

The Ekeberg Prize 2020

Tantalum recycling by solvent extraction

(page 6)

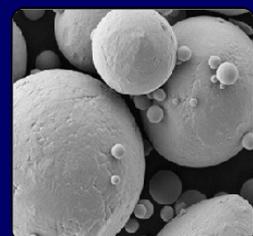


**Charles Hatchett's
London**

(p.19)



**Ta and Nb-containing
alloy powders for
application in additive
manufacturing (p.23)**



On July 1st, 2020, H.C. Starck Tantalum and Niobium became

TANIOBIS

We embody over 60 years of expertise processing and developing Ta- & Nb-based alloys and their compounds for high-end applications.



Electronics

Capacitors; Sputter targets for barrier layers in semiconductors



Medica & Optics

Biocompatible implants, high-voltage capacitors, high reliability ophthalmic and specialty glasses and lenses



Aviation & Energy

Superalloy additives for production of turbine parts



Additive Manufacturing

Customized powders for 3D printing applications

Alloyed

Our partner in 3D-printing design, process optimization and in metal digital manufacturing



Thruster by Alloyed
(LBM-printed
using **AMtrinsic**® Ta powder)

info@taniobis.com | www.taniobis.com

 **JX Metals Group**



TANI OBIS
inspiring metal evolution

President's Welcome

Dear Members and friends of the T.I.C.,

It is always a pleasure to communicate with you and I hope this note, as always, finds you safe and well.

As I write, the T.I.C. staff and Meetings Subteam are deeply engaged in setting up the venue and putting in place plans for the upcoming Virtual AGM and 61st General Assembly (GA61). The learning curve has been steep; however, the staff, Executive Committee and Meetings & Marketing Subteams have worked tirelessly to develop an agenda which is focused on meeting the needs of the broadest member and non-member audience. A broad net was cast in reviewing the approaches that have been taken by other associations and it was determined that a one-day, 4-hour AGM/GA was most appropriate for a first-time virtual meeting. Selected presentations and panel discussions will be focused on real-time issues and questions, such as what is happening in the overall market and how is the supply chain faring through the disruptions that Covid-19 has presented us.

Of course, one important aspect that will be missing is the face-to-face interactions that we all look forward to and use for catching up on real-time issues and business planning. And while I know we have all adjusted to the necessities of quarantines, social distancing and travel restrictions, the venue we have picked will accommodate one-on-one sessions between attendees through the use of private virtual meeting rooms, should they require them. I am very interested to see how this will work for our members and guests.

All-in-all, I believe the GA61 virtual conference will be interesting, informative and a learning experience for all. I firmly believe that this virtual format represents a new platform for member engagement and we will be investigating just how we might use it for this purpose in the future. That said, there is nothing like an in-person face-to-face GA, and we certainly look forward to holding GA62, in Geneva, Switzerland, in September 2021.

See you on-line for our Virtual GA61.

Sincere regards,

Dr Daniel Persico,

President

Contents

The Bulletin No.183
OCTOBER 2020



Featured articles:



The Anders Gustaf Ekeberg
Tantalum Prize: Winner
2020

Page 6



Charles Hatchett's London

Page 17



Tantalum recycling by
solvent extraction: chloride
is better than fluoride

Page 7



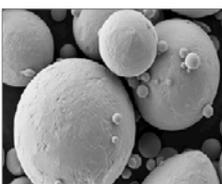
TARANTULA: Recovery of W,
Nb and Ta occurring as by-
products in mining and
processing waste streams

Page 21



Interview: Mickaël Daudin,
Pact Program Manager for
the ITSCI Programme

Page 15



Tantalum (Ta) and niobium
(Nb) containing alloy powders
for application in additive
manufacturing

Page 23

Regular articles:

3-5 President's Welcome

33 Tantalum and niobium patent update

34 Diary of forthcoming events

34 Member company and T.I.C. updates

35 Director's Notes

35 Disclaimer



主席致辞

亲爱的T. I. C. 会员和朋友：

很高兴能透过本函继续与您们交流，我希望一如既往，你们收到这封信时是健康和平安的。

当我撰写本文时，T. I. C. 的员工和会议小组成员正紧密合作，为即将举行的虚拟年度大会和第61届大会（GA61）准备场地和制定议程。尽管准备的过程非常困难，但是，我们的工作人员，执行委员会以及会议与市场营销分队努力不懈地制定了一个能够满足广泛会员和非会员需求的议程。我们在网络参考了其他协会所采用的虚拟会议方法，然而，一日内举行四小时虚拟年度大会是最佳的时间。选定的演讲和小组讨论将集中于实时问题，例如整个市场中正在发生的事情以及供应链如何渡过新型冠状病毒所带来的破坏。

当然，最重要的是我们将会丢失的一个面对面交互的机会，但仍然期待能赶上实时问题和业务计划的会议。我知道大家已经适应了隔离，社交距离和旅游限制令，而我们这次选择的场所需要与会者通过使用私人虚拟会议室来实行一对一会议。我有兴趣了解这对我们的会员和来宾将如何运作。

总而言之，我相信第61届（GA61）虚拟会议将为所有人带来有趣，丰富资讯和学习经验。我坚信这种虚拟格式代表了一个崭新的会员参与平台，我们将研究未来如何善用此平台。就是说，没有什么比面对面的年度大会更好。我们非常期待2021年9月在瑞士日内瓦举行的第62届（GA62）大会。

我们在第61届（GA61）虚拟会议上见！

送上真诚的问候

丹尼尔·佩尔西科博士（Daniel Persico），主席



Lettre du Président

Chers membres et amis du T.I.C.,

C'est toujours un plaisir de communiquer avec vous et j'espère que cette note, comme toujours, vous trouvera sain et sauf.

Au moment où j'écris, le personnel du T.I.C. et le Groupe de Travail consacré aux réunions sont profondément engagés dans la mise en place de la plateforme et des plans pour la prochaine AG virtuelle et la 61e Assemblée Générale (GA61). La courbe d'apprentissage a été abrupte; cependant, le personnel, le Comité Exécutif et les Groupes de Travail 'Réunions' et 'Marketing' ont travaillé sans relâche pour élaborer un ordre du jour axé sur la satisfaction des besoins d'un large public de membres et de non-membres. Un examen détaillé des approches adoptées par d'autres associations a été réalisé et il a été déterminé qu'un agenda de quatre heures en une journée était le plus approprié pour notre première réunion virtuelle. Les présentations et tables rondes sélectionnées sont axées sur des problématiques actuelles, telles que la situation sur le marché global et comment la chaîne d'approvisionnement traverse les perturbations que le Covid-19 nous a amenées.

Bien sûr, un aspect important qui fera défaut est les interactions en face à face que nous attendons tous avec impatience et que nous utilisons pour discuter de problèmes en temps réel et de planification commerciale. Et, même si nous nous sommes tous adaptés aux nécessités des quarantaines, de la distanciation sociale et des restrictions de voyage, la plateforme que nous avons choisie permettra des sessions individuelles entre les participants grâce à l'utilisation de salles de réunion virtuelles privées, s'ils en ont besoin. Je suis très intéressé de voir comment cela fonctionnera pour nos membres et nos invités.

Dans l'ensemble, je crois que la conférence virtuelle GA61 sera intéressante, informative et une expérience d'apprentissage pour tous. Je crois fermement que ce format virtuel représente une nouvelle plateforme pour l'engagement des membres et nous allons étudier comment nous pourrions l'utiliser à cette fin à l'avenir. Cela dit, il n'y a rien de tel qu'une réunion face à face en personne, et nous avons certainement hâte de tenir notre GA62, à Genève, en Suisse, en septembre 2021.

Rendez-vous en ligne pour notre GA61 virtuel.

Sincères salutations,

Dr Daniel Persico, Président

社長のあいさつ



T. I. C. のメンバー様、

大変ご無沙汰しておりますが、TICメンバー様は変わらず、ご健康でご活躍されていることと思います。

以前お伝えしたように、TIC スタッフとサブチームは熱心、会場の設定と、バーチャルAGMおよび第61回総会（GA61）のプランニングを打ち合わせしております。課題はありますが、スタッフ、ExComメンバー、ミーティングマーケットサブチームは最も多くのメンバーおよび非メンバーのオーディエンスのニーズを満たせるようなアジェンダに精力的に取り組んできました。様々な団体が採用しているアプローチを検討した結果、1日4時間のAGM / GAが初めてのバーチャル会議には最も適していると判断致しました。プレゼンテーションとパネルディスカッションでは市場全体で何が起きているか、Covid-19後のサプライチェーンがどのように進んでいくかなど、リアルタイムの問題と質問に焦点を当てています。

もちろん、メンバー様にとっての重要な1つであり、皆様が楽しみにして頂いているリアルタイムでの面談、打ち合わせが実現できないのは残念ではありますが、検疫、社会的距離、旅行制限の必要性に順応させながら、私たちが選んだ対策は、必要に応じて、プライベートバーチャル会議室を設定し、参加者様が1対1の打ち合わせができるように対応いたします。これがメンバーやゲストにとってどのように機能するかが私自身大変興味を持っておりません。

全体として、GA61バーチャル会議は興味深く、有益で、メンバー様にとっていい経験になると思います。このバーチャル形式は、メンバー様のための新しいプラットフォームになると私は確信しており、今後どのように利用していただけるかを検討したいと思います。とはいえ、従来の対面できる年次総会に勝るものではありません。

2021年9月にスイス、ジュネーブでGA62を開催されることを楽しみにしています。

バーチャルGA61は、オンラインでお会い致しましょう。

ダニエル・F・パーシコ、PhD、, 社長

Boas-vindas do presidente



Membros e amigos do T.I.C.,

É sempre um prazer comunicar-me com vocês, e espero que esta nota, como sempre, os encontre em segurança e bem.

Enquanto escrevo, a equipe do T.I.C. e a Subequipe de Reuniões estão profundamente engajadas em configurar o ambiente e colocar em prática os planos para as próximas AGM Virtual e 61ª Assembleia Geral (GA61). A curva de aprendizado tem sido íngreme; contudo, a equipe, o Comitê Executivo e as Subequipes de Reuniões e de Marketing trabalharam incansavelmente para desenvolver uma agenda focada em atender às necessidades do mais amplo público de membros e não-membros. Foi estabelecida uma ampla rede para revisar as abordagens feitas por outras associações, e assim determinou-se que uma AGM/GA de 4 horas em um único dia seria o mais apropriado para uma reunião virtual pela primeira vez. Apresentações e painéis de discussão selecionados serão focados em problemas e questões em tempo real, tais como o que está acontecendo no mercado como um todo e como a cadeia de suprimentos está se saindo com as interrupções que a Covid-19 nos apresentou.

Obviamente, um importante aspecto que estará ausente são as interações face a face, que todos esperamos e utilizamos para atualização sobre problemas em tempo real e planejamento dos negócios. E embora eu saiba que todos tenhamos nos ajustado às necessidades de quarentenas, distanciamento social e restrições de viagem, o ambiente que escolhemos acomodará sessões individuais entre os participantes por meio do uso de salas de reuniões virtuais privadas, caso eles assim necessitem. Estou bastante interessado em ver como isso funcionará para nossos membros e convidados.

Em suma, creio que a conferência virtual GA61 será interessante, informativa e uma experiência de aprendizado para todos. Acredito fortemente que este formato virtual representa uma nova plataforma para o engajamento dos membros, e estaremos avaliando como exatamente poderemos utilizá-la com este propósito no futuro. Dito isso, não há nada como uma GA presencial, face a face, e certamente esperamos realizar a GA62 em Genebra, Suíça, em setembro de 2021.

Vejo vocês on-line para nossa GA61 virtual.

Com sinceros cumprimentos,

Dr. Daniel Persico, Presidente



The Anders Gustaf Ekeberg Tantalum Prize: Winner 2020

Recognising excellence in tantalum research and innovation

The 2020 Anders Gustaf Ekeberg Tantalum Prize ('Ekeberg Prize'), awarded annually for excellence in tantalum research and innovation in tantalum (Ta), has been won by a team from Edinburgh University, UK, lead by Prof. Jason Love, for **Tantalum recycling by solvent extraction: chloride is better than fluoride** published in *Metals* (reprinted on page 6).

The judges' verdict

Announcing the winner, the independent judging panel lead by Richard Burt stated that tantalum recycling will continue to increase in importance, both due to dwindling reserves, and also because recycling is of great societal interest, adding that this work is an important step toward significant improvement in the chemistry of recycling, which deserves more attention.

The authors of the winning paper are Prof. Jason Love, Prof. Carole Morrison, Luke Kinsman, Rosa Crevecoeur and Amrita Singh-Morgan of the EaStCHEM School of Chemistry, University of Edinburgh, and Prof. Bryne Ngwenya of the School of Geosciences at the University of Edinburgh.



The winning team (left to right): Prof. Bryne Ngwenya, Luke Kinsman, Prof. Jason Love and Prof. Carole Morrison in a chemistry laboratory at Edinburgh University. Rosa Crevecoeur and Amrita Singh-Morgan couldn't attend.



Prof. Jason Love receiving the Ekeberg Prize medal from Roland Chavasse, T.I.C. Director

The panel wishes to congratulate all entrants whose papers are challenging the boundaries of current knowledge of tantalum, and which may well lead to significant breakthroughs into exciting new applications of the element.

The prize and award ceremony

In a normal year the Ekeberg Prize is awarded at the T.I.C.'s in-person General Assembly, where the winner is the guest of honour, but due to Covid-19 no physical meeting can take place in 2020. However, not to be outdone, on September 11th Roland Chavasse, T.I.C. Director, visited Edinburgh to award the prize in a suitably socially distanced ceremony.

There can be no doubt Anders Ekeberg himself would have found this year's winning paper particularly interesting since it was the difficulties he has with solvent extraction which caused him to name it 'tantalum' in the first place (after the Greek demi-god cursed to endure eternal thirst and hunger).

Full details about the Ekeberg Prize, including how to submit a paper for the 2021 medal, can be found at www.TaNb.org.

Tantalum recycling by solvent extraction: chloride is better than fluoride



Paper written by Luke M. M. Kinsman¹, Rosa A. M. Crevecoeur¹, Amrita Singh-Morgan¹, Bryne T. Ngwenya², Carole A. Morrison¹ and Jason B. Love¹, at: 1 - EaStCHEM School of Chemistry, University of Edinburgh, Edinburgh EH9 3FJ, UK; 2 - School of Geosciences, University of Edinburgh, Edinburgh EH9 3FE, UK.

© 2020 by the authors. This article was first published in March 2020 in the journal *Metals* 2020, 10(3), 346, available at <https://doi.org/10.3390/met10030346>. All views and opinions in this article are those of the authors and not the T.I.C.

Abstract

The recycling of tantalum (Ta) is becoming increasingly important due to the criticality of its supply from a conflict mineral. It is used extensively in modern electronics, such as in capacitors, and so electronic waste is a potentially valuable secondary source of this metal. However, the recycling of Ta is difficult, not least because of the challenges of its leaching and subsequent separation from other metals. In this work, we show that Ta(V) halides, such as TaCl₅ and TaF₅, which can potentially be accessed from Ta metal upon acid halide leaching, can be recovered by solvent extraction using a simple primary amide reagent. The need for high halide concentrations in the aqueous phase implies the formation of the hexahalide salts [TaX₆]⁻ (X = F, Cl) and that an anion-swing mechanism operates. While extraction of the fluorides is poor (up to 45%), excellent extraction under chloride conditions is found (>99%) and presents an alternative route to Ta recycling.

Keywords: tantalum; solvent extraction; WEEE; recycling; chemical separation

1. Introduction

The third-row transition metal element tantalum is critical to modern consumer technologies, finding extensive use as a component in capacitors for the microelectronics industry. Approximately 40% of the world's tantalum production is used in this application, but its recycling is limited, at only 1%^[1]. This is surprising, as electronic waste (e-waste) is becoming one of the fastest growing waste categories worldwide^[2,3]. Furthermore, it was found that metal recovery from secondary resources is gradually becoming more cost-effective than virgin mining, especially as the volume of e-waste is projected to increase substantially; over the next few decades, new technologies will become cheaper and more accessible, driving up the rate of device obsolescence^[4,5]. With the best estimates suggesting that only 20% of e-waste is properly recycled^[5], the development of sustainable, efficient hydrometallurgical techniques for the recovery of these critical resources offers huge potential to reduce the environmental impact of e-waste, lower energy costs, and move towards a more circular economy^[6]. However, this depends on the availability of inexpensive reagents for both leaching and separation processes.

The status of tantalum as a metal derived from a conflict mineral^[7], combined with its low abundance in the earth's upper crust means there is a need to design a sustainable closed-loop process to recycle tantalum from waste capacitors. Due to its very low solubility in typical mineral acids such as HCl, H₂SO₄, and HNO₃ compared with other d-block elements, current hydrometallurgical processes for tantalum involve the use of highly corrosive and toxic solutions of concentrated HF, combined with H₂SO₄ or HCl in order to generate soluble anionic metalates, such as [TaF₆]⁻ and [TaF₇]²⁻^[8,9,10,11]. As such, it is evident that there is a need to develop more sustainable processes which can not only efficiently recycle tantalum from secondary sources but do so using milder reagents^[12,13,14,15].

Recent efforts towards fluoride-free tantalum recovery processes have focused on alkaline matrices to generate polyoxotantalates that are recovered at elevated temperatures by solvent extraction^[16,17,18]. Ionic liquids (ILs) have also been investigated as potential extractants for tantalum recovery. Methylisobutylketone (MIBK)-derived ILs were shown to efficiently extract [TaF₇]²⁻ from concentrated sulfuric acid solutions with excellent selectivity for tantalum over other, potentially interfering metals^[19]. In this case, it was thought that this enhanced extraction compared with MIBK alone could be due to greater solubility of water in the IL phase, overcoming the prerequisite to displace the hydration sphere prior to transport of the metalate into nonpolar solvents. To our knowledge, there are very few reports that describe the extraction of tantalum from chloride-based media; acids such as HCl were tested in the extraction of TaF₅, but in these cases, significant solubility issues were seen^[20]. Despite the limited speciation data available for tantalum in halide acids, previous theoretical studies have postulated that TaCl₅ could behave in a similar manner to TaF₅ in aqueous solution, so forming halidometalates such as TaCl₆⁻ in the presence of excess chloride ion^[21,22].

We have shown previously that the primary amide, **L** (Figure 1), forms hydrophobic supramolecular assemblies with metalates, including $[\text{AuCl}_4]^-$, which allows for e-waste separations using anion-exchange solvent extraction processes^[23]. In this work, we describe the transport of tantalum as its halometalate TaCl_6^- into a toluene organic phase using the simple primary amide reagent **L** from acidic solutions in the presence of chloride. Subsequent back extraction (stripping) of the metalate into a fresh aqueous phase is possible with water or dilute HCl.

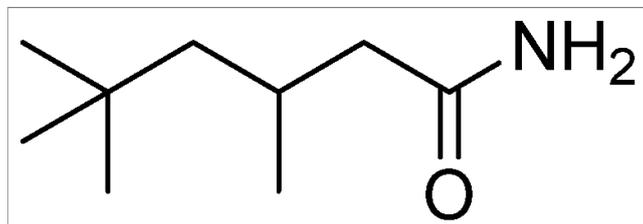


Figure 1. Structure of 3,5,5-trimethylhexanamide **L**.

2. Experimental

2.1. Materials and Instruments

Unless otherwise stated, all solvents and reagents were purchased from Sigma-Aldrich, Fisher scientific UK, Alfa Aesar (Heysham, UK), Acros Organics (Geel, Belgium), or VWR international (Lutterworth, UK) and used without further purification. Deionised water was produced using a Milli-Q purification system. The syntheses of 3,5,5-trimethylhexanamide, **L** and $[\text{H}(\text{C}_{11}\text{H}_{23}\text{NO})_2]_2[\text{SnCl}_6]$ were carried out according to the literature^[23,24].

ICP-OES analysis was carried out on a Perkin Elmer Optima 8300DC Inductively Coupled Plasma Optical Emission Spectrometer. Samples in 1-methoxy-2-propanol were taken up by peristaltic pump at a rate of 2.0 mL min^{-1} into a Gem Tip cross flow nebuliser and a glass cyclonic spray chamber. Argon plasma conditions were: 1500 W RF forward power; argon gas flows of 17, 1.0, and 0.50 L min^{-1} for plasma, auxiliary, and nebuliser flow, respectively. ICP-OES calibration standards were obtained from SCP science.

Karl-Fischer water content determinations were carried on a Metrohm 831 KF Coulometer with Hydranal Coulomat AG as the reagent mixture.

2.2. Preparation of TaCl_5 and TaF_5 Solutions

A 0.12 M stock solution of TaX_5 ($\text{X} = \text{F}, \text{Cl}$) was prepared in 12 M HCl at 25°C . This stock solution was then diluted to 0.01 M TaX_5 in 1 M HCl with varying solutions of lithium chloride in deionised water. A colourless precipitate formed over several weeks in dilute HCl solutions of TaCl_5 , and so solutions were used immediately after diluting from the 12 M stock solution. A colourless precipitate formed overnight from stock solutions of TaF_5 in 12 M HCl, and so solutions were therefore diluted and used immediately.

2.3. General Solvent Extraction Procedure

An aqueous solution of TaX_5 (0.01M, $\text{X} = \text{F}, \text{Cl}$) in 1 M HCl, 0-11 M LiCl (2 mL) was contacted with a toluene organic phase (2 mL) containing 3,5,5 trimethylhexanamide **L** (0.1 M) and stirred (1 h, 1000 rpm, 25°C). The phases were separated physically, and samples from the organic phase taken and diluted with 1-methoxy-2-propanol for ICP-OES analysis. Samples of the stock solution were analysed by ICP-OES to confirm mass balance and percentage extraction. Samples of the post extraction aqueous phase could not be analysed by ICP-OES due to the high salt content suppressing the tantalum wavelengths. Samples from relevant phases were also taken for water concentration determination and NMR analysis as required.

2.4. NMR Data for $[\text{H}(\text{C}_{11}\text{H}_{23}\text{NO})_2]_2[\text{SnCl}_6]$.

^1H NMR (CDCl_3 , 500 MHz, ppm): δH 10.17 (s, broad, 1H), 3.27 (s, 6H, NCH_3), 2.76 (dd, 2H, CH_2CO , $J = 14.2, 6.7$ Hz), 2.65 (dd, 2H, CH_2CO , $J = 14.2, 8.7$ Hz), 2.18-2.08 (m, 2H, $\text{CH}(\text{CH}_3)$), 1.32 (dd, 2H, $\text{CH}_2(\text{CH}_3)_3$, $J = 14.1, 3.3$ Hz), 1.21 (dd, 2H, $\text{CH}_2(\text{CH}_3)_3$, $J = 14.1, 7.1$ Hz), 1.05 (d, 6H, $\text{CH}(\text{CH}_3)$, $J = 6.6$ Hz), 0.90 (s, 18H, $\text{C}(\text{CH}_3)_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 126 MHz, ppm): δC 176.34, 50.65, 41.33, 38.90, 31.09, 29.99, 28.12, 22.39.

3. Results and Discussion

3.1. Solvent Extraction of Tantalum Pentachloride

The dissolution of TaCl_5 in HCl only occurs at high concentrations of HCl (12 M). Initial solvent extraction procedures were therefore developed by contacting a 0.1 M solution of **L** in toluene with a 0.01 M solution of TaCl_5 in 12 M HCl. However, at this high HCl concentration, no appreciable tantalum extraction is seen, and it is likely that the amide **L** is instead protonated and transported into the aqueous phase (Figure 2).

Upon addition of LiCl to the TaCl_5 solution at 12 M HCl, the concentration of Cl^- is increased further, although this results in the out-gassing of HCl from the solution. Under these conditions, low to moderate quantities (30%–50%) of Ta are transferred to the organic phase (Figure 2), although **L** is likely still being lost to the aqueous phase as a result of its high acidity.

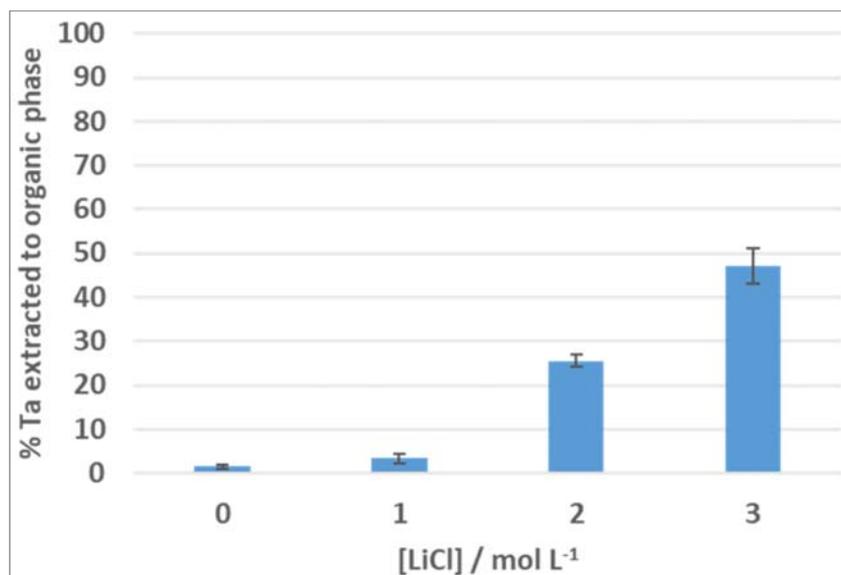


Figure 2. Extraction of tantalum from aqueous solutions of TaCl_5 in 12 M HCl with varying concentrations of LiCl into a toluene solution of **L**. Conditions: TaCl_5 (0.01 M) in 12 M HCl with 0–3 M LiCl (2 mL) stirred with **L** (0.1 M) in toluene (2 mL); phases contacted for 1 h at RT with magnetic stirring. Experiments performed in duplicate and reported as an average.

To minimize the loss of **L** to the aqueous phase while maximising Ta transfer, the acid concentration was diluted to 1 M HCl in conjunction with varying total chloride concentration through the addition of LiCl; no precipitation of Ta is seen under these conditions. In extraction experiments, no loss of **L** from the organic phase is seen (by ^1H NMR spectroscopy) and Ta is completely extracted between 7 and 11 M LiCl (Figure 3).

As tantalum begins to be extracted at 3–6 M LiCl, small quantities of a precipitate form which dissolve at higher LiCl concentrations. Quantitative ^1H NMR analysis of this third phase dissolved in deuterated dimethyl sulfoxide shows that no **L** from the organic phase is present, and ICP-OES analysis shows it comprises tantalum and lithium only, so is potentially LiTaCl_6 or a similar complex. Furthermore, **L** does not transfer significant quantities (<10 ppm) of Li into the organic phase, as the concentrations of **L** or LiCl are varied.

The need for high levels of LiCl to promote Ta extraction suggests that either the formation of the anion TaCl_6^- is a prerequisite for transport into the organic phase, or a salting-out effect is operating. To understand this, experiments were undertaken which vary the concentration of BF_4^- (using NaBF_4) as a non-coordinating anion instead of Cl^- and show that negligible Ta transfer to the organic phase occurs. This confirms that TaCl_5 is not simply “salting-out” to the organic phase and that a source of chloride is necessary to drive $[\text{TaCl}_6]^-$ formation; even so, the high salt content may aid extraction by reducing the concentration of free water in the aqueous phase^[25].

Importantly, Ta was readily back-extracted (~80%) from the organic phase to a fresh aqueous phase with either water or 1 M HCl; a white precipitate forms with water, while no precipitate is immediately observed in the strip solution with 1 M HCl.

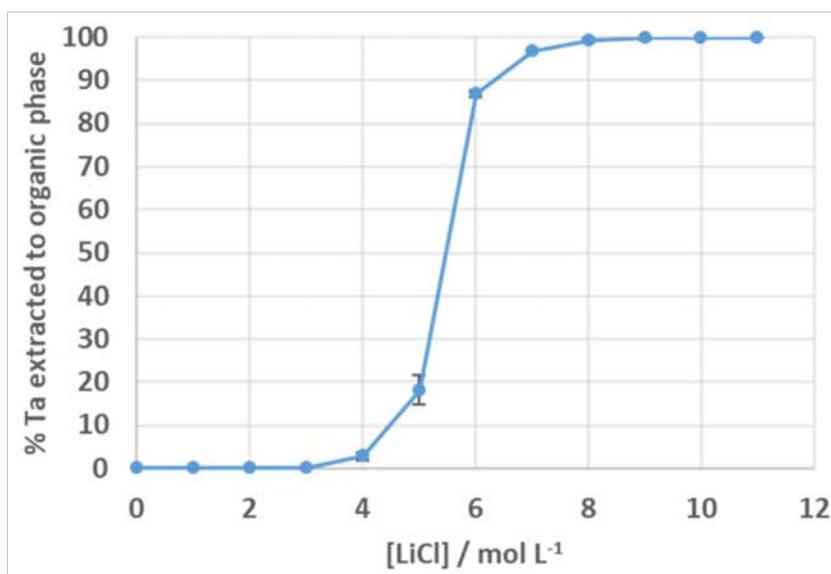


Figure 3. Transport of tantalum from aqueous solutions of TaCl₅ in 1 M HCl with varying concentrations of LiCl into a toluene solution of **L**. Conditions: 0.01 M TaCl₅ diluted in 1 M HCl, 1–11 M [LiCl] (2 mL), stirred with **L** (0.1 M) in toluene (2 mL); phases contacted for 1 h at RT with magnetic stirring. Interpolation used to aid the eye only. Experiments performed in duplicate and reported as averages.

3.2. Structure Elucidation

From the data above, it is apparent that Ta is transported into the organic phase as its ion pair [HL][L]_n[TaCl₆]. To further interrogate the organic-phase speciation, slope analysis of Log D against Log [L] was carried out (Figure 4), which results in a L:Ta ratio of approximately 2 (slope of 1.71 ± 0.13), suggesting the formation of an ion pair such as [HL₂][TaCl₆] in the organic phase.

This type of behaviour is similar to that seen previously for Au extraction using **L** in which experimental and computational analysis showed that two amides chelate a proton through the oxygen atoms to form a charge-diffuse cation that can interact with diffusely charged metalate anions through classical (N-H⋯X) and non-classical (C-H⋯X) hydrogen bonds [23,24].

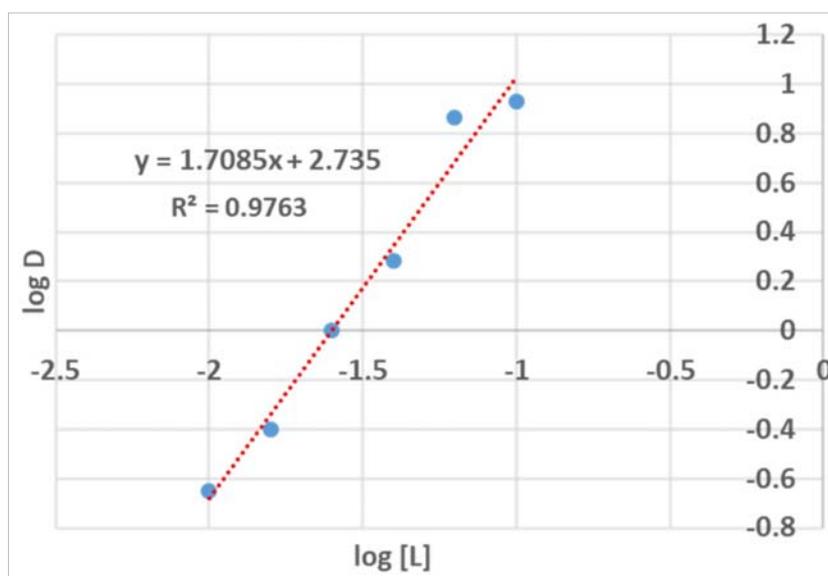


Figure 4. Slope analysis for the transport of Ta with **L**. Conditions: 2 mL 0.01 M TaCl₅ in 1 M HCl, 11 M LiCl, contacted with 2 mL of 0.01 to 0.1 M **L** in toluene for 1 h at RT with magnetic stirring.

Direct structural characterisation of the extracted species has so far proven inconclusive, although ^1H NMR studies provide an indication as to how the receptor $[\text{HL}_2]^+$ is interacting with the metalate (Figure 5). As the concentration of tantalum in the organic phase increases, the two signals at 4.61 and 6.46 ppm associated with the NH_2 protons coalesce and shift downfield to 9.63 ppm.

Variable temperature NMR spectra (Figure S1) reveal an additional signal that is attributable to associated water or hydronium, which coalesces with the amide protons upon Ta loading. There is also a large downfield shift of the signals at 1.59 and 1.87 ppm, associated with the diastereotopic CH_2 protons adjacent to the amide group, to 2.49 and 2.56 ppm respectively. These changes in the ^1H NMR spectra for Ta-loaded **L** are similar to those seen for the solid third phase formed between $[\text{SnCl}_6]^{2-}$ and a tertiary amide version of **L** (Figures S2 and S3). In this latter case, the solid-state structure showed that the two amide ligands chelate the single proton through the amido oxygen atoms, with the cation subsequently interacting with the outer-sphere of the $[\text{SnCl}_6]^{2-}$ octahedron through non-classical C-H hydrogen bonds [24,26,27]. The similarity in the ^1H NMR spectra for Ta/L, and also a relatively large downfield shift of the carbonyl carbon from 174 ppm to 180 ppm in the ^{13}C NMR spectrum (Figure S4) upon Ta loading strongly suggest that a similar structure is formed in the organic phase, with no direct interaction of the amido-oxygen donor with the Ta centre; i.e., an amide complex such as $\text{TaCl}_5(\text{L})$ is not formed.

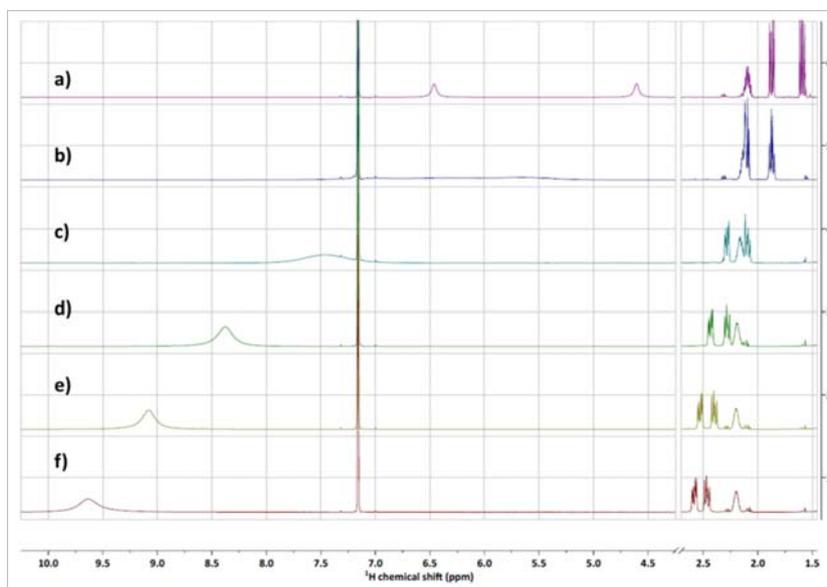


Figure 5. ^1H NMR spectra of (a) 0.1 M **L** in C_6D_6 ; then 0.1 M **L** in C_6D_6 after contact with 0.01 M TaCl_5 in 1 M HCl and: (b) 5 M LiCl; (c) 6 M LiCl; (d) 7 M LiCl; (e) 8 M LiCl; (f) 9 M LiCl.

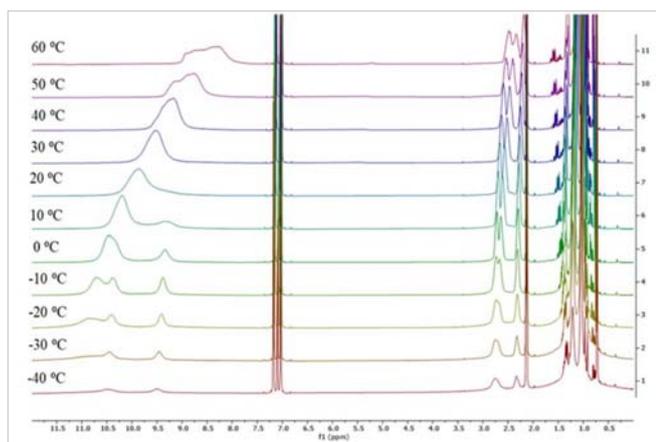


Figure S1. Variable temperature ^1H NMR spectra of 0.1 M **L** in d_8 -toluene after contact with 0.01 M TaCl_5 in 1 M HCl and 9 M LiCl from -40°C to 60°C . Presence of additional water or hydronium signal is revealed amongst the signals assigned to the amide protons (between 8.5 ppm and 10 ppm) when the sample is cooled. Y-axes are offset for clarity.

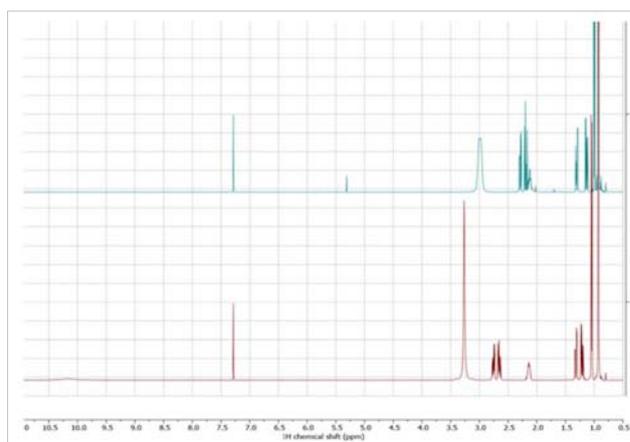


Figure S2. ^1H NMR spectra of a $\text{C}_{11}\text{H}_{23}\text{NO}$ (top) and $[\text{H}(\text{C}_{11}\text{H}_{23}\text{NO})_2]_2[\text{SnCl}_6]$ (bottom) in CDCl_3 .

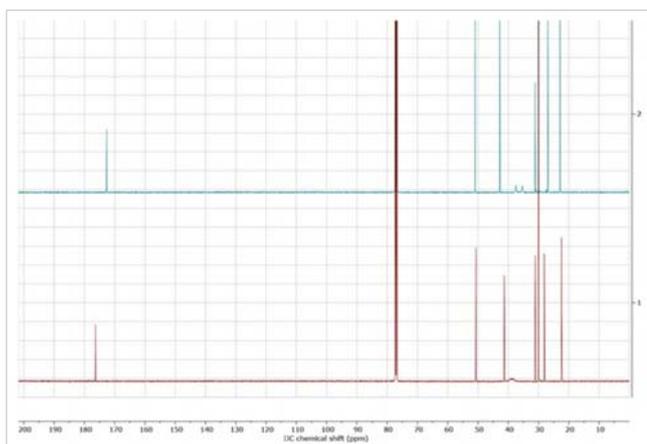


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of a $\text{C}_{11}\text{H}_{23}\text{NO}$ (top) and $[\text{H}(\text{C}_{11}\text{H}_{23}\text{NO})_2]_2[\text{SnCl}_6]$ (bottom) in CDCl_3 .

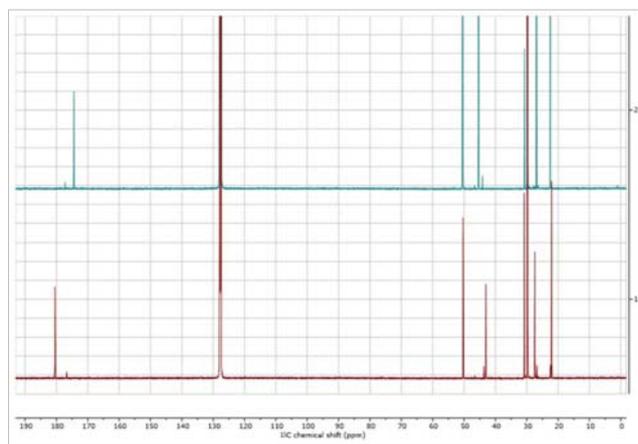


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 0.1 M **L** in C_6D_6 (top) and 0.1 M **L** in C_6D_6 after contact with 0.01 M TaCl_5 in 1 M HCl and 9 M LiCl (bottom).

Karl-Fischer titrations were undertaken to determine the role of water in the extracted species. It is seen that as more tantalum transfers to the organic phase, the concentration of water does not significantly increase, ruling out a micellar extraction mechanism (Figure 6). However, at even higher concentrations of **L** where the concentration of tantalum in the organic phase does not change, more water is transported, suggesting that water transport into the organic phase is associated with the concentration of **L**.

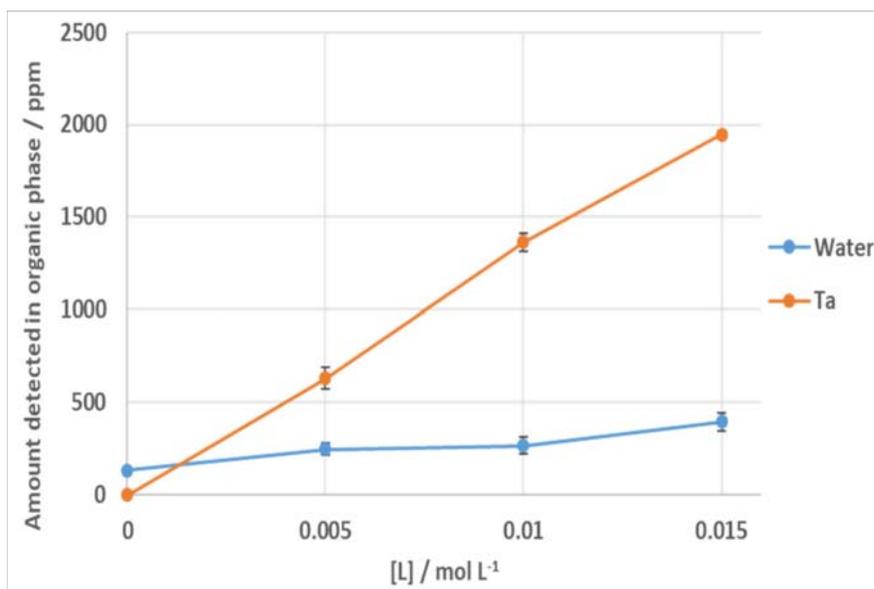


Figure 6. Karl-Fischer water measurements (1.0 mL samples from organic phase analysed for H_2O ; concentrations of Ta and H_2O are on the same scale). Interpolation used to aid the eye only. Experiments performed in duplicate and reported as an average.

During the slope analysis and Karl-Fischer titrations, a solid precipitate is seen at concentrations of **L** below 0.02 M, with more precipitate forming at lower concentrations of **L**. As with above, quantitative analysis of the organic phases by ^1H NMR spectroscopy shows that the ligand concentration remains constant (i.e., no loss of **L** to solid 3rd phase or the aqueous phase); furthermore, this phenomenon was irreproducible in the absence of either TaCl_5 or **L**.

3.3. Solvent Extraction of Tantalum Fluoride

As current commercial processes for tantalum recovery involve the use of hydrogen fluoride to leach the metal as its fluoride salts, it is important to compare how the chloride process described above would compare with its fluoride equivalent.

However, all attempts to extract TaF₅ instead of TaCl₅ were unsuccessful under the conditions used, with negligible extraction seen between 0–12 M HCl and 0–18 M H₂SO₄ with **L**; at high acid concentrations **L** is lost to the aqueous phase. When the HCl concentration is 1 M and the concentration of LiCl is varied, optimal extraction of the tantalum is 45% at 5 M LiCl before trending downwards upon further increase of LiCl (Figure 7).

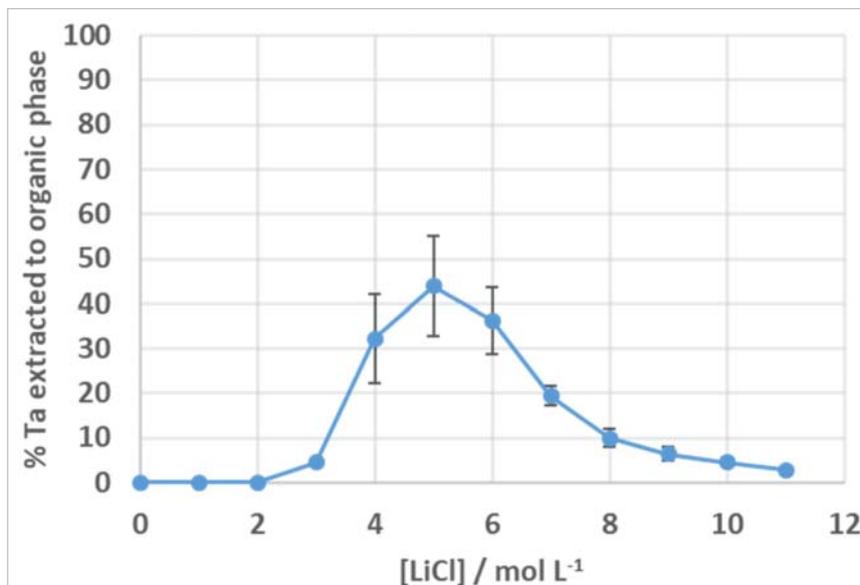


Figure 7. Extraction of tantalum from aqueous solutions of TaF₅ in 1 M HCl with varying concentrations of LiCl into a toluene solution of **L**. Conditions: 0.01 M TaF₅ diluted in 1 M HCl, 1–11 M [LiCl] (2 mL), stirred with **L** (0.1 M) in toluene (2 mL); phases contacted for 1 h at RT with magnetic stirring. Interpolation used to aid the eye only. Experiments performed in duplicate and reported as averages.

In these experiments, no solid third phase forms at any stage, and quantitative ¹H NMR experiments confirm that no amide is lost to the aqueous phase. These data contrast with the experiments using TaCl₅, perhaps because potential fluorometalates such as [TaF₆]⁻ or [TaF₅Cl]⁻ that would be formed in the aqueous phase, are smaller and have more charge dense anions with respect to [TaCl₆]⁻, and therefore will have higher hydration energies. Poor Ta extraction at high LiCl concentrations is likely to result from the competitive transport of chloride by **L** into the organic phase.

4. Conclusions

The simple primary amide, **L**, shows excellent performance for tantalum recovery by solvent extraction under high chloride conditions. The extraction mechanism is identified as similar to that seen for the recovery of gold by **L**, in which charge-diffuse protonated receptors are formed that preferentially interact with the charge diffuse monoanionic metalate [AuCl₄]⁻ [23,24]. ¹H and ¹³C NMR data are consistent with a strong outer-sphere interaction between [HL₂]⁺ and [TaCl₆]⁻. In contrast, amide **L** is a poor reagent of choice when attempting to transport TaF₅ under high chloride conditions, likely due to a combination of competitive chloride extraction and significantly weaker interactions between [HL₂]⁺ and more charge-dense species in the aqueous phase, such as [TaF₅Cl]⁻.

This latter aspect is evident from a comparison of the X-ray crystal data for [TaCl₆]⁻ and [TaF₆]⁻, which shows a 1 Å decrease in the diameter of the Ta complex moving from chloride to fluoride [28,29]. It is therefore anticipated that **L** would be a poor extractant for Ta when employed under solely fluoride conditions, in which species such as [TaF₆]⁻ and even the dianion [TaF₇]²⁻ may be present. Even so, the process described here represents an alternative, fluoride-free route to recycling Ta from waste electronics, using milder reagents than the current commercial methods.

References

1. European Commission: Critical raw materials fact sheets. Available online: https://ec.europa.eu/info/index_en (accessed on 13 January 2020). [CrossRef]
2. Ogunseitán, O.A.; Schoenung, J.M.; Saphores, J.D.M.; Shapiro, A.A. The electronics revolution: From E-wonderland to E-wasteland. *Science* **2009**, *326*, 670–671. [CrossRef]
3. Rao, M.D.; Singh, K.K.; Morrison, C.A.; Love, J.B. Challenges and opportunities in the recovery of gold from electronic waste. *RSC Adv.* **2020**, *10*, 4300–4309. [CrossRef]

4. Zeng, X.; Mathews, J.A.; Li, J. Urban mining of E-waste is becoming more cost-effective than virgin mining. *Environ. Sci. Technol.* **2018**, *52*, 4835–4841. [CrossRef]
5. Baldé, C.P.; Forti, V.; Gray, V.; Kuehr, R.; Stegmann, P. The Global E-waste Monitor-2017, 2017. United Nations University (UNU), International Telecommunication Union (ITU) & International SolidWaste Association (ISWA), Bonn/Geneva/Vienna. Available online: <https://www.itu.int/en/ITU-D/Climate-Change/Documents/GEM%202017/Global-E-waste%20Monitor%202017%20-%20Executive%20Summary.pdf> (accessed on 13 January 2020).
6. Velenturf, A.P.M.; Jopson, J.S. Making the business case for resource recovery. *Sci. Total Environ.* **2019**, *648*, 1031–1041. [CrossRef]
7. Young, S.B. Responsible sourcing of metals: certification approaches for conflict minerals and conflict-free metals. *Int. J. Life Cycle Assess.* **2018**, *23*, 1429–1447. [CrossRef]
8. Nete, M.; Purcell, W.; Nel, J.T. Hydrometallurgical separation of niobium and tantalum: A fundamental approach. *JOM* **2016**, *68*, 556–566. [CrossRef]
9. Zhu, Z.; Cheng, C.Y. Solvent extraction technology for the separation and purification of niobium and tantalum: A review. *Hydrometallurgy* **2011**, *107*, 1–12. [CrossRef]
10. Kabangu, M.J.; Crouse, P.L. Separation of niobium and tantalum from Mozambican tantalite by ammonium bifluoride digestion and octanol solvent extraction. *Hydrometallurgy* **2012**, *129–130*, 151–155. [CrossRef]
11. Nguyen, T.H.; Lee, M.S. A review on the separation of niobium and tantalum by solvent extraction. *Miner. Process. Extr. Metall. Rev.* **2019**, *40*, 265–277. [CrossRef]
12. Nelson, J.J.M.; Schelter, E.J. Sustainable inorganic chemistry: metal separations for recycling. *Inorg. Chem.* **2019**, *58*, 979–990. [CrossRef] [PubMed] *Metals* **2020**, *10*, 346 9 of 9
13. Debnath, B.; Chowdhury, R.; Ghosh, S.K. Sustainability of metal recovery from E-waste. *Front. Environ. Sci. Eng.* **2018**, *12*, 2. [CrossRef]
14. Love, J.B.; Miguiditchian, M.; Chagnes, A. New insights into the recovery of strategic and critical metals by solvent extraction: The effects of chemistry and the process on performance. In *Ion Exchange and Solvent Extraction: Changing the Landscape in Solvent Extraction*; Moyer, B.A., Ed.; CRC Press: Boca Raton, FL, USA, 2019; Volume 23, pp. 1–44. ISBN 9781315114378.
15. Wilson, A.M.; Bailey, P.J.; Tasker, P.A.; Turkington, J.R.; Grant, R.A.; Love, J.B. Solvent extraction: The coordination chemistry behind extractive metallurgy. *Chem. Soc. Rev.* **2014**, *43*, 123–134. [CrossRef] [PubMed]
16. Deblonde, G.J.P.; Bengio, D.; Beltrami, D.; Bélair, S.; Cote, G.; Chagnes, A. A fluoride-free liquid-liquid extraction process for the recovery and separation of niobium and tantalum from alkaline leach solutions. *Sep. Purif. Technol.* **2019**, *215*, 634–643. [CrossRef]
17. Deblonde, G.J.P.; Weigel, V.; Bellier, Q.; Houdard, R.; Delvallée, F.; Bélair, S.; Beltrami, D. Selective recovery of niobium and tantalum from low-grade concentrates using a simple and fluoride-free process. *Sep. Purif. Technol.* **2016**, *162*, 180–187. [CrossRef]
18. Deblonde, G.J.P.; Chagnes, A.; Bélair, S.; Cote, G. Solubility of niobium(V) and tantalum(V) under mild alkaline conditions. *Hydrometallurgy* **2015**, *156*, 99–106. [CrossRef]
19. Turgis, R.; Arrachart, G.; Michel, S.; Legeai, S.; Lejeune, M.; Draye, M.; Pellet-Rostaing, S. Ketone functionalized task specific ionic liquids for selective tantalum extraction. *Sep. Purif. Technol.* **2018**, *196*, 174–182. [CrossRef]
20. Ungerer, M.J.; Van Der Westhuizen, D.J.; Lachmann, G.; Krieg, H.M. Comparison of extractants for the separation of TaF₅ and NbF₅ in different acidic media. *Hydrometallurgy* **2014**, *144–145*, 195–206. [CrossRef]
21. Ungerer, M.J.; van Sittert, C.G.C.E.; van der Westhuizen, D.J.; Krieg, H.M. Molecular modelling of tantalum penta-halides during hydrolysis and oxidation reactions. *Comput. Theor. Chem.* **2016**, *1090*, 112–119. [CrossRef]
22. Ungerer, M.J.; van Sittert, C.G.C.E.; van der Westhuizen, D.J.; Krieg, H.M. DFT modelling of tantalum pentafluoride extraction with phosphorus-based extractants—A molecular dynamics study. *J. Phys. Chem. Solids* **2019**, *135*, 109121. [CrossRef]
23. Doidge, E.D.; Carson, I.; Tasker, P.A.; Ellis, R.J.; Morrison, C.A.; Love, J.B. A simple primary amide for the selective recovery of gold from secondary resources. *Angew. Chem. Int. Ed.* **2016**, *55*, 12436–12439. [CrossRef]
24. Doidge, E.D.; Kinsman, L.M.M.; Ji, Y.; Carson, I.; Duffy, A.J.; Kordas, I.A.; Shao, E.; Tasker, P.A.; Ngwenya, B.T.; Morrison, C.A.; et al. Evaluation of simple amides in the selective recovery of gold from secondary sources by solvent extraction. *ACS Sustain. Chem. Eng.* **2019**, *7*, 15019–15029. [CrossRef]
25. Nash, K.L. A review of the basic chemistry and recent developments in trivalent f-element separations. *Solvent Extr. Ion Exch.* **1993**, *11*, 729–768. [CrossRef]
26. Carson, I.; MacRuary, K.J.; Doidge, E.D.; Ellis, R.J.; Grant, R.A.; Gordon, R.J.; Love, J.B.; Morrison, C.A.; Nichol, G.S.; Tasker, P.A.; et al. Anion receptor design: Exploiting outer-sphere coordination chemistry to obtain high selectivity for chloridometalates over chloride. *Inorg. Chem.* **2015**, *54*, 8685–8692. [CrossRef]
27. Turkington, J.R.; Bailey, P.J.; Love, J.B.; Wilson, A.M.; Tasker, P.A. Exploiting outer-sphere interactions to enhance metal recovery by solvent extraction. *Chem. Commun.* **2013**, *49*, 1891–1899. [CrossRef]
28. Bartalucci, N.; Bortoluzzi, M.; Pampaloni, G.; Pinzino, C.; Zacchini, S.; Marchetti, F. Stable coordination complexes of α -diimines with Nb (V) and Ta(V) halides. *Dalton Trans.* **2018**, *47*, 3346. [CrossRef]
29. Kiyota, Y.; Kadoya, T.; Yamamoto, K.; Iijima, K.; Higashino, T.; Kawamoto, T.; Takimiya, K.; Mori, T. Benzothienobenzothiophene-based molecular conductors: High conductivity, large thermoelectric power factor, and one-dimensional instability. *J. Am. Chem. Soc.* **2016**, *138*, 3920–3925. [CrossRef]



The Anders Gustaf Ekeberg Tantalum Prize 2021: *recognising excellence in tantalum research and innovation*

The Ekeberg Prize is open to any published paper or patent that is judged to advance knowledge and understanding of tantalum. To be eligible the publications should be written in English and dated between October 2019 and April 2021. Submissions must be received by the T.I.C. office before May 31st 2021.

Full details will be posted at www.TaNb.org in due course.

Interview: Mickaël Daudin, Pact Program Manager for the ITSCI Programme

In Bulletin #182 we marked the 10th anniversary of the ITSCI Programme (www.itsci.org), the traceability and due diligence program for tantalum, tin and tungsten (3T) minerals operated by the International Tin Association and T.I.C. and implemented on the ground by Pact (www.pactworld.org), a US-based international not-for-profit organisation.

Here Mickaël Daudin (**MD**), Pact's Manager of the ITSCI Programme is interviewed by T.I.C. Director, Roland Chavasse (**RC**) about how Pact undertakes the day-to-day field operations of ITSCI, including working with governments, building the capacity of ITSCI member companies and partnering with local NGOs to help secure, formalise and improve the livelihoods of 3T artisanal and small-scale miners (ASM).



RC: Thank you for making time to talk with us today. What was the first thing you learned when you were assigned to the Pact team operating the ITSCI Programme?

MD: The first thing I learned was that logistics matter. Going from place to place can take a lot of time. In my last trip to Kalima, Democratic Republic of Congo (DRC), I landed at Kigali airport in neighbouring Rwanda, drove for four hours to the DRC border at Gisenyi/Goma and then boarded a one-hour flight to Kindu, the provincial capital of Maniema Province. For the last leg of my journey, I crossed the Lualaba River and drove four hours before reaching Kalima, where I was to be based while visiting mine sites in the area.



On the way to Filon site, Maniema, DRC
(photo: M. Daudin)

RC: What happened when you reached Kalima?

MD: In Kalima, I visited the Filon mine site. To get there I took a 30-minute motorcycle drive to the shore of the Ulindi river. Then we boarded a pirogue [a long, narrow canoe made from a single tree trunk] with our motorcycles to journey across the river. Once across we undertook another three-hour drive and one-hour walk (pushing the motorcycles where the road was impassable) to finally arrive at the mine site. All of this for only 35 km! For the field teams, this was not a bad journey. During the rainy season, it can be much worse. Some parts of the road have been nicknamed 'the swimming pool'.

RC: That's not an easy commute! What do you typically do when you arrive on site?

MD: During my visit to Kalima, I also met a formidable group of women miners working to support their families, despite the hard conditions. They told me how, thanks to ITSCI legitimizing the Filon site, they are no longer arbitrarily stopped on their way to the next trading town and forced to make illegal payments. This means more money in their pockets to support their families. To me, this is ultimately what ITSCI is about. Mineral resources are finite, and we have one chance to help artisanal miners benefit from these resources in a safe environment, free from abuses and human rights violations. The tremendous work of our field teams, as an important part of all ITSCI's systems, makes this possible; securing livelihoods through perseverance and shared success.

RC: Is the journey to inspect a mine site always so challenging?

MD: Not always, but this far from being an uncommon scenario for reaching a site. We monitor over 2,000 sites across the Great Lakes Region of central Africa and the long distances between places makes having local teams deployed on the ground, in the mining areas, critical to success. Site visits are part of the first step in integrating a mine in the program - conducting a baseline study. This includes visiting the site and collecting information, through interviews and additional source verification, such as who is working there, in what conditions, what state services are on site, how is the overall security in the area, are there any abuses at the site, are armed groups nearby, and more. The baseline study is about more than the site; it is about the entire route, starting from the moment you leave the closest ITSCI office.

RC: How many site visits does ITSCI make each month?

MD: On average, ITSCI field teams conduct around 400 mine site visits every month to monitor activities and follow up on risks and incidents. But visiting a site is not about ticking boxes. It is about listening to what miners have to say, observing activities, asking questions, and verifying information, assessing its plausibility and credibility, and ensuring its accuracy.

RC: And beyond logistics, what else does Pact work on, on behalf of ITSCI?

MD: Beyond logistics, implementing ITSCI on the ground includes continuously working toward improving the way we are working, addressing gaps, adjusting ITSCI procedures to local needs and enhancing management. It also takes partnership. For example, in North Kivu, improved tagging procedures were developed in 2018 to improve transparency at the different stages of mineral extraction and processing, and to improve accountability of state services and miners. ITSCI field teams held bilateral monthly meetings with the Provincial Director of SAEMAPE, the state technical service in charge of ASM in the DRC, as well as countless meetings with other state services, cooperatives and concession owners to explain the reasons behind the changes, raise awareness about the importance of the changes to the credibility of minerals on the international market. This was essential to gain their buy-in and follow-up continues even today. Whenever new recommendations for change are made, field teams begin the cycle again, making new visits and setting up new meetings. This process is the core of ongoing monitoring, but achieving results is about trust. Bilateral meetings like those we held with SAEMAPE lay the groundwork for multi-stakeholder committee meetings, chaired by local authorities and including state services, security forces, mining operators, civil society and ITSCI teams, who meet monthly to review mining activities and further embed and improve processes.



Mickaël Daudin (left) and ITSCI project manager in Maniema Province Alpy Songoli (photo: M. Daudin)

RC: How many multi-stakeholder committee meetings take place?

MD: Well, there are currently 47 local and provincial committees in the DRC and in 2019, we facilitated 267 such meetings, where security, government, industry, and civil society partners agree upon and enforce risk mitigation measures. At these meetings ITSCI field teams share information on recorded incidents, providing guidance on what should be done to mitigate and resolve the incidents. Sometimes this can be challenging, particularly if it is related to allegations of abuse by stakeholders who are in the room.



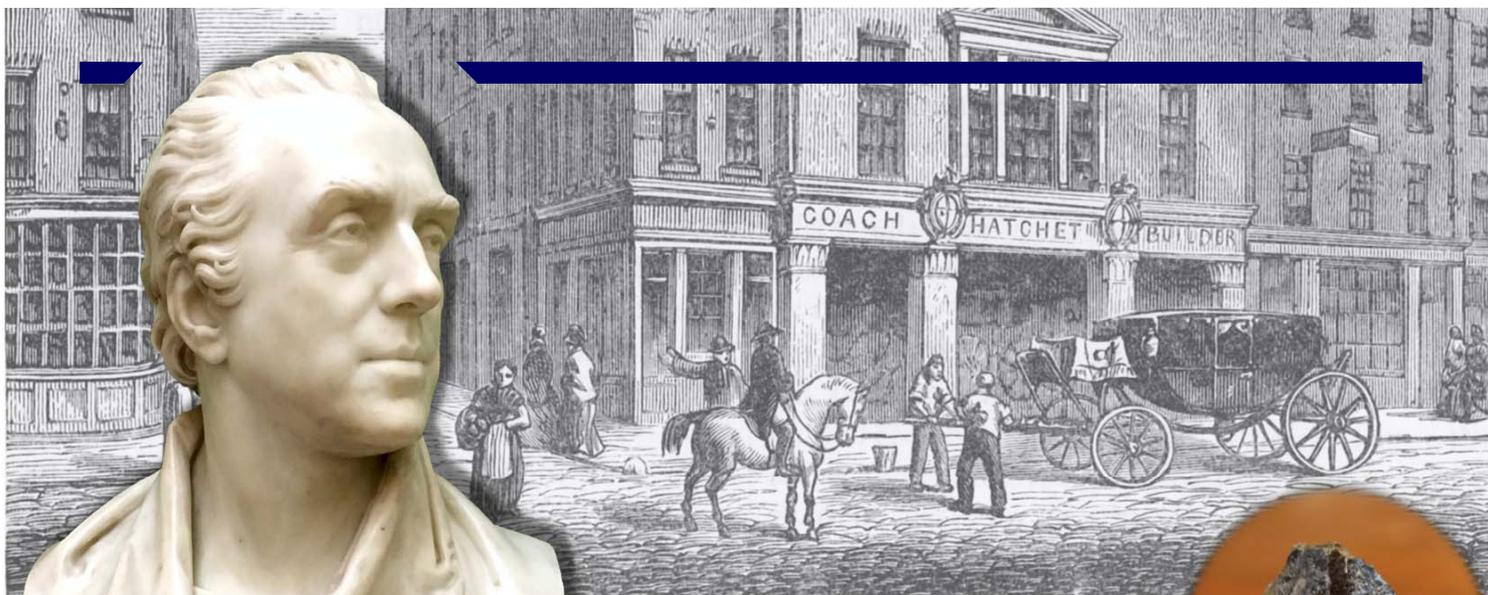
Women miners at Filon site, Maniema, DRC (photo: M. Daudin)

It requires a high degree of sensitivity and diplomacy, while maintaining trust, raising awareness of the implications of incidents in the mineral supply chain, and strengthening the capacity of stakeholders to follow DRC laws, international regulations and due diligence. ITSCI's teams have developed important relationships with senior officers in the national Congolese army and mining police, which have contributed to them taking actions or sanctioning responsible individuals. Without trust, we could not resolve risks and achieve this kind of success.

RC: How has Covid-19 impacted your work in the region?

MD: Covid-19 has had unprecedented impact on our work and resulted in significant budget cuts. Today, it has become even more critical to sustain the successes and impact we had achieved before the pandemic hit. We continue to traverse the challenging terrain to make site visits, wearing our masks and keeping our physical distance wherever possible. We are continuing to connect with stakeholders via mobile phones when in-person meetings aren't possible. Because ITSCI is about being heard and listening. It is about recognizing problems and finding solutions, instead of looking away. It is about holding government services and companies to account and having them take concrete actions to address the risks and conduct their due diligence.

RC: Mr Daudin, thank you very much for your time today. **TIC**



Left, Charles Hatchett's bust at the Linnean Society, London. Above, the Hatchett family's coach-building factory in Covent Garden. Right, the rock from Connecticut, USA, in which Hatchett discovered niobium.

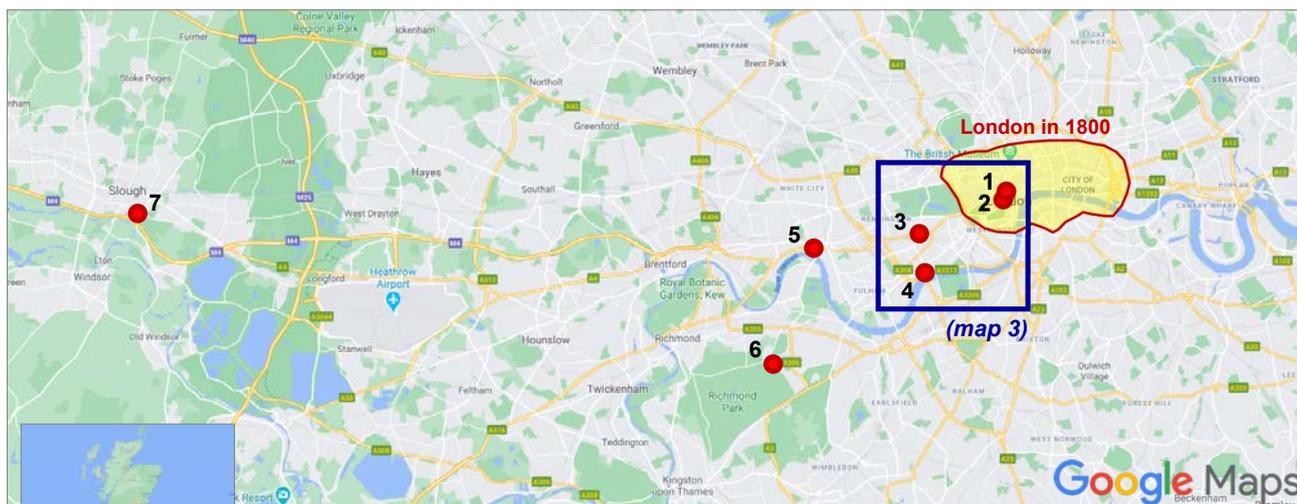
Charles Hatchett's London

Unable to leave London during the Covid-19 'lock-down' T.I.C.'s Director (and London resident) Roland Chavasse has discovered a surprising number of places and objects which Charles Hatchett would have known still exist today across the city. Join him on a walk through the streets of Georgian England...

When Charles Hatchett discovered the element niobium (or, as he called it, 'columbium') in his Hammersmith laboratory in 1801 the world was a very different place from the one in which we live. Across England the first industrial revolution was gathering steam; factories were revolutionizing productivity, a network of new roads were being constructed and Britain's economic and military superiority gave it the edge in any trade negotiation. London was a city alive with possibilities and, for some people at least, fortunes were there to be made.

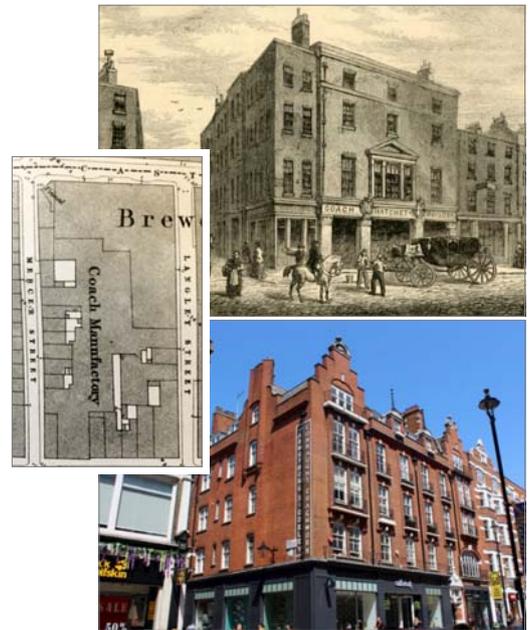
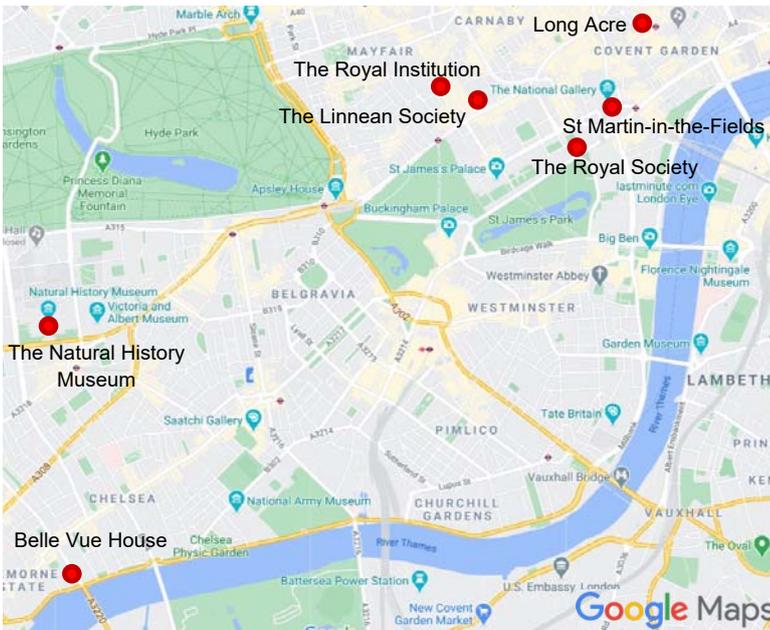
One such businessman was John Hatchett, a man born in humble surroundings but who by hard work and technical ingenuity became one of the leading carriage makers in the world, providing luxurious horse-drawn vehicles to many of the royal households of Europe, including Empress Catherine the Great of Russia and Britain's King George III.

It was into this world of commerce and new wealth that Charles Hatchett, John's only son, was born on January 2nd 1766, at "Hatchett Coaches", the family workshop and home on Long Acre, in Covent Garden, then part of an industrial cluster that focused on horse-based transport and brewing beer (location 1).



Map 1: Modern London street map showing approximate size of London in 1800 (yellow) and the locations Hatchett would have known. Key: 1 - his birth place, Long Acre; 2 - St Martin-in-the-Fields where he was baptised and married; 3 - The Natural History Museum; 4 - Belle Vue House; 5 - his laboratory in Hammersmith; 6 - Mount Clare; 7 - his tomb at Upton-cum-Chalvey.

Map 2: Ireland and the UK.



Map 3: Showing places of significance to Hatchett (Credit: Google Maps) Further information about the locations listed in this article and how they relate to Charles Hatchett is available from roland.chavasse@tanb.org.

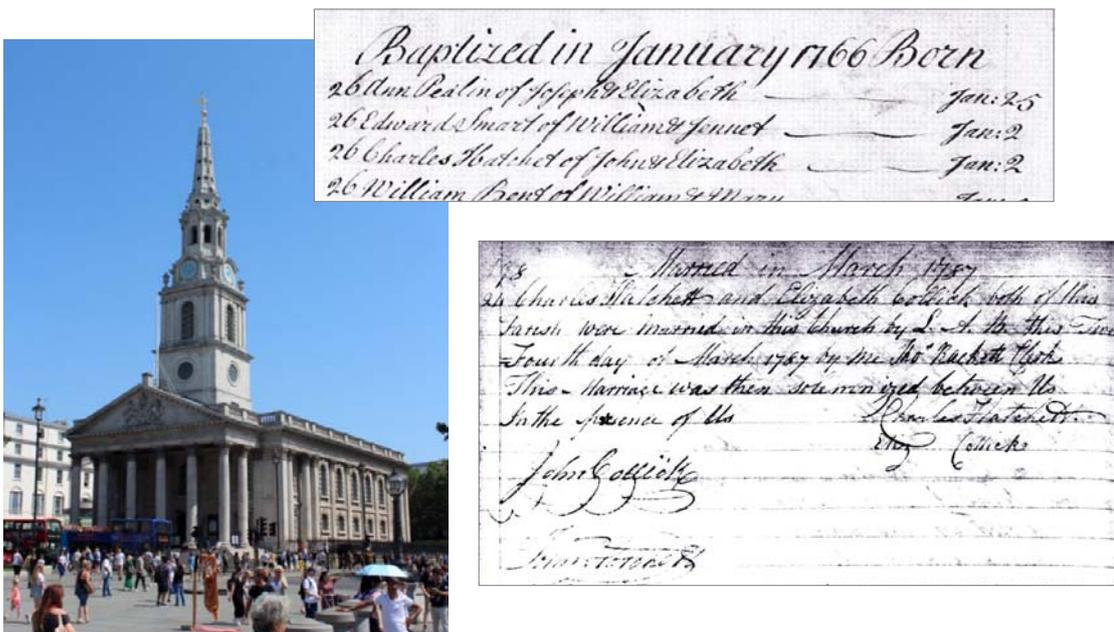
No 121 Long Acre: in 1781 and 2020, with the 19th century floor plan showing the extent of the coach workshops. (photos: Getty Images, T.I.C.)

Charles lived above the factory until the age of five, when the success of the business allowed the family to move out to Chelsea, then a rural village. Hatchett Coaches remained at No 121 Long Acre and when John died in 1806 Charles took over its day-to-day management (simultaneously giving up his practice of chemistry, much to the disappointment of his scientific friends). In 1824 “Hatchett Coaches” was bought by a rival and the name disappeared, and although the main building has since been rebuilt the floor plan remains and it is possible to walk right through the former workshop, still adorned with painted signs stating “coachwork” and similar.

Baptism and marriage

A short walk away from Hatchett’s workshop is the neoclassical gem of St Martin-in-the-Fields church, just off Trafalgar Square (location 2). Charles Hatchett was baptized here on January 26th 1766 and his birth certificate is the earliest official record of his life. This church was a focus for the local mercantile class, and just 21 years later Charles returned here to be married to Elizabeth Collick, daughter of a successful hair trader and wig maker.

St Martin’s also has a very good café in the basement, should you need refreshment.



St Martin-in-the-Fields church, baptism certificate and marriage certificate (photo T.I.C.)

A man of science (and clubs)

Hatchett was a notably urbane and talented scientist and a prototype consulting analytical chemist. Although he is now largely neglected in favour of his friend, the prolific Sir Humphry Davy (1778–1829), in his day Hatchett was a leading member of several scientific bodies, and other clubs for wealthy gentlemen.

Three of these institutions are still in operation and hold archives of Hatchett's correspondence and other effects; the Linnean Society, the Royal Society and the Royal Institution (see map overleaf). All three are within a short walk of St Martins and it is normally possible to visit them if you book in advance.

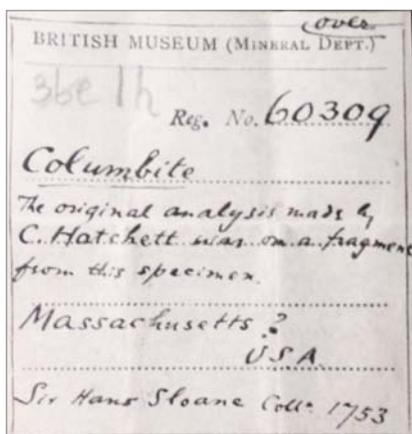
For example, at the Linnean Society on Piccadilly there is a fine bust of Hatchett (complete with bald patch) and several letters he wrote to other scientists discussing his experiments.



Hatchett's bust (photo courtesy of the Linnean Society)

The original rock

Continuing our journey westwards we come to the Natural History Museum (Cromwell Rd, SW7; location 3). Hatchett would not have known this relatively modern building, but within its collection is one of the highlights of our tour, the sample of columbite collected from Connecticut, USA, in which Hatchett first discovered niobium (see [Bulletin #178](#) for the full story of "Charles Hatchett and the origin of columbium"). Pre-booking is essential though, as the sample is not on public display, which is a pity.



Sample #60309 at the Natural History Museum, London, UK (Photo: T.I.C.)

Belle Vue House, 92 Cheyne Walk, SW10

Belle Vue House was the family home John Hatchett built once he became an established businessman in 1771 (location 4). It is a large river-side house and was the family home for most of Charles's youth. John later sold it and moved to an even larger mansion in Hammersmith (since demolished), but it was evidently a special place for Charles because in about 1818 he re-purchased it and lived there until he died.

Belle Vue is notable for being where Charles first became interested in science, according to his memoirs. The event occurred one day when his mother made some raspberry jam. Charles wanted to sample it immediately, as boys do, but his mother refused and locked it in the kitchen until supper time. Disappointed, Charles went upstairs and started to read a book to pass time. As luck would have it, the book was about chemistry. Realising the potential of science to solve his problem, Charles found some acid in the storeroom and proceeded to dissolve the lock on the kitchen door, before eating the fresh jam to his heart's content. His mother's reaction was not recorded.



Belle Vue House, Chelsea (photo: Savills)

Today it is privately occupied and can't be visited, but it is clear from the outside that this is a large and comfortable house.

Hammersmith, W6

Charles Hatchett lived in Hammersmith for many years, first at his father's vast mansion (the one since demolished), and later at his own premises on Lower Mall by the River Thames, where he established his laboratory and did his most important research, including the discovery of niobium.

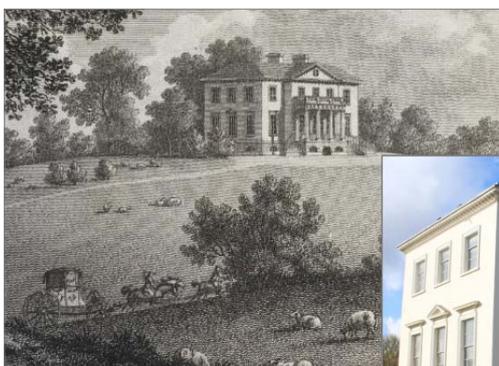
Charles's interest in chemistry was not universally welcomed, however, and his father once offered him £3,000 (enough money to buy 300 horses) and a guaranteed place in Parliament if he would abandon chemistry. Fortunately for the world, Charles followed his heart.

Today the site of Hatchett's laboratory lies within Furnival Gardens, a small public park. The exact location is unknown, however, since this area was demolished during in the 1940s. Currently there is no commemoration of Hatchett's achievements at the site (location 5).



Furnival Gardens, Hammersmith (photo: Google Maps)

Should you feel in need of refreshment at this point, a pub Charles Hatchett is known to have often visited, The Hop Poles, is just around the corner at 17 King Street (it faced the front gates of John Hatchett's mansion).



Mount Clare, Roehampton in 1784 (above) and today (right) (pictures: T.I.C. and W. Watts)



Mount Clare, Roehampton, SW15

The penultimate stop on this race through London is Mount Clare. This was Hatchett's country villa where he lived after his father died and he had taken on the management of Hatchett Coaches.

The gardens were set out by Capability Brown and this elegant villa would have been used to entertain guests and to let Hatchett escape from the cares and smells of London.

Today this building is Grade 1 listed (protected from demolition) and is currently occupied by the University of Roehampton, London. It is possible to walk around the grounds freely, but prior arrangement is required to go inside the building (location 6).

St Laurence's Church, Upton-cum-Chalvey

For the final stop on our tour you probably need a taxi as the village of Upton-cum-Chalvey (location 7), close to the royal residence of Windsor Castle, is some 30 km (20 miles) westwards.



Saint Laurence's Church, Upton-cum-Chalvey, Berkshire, UK

Here, in the 900-year old church of St Laurence's is where Charles Hatchett was buried in 1847, in a grave shared with his parents and wife. It is the only place his name is commemorated in public.

In 2019 the T.I.C. paid for the grave to be cleaned and mended (see [Bulletin #179](#)), ensuring that the memory of Charles Hatchett lives on for further generations.



Photo: T.I.C.



Photo: Julie James

Life beyond London?

Charles Hatchett was a man of his time who personified the twin spirits of commerce and science which ran through Georgian London. However, while his homes and business were always in London, in his youth he travelled extensively across Europe. These travels included an epic journey in 1790-91 to deliver one of his father's coaches to Russia, during which time it is possible that he met Anders Ekeberg who was studying in Berlin, Germany, at the time; but that is a story for another Bulletin...

TIC

TARANTULA: Recovery of tungsten, niobium and tantalum occurring as by-products in mining and processing waste streams



TARANTULA is a project funded by the European Commission. This project has received funding from the European Union's Horizon 2020 Research and Innovation program under Grant Agreement n° 821159. The T.I.C. is a partner in the TARANTULA consortium. Full details at <https://h2020-tarantula.eu/>.



Context of the project

Tungsten (W), niobium (Nb) and tantalum (Ta) are refractory metals displaying extraordinary chemical, heat and wear resistance, and are essential in a wide range of applications including capacitors for computers, mobile phones and hearing aids, high-strength steel for pipelines, superconducting magnets for MRI machines, carbides for cutting tools and drilling bits. Since 2011 the European Commission has classified them as critical raw materials (CRM)* due to their high importance for the EU economy and high supply risk.

Objective of the project and expected impacts

The TARANTULA project started in 2019 aims at reducing the dependence of EU on refractory metals imports by valorizing yet unexploited European resources such as low grade mining waste streams and process scrap. TARANTULA will achieve this goal by:

- Building a comprehensive database of existing and currently unexploited resources containing W, Nb & Ta
- Developing a toolkit of novel, cost-effective, scalable and eco-friendly metallurgical processes to increase the selectivity and recovery rates of refractory metals from low-grade waste
- Selecting the most promising routes and developing and validating a flexible prototype
- Strengthening citizen trust in mineral processing

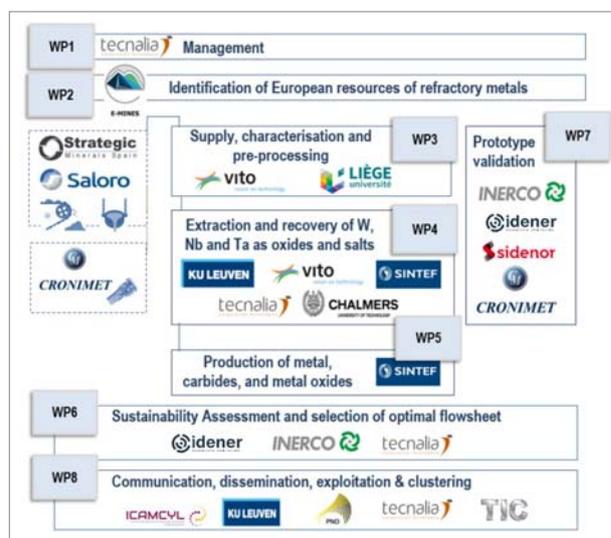
Main activities

TARANTULA's work plan is composed of 8 Work Packages (WP) along a 4-year timeline. These WP include upstream research and development (R&D) activities of the proposed metallurgical technologies (WP2-WP5) followed by a sustainability assessment to ensure an optimized selection of the most promising routes (WP6) and a prototype validation of the selected routes (WP7). Additionally, the project carries out communication, dissemination, and exploitation activities (WP8), which is where the T.I.C.'s contribution is focused.

Overview of the technologies considered

Through systematic R&D, TARANTULA aspires to bring closer to the market several highly efficient and multi-purpose technologies of different technological maturity. Each process is tuneable to the specificities of each feedstock which will add additional flexibility to the overall technology concept.

TARANTULA's technology portfolio includes bio-, hydro-, electro-, solvo-, iono- and electrometallurgical processes, while in terms of functionality, the envisioned processes can serve either as standalone treatment "modules" in place of one or more steps of the traditional W/Nb/Ta recovery routes or work in combination to form integrated solutions for maximum environmental and performance benefits.



TARANTULA Work Packages (WP). The T.I.C.'s contribution is focused in WP8.

* The European Commission's 4th critical raw materials list published in September 2020 also included these three elements. The full list is available at <https://ec.europa.eu/docsroom/documents/42849>.

Progress of the project and latest achievements

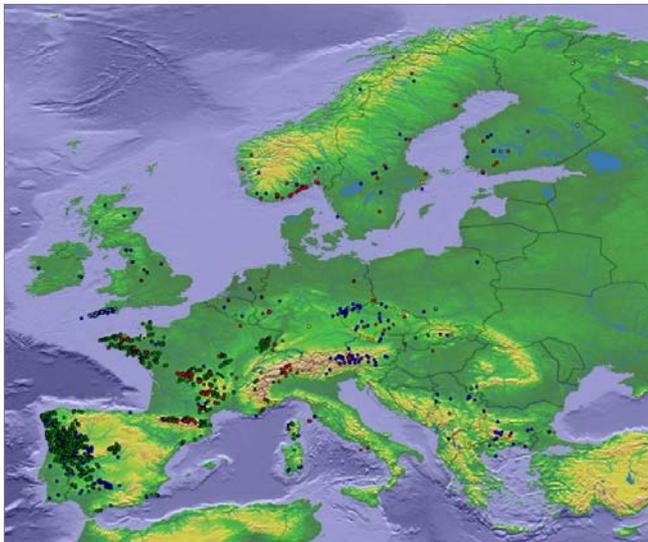
WP2: Identification of European resources of refractory metals

In Europe there are around 3750 potential sources of W, Nb and Ta, of which three are targeted by the program: Barruecopardo (W, Spain), Salau (W, France), Penouta (Ta and Nb, Spain). The methodology for selecting occurrences has been tested in Portugal and the preliminary directory of W, Nb and Ta occurrences has been delivered.

WP3: Supply, characterization and pre-processing

Samples have been collected of mineral ores from the three target sites, and also representative elements, such as carbide scraps (drills and inserts). These materials have been analysed and characterised, including testing for potentially hazardous substances in Ta-Nb concentrates and tin slags, among other samples.

Simultaneously research continues on bench-scale pre-concentration tests on W tailings and on innovative technologies for pre-concentration of tailings.



Identifying European resources forms WP2

spraying method for W, Nb and Ta oxide coatings, including development of coating process and metallographic characterization of deposited coatings, are under study.

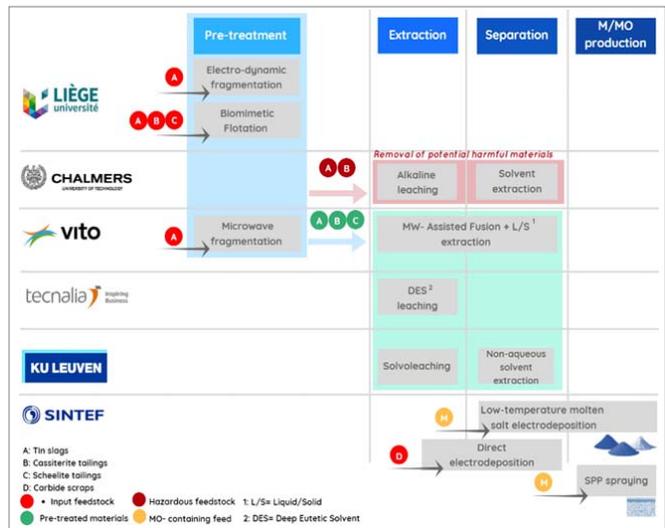
WP6: Sustainability Assessment and selection of optimal flowsheet

A questionnaire for the life cycle assessment (LCA) and life cycle costing (LCC) has been developed and the data collection from partners involved in recovery of W, Ta and Nb research activities has already been started.

WP8: Communication, dissemination, exploitation & clustering

The dissemination activities were started-up with the creation and launch of the project website, [project video](#), corporate poster, general presentation, leaflet and project logo. The analysis of the different stakeholder groups with relevance for the project was completed and the identification of related projects for clustering was achieved. Organization of and participation in dissemination activities, local events and cluster activities have taken place.

Project Partners: Coordinator: TECNALIA (Spain) / Consortium: 16 partners covering the whole value chain: Fundación Tecnalia Research & Innovation, Katholieke Universiteit Leuven, Sintef As, Vlaamse Instelling Voor Technologisch Onderzoek N.V., Universit  de Li ge, Optimizaci n Orientada A La Sostenibilidad SI, Chalmers Tekniska H ogskola Ab, Saloro S.L.U., Strategic Minerals Spain SI, Cronimet Holding GmbH, Sidenor Investigaci n Y Desarrollo S.A., E-Mines, Inerco Ingenieria, Tecnologia Y Consultoria S.A., Fundacion Icamcyl, Pno Innovation, and T.I.C.



Overview of the technologies considered

WP4: Extraction and recovery of W, Nb, Ta as oxides and salts

Identification of extractants and leaching tests of W, Ta and Nb from real samples (high grade ores and tailings) with different leaching agents together with preliminary extraction experiments for the recovery of W, Ta and Nb from leachates produced by different solid and liquid extractants are being performed. Solvometallurgical processes, including solvleaching and Deep-Eutectic Solvents (DES) and Ionic Liquids (IL), and MW-assisted fusion followed by solid phase extraction, are being applied as innovative technologies in the extraction and recovery steps.

WP5: Production of metal, carbides, and metal oxides

Evaluation of best set-up and experimental conditions for direct metal/carbide production from non-leached feedstocks and Scheelite raw material, and Plasma

Tantalum (Ta) and niobium (Nb) containing alloy powders for application in additive manufacturing

Paper written by Ilka Kaczmarek, Markus Weinmann, Melanie Stenzel and Christoph Schnitter, TANIÖBIS GmbH (formerly H.C. Starck Tantalum and Niobium GmbH), Im Schleeke 78-91, 38642 Goslar, Germany. First published in the *International Journal of Powder Metallurgy*, Volume 55, No. 4, 2019, and MPIF proceedings of the 2019 Conference on Additive Manufacturing with Powder at <https://www.mpif.org/About/IndustryAwards/MetalAdditiveManufacturingOutstandingTechnicalPaperAward.aspx>. All views and opinions in this article are those of the author and not the T.I.C.



Additive Manufacturing (AM) opens new opportunities for producing parts with complex geometries and designs that cannot be realized by subtractive machining. While AM enlarges the scope of manufacturing possibilities, the intrinsic properties of the materials applied can limit the range of accessible applications. In this context, Ta and Nb, as well as new Ta- and Nb-based alloy powders, can serve special fields of application, e.g., chemical processing, superconductors, energy, or high-temperature environments. Moreover, additively manufactured Ta/Nb-containing alloys are a promising alternative for optimization of mechanical and biological performance parameters in medical implants. The present paper gives an overview of the development of pure Ta, Nb, and Ta/Nb-containing alloy powders that have been specifically designed for application in AM processes. It is shown how spherical powders of this category are produced, optimized, and AM built in test geometries as well as for selected application-oriented complex parts. Mechanical parameters of built specimens obtained from selected prealloyed powders are discussed. Studies on the microstructure, chemical composition, and phase composition of the respective built parts are described and examples of applications provided that can derive future benefit of those materials.

Introduction

Additive Manufacturing (AM) processes such as laser beam or electron beam Powder-Bed-Fusion (PBF-LB or PBF-EB), and Directed Energy Deposition (DED), enable production of parts with a high degree in freedom of design allowing e.g., topology optimization, or complex structures that open new opportunities in wide range of applications.^{1,2} In addition to the fact that the AM process allows the creation of new designs that are not realizable by subtractive manufacturing, the materials applied can contribute further with their intrinsic properties to optimize mechanical, biological, or chemical parameters of AM parts.^{3,4} While the metal AM material landscape is still mainly dominated by steel or titanium alloys with applications being limited by their intrinsic material properties, new material candidates can further expand the scope of AM technology.^{5,6}

Tantalum and niobium are characterized by high melting points, superior corrosion resistance,⁷ superconductivity,⁸ and a high level of biocompatibility.⁹ Moreover, they are β -phase stabilizers in Ti alloys. These properties make them interesting candidates for applications such as biomedical implants, superconductors, high temperature components (e.g. engine parts), or parts for the chemical processing industry.¹⁰⁻¹² While Ta/Nb and their alloys are already applied in many of these industries, the combination of their properties with the freedom of design offered by AM processing technologies is of vital importance for the realization of new and optimized solutions. Moreover, applying AM processes for Ta/Nb materials is also beneficial for cost aspects as, for example, the number of parts for assembly can be reduced by AM, or the performance of parts can be optimized due to the realization of more complex structures and geometries. Accordingly, a major field of research activity to push existing performance beyond current boundaries has been developed for Ta/Nb-containing alloys.¹³⁻¹⁵ The key to exploit the potential of these materials in AM is the development of pure elemental or prealloyed powders that are characterized by high flowability due to optimized morphology (spherical and dense particles), suitable Particle-Size-Distribution (PSD), a low oxygen content, and a homogenous chemical composition.

Powder production and powder properties

Production process and powder morphology

Due to the high melting points of tantalum (3,017 °C) and niobium (2,477 °C), the production of spherical powders via atomization of molten metals is challenging. A suitable approach is via Electrode Induction-Melting Gas Atomization (EIGA). This crucible-free process involves melting of a suitable electrode (pure metal or prealloyed) by induction. The melt is then passed through a specifically designed nozzle and disrupted by a high-velocity argon stream to atomize the melt. The droplets of the molten metal minimize their surface energy by developing

a spherical shape. Upon passing the atomization tower they solidify forming spherical particles. This spherical shape is a major requirement in AM technology as it leads to excellent flowability. The latter is of vital importance for powder-bed-fusion processes, as it affects the feeding behavior in layer deposition and directly impacts layer quality such as uniformity of the raked layer.¹⁶ Non-spherical particles are more likely to interlock mechanically and entangle due to shape irregularity, which can adversely impact powder flow during deposition.¹⁷ The quality of the deposited layers affects the quality of printed parts substantially as it can cause lack of fusion if particles are not uniformly distributed due to gaps in the powder bed. Moreover, the density of the particles is of utmost importance as hollow particles could more easily introduce gas pores and thus lead to undesired voids in the built parts that represent defect locations and can induce mechanical failures.

TANIOBIS GmbH (formerly H.C. Starck Tantalum and Niobium GmbH) recently developed a new powder product line for application in AM under the brand name of AMtrinsic[®] that focuses on the development and production of pure Ta/Nb spherical powders as well as spherical alloy powders (also extending to complex multinary or High-Entropy Alloys (HEA)) that contain those metals. The Scanning Electron Microscope images (SEM) displayed in Figure 1 indicates that the particles of elemental niobium powder obtained by the EIGA process are perfectly spherical and their surfaces are smooth without visible cracks or other faults. Furthermore, the polished cross-section of the Nb powder particles shown in Figure 1b indicates full density in all particles without any critical voids that might lead to a lack of fusion in AM processes. Figure 2 shows that comparable results regarding morphology were achieved for a binary Ti-42Nb (42 wt% Nb) alloy despite the high melting point difference of the two elements, as well as for a binary Ta-10W (10 wt% W) alloy that is challenging due to its very high melting point. Such alloys are produced by using a prealloyed rod as the electrode in the EIGA process.

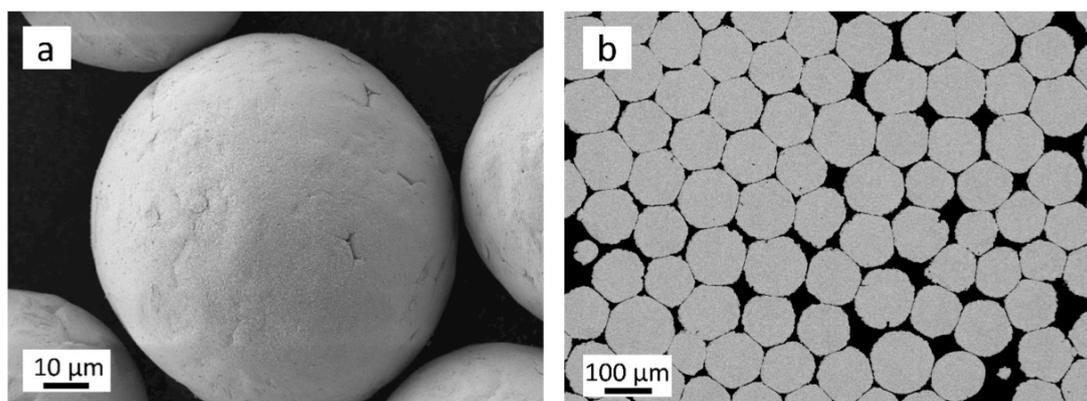


Figure 1. SEM images of AMtrinsic[®] Nb powder particles obtained by EIGA including a polished cross-section (b) displaying dense morphology of powders with no trace of voids or cracks.

Particle size distribution (PSD)

Besides the morphology and density, the particle size distribution (PSD) is an important factor determining the quality of AM parts. The PSD can be adjusted by varying among others the gas flow rate, shape of the atomization nozzle, and energy (current and frequency) applied during EIGA; directly influencing the melt flow rate in the production process.

A balanced particle size distribution results in a better packing density as small particles can fill voids between larger ones. A narrow distribution results in a higher uniformity in the melt pool, which is mandatory in achieving a high part density.¹⁸

Figure 3 shows a PSD diagram of a Ti42Nb alloy powder that has been classified to the required distribution ranges for the different AM technologies such as PBF-LB (< 63 µm), PBF-EB (63–100 µm) or DED (> 100 µm). For all fractions, the PSD is uniform and narrow. Further optimization of the individual powder fractions was achieved by a sifting step to remove very fine particles <10 µm or <15 µm. These adversely impact flow properties due to interlocking effects of particles in the powder bed, resulting in a lack of fusion in powder-bed-fusion processes. Moreover, very fine particles can impose a major risk in processing as they are easily flammable due to their high surface to volume ratio.

SEM investigations reflect the results of the optimization by removing fines. Figure 4 displays SEM images of AMtrinsic[®] Ti-42Nb powder < 63 µm at 100x and 1000x magnifications, before and after sifting. The majority of the particles (Figure 4(a)) possess a perfectly spherical shape. Figure 4(b), which is of the same powder at a magnification of 1000x, clearly shows that the particles have a very smooth surface with few satellites. In Figure 4 (b) it is apparent that particles with diameters < 15 µm are still present.

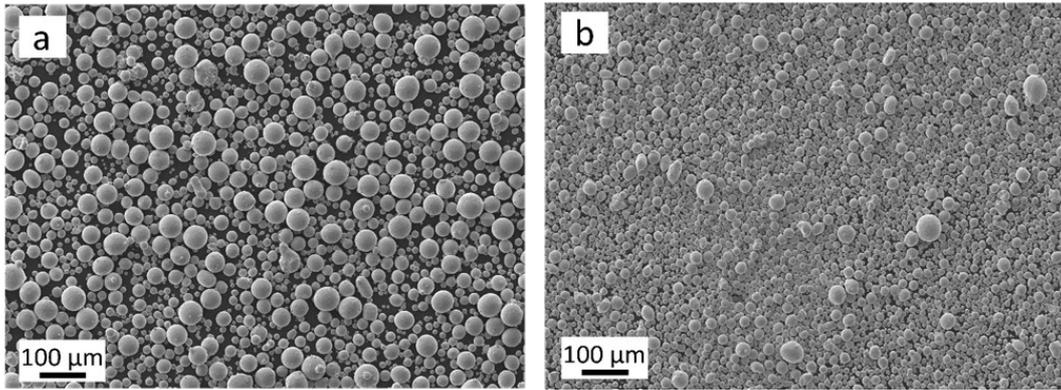


Figure 2. SEM images of AMtrinsic® Ti-42Nb (a) and Ta-10W (b) powder particles obtained by EIGA

Figure 4(c) shows a micrograph of the sifted powder at a magnification of 100x. At this magnification, the powder appears very similar to the raw powder shown in Figure 4(a). However, at a magnification of 1000x it is apparent that the number of fine particles, especially those attached to larger particles, has clearly been reduced.¹⁹

These results are very promising. A minimum number of fine particles that are attached to larger powder particles is an important prerequisite for optimal flowing behaviour in AM processes. Furthermore, a large number of satellites on the surface of larger particles formed by coalescence could negatively impact powder flowability, as they can result in friction and interlocking effects such as observed for irregularly shaped powders.

These effects can create voids that represent predetermined breaking points in AM parts. Hence, the morphology of the Ti42Nb powder, with negligible satellite formation, and the removal of fine particles by means of sifting allow excellent flow properties to be achieved.

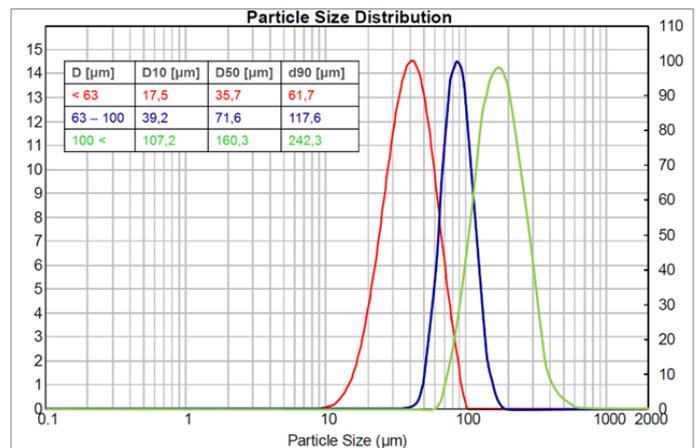


Figure 3. Relative PSD of AMtrinsic® Ti42Nb alloy after sifting and fractionizing to < 63 µm, 63 – 100 µm and > 100 µm

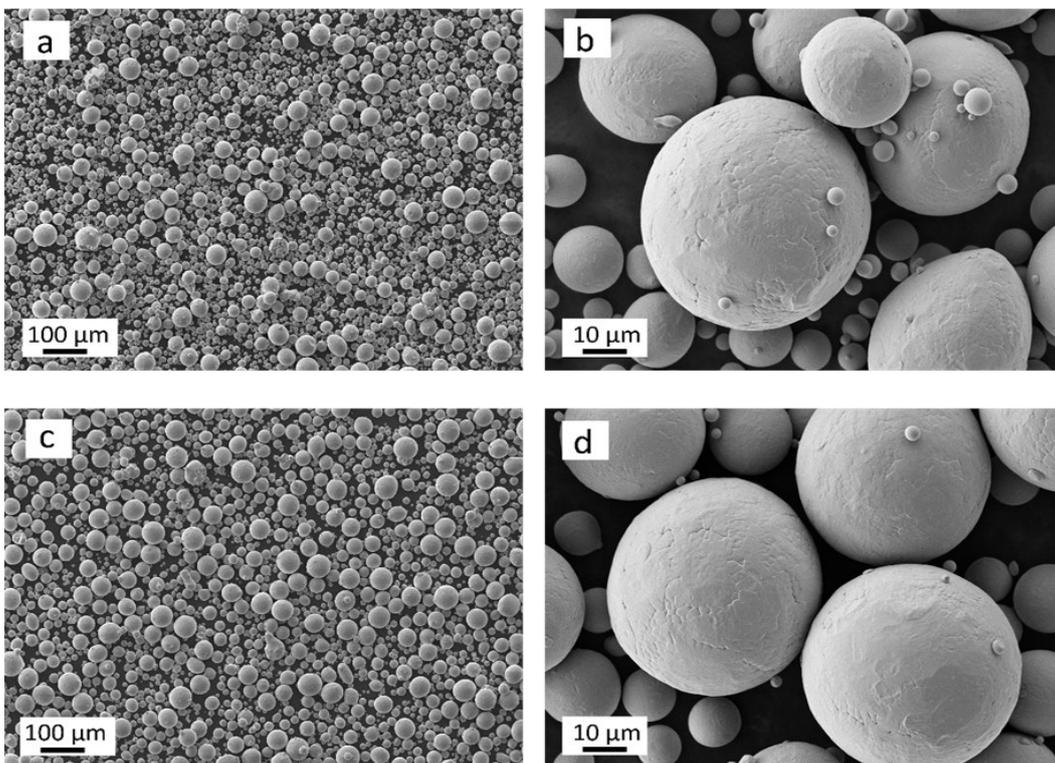


Figure 4. SEM images of AMtrinsic® Ti-42Nb powder < 63 µm as-obtained (a, b) and after sifting (c, d) at 100x (a, c) and 1000x (b, d) magnification

Oxygen content

In addition to the particle morphology and PSD, the oxygen content of powders applied in powder-bed-fusion processes plays an important role, as dissolved oxygen can adversely impact the quality and mechanical properties of built parts. Effective melting can be impeded as a large amount of oxide on the particle surface can alter flowability, with a higher risk for lack of fusion and pores due to voids in the powder bed. Oxide film layers can also decrease wettability and block molten metal flow, which can result in poor bonding between layers and can cause fusion defects.^{5,20} Several studies, especially for Ti-6Al-4V, steel, and nickel alloys found oxygen levels of powders to rise progressively with increasing reuse. This is especially critical for materials that are highly reactive with oxygen at process temperatures.^{21–23} The reusability of powder in powder-bed-based processes can directly impact the production yield and affect the costs of additively manufactured parts. If the oxygen content in the powder exceeds a predefined value after a certain number of builds, the remaining powder needs to be discarded.

Therefore, low oxygen content in the virgin powder is of high importance. A lower oxygen content can prevent an adverse impact on the mechanical properties of AM parts and can increase the number of build cycles that can be achieved before the powder properties exceed maximum tolerance limits caused by oxygen enrichment during the process. Moreover, for specific applications, such as superconducting parts, low oxygen content is indispensable to achieve critical performance parameters such as a high Residual Resistance Ratio (RRR). Deoxidation processes are applied to reduce the oxygen content in powders. The effect of deoxidation is shown in Table I by the example of a pure, spherical niobium powder. Significant oxygen reduction was achieved in all fractions (PBF-LB, PBF-EB, and DED) compared with the as-produced powders. The applied reduction process is available on an industrial scale. Moreover, the use of deoxidation can open new fields in recycling processes, where powders are not only recycled physically (readjustment of PSD, morphology) but also chemically (reduction of oxygen).

Material	Fraction (μm)	O (ppm) as-obtained	O (ppm) after deoxidation
AMtrinsic [®] Nb, DED	105-150	1512	171
AMtrinsic [®] Nb, PBF-EB	63-105	1716	268
AMtrinsic [®] Nb, PBF-LB	<63	2038	247

Table 1: Oxygen content of spherical AMtrinsic[®] Nb powder before and after deoxidation

Besides the positive impact on the oxygen content the deoxidation process can further improve powder morphologies. Due to the subsequent leaching process to remove the deoxidation agent and reaction products, satellites can be removed that are not strongly attached to larger particles. Furthermore, remaining fine particles are removed. This improves the flowability of the powder as it prevents particles interlocking during the feeding processes. Figures 5(a) and (b) show the positive effect of deoxidation processes on particle morphology. They also prove that the spherical shape of the particles is conserved in the deoxidation process.

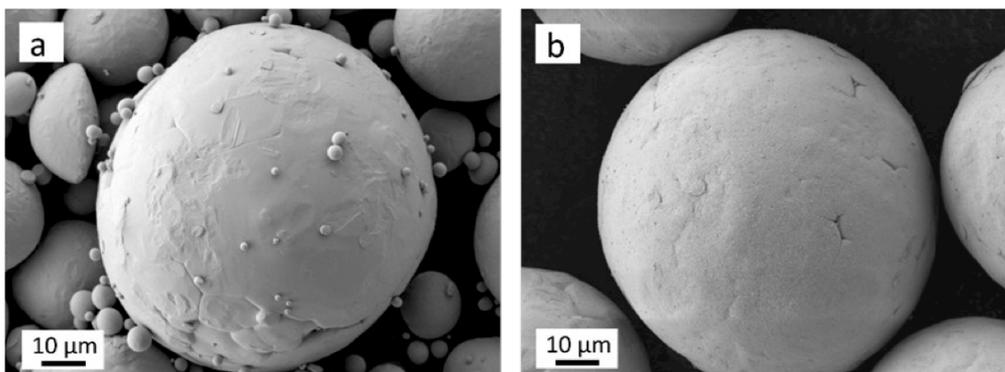


Figure 5. SEM images of spherical AMtrinsic[®] Nb powder before (a) and after deoxidation (b)

Element distribution in alloys

The chemical composition of materials is also of utmost importance as it directly translates into the AM part and impacts its mechanical and chemical properties. For high-content Ta/Nb-containing alloys (multinary or high-entropy alloys) the achievement of the desired chemical composition and required homogeneity is a major challenge. This target may become complicated for alloys in which the constituent elements have substantially different melting points, as there is a high risk of demixing, or losses by evaporation of elements during atomization.

A representative Energy Dispersive X-ray spectrometer map (EDX) of the polished cross-section of a prealloyed AMtrinsic® Ti-42Nb particle (<63 μm) is displayed in Figure 6, indicating inhomogeneous element distribution, i.e., a dendritic segregation into Ti-rich and Nb-rich regions, displayed in red and blue, respectively.

Pores or voids within the particle are not observed. The maximum chemical fluctuation within the as-atomized particle is in the range Ti32Nb (spot 2) and Ti47Nb (spot 3).²⁴ The overall composition (spot 1) is Ti42Nb. It will be shown, however, that after the application of laser-beam melting this dendritic structure transforms into a homogeneous glass-like morphology, caused by very high cooling rates. Various publications which investigate Ti-rich Ti/Nb alloy compositions reveal a cooling-rate-dependent microstructure formation for Ti/Nb alloys.^{25–28} A similar effect has been observed for a Nb-rich alloy by Weinmann et al.²⁴ revealing that the cooling rate (slow cooling vs. rapid cooling) also influences the microstructure for Nb-rich Ti/Nb alloys. It was shown for the Ti42Nb alloy that fast cooling results in glass-like morphologies, whereas slow cooling results in formation of dendritic structures like those found in the powder particles.²⁴ It is therefore important to study the chemical composition in the AM part where the powder particles are again exposed to the melting process by the laser energy with subsequent cooling. This melting and cooling directly impacts the elemental distribution in the built part.

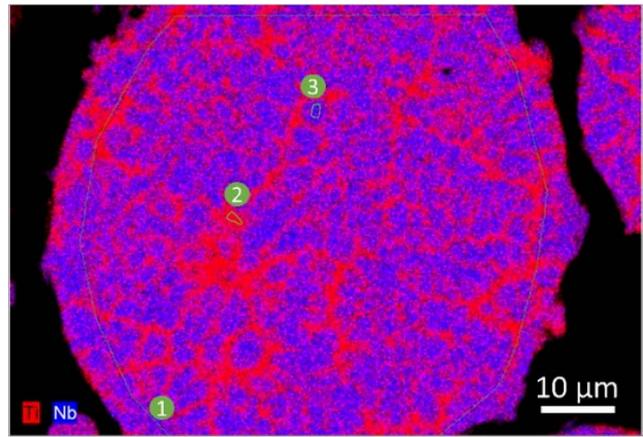


Figure 6. EDX mapping of a Ti-42Nb particle showing two distinct Ti and Nb-rich regions

A similar effect has been observed for a Nb-rich alloy by Weinmann et al.²⁴ revealing that the cooling rate (slow cooling vs. rapid cooling) also influences the microstructure for Nb-rich Ti/Nb alloys. It was shown for the Ti42Nb alloy that fast cooling results in glass-like morphologies, whereas slow cooling results in formation of dendritic structures like those found in the powder particles.²⁴ It is therefore important to study the chemical composition in the AM part where the powder particles are again exposed to the melting process by the laser energy with subsequent cooling. This melting and cooling directly impacts the elemental distribution in the built part.

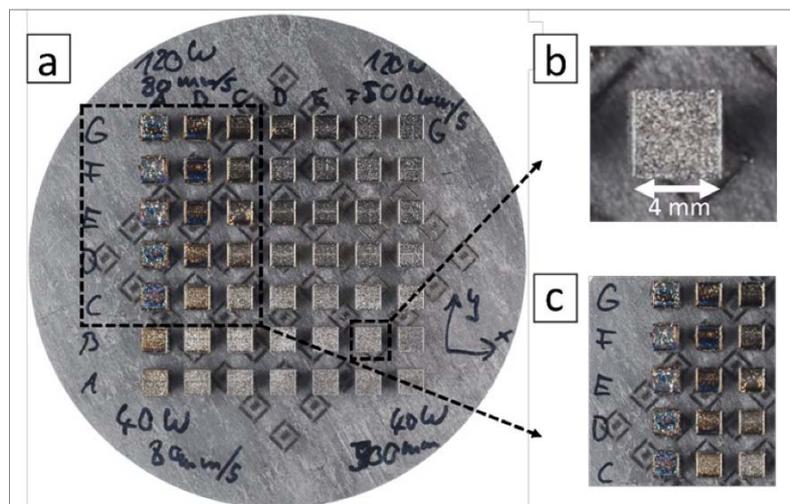


Figure 7. Experimental set-up for PBF-LB build test using Ti-42 Nb powder. The magnified images showing examples of (a) an optimum printing parameter set leading to a highly dense sample and (b) those indicating overheating effects.

PBF-LB of Ti/Nb/(Ta) alloys

The investigation of chemical and mechanical properties of AM parts is of relevance for the determination of the applicability of related powders and their potential scope of application. To study these, AMtrinsic® Ti-42Nb powder (fraction < 63 μm) was used to build parts via PBF-LB using TruPrint 1000 equipment. All build operations were performed in an Ar atmosphere to minimize process-caused oxygen pick-up. Build parameters were determined empirically by systematic variation of all relevant process parameters. For example, laser power, scan speed, hatch spacing, and powder-bed-layer thickness. The spot width of the laser applied was 55 μm. In total, 160 test specimens with dimensions 4 × 4 × 4 mm³ were investigated.

Specimens (Figure 7(a)) were built applying a hatch of 100 μm, a powder-layer thickness of 50 μm, at variable laser power (40–120 W) and scan speed (80–500 mm/s). Proper densification occurs at 50 W laser power, and a scan speed of 400 mm/s. After removal of the as-built cubes from the Nb build plate their density was qualitatively evaluated by light microscopy. Additionally, SEM/EDX investigations were performed for selected specimens. Such a specimen is shown in Figure 7(b) at higher magnification. It has relatively smooth surfaces and sharp edges. It also shows no effect of overheating unlike the printed specimen in the upper left section of the test assembly shown at higher magnification in Figure 7(c).²⁴

Microstructure of as-built specimen

To judge the quality of the specimen a detailed investigation of the microstructure is required. Figure 8 shows the results of the corresponding SEM/EDX studies of the selected cube. It was structurally investigated as-built. Post heat treatments such as diffusion annealing to reduce internal stresses or hot isostatic pressing to remove closed pores were not applied. The SEM photomicrograph indicates a very homogeneous microstructure with only minor pores identified. Based on these results, the density can be visually estimated at >99.9%. The EDX reveals that the elemental distribution in the as-built specimen has been transformed during the application of laser melting. In contrast to the EDX analysis of the spherical AMtrinsic[®] Ti-42Nb particles displayed in Figure 6, it appears that the constituent elements Ti and Nb are now dispersed homogeneously on a sub-micrometer scale.

From this analysis it is evident that the initial dendritic microstructure of the precursor powder completely vanishes during the AM process. This effect is assumed to be the result of the very high cooling rates, between 10^4 K/s and 10^6 K/s, that are achieved during laser melting.²⁹ This points to the fact that under the applied experimental conditions, the melt generated by the laser, rapidly cools in the PBF-LB process. Accordingly, local de-mixing with formation of dendritic structures, as observed for the slowly cooled melt (see Figure 6), is inhibited.²⁴ The white arrows in the EDX image displayed in Figure 8 highlight probable grain boundaries in the as-built specimen, which go along with weak chemical fluctuations or eventually the appearance of Ti/Nb phases other than β , which are, however, not shown in XRD analysis (see Figure 15). Further examination of this issue is underway.

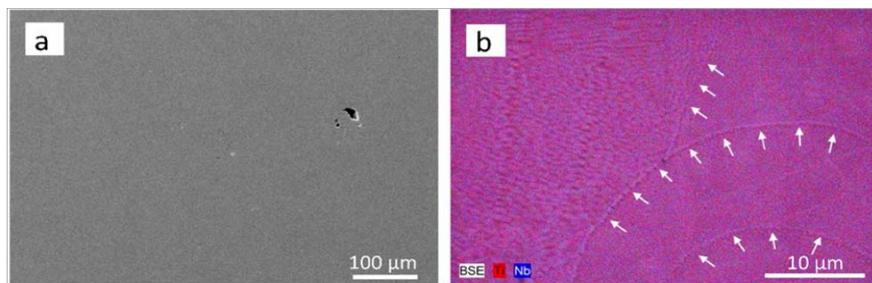


Figure 8. SEM and EDX investigations of the Ti-42Nb sample shown in figure 7 (b) at 200x and 3000x magnification, respectively

Figure 9(a) suggests that similar results i.e., homogeneous element distribution in PBF-LB built specimens are obtained for ternary TiNbTa alloy powders. Figure 9(a) confirms the excellent homogeneity in distribution of the elements. The exactly overlapping EDX spectra (9(b)) indicate a similar composition in the various spots examined. These results are promising as they prove that chemical compositions in AM parts can be defined and controlled and that special alloy compositions and their intrinsic properties can be translated into the as-built geometries.

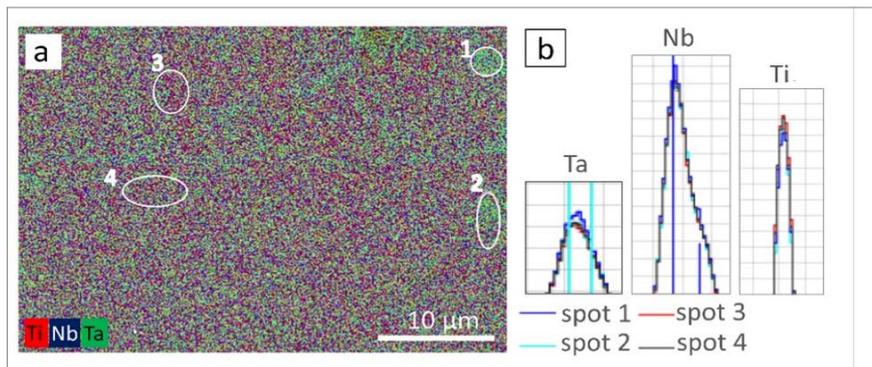


Figure 9. EDX investigations of TiNbTa sample obtained by PBF-LB processing

Mechanical properties of PBF-LB built specimens

The mechanical characteristics of AM parts are of major importance, since they determine the potential of materials applied in AM. In this study, compressive modulus, elastic modulus, and strength values have been determined for AM processed specimens made from AMtrinsic[®] Ti-42Nb powder. In a first approach, the compression test specimens shown in Figure 10 were built. Figure 10 displays a set of compression test specimens built on a Nb build plate, which are spatially separated from the build plate by 1.5-mm thick support structures. The built cylinders (without support structures) had dimensions of $d \times l = 10.7 \text{ mm} \times 16 \text{ mm}$. After removal from the build plate they were machined to $d \times l = 6.9 \text{ mm} \times 10.35 \text{ mm}$ ($d : h = 1.5$) for further testing in a compression creep test according to DIN 50106. The applied stress of $\sigma_{\max}(d_0) = 1.2 \text{ GPa}$, was increased at a rate of 30 MPa/min.

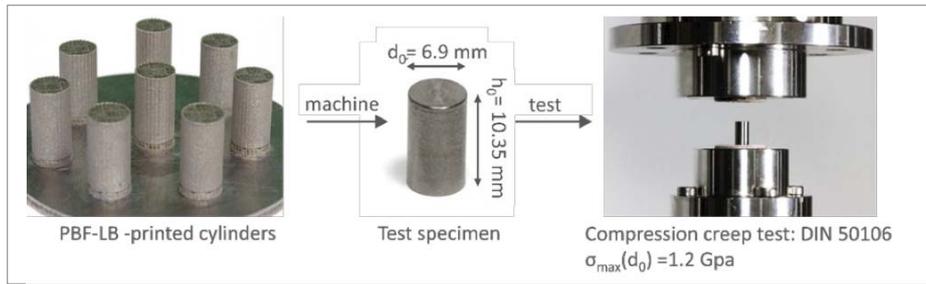


Figure 10. Compression test set of Ti-42Nb PBF-LB built specimens

Compression of the cylinders was on average 1.34 mm while the diameter increased by 0.71 mm at the widest position. The results of the compression test are displayed in Figure 11. The compressive moduli K for three samples tested were determined from the stress/strain curve to be 55.0 GPa, 63.0 GPa and 64.5 GPa.²⁴ The compressive modulus of the Ti42Nb is hence significantly lower than for Ti-6Al-4V, which is one of the most commonly applied materials in AM. Due to the Poisson's ratio (ν) of approx. 0.33 for Ti alloys such as Ti-6Al-4V or Ti/Nb alloys, the compressive modulus can be taken as a close reference for the E-modulus of the material as for this evaluation the following equation can be applied:

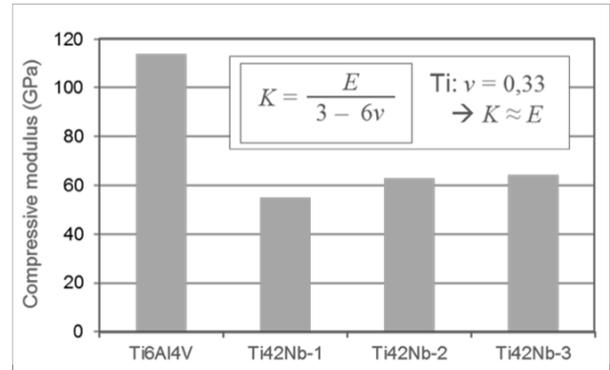


Figure 11. Compression test results of Ti-42Nb PBF-LB built specimens

$$K = \frac{E}{3 - 6\nu} = K = \frac{E}{3 - 6 \cdot 0,33} \text{ with } K \approx E$$

The E-moduli of Ti-6Al-4V and titanium are about 112 GPa and 104 GPa, respectively.³⁰ The results of the compression test reveal that the Ti42Nb alloy has a higher ductility and higher elasticity compared with Ti-6Al-4V and pure Ti.

For further characterization of the properties of the PBF-LB processed Ti42Nb, tensile tests were also performed to determine strength values and validate the measured elasticity values from the compression tests. Tensile test specimens with as-built dimensions of $d \times h = 15 \text{ mm} \times 70 \text{ mm}$ were obtained by PBF-LB processing (Figure 12a) and machined to tensile test specimen dimensions according to ISO 6892-1 (Figure 12(b)).



Figure 12. Tensile test set of Ti-42Nb PBF-LB built specimens fabricated by Laser Zentrum Hannover

For the PBF-LB processed Ti42Nb tensile specimens, an average Young's modulus of $E = 61 \pm 3.7 \text{ GPa}$ was determined. The proof strength at 0.2% plastic extension $\sigma_{0.2}$ was measured as $673.7 \pm 24.8 \text{ MPa}$ from the stress-strain curves. Due to the lack of distinct yield strength, the point of the 0.2% plastic elongation was chosen to switch the applied strain rate from $\dot{\epsilon}_1 (0.00025 \text{ S}^{-1})$ to $\dot{\epsilon}_2 (0.0067 \text{ S}^{-1})$ for determination of the ultimate tensile strength (UTS) in the plastic region of the material. An ultimate strength of $680.4 \pm 15.9 \text{ MPa}$ was observed in the tensile tests. Fracture strength was $380 \text{ MPa} \pm 29.1 \text{ MPa}$ and the maximum elongation was determined to be $10.8 \pm 1.9\%$.¹⁹ These results confirmed the high elasticity of the material measured in the compression testing. Moreover, the tensile strength test revealed that the material shows a very good combination of strength and ductility even without post processing such as diffusion annealing or hot isostatic pressing.

To investigate the fracture behaviour of the material, SEM photomicrographs of fracture surfaces of tension-tested Ti42Nb were evaluated. The SEM photomicrographs indicate a fracture appearance typical of ductile materials with a “cup-and-cone” structure (Figure 14 (b) and (c)).¹⁹ The fact that the material is not showing any brittle behaviour is of special importance to achieve good mechanical values in as-built AM parts. The high ductility of the material was also indicated by a significant necking from 6.0 mm to about 3.6 mm, corresponding to a 60% reduction in area of the initial cross-section. These ductile material properties are also reflected in the high elongation value of >10%.

The high ductility of the material is advantageous for applications as the AM parts can stand a higher stress tolerance. Thus, the mechanical properties that have been determined are very promising as they open new opportunities; for example, in the field of biomedical implant materials. The combination of high elasticity indicated by the low E-modulus of around 60 GPa and the good strength values of around 673 MPa make the Ti42Nb material a good candidate for patient-specific implants manufactured via AM technology. Ti alloys are already widely used implant materials with sufficient biocompatibility. However, as generally used, Ti materials or alloys possess relatively high elastic moduli and they may cause stress-shielding and associated implant loosening due to a mismatch of elasticity between the implant material and human bone.^{31,32,33}

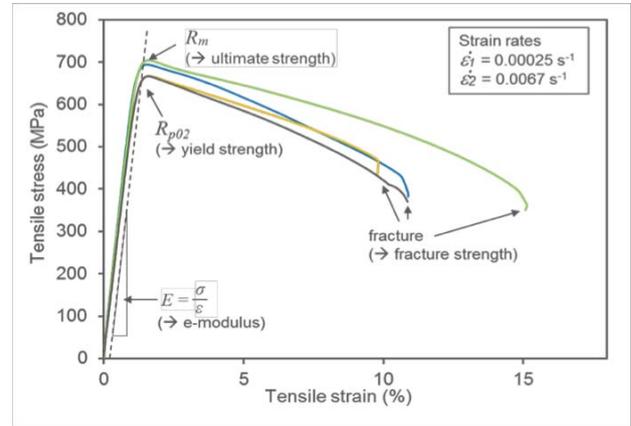


Figure 13. Tensile test results of different Ti-42Nb PBF-LB built specimens (indicated by different colour code)

The as-built Ti42Nb AM material exhibits an elastic modulus much closer to that of the human bone compared with those produced from standard Ti alloys, and can thus improve implant longevity. Besides its promising mechanical values, previous studies also have shown that PBF-LB AM parts made from AMtrinsic[®] Ti-42Nb powder are characterized by superior biological compatibility, with better cell viability for fibroblasts and osteoblasts than those made from standard Ti-6Al-4V alloys.³⁴

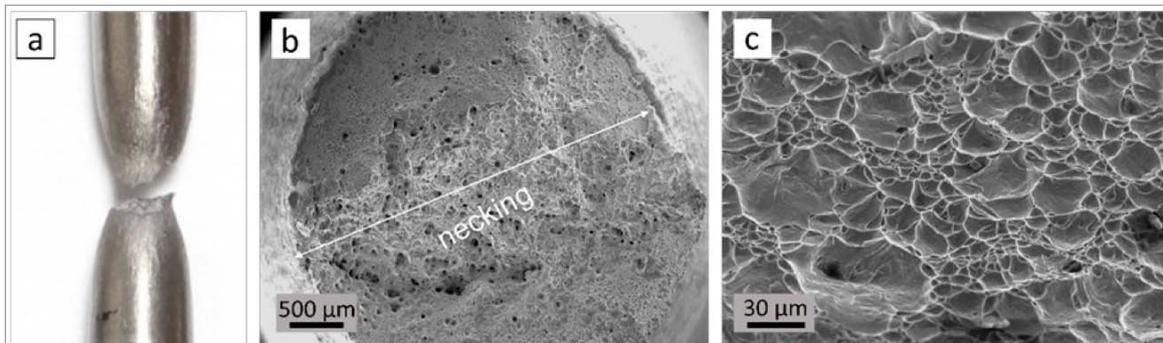


Figure 14. (a) Ti-42Nb tensile test specimen after fracture and (b, c) showing the SEM images of the fractured surface¹⁹

Phase composition of Ta/Nb-containing spherical powders for AM

The good mechanical properties that have been revealed by compression- and tension-strength testing can be also explained by the phase composition of the respective materials. Conventional Ti-6Al-4V crystallizes in a mixture of α and β phase while CP titanium crystallizes hexagonally as α phase. These phases lead to sufficient strength of the materials but also cause lower elasticity. By the addition of Nb or/and Ta, the β -phase can be stabilized. Such compositions crystallize entirely in the body-centered-cubic phase. This β -phase leads to a higher elasticity of the material at higher strength values than pure titanium. Due to this effect, β -phase materials are a primary focus of research for new, ductile materials. The X-ray diffraction analyses shown in Figure 15 show that spherical AMtrinsic[®] Nb and Ti-42Nb powders crystallize in the pure β phase with no indication for the presence of α -, α' -, or ω -phase, as reported for example for Ti/Nb alloys with higher Ti content.³⁵ The diffraction patterns for both, AMtrinsic[®] Nb and Ti-42Nb powders, are very similar. Due to the statistical replacement of Nb atoms (145 pm) with smaller Ti atoms (140 pm), the positions of the reflections of Ti42Nb powders are shifted to higher 2θ values compared with those of pure bcc Nb. Furthermore, the XRD analyses show that several investigated TiNbTa powders with varying compositions, crystallize either in pure β -phase or complex mixtures of several phases with no α phase. Due to this phase composition these materials are also expected to show good mechanical properties with high elasticity at high strength, and are suitable for applications such as biomedical implants.

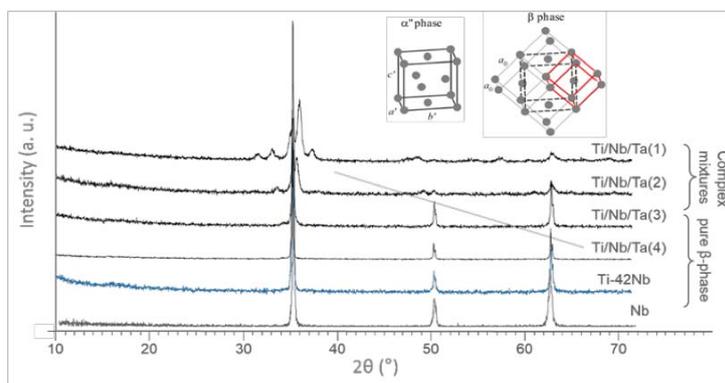


Figure 15. XRD analyses of AMtrinsic[®] Nb, Ti-42Nb and TiNbTa alloy powders



Figure 16. An example of PBF-LB processing of AMtrinsic[®] Ta powders for printing of rocket thruster with integrated cooling channels fabricated by Alloyed.

Application example for spherical Nb and Ta powders

To judge the suitability of a powder in AM applications, the transition to the production of application-relevant structures and geometries is of utmost importance. Niobium, because of its superconducting properties is the material of choice for superconductor applications. While geometries have, until now, been limited by the boundaries of subtractive manufacturing, the application of niobium powder in AM opens new opportunities in this specific field. A build parameter investigation carried out by CERN using spherical AMtrinsic[®] niobium powder has shown that over a broad processing window, samples with full density can be achieved.³⁶ The flexibility in the process window is an important aspect for reproducibility and productivity for future production on an industrial scale. The good build behavior of Nb powder was also demonstrated by building of complex structures such as cavities and Higher Order Mode (HOM) couplers which could provide new and high-performance solutions for future particle accelerator projects.³⁶

Tantalum exhibiting outstanding properties such as high strength, high ductility, excellent corrosion and heat resistance as well as biocompatibility offers unique profits for applications in aerospace, medical, nuclear, and chemical industries. AMtrinsic[®] Ta powders developed by TANI OBIS GmbH meet the requirements of AM processes i.e. sphericity, excellent flowability and high purity. In collaboration with Alloyed, processability of Ta spherical powders via PBF-LB was examined. After elaborate design and process optimization, 3D-printed parts with the highest degree of density and purity were obtained even in very complex geometries including fine feature. An example of such geometric fidelity can be seen in Figure 16 showing a PBF-LB -printed rocket thruster with its integrated cooling channels, could be easily featured by AM technology. The unique properties of Nb and Ta powders and alloys in combination with their excellent processability with AM technology is indicating their great potential to be widely exploited in various high-tech applications.

Conclusion

This paper gives an overview of pure and Ta/Nb-containing alloy powders that have been adjusted to the specific requirements of AM applications. Decisive parameters such as powder morphology, PSD, microstructure, oxygen content, as well as phase compositions have been investigated. It has been proven that the EIGA process can produce perfectly spherical powders despite the high melting point of the materials.

The application of an appropriate deoxidation process allows the production of powders with a very low oxygen content, which is beneficial for the mechanical parameters of as-built parts as well as for extending the number of printing cycles that can be realized with one powder batch. It has been further shown that for Ta/Nb-containing alloys homogeneous elemental distributions can be achieved in the powders and in the printed parts. Ti42Nb and ternary Ti/Nb/Ta alloys can be built with a broad process window to achieve dense structures. Due to the high cooling rates in PBF-LB processing, dendritic structures initially present in powder particles vanish, resulting in a fully homogeneous elemental distribution in built parts. Phase analysis by means of XRD has proven that Ti-based Ta/Nb-containing alloys crystallize either with the β -phase structure, i.e., a body-centered-cubic structure, or in complex mixtures of α' , α'' , ω , and β -phase, resulting in materials with high ductility and elasticity. This aspect makes Ti/Nb/(Ta) alloys promising candidates; for example, in biomedical applications.

In addition, the application example of Nb in superconductor part manufacturing using AM shows that the introduction of the materials in application-relevant fields has already been started. To realize the full potential that Ta/Nb and alloys containing these metals offer, further investigation and a more extensive understanding of these materials is intended. The mechanical test results discussed for PBF-LB built parts have been investigated for “as-built” structures. Investigation is required to determine how post processing steps, such as diffusion annealing (to reduce internal stresses of built geometries), or hot isostatic pressing (to close pores in the parts), affect density and mechanical properties. Moreover, such an investigation is also extended towards Ta/Nb-containing materials in complex multinary and high-entropy alloy systems.

REFERENCES

1. S. Tofail, E. Koumoulos, A. Bandyopadhyay, S. Bose, L. O'Donoghue and C. Charitidis, “Additive Manufacturing: Scientific and Technological Challenges, Market Uptake and Opportunities”, *Mater. Today*, 2017, vol. 21, no.1, pp. 22–37.
2. Y. Zhang, L. Wu, X. Guo, S. Kane, Y. Deng, Y. Jung, J. Lee and J. Zhang, “Manufacturing of Metallic Materials: A Review”, *J. of Mater. Eng. Perf.*, 2018, vol. 27, no. 1, pp. 1–13.
3. L. Murr, “Additive manufacturing of biomedical devices: an overview”, *Mater. Tech.*, 2017, vol. 33, no. 5, pp. 1–14.
4. J. Markhoff, M. Weinmann, C. Schulze and R. Bader, “Influence of Different Grained Niobium and Ti-42Nb Powders and Pellets on Human Cell Viability”, *Mater. Sci. Eng.*, 2017, vol. 73, pp. 756–766.
5. S. Yung and C. Shin, “Additive Manufacturing of Ti6Al4V Alloy: A Review”, *Mater. Design*, 2019, vol. 164.
6. X. Niu, S. Singh, A. Garg, H. Singh, B. Panda, X. Peng and Q. Zhang, “Review of Materials Used in Laser-Aided Additive Manufacturing Processes to Produce Metallic Products”, *Frontiers of Mechanical Engineering*, 2018, vol. 14, no. 3, pp. 282–298.
7. S.M. Cardonne, P. Kumar, C.A. Michaluk and H.D. Schwartz, “Tantalum and its Alloys”, *Int. J. of Refract. Met. Hard Mater.*, 1995, vol. 13, no. 4, pp. 187–191, 193–194.
8. D.K. Finnemore, T.F. Stromberg, and C. Swenson, “Superconducting Properties of High-Purity Niobium”, *Swenson Phys. Rev.* 1966, vol. 149, no.1, pp. 231.
9. N. George and A.B. Nair, “Porous Tantalum: A New Biomaterial in Orthopedic Surgery”, *Fundamental Biomaterials: Metals*, compiled by P. Balakrishnan, M.S. Sreekala and S. Thomas, Woodhead Publishing Series in Biomaterials, Woodhead Publishing, Elsevier, London, UK, 2018, pp. 243–268.
10. C. Terrazas, “Fabrication and Characterization of High-Purity Niobium using Electron Beam Melting Additive Manufacturing Technology”, *Int. J. Adv. Man. Tech.*, 2016, vol. 84, no. 5–8, pp. 1,115–1,126.
11. A. Biesiekierskia, J. Wanga, M. Abdel, H. Gepreelb and C. Wena, “A New Look at Biomedical Ti-Based Shape Memory Alloys”, *Acta Biomater.*, 2012, vol. 8, no. 5, pp. 1,661–1,669.
12. E. Eisenbartha, D. Veltena, M. Müllera, R. Thullb and J. Brema, “Biocompatibility of β -stabilizing Elements of Titanium Alloys”, *Biomaterials*, 2004, vol. 25, no. 26, pp. 5,705–5,713.
13. V. Brailovski, S.D. Prokoshkin, M. Gauthier and K. Inaekyan, “Bulk and Porous Metastable beta Ti–Nb–Zr(Ta) Alloys for Biomedical Applications”, *Mater. Sci. Eng.: C*, 2011, vol. 31, no. 3, pp. 643–657.
14. S. Maiti and W. Steurer, “Structural-Disorder and its Effect on Mechanical Properties in Single-Phase TaNbHfZr High-Entropy Alloy”, *Acta Mater.*, 2016, vol. 106, March 2016, pp. 87–97.
15. Z. Wang, S. Guo and C.T. Liu, “Phase Selection in High-Entropy Alloys: From Nonequilibrium to Equilibrium”, *JOM*, 2014, vol. 66, no. 10, pp. 1,966–1,972.
16. A. Riou, “Powders for Additive Manufacturing”, *World PM*, 2016.
17. C. Pleass and S. Jothi, “Influence of Powder Characteristics and Additive Manufacturing Process Parameters on the Microstructure and Mechanical Behaviour of Inconel 625 Fabricated by Selective Laser Melting”, *Add. Manuf.*, 2018, vol. 24, December 2018, pp. 419–431.
18. S. Dietrich, M. Wunderer, A. Huissel and M. Zaeh, “A new approach for a flexible powder production for additive manufacturing”, *Procedia Manuf.* vol. 6, pp. 88–95.
19. C. Schulze, M. Weinmann, Ch. Schweigel, O. Keßler and R. Bader, “Mechanical Properties of a Newly Additive Manufactured Implant Material Based on Ti-42Nb”, *Materials (Basel)*, 2018, vol. 11, no. 1, pp. 124–127.
20. B. Zhang, Y. Li and Q. Bai, “Defect Formation Mechanisms in Selective Laser Melting: A Review”, *Chinese J Mech. Eng.*, 2017, vol. 30, no. 3, pp. 515–527.
21. H.P. Tang, M. Qian, N. Liu, X.Z. Zhang and G.Y. Yang, “Effect of Powder Reuse Times on Additive Manufacturing of Ti-6Al-4V by Selective Electron Beam Melting”, *JOM*, 2015, vol. 67, no. 3, pp. 555–563.
22. B. Sartin, T. Pond, B. Griffith, W. Everhart, L. Elder, E. Wenski, C. Cook, D. Wieliczka, W. King, A. Rubenchik, S. Wu, B. Brown, C. Johnson and J. Crow, “316L Powder Reuse of Metal Additive Manufacturing”, *Proc. 28th Ann. Int. Solid Freeform Fab. Symposium*, 2017.
23. L. Grainger, “Investigating the effects of multiple powder re-use in AM”, <https://www.renishaw.com/en/blog-post-how-much-can-you-recycle-metal-additivemanufacturing-powder--38882>.
24. M. Weinmann, M.-Stenzel, C. Schnitter and J. Markhoff, “Development of Bio-Compatible Refractory Ti/Nb/(Ta) Alloys for Application in Patient-Specific Orthopaedic Implants”, *Int. J. Refract. Met. Hard Mater.*, 2018, vol. 75, September 2018, pp. 141–145.
25. C.R.M. Afonso, G.T. Aleixo and R. Caram, “Effects of Omega Phase on Elastic Modulus of Ti-Nb Alloys as a Function of Composition and Cooling Rate”, *Mat. Sci. Eng.*, 2007, vol. 27, pp. 908915.
26. Y. Al-Zain, H.Y. Kim, T. Koyano, H. Hosodac and S. Miyazaki, “A Comparative Study on the Effects of the w and a Phases on the Temperature Behavior of a Ti27Nb Alloy”, *Sripta Mater.*, 2015, vol. 103, pp. 37–40.
27. M. Bönsch, M. Calin, T. Waitz, A. Panigrahi, M. Zehetbauer, A. Gebert and W. Skrotzki, “Thermal Stability and Phase Transformations of Martensitic Ti-Nb Alloys”, *J. Sci. Technol. Adv. Mater.*, 2013, vol. 14, no. 5.
28. E.S.N. Lopes, A. Cremasco, C.R.M. Afonso and R. Caram, “Effects of Double Aging Heat Treatment on the Microstructure, Vickers Hardness and Elastic Modulus of Ti-Nb Alloys”, *Mat. Character.*, 2011, vol. 62, no. 7, pp. 673-680.
29. D. Herzog, V. Seyda, E. Wycisk and C. Emmelmann, “Additive Manufacturing of Metals”, *Acta Materialia*, 2016, vol. 117, pp. 371–392.
30. Y.L. Hao, S.J. Li, S.Y. Sun and R. Yang, “Effect of Zr and Sn on Young's Modulus and Superelasticity of Ti-Nb-Based Alloys”, *Mat. Sci. Eng.*, 2006, no. 441, no. 1–2, pp. 112–118.
31. B. Vandenbroucke and J. Kruth, “Selective Laser Melting of Biocompatible Metals...”, *Rapid Proto. J.*, 2007, vol. 13, no. 4, pp. 196–203.
32. L.A., Matlakhova, A.N. Matlakhov, S.N. Monteiro, S.G. Fedotov, and B.A. Goncharenko, “Properties and Structural Characteristics of Ti–Nb–Al Alloys”, *Mater. Sci. Eng. A*, 2005, vol. 393, no. 1–2, pp. 320–326.
33. D.R Sumner and J.O. Galante, “Determinants of Stress Shielding: Design Versus Materials Versus Interface”, *Clinical Orthopaedics and Related Research*, 1992, pp. 202–212.
34. J. Markhoff, M. Weinmann, C. Schulze and R. Bader, “Influence of Different Grained Niobium and Ti-42Nb Powders and Pellets on Human Cell Viability”, *Mater. Sci. Eng. C*, 2017, vol. 73, no. 73, pp. 756–766.
35. T. Ahmed and H.J. Rack, “Martensitic Transformations in Ti-(16–26 at%) Nb Alloys”, *J. Mater. Sci.*, 1996, vol. 31, no. 16, pp. 4,267–4,276.
36. R. Gerard, “Additive Manufacturing for RF and Superconducting RF Applications”, https://indico.lal.in2p3.fr/event/4990/contributions/16707/attachments/13620/16419/13DMetal_RF_Applications_at_CERN.pdf

Tantalum and niobium intellectual property update

This information is taken from the European Patent Office (www.epo.org) and similar institutions. Patents listed here were chosen because of their apparent relevance to tantalum and/or niobium. Some may be more relevant than others. Note that European patent applications that are published with a search report are 'A1', while those without a search report are 'A2'. When a patent is granted, it is published as a B document. Disclaimer: This document is for general information only and no liability whatsoever is accepted. The T.I.C. makes no claim as to the accuracy or completeness of the information herein.

Title	Applicant(s)	Publication date
-------	--------------	------------------

TANTALUM

Glass ceramics, and production method and dedicated device therefor WO2020173425 (A1)	QINHUANGDAO GLASS INDUSTRY RES AND DESIGN INSTITUTE CO LIMITED [CN]	2020-09-03
Method of measuring mass concentrations of niobium and tantalum in air of working zone by mass spectrometry... RU2730954 (C1)	FEDERALNOE BYUDZHETNOE UCHREZHDENIE NAUKI FEDERALNYJ TEKH [RU]	2020-08-26
Phase change memory with a patterning scheme for tantalum nitride and silicon nitride layers US10741756 (B1)	IBM [US]	2020-08-11
Method of making a tantalum sputter target and sputter targets made thereby US2020240006 (A1)	TOSOH SMD INC [US]	2020-07-30
Method for manufacturing tantalum sintered body KR20200088162 (A)	MTIG [KR], FOUND RES & BUSINESS SEOUL NAT UNIV SCI & TECH [KR]	2020-07-22
Semiconductor device, solid-state imaging device with tantalum oxide layer formed by diffusing a material... US2020227463 (A1)	SONY CORP [JP]	2020-07-16
High performance and reliability solid electrolytic tantalum capacitors and screening method US2020219659 (A1)	VISHAY SPRAGUE INC [US]	2020-07-09
Carbon material coated with tantalum carbide US2020216319 (A1)	TOKAI CARBON KOREA CO LTD [KR]	2020-07-09
Electrode catalyst layer composed of palladium iridium and tantalum and sterilizing water generating module... KR20200081115 (A)	COWAY CO LTD [KR]	2020-07-07
Zirconia/titanium oxide/cerium oxide doped rare earth tantalum/niobate RETa/NbO4 ceramic powder... WO2020133575 (A1)	UNIV KUNMING SCIENCE & TECH [CN]	2020-07-02
Method for manufacturing tantalum fine powders KR20200075482 (A)	INST FOR ADVANCED ENGINEERING [KR]	2020-06-26

NIOBIUM

Synthesis of a MoVTaNb catalyst from low-cost metal oxides US2020290026 (A1)	CLARIANT PRODUKTE DEUTSCHLAND [DE]	2020-09-17
Active material, electrode, secondary battery, battery pack and vehicle US2020295361 (A1)	TOSHIBA KK [JP]	2020-09-17
Steel for high temperature carburizing and its method of preparation WO2020178854 (A2)	BHARAT FORGE LTD [IN]; KALYANI TECHNOFORGE LTD [IN]	2020-09-10
High-strength welded cold-resistant steel and article made therefrom RU2731223 (C1)	PUBLICHNOE AKTSIONERNOE OBSHCHESTVO MAGNITOGORSKIJ... [RU]	2020-08-31
Preparation method for molybdenum-tellurium-vanadium-niobium-based ODH catalysts SG11202007289S (A)	NOVA CHEM INT SA [CH]	2020-08-28
A niobium carbide-containing product SE1950166 (A1)	NORDIC ELEMENTS AB [SE]	2020-08-13
Method of measuring mass concentrations of niobium and tantalum in air of working zone by mass spectrometry... RU2730954 (C1)	FEDERALNOE BYUDZHETNOE UCHREZHDENIE NAUKI FEDERALNYJ TEKH [RU]	2020-08-26
Nickel titanium niobium triple metal oxide visible photocatalyst and manufacturing method thereof KR20200090295 (A)	UNIV ULSAN FOUND IND COOP [KR]	2020-07-29
Congruently melting titanium-zirconium-niobium alloy US2020248285 (A1)	RAYTHEON CO [US]	2020-08-06

Diary of industry events

- **T.I.C.'s 61st General Assembly (virtual) and 2020 AGM, October 12th 2020**
- International Conference on Managing NORM in Industry (virtual), October 19th to 23rd 2020
- RMI (virtual) conference, October 27th to 28th 2020
- IAEA's 41st TRANSSC meeting (virtual), November 2nd to 6th 2020
- Electronica (virtual), November 10th to 13th 2020
- FORMNEXT (virtual), November 10th to 13th 2020
- Tarantula (Month 18) (virtual), December 15th to 16th 2020
- Argus Metals Week, London, UK, February 2021
- MMTA International Minor Metal Conference, Charleston, South Carolina, USA, April (tbc) 2021

* correct at time of print

Member company updates

Changes in member contact details

Since the last edition of this newsletter the following changes have been made to delegate contact details:

- **Australian Strategic Materials Ltd:** the delegate, Mr MacDonald, has a new email address amacdonald@asm-au.com, and the company has a new website www.asm-au.com.
- **Globe Metals & Mining Ltd** has moved offices to Unit 1, 26 Elliott Street, Midvale, WA 6056, Australia.
- **Guangdong Rising Rare Metals-EO Materials Ltd** has a new website www.gsxc723.com.
- **Guangdong Zhiyuan New Material Co. Ltd** has a new contact email market@zhiyuanm.com.
- **Jiujiang Fuxing Tai Trade Co. Ltd:** the delegate, Ms Shen, has a new email address jiujiangfuxingtai@vip.163.com and the company has a new website www.jjft.cn.
- **Jiujiang Tanbre Co., Ltd** has a new address: No.62 Jiuhu Road, Jiujiang City, Jiangxi Province 332014, China.
- **Mitsui Mining & Smelting Co. Ltd** has a new website www.mitsui-kinzoku.com/en/.
- **Refractory Metals Mining Co. Ltd** has moved offices to West Wing, 2/F, 822 Lai Chi Kok Road, Cheung Sha Wan, Kowloon, Hong Kong SAR.
- **Responsible Minerals Initiative (RMI)** has moved offices to 1725 Duke Street, Suite 300, Alexandria, VA 22314, United States.
- **Rwanda Mining Association (RMA)** has a new website www.rma.org.rw.
- **Specialty Metals Resources SA** has a new delegate, Mr Quentin Lamarche, who can be contacted at quentin.lamarche@smr.hk.
- **Tantec GmbH** has a new website www.tantec-group.com.
- **ThreeArc Mining LLC:** the delegate, Mr Bovykin, has a new email address dbovykin@threearc.ru.



Join our mailing list to receive the Bulletin by email each quarter

Our mission with the Bulletin is to provide the global tantalum and niobium community with news, information and updates on our work. We hope you enjoy reading it! Recipients will also receive messages about the T.I.C. and our General Assemblies.

Email info@tanb.org to join our mailing list and keep up to date with the T.I.C.



Director's Notes

London, UK

Dear T.I.C. Members and stakeholders,

I hope that you, your family and friends are staying well during these challenging times.

First, the good news is that by working night and day Emma Wickens and I, with Dan Persico, Candida Owens and the Meetings Subteam, have created a virtual General Assembly and annual general meeting within the space of a month.

We have assembled a truly world-class group of speakers and panellists and with the support of our Gold sponsor, A&R Merchants, and in association with MIRU, the leading Japanese metals news organisation, it should be an event to remember for all the right reasons. Personally, I am very excited about the virtual conference which offers us a whole new platform to provide members and stakeholders with added value.

However, as I mentioned in the last Bulletin, this Association has not been immune to the effects of the Covid-19 pandemic. The unavoidable decision not to hold a face-to-face conference this year (our second largest source of income, after the membership fees) has determined that we must take action to stem the outflow of funds. As a result, I'm sorry to say that this will be my last letter as Director, the role being cut back as a cost-saving measure.

Let's take this opportunity to look back over the last 5 years and reflect on the changes which have taken place. In 2015 the Executive Committee decided that the T.I.C. would invest a small portion of its significant funds to expand its core competencies and develop additional capabilities by hiring additional staff to improve not only the value proposition for members, but also the tantalum and niobium industry as a whole. To satisfy this goal, in January 2016 I was hired as Director, taking staffing levels from the equivalent of 1.4 to 2.4 full time positions.

Since then, some highlights have included:

- Developing a more proactive industry body that better promotes members' interests at the many forums, working groups and bodies in which we participate (OECD, TRANSSC, ITSCI, EPRM, TARANTULA, PPA, TFWG, the NORM Exemption Group etc)
- Greatly increasing our outreach and stakeholder engagement, especially with governments, international organisations and academia
- Developing transport guides to NORM (naturally occurring radioactive material) in multiple languages
- Launching an internationally recognised award for excellence in tantalum research and innovation; the Anders Gustaf Ekeberg Tantalum Prize
- Redeveloping and enlarging the Bulletin newsletter to become the flagship journal of this industry; and introducing annual editions in French, Chinese, Portuguese and Japanese
- Giving more presentations promoting the T.I.C., tantalum and niobium at more conferences than ever before
- Creating a new and expanded website with extensive resources for members
- Holding the first ever General Assembly in central Africa, when we visited Kigali, Rwanda, in 2018

It has been a pleasure serving members as the inaugural T.I.C. Director and I wish the Association well. I look forward to meeting you all once Covid-19 allows international travel once more, but, until then, look after yourself and those dear to you.

Kind regards,

Roland



Visiting Edinburgh University in September 2020 to award the 2020 Ekeberg Prize.

The Bulletin is published by the Tantalum-Niobium International Study Center (T.I.C.); ISSN 1019-2026. Editor: Roland Chavasse; Production Director: Emma Wickens. The T.I.C. can be contacted at info@tanb.org; www.tanb.org; +32 2 649 51 58, or at the registered address: Chaussée de Louvain 490, 1380 Lasne, Belgium.

The T.I.C. is an international, non-profit association founded in 1974 under Belgian law that represents around 90 members from over 30 countries involved with all aspects of the tantalum and niobium industry. The T.I.C. is managed by an Executive Committee elected from the membership and representing all segments of the industry. Corporate membership costs EUR 2750 per calendar year and full details of benefits are available at www.TaNb.org

Disclaimer: Tantalum-Niobium International Study Center (T.I.C.) has made every effort to ensure that the information presented is technically correct. However, T.I.C. does not represent or warrant the accuracy of the information contained in the Bulletin or its suitability for any general or specific use. The reader is advised that the material contained herein is for information purposes only; it should not be used or relied upon for any specific or general application without first obtaining competent advice. The T.I.C., its members, staff and consultants specifically disclaim any and all liability or responsibility of any kind for loss, damage, or injury resulting from the use of the information contained in this publication.



a **YAGEO** company

**KEMET continues to be a leader
in the responsible sourcing of tantalum**



ECV

Environmental Claim Validation Certificate

Vertically Integrated Tantalum Sourcing

RMAP Validated

Responsible Minerals Assurance Program

Partnership for Social & Economic Sustainability

CONNECT WITH KEMET



kemet.com