



A new technology platform for the production of electronic grade tantalum nanopowders from tantalum scrap sources



Joseph D. Lessard, Leonid N. Shekhter, Daniel G. Gribbin, Yuri Blagoveshchensky, Larry F. McHugh*

Orchard Material Technology, LLC, 790 Turnpike Street, Suite 202, North Andover, MA 01845, USA

ARTICLE INFO

Article history:

Received 30 May 2014

Received in revised form 22 September 2014

Accepted 25 September 2014

Available online 5 November 2014

Keywords:

Tantalum

Scrap recycling

Iodine

Plasma

ABSTRACT

Conversion of tantalum alloy scrap into high-value, electronic-grade tantalum nanopowders is a significant economic and technological advancement. At present, it is only possible to recycle tantalum alloy scrap into low-value tantalum mill products; however, upgrading this metal stream into the raw materials for the capacitor industry offers economic payback and environmental savings. A new technology platform based on the iodization of tantalum alloy scrap produces volatile tantalum(V) iodides that can be condensed to form fine powders. Subsequent hydrogen reduction of the iodide powders in a plasma furnace produces high surface area tantalum metal powder precursors, which, after annealing, yield high-purity nanopowders with uniform particle size distribution, low oxygen content, and high surface area and capacitance. The hydrogen iodide produced during plasma reduction can be captured, dissociated into molecular hydrogen and molecular iodine, and recycled. The total process flow sheet is presented.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Tantalum (Ta) is valued for its refractory properties and superior electronic properties. Tantalum capacitors are valued for their high capacitance to volume ratio, allowing for miniaturization in consumer electronics that demand performance under difficult conditions. Additionally, due to its high melting point, chemical corrosion resistant nature, and hardness, tantalum is employed in several chemical processing equipment applications, alloys, and superalloys. Due to its rarity, association with conflict regions, and difficulty to isolate and process, the use of recycled tantalum is likely to increase in the coming years; between the years 2000 and 2011, tantalum waste and tantalum scrap accounted for 15–30% of the total global tantalum supply [1].

Depending on the nature of the tantalum waste, the material is currently recycled in one of several ways. Capacitor waste streams, depending on the extent of their processing before rejection, are either reprocessed by capacitor manufacturers, or – in the least desirable outcome – sent back to the start of ore concentrate processing for digestion, solvent extraction and K_2TaF_7 salt or Ta_2O_5 production. At present, the capacitor market makes up approximately 40% of tantalum demand [1]. Superalloys, which make up 21% of the market demand, are traditionally recycled by remelting the alloy scrap into the molten alloys [1]. The tantalum mill product industry for chemical process equipment makes up 5–8% of the market and is projected to grow at a rate of 5% per year; these tantalum alloys, usually very rich in Ta, are often remelted into alloy melts for recycling [1].

During the recycling of all of these tantalum products the net value of the tantalum either remains unchanged (in the case of the alloys) or decreases (in the case of the capacitor scrap). An attractive alternative recycling technology would not only produce tantalum of the requisite purity, but it would also offer the potential to *upgrade* the tantalum value. Today, no technology exists that can economically convert tantalum alloy scrap into high value capacitor-grade tantalum.

At present, tantalum purification proceeds via either sodium (Na) reduction [2,3] or magnesium (Mg) vapor reduction [4,5], with the latter offering more contemporary improvements over the former. In general, Na reduction was used to take tantalum salts extracted from Ta–Nb ores via leaching and solvent extraction to metallic Ta. In this process, however, dissolution of NaF and KF leads to a limited Ta solubility in the aqueous solution, which reduces the direct yield of Ta. During Na reduction, process conditions limit the extent to which high surface area Ta powders can be produced effectively; subsequent production of high capacity powders is challenging [6]. Reduction of Ta_2O_5 with gaseous Mg leads to higher surface area Ta metal powders as compared to Na reduced powders; in turn, Mg reduction produces higher capacitance Ta powders. However, the unavoidable formation of acid insoluble magnesium–tantalum oxide phases requires additional reduction with Mg (deoxidation); it normally takes 1–2 deoxidation steps to produce the final powder. Overall, both Na and Mg reduction technologies require multiple steps (reduction, leaching, sintering, deoxidation) to produce the finished powder.

Both Na and Mg reduction technologies call for multiple passivation steps after reduction, sintering, and deoxidation. After passivation, the O_2 content becomes a function of the powder surface area: the higher the surface area, the higher the O_2 content. Typically, the O_2 content is

* Corresponding author.

E-mail address: lmmc@orchardtec.com (L.F. McHugh).

on the order of thousands of ppm, reaching more than 1% for high surface area/capacitance powders.

The goal of the newly proposed iodization process to be outlined in this manuscript is to upgrade tantalum scrap streams into high-value, capacitor-grade tantalum powders via a streamlined flow sheet without leaching or deoxidation steps. The final process has minimal environmental impact.

2. Iodization and purification of tantalum alloy scrap

2.1. Tantalum scrap compositions

The tantalum scrap used in this study were two compositions of tantalum alloy streams; the first is a high purity (>99%) tantalum mill product and the second is a Ta–2.5W alloy used in the chemical processing industry. These two compositions were chosen to demonstrate the ability of this technology to purify tantalum from different sources with various levels of metal impurities; additionally, this relatively low-value tantalum source can be upgraded to high-value capacitor grade tantalum. The compositions of the two tantalum feed streams are presented in Table 1.

After sufficient milling of the scrap material, treatment of the scrap powder with iodine (I_2) vapors at elevated temperatures leads to the rapid formation of metal iodides [7]. As will be shown below, depending on the nature of the scrap and its impurities a fractional distillation of the metal iodides is possible with the isolation of tantalum(V) iodide, TaI_5 . The primary chemical reaction to proceed under these conditions is outlined in Eq. (1), where Me refers to an arbitrary metal, which is primarily Ta in this work.



Depending on the metal iodide formed, and the prevailing conditions of the reaction, the product of Eq. (1) may be solid or gaseous. Several side reactions (e.g. carburization reactions, oxidations) can also take place, though these are minor relative to the iodization reaction. Thermodynamic calculations to understand these chemical processes were performed with FactSage® 6.4 simulation software [8].

2.2. Tantalum mill product scrap iodization

Using a basis of 100 g (0.22 lb) Ta scrap, a 5:1 mass ratio (3.6:1 molar ratio) of I_2 to scrap was used in the iodization investigations. As demonstrated in Fig. 1, iodization and vaporization of tantalum to form TaI_5 are thermodynamically favored over the temperature range 400–600 °C (752–1112 °F). Provided the scrap material is sufficiently well milled, excessively high temperatures will not be required to vaporize the tantalum from the scrap material and effect the purification.

Interestingly, and critical to the ultimate success of this technology, the impurity metals largely remain in the solid state, even after iodizing. Complete iodization of the niobium, manganese and iron contents is predicted thermodynamically with 100% of the NbI_5 and MnI_2 remaining in the solid phase. The tungsten content forms WC (due to the impurity of carbon present in the scrap) under the process conditions and remains in the solid phase. The formation of other metal carbides (i.e. Fe, Nb) is not thermodynamically favored under these conditions. Interestingly, the FeI_2 that is formed from the iron impurity reports to both the solid and gas phases under the conditions investigated here

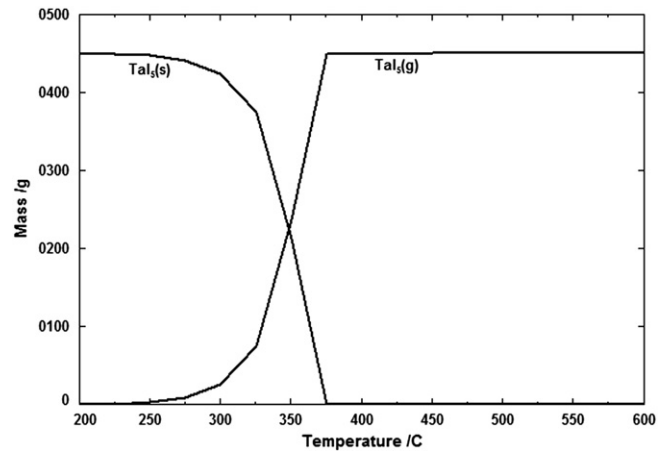


Fig. 1. Tantalum iodization with 5:1 I_2 to scrap ratio determined using FactSage.

(Fig. 2). At the onset of TaI_5 vaporization roughly 1.6% of the total Fe joins the vapor phase as FeI_2 and $(FeI_2)_2$, for a Fe content of <2 ppm in the Ta. By comparing Figs. 1 and 2, it is apparent that careful control of the process conditions during iodization can lead to effective purification of Ta from the impurity metals, principally Fe. Recovery of Ta during this step is >99%.

2.3. Ta–2.5W alloy scrap iodization

A similar basis of 100 g (0.22 lb) Ta–2.5W scrap and a 5:1 I_2 to scrap ratio were used in the investigation of the iodization of the alloy. The Ta–2.5W scrap contains a wider range of impurities than the mill product material. Of particular interest, the Ti content in the alloy scrap forms TiI_4 , a compound even more volatile than TaI_5 . As such, a fractional distillation or stepped temperature profile during reaction will be required. Based on the thermodynamic simulation iodization at 200 °C (392 °F) will lead to the quantitative iodization and complete vaporization of the Ti content as TiI_4 with minimal (<0.04%) loss of TaI_5 to the gas phase. All other impurities remain in the solid phase in various forms (TaI_5 , NbI_5 , W, WC, MoI_4 , WO_2 , MnI_2 , FeI_2 , NiI_2 and SiO_2). Further heating of the solid residue after removal of the TiI_4 gas phase under an Ar purge to 400 °C (752 °F) results in complete vaporization of the TaI_5 and >99% Ta recovery (Fig. 3). A comparison of the TiI_4 and TaI_5 partitioning between the gas and solid phases is presented in Fig. 4.

Condensation of the TaI_5 gaseous phase from the processing of both scrap streams yields high-purity tantalum source. The gas phase can be collected by purging the iodization furnace and collecting the condensate after cooling. Subsequent sizing of the resulting condensate may be required to facilitate further processing and Ta reduction.

3. Hydrogen plasma reduction of metal iodides

3.1. Comparison of metal iodide reduction thermodynamics

The two principle metal iodides to be considered for H_2 reduction are FeI_2 and TaI_5 , in which the former is present at ppm levels as an impurity in the latter (Eqs. (2) and (3)).



Table 1
Compositions for tantalum scrap sources (wt.%).

Scrap source	Ta	O	W	C	N	Nb	Fe	Mn	H	Mo	Ni	Si	Ti
Mill products	99.8	0.01	0.05	0.01	0.003	0.05	0.01	0.01					
Ta–2.5W alloy	96.8	0.015	2.5	0.01	0.01	0.5	0.01	0.01	0.0015	0.02	0.01	0.005	0.01

Download English Version:

<https://daneshyari.com/en/article/1603125>

Download Persian Version:

<https://daneshyari.com/article/1603125>

[Daneshyari.com](https://daneshyari.com)