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Tailoring Nb-based alloys for Additive Manufacturing: From powder production to parameter optimization



Tantalum and Additive Manufacturing - Development of high-purity tantalum powder used for high purity tantalum sputtering target.

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President's Welcome

Dear Members and Friends:



Once again, we are approaching the time when a significant amount of T.I.C. staff activities and effort are focused on the upcoming GA65 Tokyo. I am especially excited about this GA as it is the 50th anniversary of the T.I.C.

Some may wonder how we are celebrating GA65 with only 50 years of T.I.C. existence. Well, let's look t a bit of T.I.C history. The T.I.C. was founded in 1974, with two GAs having been held per year. Early on, membership was limited to tantalum miners and processors, with the by-laws changing over time to include traders, industrial consumers, commercial intermediaries, end-users, etc., resulting in a broad representation of the entire supply chain for tantalum and niobium that we have today.

From 1974 – 1987 the two bi-annual GAs were both held in Brussels. The geographic expansion of the GAs began in May of 1977 with GA7 having been held in Winnepeg, Canada at the old TANCO site. The second GA of 1977 was still held in Brussels in October. GA7 also started the tradition of member-site related GAs. It wasn't until the GA29, held in Orlando, Florida USA, that the T.I.C. moved to one GA per year, as it is today. For those doing the math, there were therefore 28 GAs held during the first 14 years of existence.

Something I was not aware of is that the T.I.C. was founded as the "Tantalum Producers International Study Center" chartered under Belgian law on October 24, 1974. In June, 1984, at GA21, the name was changed to the "Tantalum International Study Center", reflecting the broader membership. At GA25, held in May, 1986, the name was again changed to what we have today, the "Tantalum–Niobium International Study Center", reflecting the influx of niobium producers and processors that started around 1983. And while membership has waxed and waned with economic conditions, consolidations, etc., the membership continued to reflect the landscape of the tantalum and niobium supply chains, as it does today.

Leading up to the 50th anniversary celebration of the T.I.C., I thought this short summary of the evolution of the T.I.C. would be of interest to our members and friends. I hope you find it as interesting as I did when I was piecing it together (actually summarizing the information from an existing document written by Emma Wickens for the GA50 bulletin in 2009).

As we move into the summer holiday season, here in the northern hemisphere, I wish everyone safe and enjoyable ventures. And for our southern hemisphere friends, keep your scarves handy as the cold winter winds are not far away.

In closing, as the famous American pop song goes..."See You in September"...in Tokyo.

Stay safe

Daniel F. Persico, Ph.D., President

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亲爱的会员和朋友们



又到了T.I.C.工作人员的大量活动和精力都集中在即将召开的东京GA65大会上的时候了。我对这次大会感到特别兴奋,因为它是 T.I.C. 成立 50 周年纪念。

有些人可能会问, T. I. C. 成立才 50 年,我们怎么会庆祝 GA65 呢? 让我们回顾一下 T. I. C. 的历史。T. I. C. 成立于 1974 年,每年举行两次全球 大会。早期的成员仅限于钽矿开采商和加工商,随着时间的推移,其章程也发生了变化,纳入了贸易商、工业消费者、商业中间商、最终用户等,从 而形成了今天钽和铌整个供应链的广泛代表性。

从 1974 年到 1987 年,每年两次的全球钽铌大会都在布鲁塞尔举行。1977 年 5 月,第七届大会在加拿大温尼伯的 TANCO 旧址举行,大会的地域 范围开始扩大。1977 年第二届大会仍于 10 月在布鲁塞尔举行。 大会第七届会议也开启了与会员站点相关的大会传统。直到在美国佛罗里达州奥兰 多举行的第 29 届大会,T.I.C.才改为每年举行一届大会,即现在的做法。 因此,T.I.C.成立后的前 14 年共举办了 28 届大会。

我不知道的是, T. I. C. 的前身是 1974 年 10 月 24 日根据比利时法律特许成立的 "钽生产商国际研究中心"。1984 年 6 月,在第 21 届大会 上,该中心更名为 "国际钽研究中心",以反映更广泛的成员组成。在 1986 年 5 月举行的第 25 届大会上,该中心再次更名为今天的 "钽铌国 际研究中心",以反映 1983 年左右开始的铌生产商和加工商的涌入。虽然成员数量随着经济状况、合并等因素而时有时无,但成员数量一直反映着 钽和铌供应链的格局,就像今天一样。

在 T.I.C.成立 50 周年庆典之前,我想我们的会员和朋友会对 T.I.C.的发展历程感兴趣。我希望你们能像我当初拼凑这篇文章时一样感到有趣(实际上是对艾玛-威肯斯(Emma Wickens) 2009 年为 GA50 简报撰写的现有文件中的信息进行总结)。

北半球的暑假即将来临,祝大家假期平安愉快。南半球的朋友们,请随身携带围巾,因为寒冷的冬风离我们不远了。

最后,正如那首著名的美国流行歌曲所唱的那样...... "九月东京见"。

注意安全

Boas-vindas do Presidente

Prezados associados e amigos:



Mais uma vez, estamos nos aproximando do momento em que uma quantidade significativa de atividades e esforços da equipe do T.I.C. está concentrada na próxima GA65 em Tóquio. Estou especialmente entusiasmado com essa GA, pois é o 50º aniversário do T.I.C..

Alguns podem se perguntar como estamos comemorando a GA65 com apenas 50 anos de existência do T.I.C.. Bem, vamos dar uma olhada em um pouco da história do T.I.C.. O T.I.C. foi fundado em 1974, com a realização de duas AGs por ano. No início, a filiação era limitada a mineradores e processadores de tântalo, com os estatutos mudando ao longo do tempo para incluir comerciantes, consumidores industriais, intermediários comerciais, usuários finais, etc., resultando em uma ampla representação de toda a cadeia de suprimentos de tântalo e nióbio que temos hoje.

De 1974 a 1987, as duas AGs bianuais foram realizadas em Bruxelas. A expansão geográfica das GAs começou em maio de 1977, com a GA7 sendo realizada em Winnepeg, Canadá, nas antigas instalações da TANCO. A segunda GA de 1977 ainda foi realizada em Bruxelas, em outubro. A GA7 também iniciou a tradição de GAs relacionadas aos sites dos membros. Foi somente na GA29, realizada em Orlando, Flórida, EUA, que a T.I.C. passou a realizar uma GA por ano, como acontece atualmente. Para aqueles que estão fazendo as contas, houve, portanto, 28 AGs realizadas durante os primeiros 14 anos de existência.

Algo que eu não sabia é que o T.I.C. foi fundado como o "Tantalum Producers International Study Center" (Centro Internacional de Estudos dos Produtores de Tântalo), fundado sob a lei belga em 24 de outubro de 1974. Em junho de 1984, na GA21, o nome foi mudado para "Tantalum International Study Center", refletindo a ampliação do número de associados. Na GA25, realizada em maio de 1986, o nome foi novamente alterado para o que temos hoje, o "Tantalum-Niobium International Study Center", refletindo o influxo de produtores e processadores de nióbio que começou por volta de 1983. E, embora o número de membros tenha aumentado e diminuído com as condições econômicas, as consolidações etc., os membros continuaram a refletir o cenário das cadeias de suprimentos de tântalo e nióbio, como acontece atualmente.

Em preparação para a comemoração do 50º aniversário do T.I.C., achei que este breve resumo da evolução do T.I.C. seria de interesse de nossos membros e amigos. Espero que o ache tão interessante quanto eu achei quando o estava montando (na verdade, resumindo as informações de um documento existente escrito por Emma Wickens para o boletim GA50 em 2009).

À medida que entramos na temporada de férias de verão, aqui no hemisfério norte, desejo a todos uma viagem segura e agradável. E para nossos amigos do hemisfério sul, mantenham seus cachecóis à mão, pois os ventos frios do inverno não estão longe.

Para encerrar, como diz a famosa canção pop americana... "See You in September" (Vejo você em setembro)... em Tóquio.

Fique bem

社長のあいさつ

会員の皆様、そしてご友人の皆様:



今年もまた、T.I.C.スタッフの活動と努力が、来るGA65東京大会に集中する時期が近づいてきました。今回のGAがT.I.C.創立50周年ということで、私は特に興奮しています。

T.I.C.が誕生してまだ50年しか経っていないのに、どうやってGA65を祝うのか不思議に思う人もいるかもしれない。では、T.I.C.の歴 史を少し振り返ってみよう。T.I.C.は1974年に設立され、年に2回のGAが開催されてきた。設立当初は、タンタルの採掘業者と加工 業者に限定されていましたが、時間の経過とともに規約が変更され、貿易業者、工業消費者、商業仲介業者、エンドユーザーなどが 含まれるようになり、その結果、今日のようにタンタルとニオブのサプライチェーン全体を幅広く代表するようになりました。

1974年から1987年まで、年2回の総会はいずれもブリュッセルで開催された。GAの地理的拡大は1977年5月に始まり、GA7はカナダのウィニペグ、旧TANCOサイトで開催された。1977年の第2回総会は、やはり10月にブリュッセルで開催された。GA7はまた、メンバーサイト関連のGAの伝統を始めた。T.I.C.が現在のように年1回のGAに移行したのは、米国フロリダ州オーランドで開催されたGA29からである。計算すると、設立から14年間で28回のGAが開催されたことになる。

私が知らなかったことは、T.I.C.は1974年10月24日にベルギーの法律に基づいて設立された「タンタル生産者国際研究センター」であったということです。1984年6月のGA21では、より広範な会員を反映し、名称が「タンタル国際研究センター」に変更された。1986年5月に開催されたGA25では、1983年頃に始まったニオブの生産者と加工業者の流入を反映し、名称が再び現在の「タンタル・ニオブ国際研究センター」に変更されました。そして、経済情勢や統合などによって会員数は増減を繰り返しましたが、会員数は今日と同様にタンタルとニオブのサプライチェーンの状況を反映し続けました。

T.I.C.創立50周年記念式典に先立ち、T.I.C.の変遷を短くまとめた本書は、T.I.C.の会員および友人の皆様に興味を持っていただける ものと思います。2009年にGA50会報のためにエマ・ウィッケンズが書いた既存の文書から情報を要約したものです)私がこの文章 をまとめたときと同じように、皆さんがこの文章を興味深く思ってくださることを願っています。

北半球では夏休みに入るが、皆の安全で楽しい旅を祈っている。南半球の友人たちは、冬の寒風がそう遠くないうちにやってくるので、マフラーを手放さないように。

最後に、アメリカの有名なポップソングにあるように...「See You in September」...東京で。

ご安全に

Lettre du Président

Chers membres et amis:



Une fois de plus, nous approchons du moment où une grande partie des activités et des efforts du personnel du T.I.C. se concentre sur la prochaine AG65 à Tokyo. Je suis particulièrement enthousiaste à l'idée de cette assemblée générale, car elle marque le 50e anniversaire du C.I.T.

Certains se demanderont peut-être comment nous pouvons célébrer l'AG65 alors que le T.I.C. n'a que 50 ans d'existence. Voyons un peu l'histoire du T.I.C. Le T.I.C. a été fondé en 1974, avec deux AG par an. Au début, les membres étaient limités aux mineurs et aux transformateurs de tantale, mais les statuts ont évolué au fil du temps pour inclure les négociants, les consommateurs industriels, les intermédiaires commerciaux, les utilisateurs finaux, etc.

De 1974 à 1987, les deux assemblées générales semestrielles se sont tenues à Bruxelles. L'expansion géographique des AG a commencé en mai 1977 avec l'AG7 qui s'est tenue à Winnepeg, au Canada, sur l'ancien site de TANCO. La deuxième AG de 1977 s'est toujours tenue à Bruxelles en octobre. L'AG7 a également lancé la tradition des AG liées aux sites des membres. Ce n'est qu'à l'occasion de l'AG29, qui s'est tenue à Orlando, en Floride (États-Unis), que le T.I.C. est passé à une AG par an, comme c'est le cas aujourd'hui. Pour ceux qui font le calcul, il y a donc eu 28 AG au cours des 14 premières années d'existence.

Je ne savais pas que le T.I.C. avait été fondé sous le nom de "Tantalum Producers International Study Center" (Centre d'étude international des producteurs de tantale) et qu'il avait été créé en vertu de la loi belge le 24 octobre 1974. En juin 1984, lors de l'AG21, le nom a été changé en "Tantalum International Study Center", reflétant l'élargissement des membres. Lors de l'AG25, qui s'est tenue en mai 1986, le nom a de nouveau été modifié pour devenir ce que nous connaissons aujourd'hui, le "Tantalum-Niobium International Study Center", reflétant l'afflux de producteurs et de transformateurs de niobium qui a commencé aux alentours de 1983. Bien que le nombre de membres ait varié en fonction des conditions économiques, des consolidations, etc., il a continué à refléter le paysage des chaînes d'approvisionnement en tantale et en niobium, comme c'est le cas aujourd'hui.

À l'approche de la célébration du 50e anniversaire du T.I.C., j'ai pensé que ce bref résumé de l'évolution du T.I.C. serait intéressant pour nos membres et amis. J'espère que vous le trouverez aussi intéressant que je l'ai été lorsque je l'ai assemblé (en fait, j'ai résumé les informations d'un document existant écrit par Emma Wickens pour le bulletin GA50 en 2009).

Alors que nous entrons dans la période des vacances d'été, ici dans l'hémisphère nord, je souhaite à tous de bonnes vacances. Et pour nos amis de l'hémisphère sud, gardez vos écharpes à portée de main car les vents froids de l'hiver ne sont pas loin. Pour conclure, comme le dit la célèbre chanson américaine : "See You in September"... à Tokyo.

Soyez prudents

Editor's notes

Dear Members and Friends,



As the summer seems to be gradually coming to an end, I can't help but have envious thoughts of our members enjoying the prolonged warmth in more temperate climates. While the season shifts, it serves as a reminder of the

diversity within our global community and the unique experiences each of us brings to the table.

As we look forward to the upcoming GA65 in Tokyo this September, I'm filled with anticipation for the opportunities it will present. Despite the challenges we've faced this quarter.

It is also with deep sadness that I inform you of the passing of two esteemed members of the Tantalum family, Mr. Jim McCombie and Mr. Terrance "Terri" Tripp. Their contributions were invaluable, and they will be greatly missed. On behalf of the entire community, we extend our heartfelt condolences to their families.

Please remember that the T.I.C. is your organization, and we are here to serve you. Your input, participation, and feedback are crucial to our success, and we are committed to supporting your needs and interests.

Thank you for your continued dedication and support.

Warmest regards,

lan.

Ian Margerison

Executive Marketing Manager and Technical Officer.

Sign up to attend at www.tanb.org/view/65th-general-assembly

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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 year and full details of benefits are available at www.TaNb.org

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Passing of industry colleagues

The passing of Jim McCombie - Stapleford Minerals and Metals Limited

I have sad news to pass on that Jim McCombie passed away on Saturday February 17th, 2024.

As long standing member of the T.I.C. and well known personality in the trading of refractory metals for the family business, Stapleford Minerals and Metals Limited, he will be missed.

Terrance "Terri" Tripp

Terrance B. "Terri" Tripp, 86, passed away on Friday, April 12, 2024, He was the husband of 68 years to his college sweetheart, Eugenia (Murray) Tripp.

Dr. Tripp was born on August 6, 1937. He was the son of the late Lloyd and Iva (Usher) Tripp. He was raised in Saco, Maine, USA and earned his bachelor, master's, and PhD from the University of Maine.

Dr. Tripp was a chemist and had been employed at Sprague Electric Co. in N. Adams, MA and at H. C. Stark in Newton, MA. He was also a professor of Chemistry and Chair of the Math-Science Department at the University of Maine at Presque Isle. Terri was a giant in our industry having pushed the boundaries of the fundamental understandings of tantalum dielectrics focused on tantalum capacitors.

In addition to his wife, he is survived by two children, one sister, and one grandson.

Terri was a scientist, educator, and gentleman, and will be missed by his many industry friends and colleagues.

Member company updates

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

- CCMA, LLC has relocated to 2410 N. Forest Rd. Suite 100, Getzville, NY 14068, United States.
- Globe Metals & Mining Ltd has a new delegate, MrtPaul Smith, he can be contact on paul.smith@globemm.com.
- Halcyon Inc. has relocated to Level 6, Trade Centre Second, Sheikh Zayed Road, Dubai.
- MERSEN Deutschland Linsengericht GmbH has changed its name to Cometec GmbH.
- Plansee SE has a new delegate, Mr Eric Rowe, he can be contacted on eric.rowe@globaltungsten.com.
- RC Inspection Metals B.V has changed its name to RC Inspection B.V. and has relocated to Pieter Zeemanweg 167, 3316 GZ, Dordrecht, Netherlands.
- Wood Mackenzie has a new delegate, Ms Ankita Chakarabortty, she can be contacted on Ankita.Chakrabortty@woodmac.com.
- Ulba Metallurgical Plant JSC celebrates its 75th Anniversary, 102 Abay Avenue, 070005 Ust-Kamenogorsk, Republic of Kazakhstan and can be contacted on marketing_ta@ulba.kz or by the website: www.ulba.kz/en





Tailoring Nb-based alloys for Additive Manufacturing: From powder production to parameter optimization

Authors: Dr. Markus Weinmann (TANIOBIS GmbH), Shaumik Lenka (Alloyed), Dr. André Németh (TANIOBIS GmbH), Dr. Melanie Stenzel (TANIOBIS GmbH)



Abstract -

Niobium-based alloys, such as C-103 and Tantalum-modified FS-85, are of particularly interest due to relatively low density, good thermal conductivity and excellent temperature & time-dependent mechanical properties especially when Ni- and Co-based superalloys reach their application limits at temperatures exceeding ~1050 °C.

While C-103 is widely used processed with traditional manufacturing methods, the Tantalum-bearing alloy FS-85 provides a superior high temperature performance and creep resistance at high temperatures. However, the production of parts using conventional processing such as casting and machining has always been challenging. The development of commercially available FS-85 alloy powders for Additive Manufacturing, has enabled to target new, high-value applications for complex-shaped, highperformance components. Understanding the workflow from powder production and characterization, to the determination of optimized process parameters is a precondition for the development of such powders. In this paper, TANIOBIS GmbH and Alloyed Ltd detail the process of preparing, characterizing, and processing two alloy powders – C-103 and FS85 - by laser powder bed fusion.

Motivation

Ultra-high temperature refractory alloys have the potential to perform at temperatures exceeding ~1050 °C, outperforming even the most advanced Ni- and Co-based superalloys due to their ceiling imposed by the strengthening phase stability as well as their high melting point. Niobium-based alloys, such as C-103, are of particularly interest due to relatively low density, good thermal conductivity and excellent temperature & time-dependent mechanical properties (Fig. 1). ^{1,2}

Fig. 1: Creep performance of various high temperature alloys showing the superiority of Nb alloys. Data for superalloys extracted from Ref.

As a result, Niobium-base alloys are commonly used in propulsion systems within the space and defense industry. Typical applications have until recently been limited to simple shapes such as products made from sheet and bar such as expansion chamber skirts made from TIG welded sheet. This is as ingot production is expensive and they are challenging to fabricate into complex shapes due to their high hot working temperature. Because of the high cost of manufacture not the strongest but most readily manufacturable alloy C-103 is left in the market today.

Until now near net-shape manufacture was not possible as investment casting has challenges around mold reactions, insufficient superheating as well as economic reasons such as loss of the alloy in T.I.C. Bulletin No. 191: August 2024 © T.I.C. 2024 gates. Processing these unique high temperature alloys in powder form allows for near-net shape manufacture using laser powder bed fusion (L-PBF), electron beam powder bed fusion (EB-PBF), direct energy deposition (DED), as well as advanced powder metallurgy (PM). These technologies have major advantages over conventional processing such as cheaper part production due to more efficient use of material and the ability to produce complex components.

The ability to manufacture complex shapes from C-103 and FS-85 (here described for the first time) via L-PBF enables new applications such as structures for high velocity flight and re-entry guidance but also to enable higher temperature gas turbines for power generation and jet propulsion.

Alloy powder preparation

Niobium-base C-103 and FS-85 alloy powders have been developed at TANIOBIS GmbH, Germany, and are commercially available as AMtrinsic® C-103 or AMtrinsic® FS-85 pre-alloyed powders. Due to the lack of suitable crucible materials they are atomized by electrode induction-melting gas atomization (EIGA) of pre-alloyed electrodes. The electrodes were electron beam-melted with dimensions of ca. d x I = 45 mm x 650 mm. Prior to their use a 90° tip was machined to fit shape and dimension of the induction coil. The pre-alloyed rods were atomized in a purified Ar (4.6, Linde) atmosphere through a Laval nozzle and the asobtained raw powders sifted to remove the fine powder fraction < 10 μ m. Finally, the sifted powders were fractionized through 63 μ m, 105 μ m and 150 μ m meshes. The classification releases powders with particle size distributions typically applied in L-PBF (10 – 63 μ m), EB-PBF (63 – 105 μ m) or in DED (105 – 150 μ m).

Alloy powder characterization

Niobium-base C-103 and FS-85 L-PBF alloy powders have fully been characterized, chemically by a combination of ICP-OES and carrier gas hot extraction and/or combustion analysis as well as morphologically by XRD and SEM/EDX. Their flowability was investigated using Hall Flow measurements.

The chemical composition of C-103 and FS-85 powders determined spectroscopically (ICP-OES) and by carrier gas hot extraction/combustion analysis is provided in Table 1. For comparison, the overall composition and the composition of selected spots determined by EDX are given.

The chemical compositions of the atomized powders correspond well with those of conventionally processed materials. However, due to the much higher surface areas, the contents of the light elements, i.e. C, N and O are slightly higher than in the cast solids.

Investigations by XRD shown in Fig. 2 point to the fact that C-103 and FS-85 alloy powders crystallized in the body-centered cubic crystal structure. A comparison with pure Nb shows the very similar appearance of the XRD patterns with the typical 110, 200 and 211 ß-phase reflections. Accordingly, C-103 as well as FS-85 can be considered as single-phase materials.

Fig. 3 SEM images of C-103 and FS-85 alloy powders recorded at 100x magnification For application in powder bed additive manufacturing processes a good processability of the powder is mandatory. A spherical shape is one important requirement to guarantee free flow and ensure a homogeneous distribution of the powder in each individual coating step. Other prerequisites are the absence of satellites, i.e. attachment of smaller particles on the surface of bigger particles or agglomerates. The absence of pores or voids in the powders is necessary to avoid the inclusion of porosity in the built part.

Both C-103 and FS-85 L-PBF powders show an ideally spherical microstructure, as can be seen from the SEM images in Fig. 3. They have smooth surfaces and are fully deagglomerated. In addition, satellites are absent and consequently the powders possess very appreciable flow properties. Their Hall Flow according to ASTM B213 is 12 s (C-103) and 8 s (FS-85). Particle size measurements by means of laser diffraction indicates narrow distributions with d50 values of 34 μ m and 39 μ m. Tap densities are in the range of 5.5 g/ cm3 (C-103) and 6.5 g/cm3 (FS-85). The higher density of FS-85 is attributed to its substantial amounts of Ta and W.

Fig. 4 BSE images of polished cross sections of C-103 and FS-85 alloy powders recorded at 2500x magnification

From the polished cross-sections shown in Fig. 4 it can be concluded that the particles are fully dense.

Voids, defects or inhomogeneities are not observed. Interestingly, the BSE images of both C-103 and FS-85 show structural features with a more or less pronounced dendritic appearance. Similar observations have been made for Nb and Ta-modified Ti base alloys. In C-103 they do not appear clearly, while the BSE image from FS-85 undoubtedly shows flower-like dendritic features. In addition, the contrast in the image of FS-85 is significantly higher than that of C-103.

The EDX images of C-103 and FS-85 provided in Fig. 5 show clear differences in the distribution of the elements. In C-103, chemical variation of the main components Nb and Hf is observed. Nb appears enriched in the dendritic phase while Hf is enriched in the inter-dendritic phase. This is clearly expressed by the different chemical compositions, which are highlighted in Table 1 of spots 1 and 2 in the Hf map of C-103. While the dendrite-type features contain 90.5 wt% Nb and 8.5 wt% Hf, the volumes between the dendrites consist of 79.2 wt% Nb and 19.6 wt% Hf. The secondary components Ti and Zr appear homogeneously distributed over the particle.

The element distribution in FS-85 is very different. None of the elements appears homogeneously distributed throughout the particles. There is a clear separation into Nb/Zr and Ta/W enriched volumes. In contrast to C-103, Nb appears with higher concentration in the inter-dendritic phase associated with Zr. In contrast, Ta and W occur preferentially in the dendrite phase. The chemical fluctuations of the elements in both phases are significantly more pronounced than with C-103. While spot 1, which indicates the composition of the inter-dendrite phase, consists of 68.2 wt% Nb, 21.1 wt% Ta, 5.8 wt% W and 4.9 wt% Zr, respectively the values in the dendritic structures (cf. spot 2) are 58.3 wt%, 29.3 wt%, 10.4 wt% and 1.9 wt%.

Fig. 5 EDX images of polished cross sections of C-103 (top) and FS-85 (bottom) alloy powders recorded at 2500x magnification. The chemical composition of the entire are and selected spots 1 and 2 is provided in Tab. 1

C-103 and FS-85 powder particles were also investigated by means of Electron Backscatter Diffraction (EBSD) to receive information of crystal size, structure and orientation. Powder samples were therefore hot mounted by mixing with a conductive mount and subsequently mechanically polished using 600-4000 abrasive grit papers. The polishing was then continued using diamond paste from 10 to 1 μ m to have a mirror finish and finally finishing the polishing with 0.25 μ m colloidal silica solution to get surface conducive for electron backscattered diffraction scans. The high angle boundaries in these images are the boundaries between two different grains and the low angle grain boundaries are the inter-dendritic boundaries within the same grain.

Fig. 6 EBSD of C-103 (left) and FS-85 (right) powders showing the grain structure within the powder particles.

The average grain size of C-103 particles, which measures up to approx. 20 μ m appears to be slightly higher than in FS-85. This might be a consequence of the higher number of constituents in FS-85 than in C-103 and consequently a higher entropy of the FS-85 system, exhibiting extensive crystallization. Such effect is well known for refractory metal high entropy alloys, which have recently been discribed in the literature.

Method of manufacture (Alloyed process for parameter development)

The additive manufacturability of C-103 and FS-85 has been assessed by laser powder bed fusion (L-PBF) in a protective argon atmosphere using a Renishaw AM400 (Fig. 7) pulsed fiber laser system with 1075 nm wavelength. Printing any new alloy or composition requires single track experiments (Fig. 8) to be done at the various additive manufacturing machine settings to get the information about melt-pool thickness and depth. This is key to make sure the melt-pools overlap creating sound builds without any remnant unfused powder. Single track also helps parameter selection by adjusting the tradeoff between a stable scan track and keyhole formation due to high enthalpy. Fig. 8 provides a schematic of the various AM machine parameters that have been tested. A snapshot of the single track samples has also been shown in Fig. 8 which were metallographically analyzed to determine scan track stability and soundness.

Fig. 7 Renishaw AM 400 machine used at Alloyed Inc to build cubes and test bars in a reduced build volume.

Fig. 8 Single track DOE (top) and experiments (bottom) conducted in Renishaw AM 400 machine at 300-400 W with 50-90 μs exposure time and 10-50 μm point distance.

The scan track width and 1 dimension energy density were plotted along with the ranking of the tracks based on the stability post metallographic analyses. This is shown in Fig. 9 and can then be used as a map to visualize effect of operating parameters on printability.

Fig. 9 Process parameter and microstructure stability plot generated by characterizing single tracks made from various operating conditions for FS-85.

The AMtrinsic® C-103 and FS-85 powders after being thoroughly characterized as described in Section 1 were printed with varied process parameters according to the design of experiment strategy. Cubes of the dimension of 10x10x10 mm3 were manufactured with varying processing parameters as shown in Table 1 at a fixed layer thickness of 30 µm. A meander laser scan path was applied with a rotation of 67 deg with each layer.

Table 1: Range of parameters used for design of experiment to determine the printability of FS-85 and C-103 alloys.

Fig. 10 shows a snapshot of one particular DOE strategy of 12 cubes being printed. Once the optimized process parameter was narrowed down, a full test bar build was done as shown in Fig. 10. Post printing of the cubes a full microstructural characterization was done to correlate the process parameters and microstructural attributes. The density of the cubes and the AM defects concentration (cracks and porosities measured through microstructural characterization) were correlated with the build parameters such as laser power, exposure time, hatch and point distance.

Fig. 10 Cube build of C-103 and FS-85 (top) as a part of the design of experiment strategy. Full test bar build (bottom) with the optimized printing parameters.

The influence of the processing parameters such as laser power, scan speed, hatch, powder bed thickness etc. on the quality of the print can be assessed by investigating its density/porosity. It can be seen that as the laser power (all other parameters remain unchanged) is lowered from 300 W to 200 W defects or pores around the corners, borders and bulk are significantly reduced.

Fig 11. Optical micrograph of DOE cubes processed at 300W (left) and 200W (right) showing significant difference in defect concentration, size and shape.

Characterization of additive manufacturability (Comparison of density of C-103 and FS-85)

Cubes with density \geq 99.9 % were obtained applying optimized processing parameters. The comparison of corners, borders and bulk microstructure has been done and the micrographs for C-103 and FS-85 have been shown in Fig. 12 and Fig. 13, respectively. It can be seen that both alloys are readily processable through laser powder bed fusion.

Fig 12. Optical micrograph of corner (left), bulk (middle) and border (right) micrographs showing feeble presence of defects/porosities for C-103 cube build with optimized parameters.

Fig 13. Optical micrograph of corner (left), bulk (middle) and border (right) micrographs showing feeble presence of defects/porosities for FS-85 cube build with optimized parameters.

Characterization of additive manufacturability (Advanced chemical and micro characterization / EBSD)

Additive manufacturing using selective laser beam melting has a significant impact on the development of the morphology of the materials used. This can be seen exemplarily for FS-85 by comparing the powder morphology shown in Fig. 5 with that of the L-PBF-printed material shown in Fig. 14. © T.I.C. 2024 T.I.C. Bulletin No. 191: August 2024 1 Fig. 14 EDX images of polished cross sections of FS-85 printed specimens recorded at 3000x magnification. Build direction from right to left. The dashed line in the W map highlights melt pool boundaries along which a slight de-mixing occurs.

During the impact of the laser beam on the powder bed, it melts completely. Moreover, the underlying layers are also melted and accordingly each individual layer is therefore remelted several times in the process. In the molten layers, the individual atoms are randomly distributed, with maximum disorder; they exhibit a maximum entropy. Since the cooling rates for L-PBF are extremely high at around 105 K/min, a thermodynamically favored partial de-mixing with the formation of dendrite-like structures observed in the powder particles can no longer take place. The remaining structure therefore has a very high entropy and random element distribution.

At the deepest part of the melt pool, i.e. at the solid/liquid boundary, a slight segregation of the alloy may occur. The reason is that the individual alloy components solidify with different rates which causes the segregation. Two such melt pool boundaries are indicated in Fig. 5 in the tungsten map by a dashed line. The melt pool boundaries are likewise visible, though not highlighted, in the Nb, Ta and Zr map. To make sure all printed components fulfill the composition specification for C-103 and FS-85 standards, advanced chemical analysis such as ICP and LECO were done. Table 2 shows the oxygen concentration measured using LECO for powders and the components made through additive manufacturing. This level of quality check is required for stringent qualification of various classes of components for space applications. In general, a slight increase of oxygen caused by the L-PBF processing of 140 – 250 ppm is observed.

Table 2. Oxygen content of powders and additively manufactured components measures through LECO for qualification and understanding the oxygen pickup during printing.

Advanced electron back scattered diffraction examination of the AM printed parts were done to see the grain structure in the as-printed components. EBSD map of C-103 and FS-85 (Fig.15) shows predominant (101) and (111) texture, respectively. This change in texture from cube on the edge to cube on the corner dependence could be attributed to the difference in chemical composition leading to a difference in solidification texture during printing of powders using L-PBF.

Mechanical Performance (room temperature tensile performance)

Mechanical performance of the additively manufactured FS-85 and C-103 at room temperature was measured using standard ASTM E8 tests. Rectangular blanks of dimension 55x10x10 mm3 were machined into cylindrical dumbbell specimen with threads on either end. The samples were tested in tension in a 30 kN Intron tensile testing machine at a strain rate of 0.005 mm/min. Figure 16 shows the room temperature performance of additively manufactured FS-85 and C-103.

Fig. 16 Mechanical properties of C-103 and FS-85 alloys at room temperature processed by L-PBF.

It is found that FS-85 is significantly stronger than C-103. The corresponding ultimate strengths are ca. 750 MPa and 565 MPa, respectively. On the other hand, C-103 exhibits a significantly higher strain-to-failure of ca. 20 - 22 % compared with ca. 6 - 7 % in FS-85. Both alloys are currently being mechanically tested at higher temperatures up to 1500°C to evaluate their potential for service in high temperature environments.

As evident from Fig. 17, an excellent high-temperature performance can be observed for both alloys at elevated temperature. Either of the alloys produced by PBF-LB clearly outperforms wrought C-103 in terms of strength and density-compensated strength. In accordance with room temperature investigations, the tantalum-modified FS-85 alloy is the first choice when searching for new alloys for service in high-temperature environments.

Fig. 17 Yield strength obtained in high-temperature tensile tests (ETMT) of PBF-LB-processed C-103 and FS-85.

Outlook, component manufacture

C-103 and tantalum-containing FS-85 alloys prove to have superior printability and mechanical properties comparable to the conventionally processed alloys. These alloys therefore need to be manufactured into prototype components to prove the validity of these alloys in actual component manufacture for space applications. Fig 18 shows such a particular prototype thruster manufactured using FS-85 alloy processed by laser powder bed fusion.

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Tantalum and Additive Manufacturing



Development of high-purity tantalum powder used for high purity tantalum sputtering target

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Abstract -

This paper introduces the development trend of high-purity tantalum powder for high-purity sputtering tantalum targets and mainly elaborating on the preparation methods of this kind of high-purity tantalum powder. Through the research on the deep removal technology of W, Mo, Nb in the preparation process of high-purity Potassium heptafluorotantalate, the research on the physical property control technology and anti-corrosion mechanism in the reaction process of sodium reduction of Potassium heptafluorotantalate, and the research on the subsequent impurity control technology of high-purity tantalum powder, then high-purity tantalum powder with purity (GDMS detection) of more than 99.998% has been developed, of which the total amount of three high-temperature Refractory metals such as W, Mo, Nb is less than 0.35ppm, It meets the specification requirements for high-purity sputtering tantalum targets with a purity of over 99.9998%.

Key words: high purity; tantalum sputtering target; tantalum powder; preparation technology; development

1. Introduction

Tantalum is an important rare refractory metal material with excellent heat resistance, corrosion resistance, anti-oxidation and superior anti atomic migration ability. It is a preferred sputtering target material for semiconductor chip barrier layer in the integrated circuit with line width of below 45nm. At present, the rapid development of integrated circuit technology promote the large-scale application of Ta/Cu high purity metal in manufacturing integrated circuit, so a huge industrial expansion happens during the past three years. High purity tantalum sputtering target is usually produced in the way that ultra-high purity tantalum powder is first melted into ingots through electron beam melting, and then the sputtering

target blank for semiconductor is finally prepared through repeated shaping deformation and heat treatment. During the whole processes above, it is difficult to remove such refractory metals as W, Mo and Nb, so the purity of tantalum sputtering target depends on that of tantalum powder used. The impurity level of W, Mo and Nb become important indicators whether tantalum powder is suitable for high purity tantalum target.

In 2020, some international top companies have resolved the problem of high impurities of refractory metals W, Mo and Nb in tantalum powder, resulting in the total concentration of W, Mo and Nb lower than 0.8ppm, so that tantalum sputtering targets for semiconductors can be produced with high purity of above 99.9998% (5N8 Grade). Meanwhile the development of China's tantalum industry was hindered by the problem of that the total impurity of W, Mo and Nb of tantalum potassium fluoride is higher than 1ppm, so the tantalum sputtering targets for semiconductors could only reach the purity of 99.999% (5N Grade).

In keeping with the market trends, high-purity tantalum powder (99.998% (4N8) was independently developed with great efforts by our technicians in the past years, in which the total impurity of W, Mo and Nb is lower than 0.35ppm through developing many processing techniques in deeply removing W, Mo and Nb inclusive of preparing high purity tantalum potassium fluoride, physical property modification during sodium reduction reaction with tantalum potassium fluoride and making an analysis on anti-corrosion mechanism and developing post-steps impurity control method in the production of high purity tantalum powder. As a result, the tantalum powder we produced with high purity of above 99.998% (4N8 Grade) can meets the requirements of high purity tantalum sputtering target (5N8 Grade and above) in worldwide market and stably supplying to our customers.

This paper emphasizes on the preparation technology and development process covering high purity tantalum potassium fluoride and high purity tantalum powder, and finally came to a conclusion on successful development.

2. Experiment



Technical route for Preparing high purity tantalum potassium fluoride

Fig. 1 Technical route for preparing high-purity K2TaF7

As shown in Figure 1, high purity tantalum potassium fluoride(K2TaF7) was prepared by using the MIBK organic extraction system. In the organic phase, the proportion of tantalum pentoxide (Ta2O5) vs niobium pentoxide (Nb2O5)= (1~5): (1~5). We analyzed the influence of extraction separation, acid leaching and tantalum stripping processes with the different proportion on the impurity removal of W, Mo and Nb during preparing high purity tantalum potassium fluoride. At the same time, the preparation process of high purity tantalum potassium fluoride was determined based on analyzing the influence of crystallization and synthesis process on the chemical impurities and crystalline morphology.

2.2 Preparation of high-purity tantalum powder

High purity tantalum powder for sputtering target was prepared by using mature and advanced sodium reduction process while blending tantalum potassium fluoride, and the reduction reaction equation is as follows:

$$K_{2}TaF_{7} + 5 Na = 2 KF + 5NaF + Ta$$
 (powder)

The detailed process flowchart is shown in Figure 2. The preparation technology of high purity tantalum powder for high purity tantalum sputtering target was established based on studying on the micro modification techniques of tantalum powder, the corrosion behavior and mechanism of high temperature complex molten salt system, deeply removing refractory metal impurity during acid leaching, the post-step heat treatment, oxygen reduction and the control method for refractory metal impurities.



Fig. 2 Technical route for preparation of high purity tantalum powder

2.3 Main equipment and raw materials

Main equipment: extraction tank, crystallization tank, sodium reduction furnace, vacuum heat treatment furnace, water washing tank, acid leaching tank and oxygen reduction furnace.

2.3.2 Main raw materials: tantalum ore, K2TaF7, NaCl, hydrochloric acid, nitric acid, hydrofluoric acid.

2.4 Analytical instruments

The impurities of Fe, Ni, Cr and Si in tantalum potassium fluoride (K2TaF7) were tested by using JY ULtima2 inductively coupled plasma atomic emission spectrometer produced by HORIB JY, France; the concentration of Ta2O5 in tantalum potassium fluoride was tested by using color layer

separation-weight method; The impurity of O and N in tantalum powder was tested with the ON-600 type oxygen and nitrogen analyzer produced by LECO, USA; The impurity of K and Na in tantalum powder was tested with Model AA220Z/220FS atomic absorption spectrometer produced by Varian, USA; The impurity of C in tantalum powder was tested with Model CS-600 carbon-sulfur analyzer manufactured by LECO, USA; Elemental spectra in tantalum powder was analyzed with Model DV-5 DC arc photoelectric spectrometer produced by Baird, USA; glow discharge mass spectrometry (GDMS) analysis for tantalum powder with Model ELEMENT GD PLUS instrument manufactured by Thermo Fisher Scientific, USA; The impurities of W, Mo, Nb in tantalum powder were analyzed with Model iCAP TQ triple four-stage rod mass spectrometer produced by Thermo Fisher Scientific, USA,; A SEM Analysis for tantalum powder with Model JSM-5-610 LV high-low resolution SEM tester produced by Japan Electronics Corporation; The bulk density of tantalum powder was analyzed with Model FL4-1 tester self-made according to the Chinese National Specification GB1479-84; The particle size distribution of tantalum powder was measured by Model LS230 tester produced by Coulter, USA.

3. Results and Discussions

3.1 Deeply removing impurities of W, Mo and Nb in the preparation of high purity tantalum potassium fluoride (K2TaF7)

There are many important factors affecting the impurity level of W, Mo and Nb during the preparation of tantalum potassium fluoride, such as selection of tantalum minerals, the acidity when acid leaching, accurate control process parameters for Ta & Nb separation and tantalum stripping during liquid extraction, crystallization synthesis, gradient cooling, filtration, washing and drying. Based on Ta & Nb extraction mechanism and the extraction distribution coefficient of W and Mo, the impurity of W and Mo can be controlled during the ore digestion and extraction processes, and then the low impurity minerals could be selected. The impurities of W, Mo and Nb can be effectively removed during the extraction process through adding extraction stages, setting Ta2O5 / Nb2O5 ratio in the organic stage: Ta2O5 / Nb2O5= (1~2) / 1 while precisely controlling the acidity of acid leaching solution and liquid flow rate of niobium reextraction. We made use of the existing crystallization synthesis process. The gradient cooling was used for crystallization so as to ensure that Ta5 + only binds to K + and F- during crystallization, and tantalum potassium fluoride has a sufficient nucleation period and crystal core growth period. Finally, the tantalum solution was synthesized and crystallized, washed and dried separately thus effectively preventing the impurities of W, Mo and Nb from bringing in.

Through the above studies, high-purity $K_2 TaF_7$ samples in the three batches of K-1, K-2 and K-3 were developed in compliance with above preparation process of high-purity tantalum potassium fluoride. The testing results are shown in Table 1.

| Table 1 chemical analysis of high-purity K ₂ TaF ₇ samples | | | | | | | | | | |
|--|------|-----------|----|--|--------|----------|----------|-------|-----|--|
| Sample No. | Impu | rities le | | Ta ₂ O ₅ Content | Weight | | | | | |
| | Fe | Ni | Cr | Si | Nb | W | Мо | % | Kg | |
| K-1 | <5 | <5 | <5 | 5 | <1 | \leq_1 | \leq_1 | 56.61 | 800 | |
| K-2 | <5 | <5 | <5 | 5 | $<_1$ | $<_1$ | \leq_1 | 55.81 | 800 | |
| K-3 | <5 | <5 | <5 | 5 | $<_1$ | \leq_1 | \leq_1 | 56.48 | 800 | |

Table 1 chemical analysis of high-purity K₂TaF₇ samples

As seen from the results in Table 1, the metal impurities of W, Mo and Nb in high purity K_2TaF_7 in three batches were <1ppm, reaching the lowest limit of detection through detection by inductively coupled plasma mass spectrometer (ICP-MS), so the impurities analysis of W, Mo and Nb in high purity K_2TaF_7 has no guiding significance. The high purity tantalum powder was prepared in 6 batches from Ta-1 to Ta-6 by using the high purity K_2TaF_7 samples in three batches, so the impurity level of W, Mo and Nb in the high purity K_2TaF_7 samples was characterized by that of the high purity tantalum powder. The detection results are shown in Table 2.

| Sample No. | Impurities level (ppm) | | | | | | | | | | | |
|------------|-------------------------|------|------|------|------|------|-------|-------|------|--|--|--|
| | Fe | Ni | Cr | к | Na | Si | W | Мо | Nb | | | |
| Ta-1 | 3.07 | 5.79 | 2.41 | 0.84 | 5.99 | 1.56 | 0.018 | 0.012 | 0.18 | | | |
| Ta-2 | 2.26 | 2.74 | 3.71 | 0.5 | 4.94 | 1.61 | 0.051 | 0.014 | 0.17 | | | |
| Ta-3 | 1.15 | 0.96 | 1.17 | 0.31 | 3.66 | 3.54 | 0.08 | 0.02 | 0.25 | | | |
| Ta-4 | 4.66 | 2.64 | 1.23 | 0.94 | 7.55 | 2.26 | 0.036 | 0.026 | 0.21 | | | |
| Ta-5 | 2.61 | 1.36 | 1.76 | 0.76 | 6.45 | 1.8 | 0.034 | 0.051 | 0.15 | | | |
| Ta-6 | 5.99 | 1.09 | 1.66 | 0.33 | 3.02 | 0.89 | 0.014 | 0.032 | 0.14 | | | |

Table 2 Impurity analysis of high-purity Ta powder samples

As seen from the analysis results of glow discharge mass spectrometry (GDMS) on high purity tantalum powder samples in Table 2, the total impurity of three refractory metals W, Mo and Nb is less than 0.8ppm, which meets the technical goal and requirements of high purity K_2TaF_7 . The purity of high purity K_2TaF_7 is calculated as an example in the Chinese Patent CN108910949A with the title of "Preparation method of high purity K_2TaF_7 ", and the high purity of tantalum powder samples in 6 batches is more than 99.998% (4N8 Grade).

3.2 Physical property and impurity control for deeply removing W, Mo and Nb in the preparation of high purity tantalum powder for high purity tantalum sputtering targets

3.2.1 Influence of accessory parts on the impurities of W and Mo in high purity tantalum powder

During the reduction process of $K_2 TaF_7$, an acidic atmosphere with F- formed, thus causing certain corrosion to the special tools for reduction reaction. A main special tool used in the reduction process is the mixing agitator being made of heat-resistant stainless steel (3128 Steel Grade No.) Surface peeling and green phenomena occur during use, resulting in increasing impurities in tantalum powder. it is found to contain a certain amount of W and Mo after the paddle and rod of the mixing agitator were analyzed using handheld spectrometer (see Table 3 for detailed results), so corrosion to the mixing agitator bring tiny amount of W and Mo impurities into the tantalum powder, causing the impurity level fluctuation of W and Mo in the high purity tantalum powder.

Table 3 Chemical composition of the mixing agitator (3128 steel No.)

Unit 04

| Unit | - 70 | | | | | | | | |
|--------------|--------|------|-------|-------|------|------|------|------|------|
| Agitator No. | Site | Fe | Ni | Cr | Mn | Мо | W | Ti | Ta |
| No.1 | Paddle | 1.28 | 60.54 | 19.85 | 0.31 | 8.35 | 7.9 | 0.73 | 0.86 |
| | Rod | 1.25 | 60.33 | 19.98 | 0.29 | 8.2 | 7.27 | 0.27 | 2.25 |
| No 2 | Paddle | 0.86 | 66.87 | 15.65 | 0.27 | 8.04 | 7.88 | 0.43 | |
| | Rod | 1.21 | 60.75 | 20.06 | 0.34 | 8.4 | 7.9 | 0.77 | 0.42 |
| No.3 | Paddle | 0.94 | 63.48 | 17.05 | 0.29 | 7.89 | 7.65 | 0.69 | 2 |
| | Rod | 1.43 | 58.49 | 19.23 | 0.38 | 8.42 | 7.56 | 0.73 | 3.62 |

During the study in this paper, we selected the mixing agitator combined with tantalum rod and a bushing protection, and tantalum coating layer was coated on the surface of agitator to protect the contact site when the mixing agitators in contact with the molten salt so as to avoiding impurity level fluctuation of W and Mo because for the agitator's peeling and wear. In addition, The samples in a batch were prepared respectively through reduction reaction with above three protection methods and the results are shown in Table 4. As seen from the analysis results in Table 4, the impurities W and Mo were effectively prevented from intrusion into high purity tantalum powder through adopting above three protection methods. Therefore, the impurity level of W and Mo is under control in the production high purity tantalum powder. Considering the economic cost of production, the mixing agitator with bushing protection is mostly economical and practical, and can be widely used.

| Sample No. | Impurity level | (ppm) | | Type of agitator | | |
|-------------|----------------|-------|------|---|--|--|
| Sample 100. | W | Мо | Nb | Type of agriator | | |
| Ta-4 | 0.051 | 0.019 | 0.16 | With bushing protection | | |
| Ta-5 | 0.074 | 0.050 | 0.19 | Combined with Ta rod | | |
| Ta-6 | 0.087 | 0.069 | 0.22 | Coated with Ta layer on the surface of agitator | | |

| Table 4 | Impurity | v level of W. | Mo and Nb in | hiah-purity | Ta powder |
|---------|----------|---------------|--------------|-------------|-----------|
| | mpanty | , | | | |

3.2.2 Physical property control of Ta powder during the reduction of K2TaF7

High purity tantalum puttering targets is prepared by using high purity tantalum ingot which is first prepared through following processes of putting metallurgical grade tantalum powder into the envelope, and then pressing the tantalum powder into tantalum bars through cold isostatic pressing, and then pre-firing and melting of tantalum bars by electron beam melting, finally obtaining tantalum ingot. The density of the sintered body will increase with raising the loading density when isostatic pressing, thereby reducing irregular shrinkage during sintering, reducing the broken bars, and improving the productivity. The filling density of the envelope mainly depends on the bulk density of high purity tantalum powder. It is well known that the optimal loading density of tantalum powder is 3.5-5 g/cm3, correspondingly high purity tantalum powder for high purity tantalum sputtering target is also required for the bulk density of 3.5-5 g/cm3.

To meet the requirement for the bulk density of 3.5-5 g/cm3, such important process parameters as the reduction procedure, reduction temperature, input rate of sodium, processing atmosphere, mixing speed must be accurately controlled. Otherwise as shown in Table 5 and Figure 3, high purity tantalum powder produced before modification has a violent reduction reaction, and the reduced native particles have no time to leave the reaction area (reaction point) into the molten salt body, but form mutual adsorption and binding within the high-temperature region near the reaction point while the native particles grow up and the over burned particles generate due to high temperature, and simultaneously creating cladding phenomenon, resulting in coarse particles, uneven particle distribution of materials, higher impurities in the original Ta powder. A large number of over sintered particles wrap around the inclusion of impurities, causing inadequate purification which has a great impact on the later use.

Based on micromorphology analysis of tantalum powder particles and studying on the sodium reduction process with K_2TaF_7 for preparing high-purity tantalum powder. The accurate charging and sodium injection speed were optimized, thus reducing the concentration of the reactants in the molten salt system, lowering the temperature of the reaction point, the over-sintering of native particles at high temperature; Reducing ultrafine particles by using the appropriate amount of additives and proper addition method; The oversintering of different molten salt layers was resolved by using mixing control techniques and reasonable holding and sintering process; Reducing overburned particles and improving the physical properties of high purity tantalum powder samples for high purity tantalum sputtering target (For modified samples, see Table 5 and Figure 3); The particle size was significantly improved and the microscopic morphology is much more homogeneous, meanwhile eliminating the generation of over-sintering particles in the feedstock, which plays a decisive role in the later purification.

| Sample No. | Impurity level | | | (ppm |) | | | Fisher particle size | Bulk density (SBD) | Note |
|---------------|----------------|----|---|------|----|----|----|-----------------------------------|-----------------------|------------------------|
| | 0 | Ν | С | Fe | Cr | Ni | Si | μm | g/cm ³ | |
| Ta-7 | 880 | 50 | 9 | 8 | 3 | 14 | 5 | 10.02 | 4.06 | |
| Ta-8 | 790 | 35 | 8 | 11 | 3 | 13 | 5 | 10.16 | 3.6 | Before modification |
| Ta-9 | 860 | 45 | 7 | 12 | 3 | 13 | 5 | 11.8 | 3.69 | |
| Ta-10 | 980 | 35 | 8 | 3 | 3 | 3 | 5 | 6.1 | 3.2 | |
| Ta-11 | 98 0 | 25 | 8 | 3 | 3 | 3 | 5 | 6.14 | 3.31 | After modification |
| Ta-12 | 880 | 40 | 7 | 3 | 3 | 3 | 5 | 5.52 | 3.16 | |

Table 5 Chemical composition of high purity tantalum powder samples

Before modification



SEM photo of Ta-7 sample (X500)

After modification



SEM photo of Ta-10 sample (X500)



SEM photo of Ta-7 sample (×5K)



SEM photo of Ta-10 sample(×5K)

Fig. 3 SEM photo of high purity tantalum powder samples

3.2.3 Purification of high-purity tantalum powder through acid leaching

We studied on the microscopic morphology of the reduced tantalum powder. Due to the temperature distribution inhomogeneity during the reduction process, the particle size distribution is also non-uniform, resulting in particle sintering and cladding of the impurities.

In view of the above problems, we developed the physical property control technology for tantalum powder. the original powder particles was fully crushed, the such impurities included in the particles as W, Mo released, meanwhile some contaminants on the surface of tantalum powder was removed by reasonable acid leaching, and partial refractory metal impurities such as W, Mo was further removed, thereby finally achieving the purpose of purification.

The glow discharge mass spectrometry(GDMS) analysis results were shown in Table 6, which is to make a comparison for the high purity tantalum powder developed before and after modifying acid leaching process and by using the same reduced samples. As seen from the data results in the Table 6, the impurities of W and Mo in the samples numbered as Ta-13-1 were significantly reduced by the physical property regulation technology and the modified acid leaching process.

Table 6 GDMS analysis comparison for the tantalum powder produced before and aftermodifying acid leaching process

| Sample | Impu | | Note | | | | | | | |
|---------|------|------|------|------|------|------|-------|-------|------|---|
| No. | Fe | Ni | Cr | к | Na | Si | W | Мо | Nb | Note |
| Ta-13 | 5.24 | 1.49 | 3.45 | 5.66 | 4.62 | 6.71 | 0.067 | 0.13 | 0.26 | Original process |
| Ta-13-1 | 5.12 | 1.09 | 1.66 | 0.33 | 3.02 | 0.89 | 0.014 | 0.032 | 0.24 | Crushing material and modifying acid leaching process |

3.2.4 Purification of high purity Ta powder when some accessory parts used in heat treatment

Through analyzing the heat treatment process where the impurities of W and Mo probably increase, it is found that insulation screen for heat treatment is mainly made of the stainless steel and heat-resistant molybdenum material, and the support rod and baffle plate are molybdenum parts, by which Mo impurities will be introduced into the product during production.

In order to better resolve the problem of heat insulation screen carrying impurity, its inner screen was changed to tantalum alloy screen for reducing the intrusion of Mo impurity in the heat treatment process. Table 7 shows the analysis results of glow discharge mass spectrometry (GDMS) for the impurities of of W, Mo and Nb in the tantalum powder prepared by using heat insulation screen being made of Mo and Ta alloy respectively. As seen from the data results of Table 7, After heat treatment, the heat treatment furnace with Ta or Ta alloy screen has no obvious influence on the impurity level of W, Mo and Nb in the samples of high purity tantalum powder, while the impurity level of Mo increased significantly after heat treatment when the heat treatment furnace with Mo screen was used.

Table 7 GDMS analysis on the impurity level of W, Mo and Nb in high purity tantalumpowder

| Sample No | Impurity | y level | (ppm) | Material for heat |
|---|----------|---------|-------|-------------------|
| Sample No. | W | Мо | Nb | insulation screen |
| Ta-14 (original Ta Powder) | 0.13 | 0.060 | 0.34 | |
| Ta-14 (surface test after heat treatment) | 0.061 | 0.180 | 0.35 | Mo screen |
| Ta-14 (Product) | 0.095 | 0.070 | 0.35 | |
| Ta-15 (original Ta Powder) | 0.056 | 0.045 | 0.23 | |
| Ta-15 (surface test after heat treatment) | 0.09 | 0.046 | 0.20 | Ta screen |
| Ta-15 (Product) | 0.092 | 0.037 | 0.19 | |
| Ta-16 (original Ta Powder) | 0.039 | 0.056 | 0.35 | |
| Ta-16(surface test after heat treatment) | 0.031 | 0.065 | 0.34 | Ta alloy screen |
| Ta-16 (Product) | 0.045 | 0.045 | 0.22 | |

During heat treatment, such Mo fabricated parts as support rod, baffle plate were replaced with Ta parts whose heat-resistant strength are not enough higher and easy to deform, thus causing abnormal production. The Mo fabricated parts were pre-sintered at high temperature before use and the volatilization of Mo can be effectively reduced so as to better reducing the influence of some accessory parts on impurity level.

3.2.5 Effect of oxygen reduction process on purification of high-purity tantalum powder

The oxygen reduction process is mainly redox reaction of solid-liquid phases. Mg is added as a reducing agent during the production, and is also regarded as an impurity, so the removal process is particularly important. The sintering at an extremely high temperature will cause the sintering of tantalum powder particles, and form an inclusion of Mg cladding, causing the residue of impurities. The particles can be effectively crushed through adding proper crushing process when performing oxygen reduction, thereby providing a favourable condition for subsequent purification.

As shown in Table 8, the chemical impurities of high purity tantalum powder samples were analyzed, which were prepared by modifying different oxygen-lowering temperature and acid leaching techniques. As seen from the data results in Table 8, the oxygen concentration was greatly reduced by higher oxygen- lowering temperature, but due to its high sintering strength, the materials are difficult to crush into powder and remove the impurity of Mg from the material. Appropriate oxygen reduction process at low-temperature can keep the oxygen concentration controlled at an appropriate level while reducing sintering strength of the material, moreover effectively reducing the inclusion of impurities of Mg controlled at the level of below 5ppm.

| Sample | Impurity level (ppm) | | | | | | Particle | density (SBD) | Oxygen reduction | Acia leaching |
|---------|----------------------|----|----|----|----|----|----------|-------------------|---------------------|-----------------------|
| No. | | | | | | | size | (SDD) | process | process |
| | 0 | Ν | Fe | Cr | Ni | Mg | μт | g/cm ³ | - | - |
| Ta-17-1 | 450 | 40 | 5 | 3 | 3 | 11 | 9.4 | 3.77 | | 1 |
| Ta-18-1 | 410 | 27 | 4 | 3 | 3 | 10 | 9.76 | 3.64 | Oxygen | Lower acid volume |
| Ta-19-1 | 460 | 41 | 4 | 3 | 3 | 10 | 9.2 | 3.18 | reduction | |
| Ta-17-2 | 350 | 34 | 4 | 3 | 3 | 7 | 9.25 | 3.67 | At high | |
| Ta-18-2 | 410 | 30 | 4 | 3 | 3 | 9 | 10.16 | 3.44 | temperature | Higher acid volume |
| Ta-19-2 | 370 | 31 | 5 | 3 | 3 | 11 | 9.6 | 3.36 | | |
| Ta-20-1 | 390 | 42 | 3 | 3 | 3 | <1 | 7.55 | 3.19 | | |
| Ta-21-1 | 330 | 32 | 3 | 3 | 3 | <1 | 7.32 | 3.34 | Oxygen | Lower acid volume |
| Ta-22-1 | 410 | 32 | 3 | 3 | 3 | <1 | 7.26 | 3.28 | reduction | |
| Ta-20-2 | 410 | 45 | 11 | 3 | 3 | <1 | 7.28 | 3.13 | At low | |
| Ta-21-2 | 460 | 35 | 5 | 3 | 3 | <1 | 7.18 | 3.08 | temperature | Higher acid volume |
| Ta-22-2 | 460 | 38 | 3 | 3 | 3 | <1 | 7.28 | 3.04 | | |

Table 8 Impurity level in high purity tantalum powder samples

3.3 Analyzing the Physical property and chemical impurities of high purity tantalum powder developed

Based on the above research work, we developed the preparation technology of high purity $K_2 TaF_7$ and high purity tantalum powder. We developed high purity tantalum powder samples for high purity sputtering tantalum target and analyzed the physical and chemical properties as shown in Table 9 and 10. As seen from the data results in Table 9 and 10, we developed high purity tantalum powder that has the purity of above 99.998% (4N8 Grade) and the total impurity level of W, Mo and Nb is less than 0.35ppm, the oxygen concentration is less than 600ppm, and the bulk density is 3-4 g/cm3, which fully meets the requirements in semiconductor application where tantalum sputtering targets with high purity of above 99.9998% (5N8 Grade) are required.

| Table 9 | Chemical | propertv | of hiah | purity | v tantalum | powder |
|---------|----------|----------|---------|--------|-------------|--------|
| | ononioui | proporty | or mgn | pairty | , cancarann | pomaon |

| | | | | | | | | | | Fisher | Bulk |
|-----------------------------|-----|------|-----|------|-----|-----|-------|-------|-------|--------|-------------------|
| Sample Impurity level (ppm) | | | | | | | | | | | density |
| No. | | | | | | | | | | size | (SBD) |
| | 0 | CN | Fe | Ni | Cr | Mg | W | Мо | Nb | μш | g/cm ³ |
| FTa-1 | 390 | 7 38 | 3.1 | 0.53 | 1.1 | 1.1 | 0.027 | 0.025 | 0.205 | 8.0 | 3.9 |
| FTa-2 | 410 | 7 30 | 4.6 | 0.72 | 1.4 | 1.2 | 0.04 | 0.041 | 0.131 | 7.2 | 3.6 |
| FTa-3 | 440 | 9 32 | 5.5 | 0.47 | 1.3 | 1.3 | 0.036 | 0.034 | 0.157 | 7.9 | 3.8 |
| FTa-4 | 380 | 8 30 | 3.3 | 1.3 | 1.1 | 1.0 | 0.031 | 0.022 | 0.145 | 7.8 | 3.8 |
| FTa-5 | 440 | 7 33 | 5.3 | 0.98 | 1.6 | 1.2 | 0.019 | 0.045 | 0.191 | 8.1 | 4.0 |

| | Fisher | Bulk | | | | | | | | |
|---------------|------------------|-------------------|--------------------|----------|-----------|-----------|-------|--|--|--|
| Sample No. | Particle size | density (SBD) | Mesh screening (%) | | | | | | | |
| | μm | g/cm ³ | +80 | -80/+200 | -200/+325 | -325/+400 | -400 | | | |
| FTa-1 | 8.0 | 3.9 | 0.08 | 29.52 | 20.8 | 5.76 | 43.84 | | | |
| FTa-2 | 7.2 | 3.6 | 0.2 | 30.68 | 19.44 | 5.92 | 43.76 | | | |
| FTa-3 | 7.9 | 3.8 | 0.34 | 28.86 | 19.54 | 5.68 | 45.58 | | | |
| FTa-4 | 7.8 | 3.8 | 0.28 | 30.52 | 20 | 0.88 | 48.32 | | | |
| FTa-5 | 8.1 | 4.0 | 0.2 | 30.24 | 19.32 | 7.52 | 42.72 | | | |

Table 10 Physical property of high purity tantalum powder

4. Conclusion

4.1 Through research on the decomposition, extraction and crystallization of high purity tantalum potassium fluoride (K2TaF7), we achieved a technological breakthrough in deeply removing refractory impurities of W, Mo and Nb during the extraction and purification of Ta & Nb minerals and improving the purity of K2TaF7, thus meeting the requirements of ultra-high purity tantalum powder for high purity tantalum targets.

4.2 We studied the sodium reduction, acid leaching, heat treatment and oxygen reduction processes, which are the four key process steps for preparing high purity tantalum powder used for high purity tantalum sputtering target, and moreover we achieved a technological breakthrough in controlling such impurities as W, Mo, Nb, and O during sodium reduction process, and have established a complete technical system in preparing high purity tantalum powder used for high purity tantalum target.

4.3 We developed high purity tantalum powder that has the purity of above 99.998% (4N8 Grade) and the total impurity level of W, Mo and Nb is less than 0.35ppm, the oxygen concentration is less than 600ppm, which completely meets the requirements in semiconductor application where tantalum sputtering targets with high purity of above 99.9998% (5N8 Grade) are required.

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