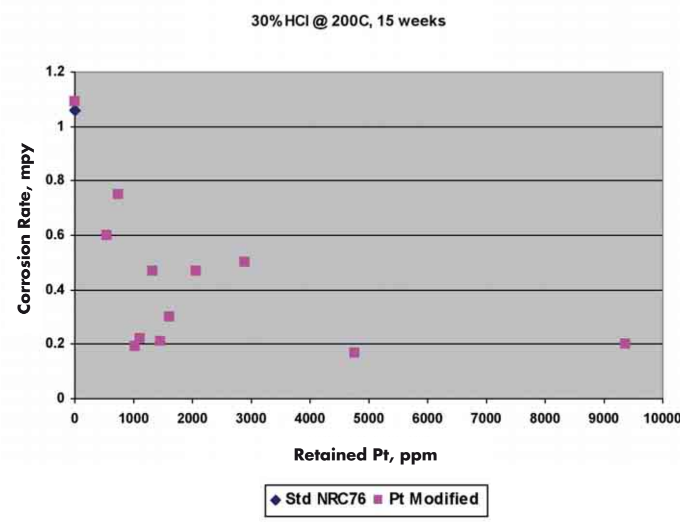


Figure 7a: 30% HCl @ 200°C for 15 weeks: Corrosion Rate

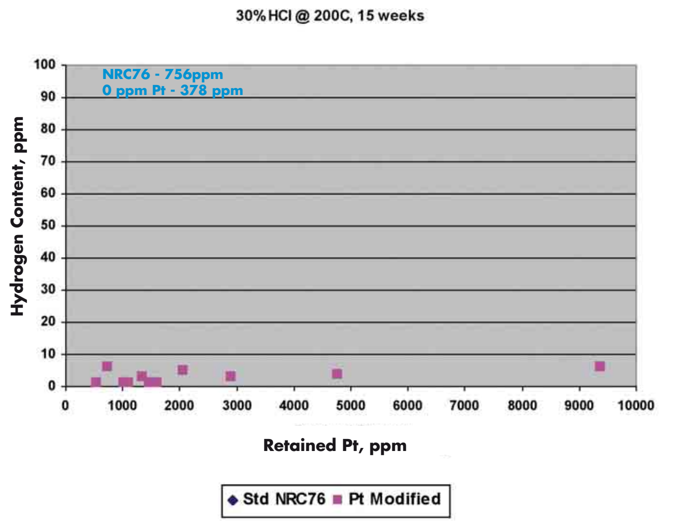


Figure 7b: 30% HCl @ 200°C for 15 weeks: Hydrogen Content

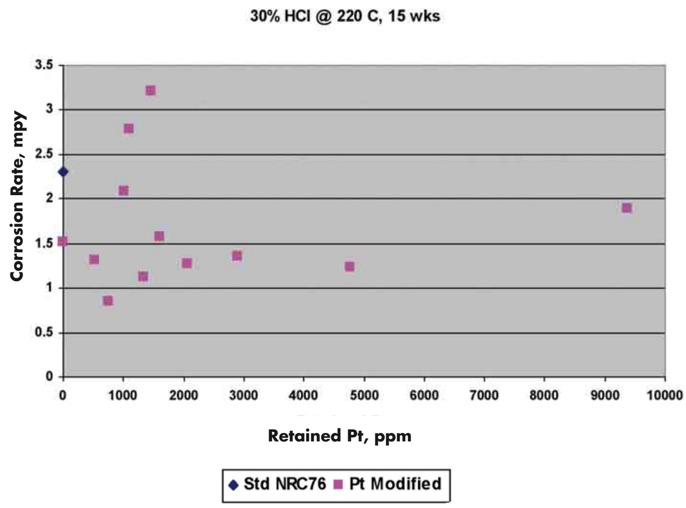


Figure 8a: 30% HCl @ 220°C for 15 weeks: Corrosion Rate

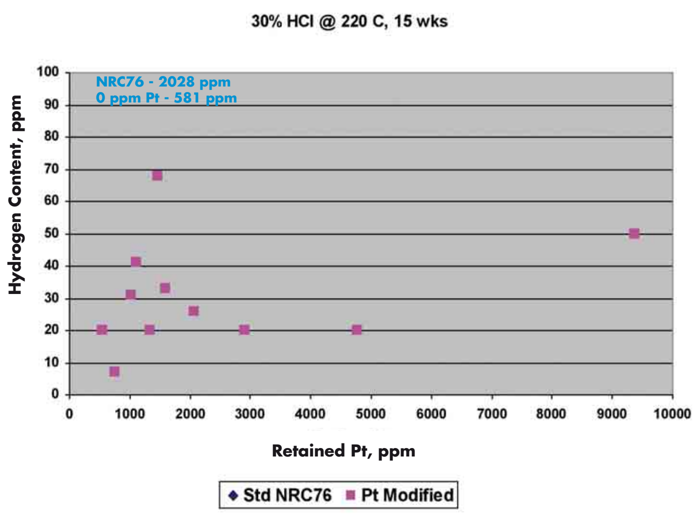


Figure 8b: 30% HCl @ 220°C for 15 weeks: Hydrogen Content

Discussion

The results presented above show that low level platinum additions to the NRC®76 alloy improve corrosion and hydrogen (enrichment) embrittlement resistance in both HCl and H_2SO_4 acids at high temperatures. Previous[2] research demonstrated that platinum spotting had an almost insignificant effect on the corrosion and hydrogen (enrichment) embrittlement resistance of NRC®76. While platinum spotting (cathodic protection) is an accepted technique for improving corrosion and hydrogen embrittlement resistance of tantalum, over time the spots will dissolve and need to be replaced. Since the platinum has been alloyed into the NRC®76 alloy and no platinum particles were present in the microstructure, cathodic protection is most likely not the mechanism by which the improved corrosion and hydrogen embrittlement resistance is achieved.

Compared to pure tantalum, the improved corrosion resistance of Ta-W alloys results from the effect of the additional outer valence electrons in tungsten helping to reduce the number of oxygen vacancies in the Ta_2O_5 oxide layer[1]. The addition of molybdenum and rhenium also improved the corrosion resistance of pure tantalum. However, ternary alloys showed increased corrosion rates compared to the binary alloys[4]. Consequently, it is theorized that platinum improves corrosion and hydrogen embrittlement resistance in NRC®76 by producing low hydrogen overvoltage sites within the NRC®76 alloy that shift its electrical potential in a more noble (positive) direction. This would help stabilize and preserve the protective Ta_2O_5 surface oxide film. This is very similar to the mechanism by which palladium and ruthenium additions enhance the corrosion resistance of titanium.

CONCLUSIONS

The results presented above show that low level platinum additions to the NRC®76 alloy significantly improve corrosion and hydrogen (enrichment) embrittlement resistance in both HCl and H_2SO_4 acids at high temperatures. Platinum additions may produce a slight strengthening effect with almost negligible effects on ductility. While an exact mechanism is unclear at this time, it is theorized the platinum addition produces low hydrogen overvoltage sites within the NRC®76 alloy that shift its electrical potential in a more noble direction thereby stabilizing the protective Ta_2O_5 surface oxide film.

BIBLIOGRAPHY

[1] C.R. Bishop & M. Stern, Union Carbide Metals Co., Hydrogen Embrittlement of Tantalum in Aqueous Media, 17th Annual NACE Conference, Buffalo, NY, March 1961.

[2] J. Chelius, Use of Refractory Metals in Corrosive Environment Service, Mater. Eng. Quart., August 1957, pp. 57-59.

[3] P. Aimone & E. Hinshaw, 'Tantalum Materials in the CPI for the Next Millenium', 57th Annual NACE Conference, Houston, TX, March 2001.

[4] L.A. Gypen, M. Brabers, A. Deruyttere, Werkstoffe und Korrosion, v35, 1984, pp. 37-46.

FIFTY-FIRST GENERAL ASSEMBLY: TECHNICAL PROGRAMME

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

Hermetically sealed polymer tantalum capacitors
by Y. Freeman, J. Chen, T. Kinard and S. Hussey, Kemet Electronics

The use of tantalum based materials in industrial scale hydrogen production – a case study
by Bo Gillesberg and Dean Gambale, Tantaline

A strong new link in the tantalum chain
by Jack Telford, Gippsland Limited

High CV/g tantalum flake powder from plasma spray technology
by John Crawley, Niotan Inc.

Progress with Nb_3Sn conductors for fusion and particle accelerator applications
by Scott Reiman and Jeff Parrell, Oxford Superconducting Technology

2010: a statistics and transport odyssey
by Ulric Schwela, Tantalum-Niobium International Study Center

How to make tantalum
by James Fife, Niotan Inc.

Production of superconductor niobium materials at TVEL Corporation
by M. Shlyakhov (JSC TVEL), V.V. Rozhdestvenskiy (JSC TVEL), Abramushin K.M. (JSC ChMP) and Vorobieva A.E. (Bochvar Institut)

Tantalum sputtering targets: application, attributes and future
by Paul Gilman, Praxair Electronics

Green manufacture of tantalum capacitor powder
by Lee Ruch, Niotan Inc.

Direct conversion of tantalum scrap to metallurgical and capacitor grade powder
by Craig Hafner, Hi-Temp Specialty Metals

Order out of chaos: ongoing developments with the Supply Chain initiative
by Richard Burt, GraviTa Inc., and William Millman, AVX Ltd

iTSCi - a report from the field
by Karen Hayes, PACT

OEM requirements for responsible sourcing in the metals Supply Chain
by Jerry Meyers, Intel

WORKING GROUP ON TANTALUM AND NIOBIUM MINING

Last October, at the Fiftieth General Assembly held in Tallinn, Estonia, the T.I.C. ratified an 'Artisanal and Small Scale Mining Policy'. The initial focus of this Policy remains the mining & trading of minerals from 'areas of weak governance' – essentially the Democratic Republic of the Congo (DRC) and adjoining States.

Since that meeting, the T.I.C. has been involved in extensive discussions with a variety of bodies also focusing on this subject, including the electronics and telecommunications (GeSI/EICC) Initiative, the Tin Industry (ITRI), the OECD and the US House of Representatives, and has been following progress with such other initiatives as the International Conference of the Great Lakes Region (ICGLR) and the United Nations. Resulting from these discussions, the T.I.C. decided that a separate T.I.C. project would be counter-productive; we have therefore provided one-time seed capital to the International Tin Research Institute for the iTSCi initiative. Ongoing operating funding will be provided by an Exporter Levy of US$1 per pound of contained Ta_2O_5 (as well as a levy that is already being paid by participating tin smelters).

This initiative has the full financial and technical support of the electronics and telecommunications (GeSI/EICC) industries – the eventual users of well over 50% of the world's tantalum, as well as support from and cooperation of the Government of the DRC.

The iTSCi project will be commencing a Pilot Programme very shortly, with full roll-out throughout the DRC later this year. Two mines have already been designated as Pilot Sites by the DRC Government, and a Press Release naming these is expected shortly. A third site is expected to be added in the near future. There is little doubt that GeSI/EICC will be expecting its suppliers to be participating in the scheme – indeed all processors who supply tantalum (or tin) to its members can expect to be audited before year end by GeSI/EICC. It should also be noted that the GeSI/EICC supply chain initiative is extending, to include non electronic applications such as special alloys, fine oxides and cutting tools.

MEMBER COMPANY NEWS

AS Silmet

David O'Brock was appointed CEO of AS Silmet by the supervisory board at its regular meeting in Tallinn, Estonia, on May 20th.
Continuing on the Management board are Mr Alexandr Kyutt (Financial Director) and Mr Alexandr Gurjanov (Production Director). Mr Tiit Vau will be assuming the duties of Commercial Director.
Silmet is one of the largest chemical companies in Estonia and is the only non-Chinese raw material based producer of Rare Earth elements outside of Asia. AS Silmet is also one of the world's leading Niobium producers and employs about 500 people in its factory in Sillamäe, Estonia.

Changes in member contact details

A&R Merchants

A&R Merchants has announced new contact details.
Address: 3140 Emmons Avenue, Suite – 4U, Brooklyn NY11235-1723, U.S.A.
Tel.: +1 718 790 7757

Crevier Minerals Inc.

Crevier Minerals Inc. has a new address: 1010 Rue de la Gauchetière Ouest, Bureau 680, Montreal, Quebec, Canada H3B 2N2.

Tantalite Resources

Tantalite Resources has nominated a new delegate to the T.I.C.: Mr Russell Heins replaces Mr Gary Marx, who has left the company. E-mail: russell.heins@tantalitesa.co.za

Traxys

The office of Traxys has recently moved to Route d'Arlon 19-21, 8009 Strassen, Luxemburg.

Wah Chang

Mr Barry Valder, delegate to the T.I.C. for Wah Chang, has a new e-mail address: barry.valder@atimetals.com

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