PRESIDENT’S LETTER

Dear Fellow T.I.C. Members and Friends,

Summer is in full swing, at least here in the northern hemisphere, and I trust you are enjoying it. These are clearly both interesting and challenging times for the tantalum and niobium industries.

As previously mentioned, the T.I.C. exists for and on behalf of our members and your Executive Committee is constantly looking for ways to build upon the momentum of the past and to improve. We want to generate more value for you, although some of it is not readily apparent. Over the years, the T.I.C. has taken leadership roles, for example, in the fields of conflict minerals and transport of radioactive materials and will continue to do so. Such efforts may not appear to be immediately relevant to some individual members, but they are essential for the long term strength of our industry as a whole.

In this quarterly Bulletin, we highlight the technical presentations scheduled to be given at the Fifty-sixth General Assembly in Penang, 25-28 October 2015. In addition, we will change the program slightly this year to allow a more detailed discussion of some of the initiatives we have underway. As you can see, we plan to have a session dedicated to the four subteam initiatives we currently have, with the head of each subteam leading the presentation:

- we are revising our website and work is proceeding well,
- on staffing, a job description for the proposed new Director position is almost finalized and I would hope to be able to get back to you later this summer with more details, including seeking your help in identifying and attracting potential candidates,
- on meetings, you’ll find more in this Bulletin about the Penang meeting, with further details, including online hotel booking, being issued in early August. Please also mark the dates of 16-19 October 2016 in your calendars, as we plan to hold the Fifty-seventh General Assembly then in Toulouse, France,
- we continue our focus on the supply chain, whether it’s monitoring ongoing possible regulatory impacts, such as the ones currently being discussed in the EU or OECD, or working with such organizations as CFSI on improving their audit protocols and procedures. The supply of Ta units from central Africa and our role with iTSCI also continue to be critical aspects of maintaining a healthy supply chain and industry. We welcome your thoughts on how the supply chain initiatives can be strengthened and improved.

The efforts mentioned above are undertaken to consistently add value for you, our members. However, these efforts and results come at a cost. With this in mind, the Executive Committee has made the difficult decision to increase the annual dues for corporate members to Euros 2,400. This decision was made after much thought and discussion, through benchmarking ourselves against other specialty metal trade associations, as well as the consideration that corporate member dues have been constant for nine years.

As always, we appreciate your feedback.

Yours sincerely,

David R. Henderson
President
The Fifty-sixth General Assembly and associated technical meeting of the T.I.C. will be held in Penang, Malaysia, from Sunday October 25th to Wednesday October 28th 2015. The conference will take place at the Shangri-La Rasa Sayang Resort, where a block booking of bedrooms has also been reserved.

On Sunday October 25th, 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 that evening, from 6p.m. to 8p.m.

The formal General Assembly of the association will be held at 9a.m. on Monday October 26th. 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 September 26th at the very latest. For any further information on becoming a member, please refer to the following page of our website: http://tanb.org/applmemb.

The General Assembly will be followed by presentations dedicated to each of the four subteam initiatives currently ongoing within the T.I.C. (see details below). This special session, restricted to delegates from member companies, is scheduled until noon.

After a break for a buffet lunch, technical presentations will extend until mid-afternoon.

On Monday evening, all participants are invited to a Gala Dinner to be held in a marquee in the gardens of the hotel.

A further technical session will be held on Tuesday October 27th, breaking for a buffet lunch and ending mid-afternoon.

The full programme of presentations is published here below.

On Wednesday October 28th, delegates will be given the opportunity to visit the facility of Malaysia Smelting Corporation located in Butterworth, around one hour away from the hotel.

Tours for accompanying persons are also being arranged for Monday and Tuesday.

An invitation (including a link to the online booking system of the hotel) will be sent to the nominated delegate of each member company in the first half of August. Non-members who would like to attend should contact the T.I.C. Secretary General.

**PROGRAMME OF PRESENTATIONS**

As explained above, a special session of presentations on the morning of Monday October 26th, restricted to delegates from member companies, will focus on the various subteam initiatives currently ongoing within the T.I.C.:

**Update on website revision**
by Daniel Persico

**Update on T.I.C. staffing**
by William Millman

**Update on General Assemblies and associated technical meetings**
by David Gussack

**Update on supply chain initiatives**
by David Henderson

On the afternoon of Monday October 26th and on Tuesday October 27th, the following technical papers are expected. The announced presenter is the first author listed, unless otherwise specified. The papers are shown in alphabetical order of first author (not in running order).

**H.C. Starck's central Africa sourcing activities**
by Marc Hüppeler, H. C. Starck

**Miniaturization of chip tantalum capacitors**
by Tomoharu Kumada, NEC TOKIN Corporation
To source or not to source from the DRC, that is the question!
by Mike Loch, RESOLVE

Biomedical porous tantalum synthesized via 3D wire frame and chemical vapour deposition
by Lu Dong, He Jilin, Wang Li, Marko Hututla, Li Bin, Shi Wenfeng and Cao Wei, CNMC Ningxia Orient Group
(presented by Jiang Bin)

Tomtor niobium and rare earths deposit
by Alexander Malakh and Oleg Anikin, TriArc Mining

Applications and properties of Metalysis FPC-produced spherical tantalum powder
by Ian Margerison, Kartik Rao and Ian Mellor, Metalysis Ltd

Japanese economy outlook and tantalum market situation
by Shigeo Nakamura, Advanced Material Japan Corporation

The iTSCi Programme: enabling tantalum supply from high risk areas by satisfying international expectations
by Kay Nimmo (ITRI Ltd) and Karen Hayes (Pact Inc)

Hermetically sealed low ESR, high reliability tantalum capacitors
by Jan Petržílek, Martin Biler, Jiří Navrátil and Miloslav Uher, AVX Corporation
(presented by William Millman)

EU Conflict Minerals Regulation (state of play)
by Signe Ratso, EU Commission, DG Trade

Responsible sourcing: roadmap to a sustainable supply chain for tin and tantalum
by Raveentiran Krishnan and Chua Cheong Yong, Malaysia Smelting Corporation

Conflict-Free Sourcing Initiative: only one part of due diligence
by Michael Rohwer, Leah Butler and Tara Holeman, Conflict-Free Sourcing Initiative (CFSI)

Statistics and more statistics: what are they and where do they come from?
by Ulric Schwela, Tantalum-Niobium International Study Center

Production of ultra-high capacitance powders using a Na flame process
by Craig Sungail, Ashish Rai and John Koentzzer, Global Advanced Metals
(presented by Stephen Krause)

Conductive polymer based tantalum capacitors for automotive applications
by Jane Ye, Chris Stolarski and Mei Yuan, KEMET Electronics (Suzhou) Co. Ltd.

KING-TAN TANTALUM INDUSTRY LTD PASSES CFS COMPLIANCE AUDIT

At the October 2013 General Assembly in York, England, the decision was made to suspend the membership of King-Tan Tantalum Industry Ltd. This decision was made based on the failure of King-Tan to adhere to the due diligence and traceability requirements set out in the T.I.C. Artisanal and Small Scale Mining Policy*. All members of the T.I.C. are bound by this policy which was adopted in 2009. The General Assembly was informed of the unanimous decision of the Executive Committee on this point in accordance with the T.I.C. Charter, with no formal vote by the Assembly. The T.I.C. Charter makes no mention regarding a re-instatement process; however, the Executive Committee determined that it would be up to the General Assembly to re-instate membership.

At the Executive Committee meeting held in New York City in October 2014, a request was made to King-Tan to carry out a CFS pre-audit before April 2015. This request was a condition of membership re-instatement. King-Tan has exceeded this condition and has passed the final audit for CFS compliance in February this year. Both CNMC Ningxia Orient Group and EICC/CFSI contributed to this successful effort.

During the Executive Committee’s meeting on 20 April 2015 in Brussels, it was therefore decided to make the recommendation to the General Assembly, to be held this coming October in Penang, Malaysia, to lift the suspension. King-Tan has been formally notified of this decision.

*: the T.I.C. Artisanal and Small Scale Mining Policy can be found at http://tinyurl.com/TIC-ASMP
The major trend in modern electronics is miniaturization which requires a constant increase of the volumetric efficiency of all the electronic components in the end electronic devices. The traditional way to increase volumetric efficiency [CV/cc] of tantalum [Ta] capacitors is by using finer Ta powder and thereby increasing the specific surface area of the Ta anodes.1 The old coarsest Ta powders obtained by hydrating and crushing of Ta ingot had an average size of primary particles in tens of microns and CV/g below 1000 CV/g. The new finest Ta powders obtained by sodium reduction, direct reduction by magnesium or flame synthesis have an average size of primary particles just a fraction of a micron and CV/g equal or above 200,000 CV/g.

Applications of high CV Ta powders in Ta capacitors are limited to low voltage capacitors with thin oxide dielectrics. When the dielectric thickness increases due to a higher formation voltage, CV of the capacitors with high CV powder rapidly decreases. This phenomenon was explained by the necks-pores model.2,3 During formation, the anodic oxide film of Ta is partially growing inward on the Ta substrate and partially outward from it. The inward growth of the oxide film results in disruption of the thinnest parts of the porous Ta anode, the necks between the primary particles. The outward growth of the oxide film clogs the pores between the primary particles. Both processes decrease the surface area of the anode and, thereby, capacitance and CV of the Ta capacitor. The neck size can be increased by higher press density and sintering temperature and time; however, this will also result in higher shrinkage and smaller pore size.

There is one more limitation for the highest CV Ta powders which relates to the amount of oxygen in Ta anodes sintered with these powders. During sintering in vacuum at temperatures exceeding 1000 °C, oxygen from the native surface oxide dissolves in the bulk of Ta particles. The oxygen increase in the sintered Ta anode versus the Ta powder is higher in finer Ta powders due to the larger surface-to-volume ratio in their primary particles. The paper presents experimental data on how excessive oxygen in Ta anodes affects their mechanical and electrical properties and limits usage of the high CV/g Ta powders in Ta capacitors. It also shows a possibility to overcome this limitation and make reliable Ta capacitors with the highest CV/g Ta powders and record high volumetric efficiency.

RESULTS AND DISCUSSION

Figure 1 shows typical sintering temperatures and oxygen content in Ta powders as a function of their specific charge CV/g.

As one can see in Figure 1, the oxygen content is increasing and the sintering temperature is decreasing with higher CV/g powder. Oxygen increase is due to the smaller size of primary particles in higher CV powders with higher surface to volume ratio and, thereby a stronger effect of the oxygen in the native oxide. Sintering temperature should be reduced with higher CV powders to avoid higher sintering activity of the smaller powder particles.

There are two critical points on the graphs presented in Figure 1. The first point is the critical sintering temperature Ts* = 1880 °C, which separates sintering temperatures [Ts] when oxygen evaporates from Ta in vacuum (Ts ≥ Ts*) and temperatures when oxygen dissolves in Ta in vacuum (Ts < Ts*). From Figure 1, only very coarse Ta powders can be sintered at Ts > Ts*, and these powders are still in use in highly reliable Ta capacitors for military and space applications.
The second critical point in Figure 1 is oxygen content about 15,000 ppm in Ta powder with CV/g close to 200,000 CV/g. Figure 2 shows the X-ray diffraction (XRD) pattern of this powder prior to the anode sintering.

![Figure 2: X-ray diffraction pattern of 200,000 CV/g Ta powder](image)

According to Figure 2, the powder consists of Ta with cubic crystalline structure and lattice parameter $a = 3.3088 \, \text{Å}$. This lattice parameter is close to that in pure Ta, indicating that the bulk of the Ta particles is practically free of oxygen due to deoxidizing during the powder manufacturing and almost all of the oxygen in this powder comes from the native oxide on the surface of the powder particles. There is a small amount of Ta hydride in the powder which will be decomposed at the sintering temperature with full evaporation of hydrogen.

When this powder was sintered in vacuum, the oxygen content in the sintered anodes increased to approximately 22,000 ppm. The XRD pattern of the sintered anodes (Figure 3) is also different from that in the powder.

![Figure 3: X-ray diffraction pattern of Ta anodes sintered in vacuum with 200,000 CV/g powder](image)

The lattice parameter $a = 3.3192 \, \text{Å}$ in the sintered anode is higher than that in the powder and indicates saturation of solid solution of oxygen in tantalum. Besides Ta, there is a clear evidence of the crystalline Ta$_2$O$_5$ phase on the XRD pattern. The inclusions of the oxide crystals can be seen on the surface and inside the sintered anodes (Figure 4).
Presented in Figures 3 and 4, data show that during sintering of the 200,000 CV/g Ta powder the bulk of the Ta particles saturates with oxygen and the excess of oxygen reacts with Ta forming Ta oxide. Inclusions of hard crystalline Ta oxide in the sintered Ta anode affect its mechanical properties provoking anode cracking and chipping, which were found in failed Ta capacitors with these anodes. Crystalline Ta oxide also affects the electrical properties of Ta anodes since crystalline oxide is not as good a dielectric as amorphous oxide, the latter formed when anodizing Ta.

To address these issues, deoxidizing of sintered Ta anodes was performed in magnesium vapor similarly to that described in [1]. As a result of the deoxidizing, the oxygen content in the anodes is reduced to about 9,700 ppm, 50% below that in the original powder. This indicates a presence of the very fine primary particles in the powder which were dissolved in the larger particles during the sintering process. The XRD pattern of the sintered and deoxidized anodes was similar to that in the powder (Figure 2) with oxygen free bulk of Ta particles and no Ta oxide or any other phases. The drawback of deoxidizing of the sintered anodes with 200,000 CV/g Ta powder was total disconnecting of the Ta powder from the Ta lead wire embedded into Ta anode at pressing (Figure 5), while there was good powder-wire bond after the sintering in vacuum (wire was snapping during the pull-out test).
This effect evidences that the powder-wire bond formed during the anode sintering in vacuum was mostly made of Ta oxide due to the diffusion flow of oxygen from the powder particles saturated with oxygen into the wire with low oxygen content. During deoxidizing, Ta oxide transforms into porous Ta with very weak mechanical properties. It’s obvious that similar transformations take place inside the Ta anode where crystalline oxide inclusions were situated before the deoxidizing.

The technology that addresses chemical, mechanical, and electrical properties in Ta anodes with 200,000 CV/g Ta powder is deoxidizing-as-sintering (DAS). The X-ray pattern of DAS anodes was similar to that in the original powder (Figure 2) demonstrating oxygen free bulk of Ta particles and no oxide or other phases. There was a strong powder-wire bond in DAS anodes despite the fact that these anodes had very little or no shrinkage. DAS anodes also demonstrated improved electrical properties with dc leakage at wet test about half of that in anodes sintered in vacuum. The morphology of the finished anodes was different from that in anodes sintered in vacuum and depended on the DAS conditions and final oxygen content in the sintered anodes. Figure 6 shows with the same magnification typical morphology of the Ta anodes with 200,000 CV/g powder sintered in vacuum (a, oxygen 22,000 ppm) and deoxidizing-as-sintering (b, oxygen 6500 ppm and c, oxygen 4800 ppm).

As one can see from Figure 6, in comparison with anodes sintered in vacuum, DAS anodes have thick necks and open pores between the primary particles, especially in the case of lower oxygen content. Different sintering mechanisms could be responsible for these differences in morphology of the Ta anodes. The bulk diffusion of tantalum atoms is the major mechanism of sintering in vacuum providing mutual penetration of Ta particles and, thereby, shrinkage of Ta anodes. The surface diffusion of tantalum atoms is the major mechanism of DAS that takes place at lower temperatures than those at bulk diffusion, and provides growth of the necks between adjacent particles due to material redistribution without anode shrinkage. Since oxygen is a sintering inhibitor in Ta, surface diffusion is efficient only when oxygen is removed from Ta by deoxidizing.

Different morphology of Ta anodes with 200,000 CV/g powder sintered in vacuum and DAS results in different CV/g in finished anodes and different CV/g dependence on formation voltage. Figure 7 demonstrates CV/g versus formation voltage for a, b, and c anodes shown in Figure 6.

As one can see from Figure 7, at low formation voltage, Ta anodes with DAS have lower CV/g in comparison to that in Ta anodes sintered in vacuum, especially, in case of DAS anodes with the lower oxygen content. This difference in initial CV/g is expected from the morphology of these anodes (Figure 6) that shows smaller surface area of DAS anodes versus anodes sintered in vacuum. The difference between CV/g in anodes sintered in vacuum and DAS anodes can be reduced by allowing higher oxygen content and less morphology change in DAS anodes. At the same time, CV/g of the DAS anodes with
lower oxygen content is more stable with formation voltage and exceeds that of anodes sintered in vacuum at higher formation voltages. This is due to the ideal morphology of DAS anodes with thick necks and large pores between the primary particles. Presented in Figures 6 and 7, results show that DAS technology can be used with the highest CV/g Ta powder to address the oxygen limitation and achieve record high CV/cc in low voltage Ta capacitors and also to modify the anode morphology and increase CV/cc in higher voltage Ta capacitors.

CONCLUSION

The results presented in this paper show that oversaturation of Ta powder with oxygen and precipitation of the oxide phase during sintering in vacuum affect the mechanical and electrical properties of Ta anodes and limit the applications of the newest Ta powders with CV/g ≥ 200,000 CV/g even in the lowest voltage Ta capacitors. This limitation can be overcome by deoxidizing-as-sintering (DAS) technology, which provides good mechanical and electrical properties to Ta anodes with the highest CV/g Ta powders. Besides that, DAS technology can modify morphology of the Ta anodes without anode shrinkage, approaching ideal morphology with large necks and open pores between the primary particles. From a practical point of view this means that Ta anodes can be not just sintered with Ta powder keeping the powder morphology practically unchanged, but can be formed from the higher CV/g powder to the best suited morphology for the given formation voltage. These anodes will provide record high volumetric efficiency to the Ta capacitors in the whole range of rated voltages.

ACKNOWLEDGMENT

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REFERENCES

1. Y. Freeman, Proceedings of CARTS USA 2005, p. 232-238, Palm Springs, CA

MEMBER COMPANY NEWS

CHANGES IN MEMBER CONTACT DETAILS

NAC Kazatomprom
Mr Askar Zhumagaliyev, recently appointed CEO of NAC Kazatomprom, has become the delegate to the T.I.C. for his company. The contact e-mail address is nac@kazatomprom.kz.