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A review of tantalum resources and its production

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Abstract: Tantalum (Ta) is a technology-critical metal, which has important applications in many strategic emerging industries, such as electronic, and aerospace, and there are no substitute materials for Ta so far. The supply crisis of Ta has kept growing globally over the past two decades. This work presents a comprehensive review of tantalum resources and its production. There is less than 300 kt Ta in the earth's crust, and the production of primary Ta is an energy- and materials-demanding process. Ta can also be recovered from tin smelting slag, lithium ores, end-of-life tantalum products, etc., and they can account for 37% of the total Ta production. The HF leaching−solvent extraction−sodium potassium fluorotantalate reduction process is the most widely used technology in producing Ta. However, long process and environmental issues have limited the sustainable development of this method. Clean production technologies and efficient recycling of Ta should receive continuous attention.

Key words: tantalum; application; resource; production; recycling

1 Introduction

Tantalum (Ta) is a high melting point metal, and has fancy properties, such as good conductivity of heat and electricity, excellent machinability, and high stability in acidic environment, which makes it an important material in many fields, such as electronics, chemicals, aerospace, and medicine [1]. The production and recycling of Ta have significant influences on the development of these strategic emerging industries. However, the resource of tantalum is scarce (less than 300 kt Ta in the earth's crust) [2], and this could easily lead to Ta supply crisis. Ta has been labelled as critical raw materials by the European Union since 2020, and it is noted that the supply crisis of Ta has kept increasing since 2017. In the era of economic globalization, the production and supply of tantalum affect the development of related industries. Therefore, it is essential to know the supply chain of tantalum.

There are three critical parts of the Ta supply chain, which are Ta resources, metallurgical production and manufacturing, and downstream application. It is urgent to diagnose these critical parts to know how to improve its supply resilience. Limited numbers of works can be found in literatures. However, the researches were mainly focused on the primary resources of tantalum, but the secondary and associated resources are seldom mentioned [3−6]. Referring to the tantalum-making process, some work has been done to study the reduction process of tantalum oxides [7−9]. But the decomposition process of tantalum concentrates and the separation of tantalum and niobium are still not well known. Some studies [10−12] have analysed

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the supply and demand of Ta, but they didn’t consider political, economic and cultural factors.

In order to show the life-circle of Ta, this work has made a comprehensive review of the catalogue of resources, applications, supplies and production of the tantalum. Existing theories are analysed and integrated to fill in the gaps in existing research, and suggestions have been put forward to enhance the stability of the tantalum supply chain.

2 Applications and supply of Ta

2.1 Ta applications

Tantalum was firstly separated as a discrete element in 1802 [13], and then started to be used as filaments, rectifiers and detector materials [14,15]. Due to the unique properties, the application of Ta keeps developing. Nowadays, tantalum has been widely used in electronics, chemical industry, aerospace, optics, medical treatment, nuclear industry, etc., and it has been categorized as a technology-critical metal [1,16]. Figure 1 shows the life circle of Ta, including the resources, production, value-adding manufacturing and end-users in each material flow [3,17−23].

The electronics industry, accounting for around 50% of consumption, has consumed the largest part of tantalum, in which met-grade tantalum powder, capacitor-grade tantalum powder and Ta mill production are used in manufacturing sputtering targets and tantalum capacitors. Ta is an important alloying element in preparing high-temperature alloys, which are key materials for aerospace engines [24]. Tantalum compounds, which are mainly in the forms of tantalum oxide, sodium tantalate, lithium tantalate, etc., are widely used in optics, semiconductors [25] and catalysis industries [26].

Figure 2 shows the compound annual growth rate of tantalum worldwide between 2016 and 2021, by the end product [3,27]. The overall growth rate of tantalum consumption is 4%−5%, and more Ta is needed in preparing sputtering targets, superalloys and Ta compounds. The Ta consumption in the capacitor filed grows by 1.5%, a value below average, and saturation of the market and miniaturisation of capacitors are the main reasons. However, the construction of 5G base stations all over the world and the fast growth of electric vehicles are expected to be new points of growth [28,29] in the future. Due to the low substitutability of tantalum, the consumption in the high-temperature alloy field increases by 7%, and this is mainly a result of the rapid development of the aerospace field [23]. Ta consumption for sputtering targets and tantalum chemicals will also grow at an above-average rate. The use of tantalum in carbides is expected to decline slowly in following years.

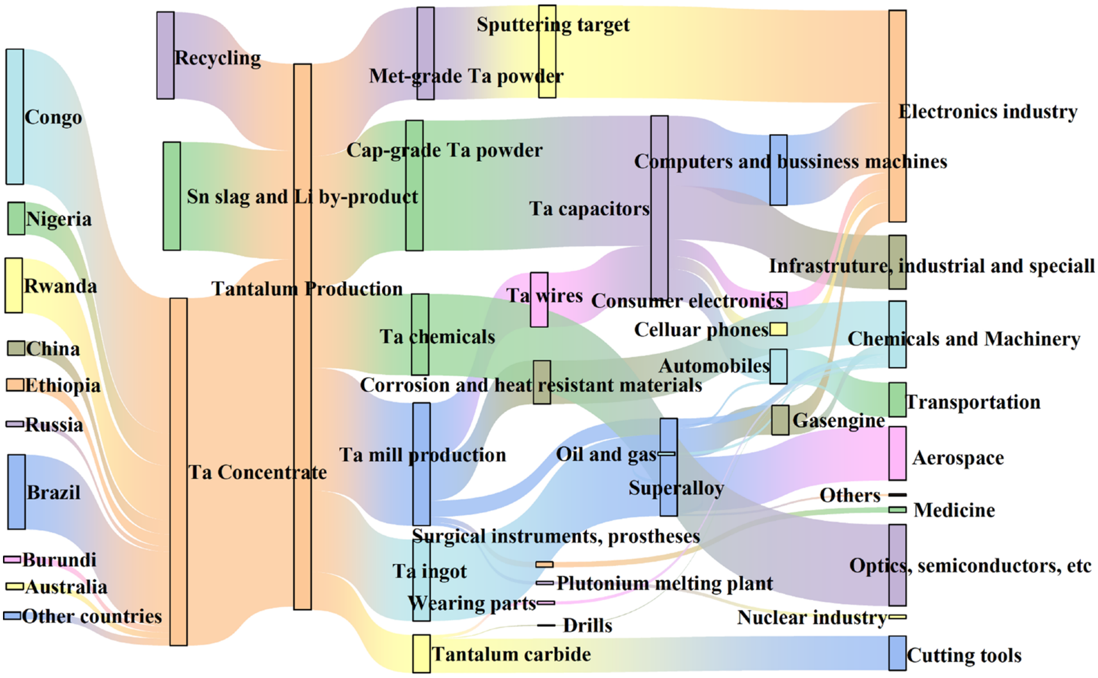

Fig. 1 Material flows of Ta resources, production, value-added manufacturing and applications between 2015 and 2019

2.2 Supply

The supply of tantalum in the world had several disruptions and subsequent price swings in the past 20 years, and this implies resilience and stability problems in the supply chain. Figure 3 shows the global production of tantalum metal from 1999 to 2021 [3,30].

Because of the benign economic climate between 1999 and 2005, global tantalum production gradually increased to 1916 t. However, Ta production has decreased for several years in a row since 2006, and it was mainly a result of the global financial crisis at that time [3]. And then, Ta production started to grow in 2013, and maintained a high production value between 2017 and 2019. This could be explained by the improvement of the global economy, especially the rapid development of global electronics, aerospace and other industries. New Ta projects in Congo, Rwanda, etc., also improve the global tantalum supply [31]. However, the yield decreased slightly in 2019 and 2020, and it is caused by the COVID-19 pandemic. When Ta production resumed in 2021, its supply reached a ten-year peak value of 2494 t [24,32]. Overall, the outlook for tantalum continues to remain robust. Figure 4 shows the tantalum price between 1976 and 2020 [21,33,34].

Tantalum is usually traded with long-term contracts, or parceled on a confidential basis among miners, traders and producers [35,36]. A prisoner's dilemma is easily caused by some traders and buyers [34], and this may result in short-term market volatility. The price of tantalum will rise in the future when the world gradually recovers from

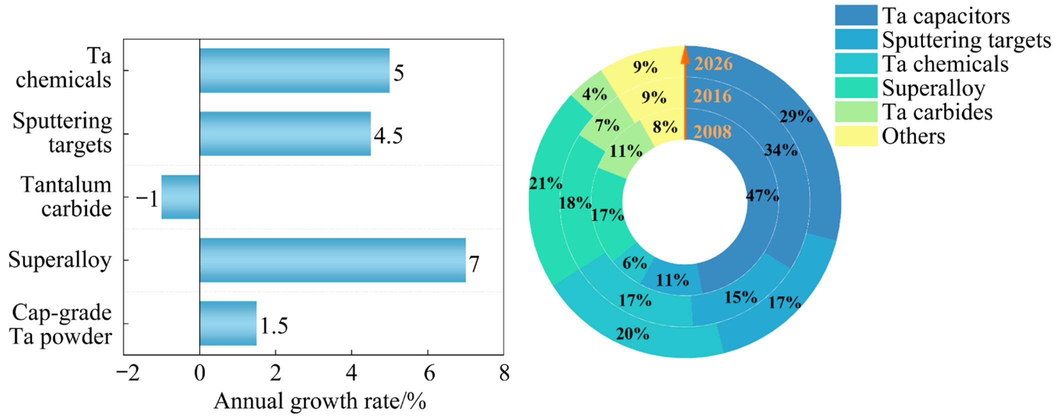

Fig. 2 Portion of Ta products between 2016 and 2021, and forecast before 2026

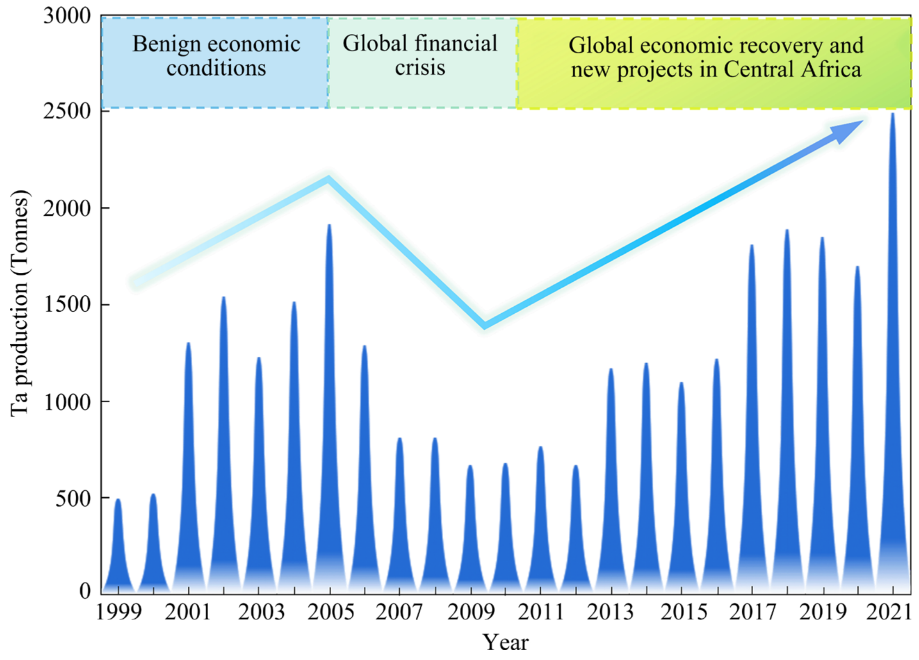

Fig. 3 Global production of tantalum between 1999 and 2021

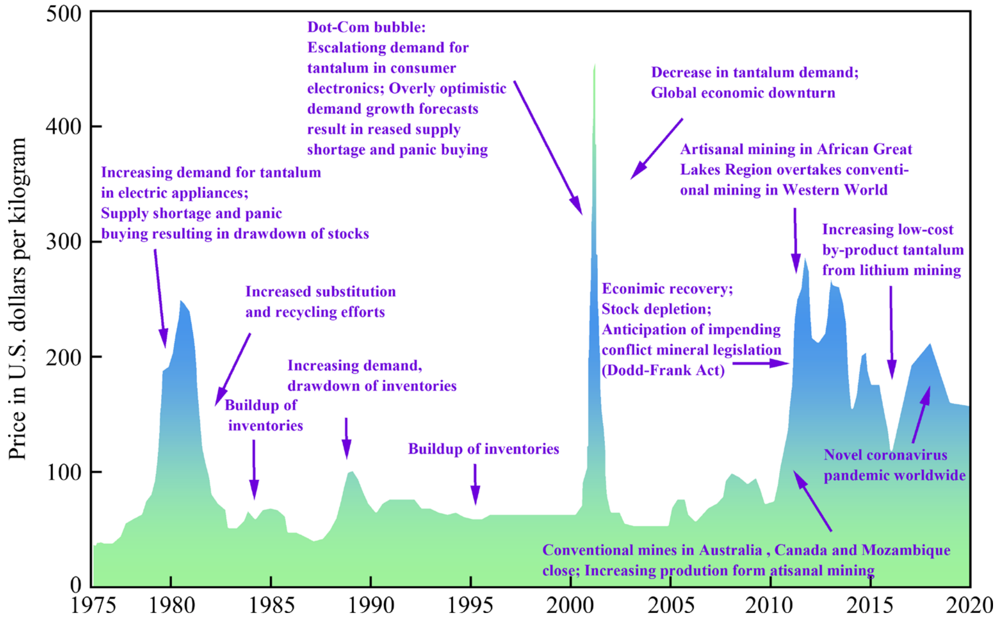

Fig. 4 Price of tantalum between 1975 and 2021

the pandemic. There are about 48 tantalum smelters worldwide, and primary tantalum is mainly produced in China, Thailand, India, Kazakhstan, Brazil and Europe. However, most of the value-adding manufacturing works of Ta are carried out in the USA, Japan, Korea and Germany [10,37]. Commercial data about Ta concentrate importing and exporting between 1990 and 2020 have been reviewed and presented in Fig. 5 [38].

There is a great increase in the tantalum−niobium−vanadium concentrate trading and unwrought tantalum exporting from the 1990s to 2000s, and this is mainly contributed by the fast development of the Ta-making industry and other Ta-related immerging industries. About 50% of the tantalum−niobium−vanadium concentrates are processed in China nowadays, but China is only the third largest country in exporting primary Ta. The United States used to be the biggest country in both concentrate importing and Ta exporting. Because of the financial crisis in 2009, the tantalum−niobium−vanadium concentrate imported to the USA decreased to a low level, and started to recover gradually in 2012. But the amount of concentrate imported in recent years was much smaller than that in 1990—2008, and this can be explained by the industry structure adjustment. Malaysia and Estonia also import tantalum concentrate, but their portion is small. About 60% of the global tantalum exporting is contributed by the United States and Japan, which revealed that Ta refiners are still important in these developed countries. Thailand and Kazakhstan export more than 20% of global unwrought Ta, and this is determined by the Ta resources in these countries.

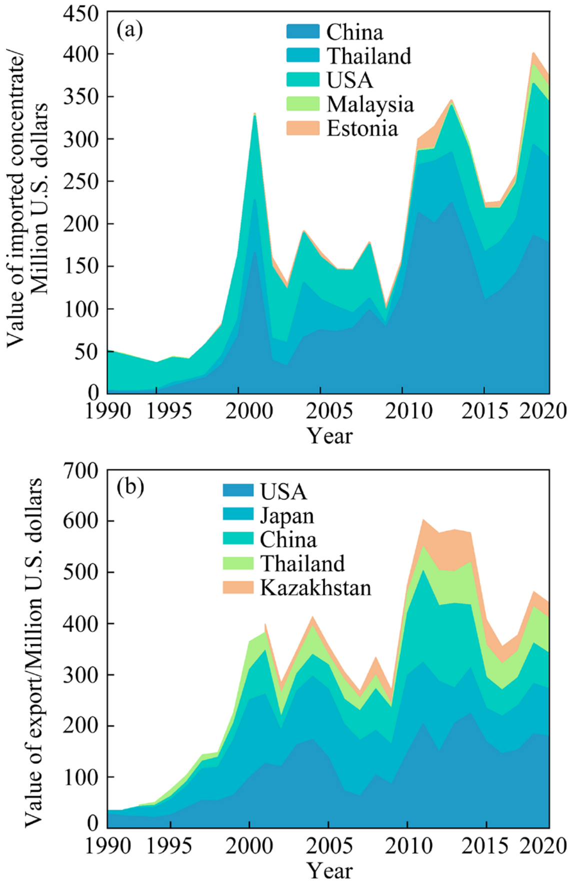

Fig. 5 Values of imported tantalum−niobium−vanadium concentrate and exported unwrought tantalum by countries between 1990 and 2020

It is noted that shipments of different tantalum materials show different trends over time. Figure 6 shows the annual shipments of the six different tantalum materials in TIC members [39,40]. The supplies of all tantalum materials except met-grade tantalum powder and tantalum ingots decreased in 2019, which was affected by COVID-19. The demand for tantalum carbide declined due to the substitution of tungsten and other hard alloys. Shipments of capacitor-grade tantalum powder fluctuated slightly, but kept at high values. The supply of Ta milling products decreased. The demand for met-grade tantalum powders and tantalum compounds is increasing because of the development of sputtering targets, semiconductors and optics. In general, the change in the shipment of different Ta materials has revealed that high-temperature alloys and tantalum compounds are nibbling away at the Ta in carbides and capacitors in the market.

3 Ta resources

Ta could be produced from Ta concentrates, associated resources (tin slag, lithium by-products, etc.), and end-of-life Ta products. Public data have been reviewed and analysed, and the portions of Ta produced from these above resources are 64%, 20%, and 16%, respectively [4,41].

3.1 Ta minerals

Tantalum is a rare metal, and its abundance in the earth crust is only 0.9×10^{-6} [42,43]. There are approximately 65 large tantalum and niobium deposits worldwide, and according to their geological characteristics, they can be classified into five types [5], namely pegmatitic, granitic, alkaline granitic, crystal-rich and carbonatite. Tantalum is mainly found in lithium−caesium−tantalum-rich granite deposits and lithium−caesium−tantalum-rich pegmatite deposits [44]. There are over 150 minerals [45], which contain tantalum, and only several tantalum minerals could be used in Ta extraction, such as tantalite, columbite, microlite, wodginite, struverite, and cassiterite. About 50% of present tantalum has been produced from tantalite [46,47].

Geologists have speculated that tantalum resources are abundant, but no definitive data on reserves are available. The mineral report published in 2011 by the British Geological Survey (BGS) mentioned that the tantalum reserves (in Ta_2O_5) are over 150000 t, but the tantalum resources (in Ta_2O_5) are over 300000 t [48], which is consistent with the tantalum resources estimated by TIC [2]. According to the United States Geology Survey (USGS 2022), the global tantalum reserves (in Ta_2O_5) are estimated to be 189000 t, and the reserves in Australia, Brazil, and the USA are 94000, 40000 and 55000 t, respectively [32,49]. Figure 7 depicts the tantalum resources and reserves in different countries.

Figure 8 [50] shows the annual supply of tantalum concentrates in different countries between

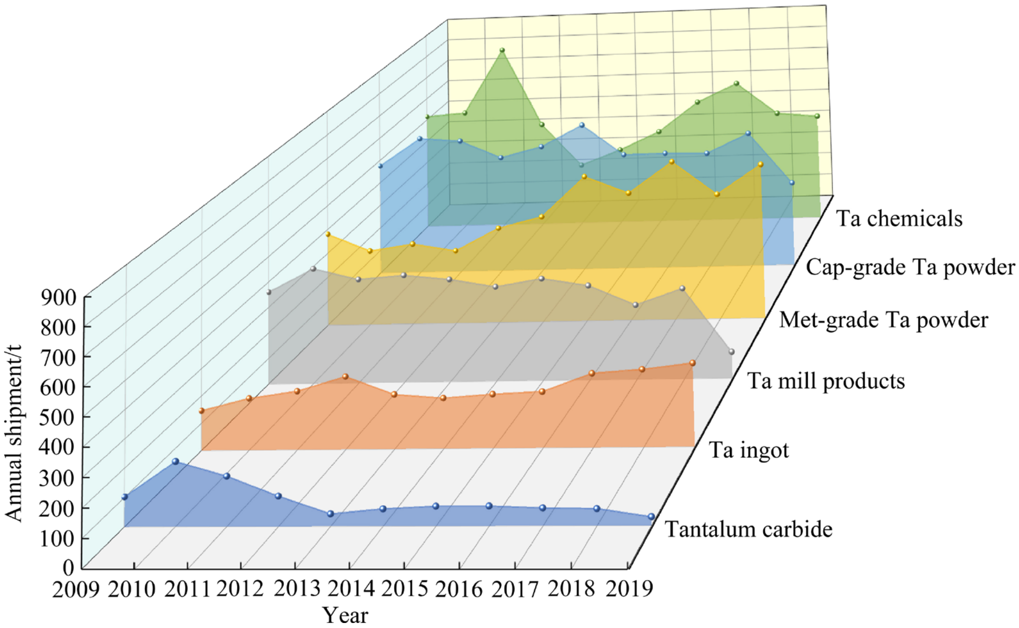

Fig. 6 Annual shipments of different tantalum products

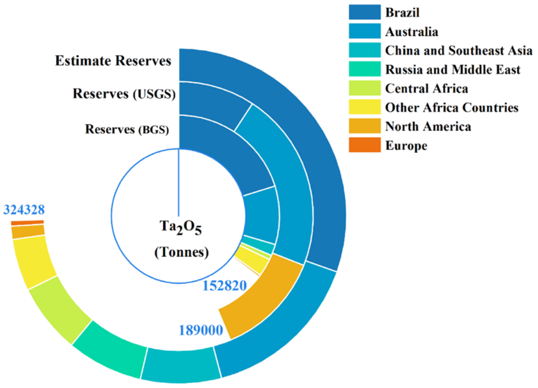

Fig. 7 Global tantalum reserves (Source: USGS, BGS, TIC)

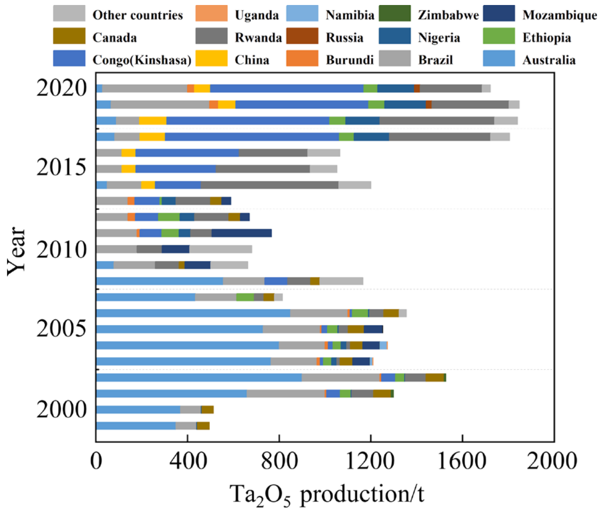

Fig. 8 Tantalum concentrate production in different countries (Source: USGS)

1999−2020. Australia and Brazil were major suppliers in the world before 2008, and they used to have 90% of the global tantalum concentrate market. However, Australia closed tantalum mines in 2008 with the background of the global financial crisis, and the supply of Ta concentrate from Australia was zero between 2010 and 2013. When Ta price increased rapidly after 2013, some mines in Australia resumed, but still cannot regain their old share [5]. Tantalum supplies from Africa's "Great Lakes" region, such as the Congo and Rwanda, are gradually assuming global dominance, and both countries consistently accounted for more than 50% of the supply since 2014.

The supply of Ta concentrates also varies with time, and the surge from 1999 to 2000 could be interpreted by the rapid increase in demand for tantalum capacitors. The "internet bubble burst" from 2002 to 2005, which led to a decrease in demand for tantalum and a surplus of stocks, made mines worldwide reduce production [51]. Global tantalum concentrates declined in 2005 and 2006 due to the shrinking of the Greenbush mine in Australia. Then, the production of tantalum concentrates increased significantly after 2006, and this could be explained by the rapid development of artisanal mining in African countries, such as the Congo, and Rwanda. However, the financial crisis in 2008 resulted in the breakdown of many tantalum mines. From 2009 to 2013, the production of tantalum concentrates decreased to a low value, and it increased significantly in 2014 with the global economic rejuvenating. The supply of tantalum concentrates remained stable from 2014 to 2016. Along with the fast development of the electronics industry, Ta concentrates supply reached a high value between 2017 and 2019. However, some countries closed mines with the background of COVID-19 pandemic in 2019, and this resulted in 8% decrease in 2020 [5,32].

Tantalum has been listed in the EU's fourth Critical Raw Materials List, and the EU has raised the level of Ta supply risk [52]. In addition to the geological availability, most of the tantalum mines in the "Great Lakes" region of Africa are "Conflict minerals" [10,53,54], and they are mined by artisanal approach [17,55,56], which is lack of accurate data.

The long-term continuity of tantalum supply is difficult to predict in a dynamic global market environment. The transfer of tantalum production from industrialised, politically stable countries to developing, politically volatile regions has attracted international concerns about the risk to the tantalum supply chain [19]. The "conflict minerals" of Central Africa have also attracted widespread international attention. With the gradual increase in public awareness of conflict minerals and the successive introduction of relevant bills [5,54], the share of tantalum supply from the "Great Lakes" region of Africa will decline significantly. On the other hand, the development of larger tantalum mines is actively considered in the international tantalum market in industrialised countries, such as Canada, Australia and Brazil. Therefore, a significant increase in tantalum concentrate production is expected to follow [18].

3.2 Tin slag

Tantalum has also been detected as an associated mineral in cassiterite ores, and these Ta sources mainly enter the slag phase in the pyrometallurgical processing of tin. The tantalum in the tin slag can be enriched with acid leaching, alkaline leaching or chlorination roasting, and the Ta content in the products can be up to 50 wt.%, which can be regarded as a synthesised Ta concentrate [57−63]. Tin slag was once an important raw material for primary tantalum production in some countries, such as Thailand, Malaysia, and Brazil. Tantalum extracted from tin slag was used to account for more than 50% of total primary tantalum production in the 1970s and 1980s. However, the portion decreased in 1985 since the collapse of the tin market [19,37]. Figure 9 shows the share of primary Ta produced from tin slag between 1991 and 2019 [39,64].

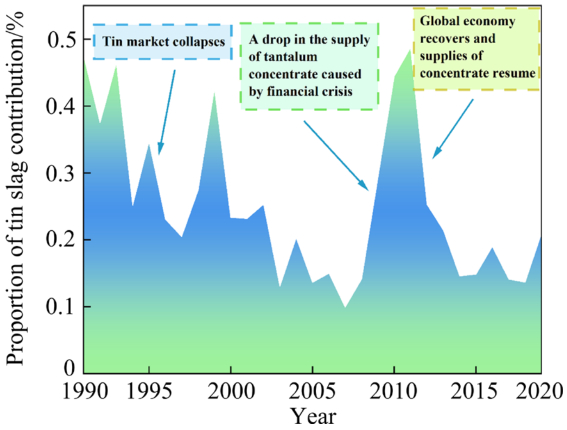

Fig. 9 Share of primary Ta produced from tin slag between 1991 and 2019 (Source: TIC)

As shown in Fig. 9, the proportion of primary tantalum produced from tin slag generally decreased in the past 30 years. But in some specific periods, it increased as substitute raw materials when the supply of tantalum concentrate was not sufficient. Tin is mainly used in containers, construction materials, transport materials and solder [17,65], but cheaper alternatives are available for these applications [66]. As a result, demand has grown slowly over the past 30 years and it is expected to grow by 2% in the following 5−10 years [65], which indicated that Ta extraction from tin slag will not increase significantly in the future. Another reason is the environmental requirements and economic challenges in extracting tantalum from tin slag are also negative [58].

3.3 Lithium ore

Tantalum has historically been an important by-product of lithium-making processes [67]. The tantalum can be recovered from polymetallic lithium ores during beneficiation [68]. Currently, primary lithium comes mainly from brines and pegmatite minerals in roughly equal proportions [69]. In the long term, the explosion of lithium supply capacity is most likely to occur in large brine deposits [70], but the mining of brine deposits is still challenging. Only 2 of the top 10 brine deposits are operating nowadays. Lithium ores mining is still attracting attention due to the short investment cycle [71]. Table 1 gives estimated global statistics for significant lithium mineral resources and by-product tantalum resources [69].

Due to the rapid development of smartphones, tablets, electric vehicles, etc., the manufacturing of lithium-ion batteries has been growing rapidly in the past 20 years. At the same time, concerns of the international community on energy saving and emission reduction provide new opportunities for lithium-ion batteries in the following decades, and it is expected that the lithium-ion battery market may grow 10 times larger by 2032 [69]. Lithium ores, an important resource for Li extraction, are supposed to increase dramatically, and there are seven major lithium pyroxene mines put into operation in Australia by the end of 2019 [71]. The rapid growth of lithium ores mining will also boost the supply of its by-product, tantalum [55]. According to Roskill's report, Australia accounted for 5% of global tantalum concentrate production in 2018, and it increased rapidly to 17% in 2019, which is a result of the mining of lithium pyroxene. Tantalum resources recovered from minerals such as lithium pyroxene and tin slag in Australia are expected to supply 20% of the world's tantalum demand by 2026 [1]. Based on future global requirement trends for lithium resources, tantalum as a by-product of lithium-making processes is likely to become an important source of primary tantalum production in the next 10 years.

3.4 Secondary resource

Tantalum is easy to lose in the environment, other material streams and landfills, and the global

Table 1 Large lithium−tantalum deposits and operators in world

Company	Deposit	Country	LCE[1] grade/wt.%	Ta grade[2]/wt.%	Status
Xinjiang Non-Ferrous	Koktokay	China	−	−	Operating
Talison	Greenbushes	Australia	5.93	0.03	Operating
Galaxy	Mt Cattlin	Australia	2.68	0.02	Operating
Process Minerals Int.	Mt Marion	Australia	3.38	0.01	Operating
Yichun Tantalum	Yichun	China	−	0.02	Operating
Bikita Minerals	Bikita	Zimbabwe	−	−	Operating
Mineral Resources	Wodgina	Australia	3.18	0.02	Operating
Jilin Jien	Val d'Or	Canada	2.95	−	Recommissioning
AMG	Mibra	Brazil	2.60	0.03	Constructing
Pilbara	Pilgangoora	Australia	3.08	0.01	Constructing
Tawana	Bald Hill	Australia	2.91	0.02	Constructing
Altura	Pilgangoora	Australia	2.46	−	Constructing
Nemaska	Whabouchi	Canada	3.62	−	Financing
Keliber	Various	Finland	2.96	0.01	Planning
European Metals	Cinovec	Czech Republic	1.04	−	Planning
Critical Elements	Rose	Canada	2.34	0.02	Planning
Sayona	Authier	Canada	2.64	−	Planning
Pock Tech	Georgia Lake	Canada	2.55	−	Planning
Kidman/SQM	Earl Grey	Australia	3.55	−	Planning
Global Geoscience	Rhyolite Ridge	USA	0.87	−	Planning
Galaxy Resources	James Bay	Canada	3.09	−	Planning
Avalon	Separation Rapids	Canada	3.24	0.01	Planning
European Lithium	Wolfsburg	Austria	2.89	−	Planning
Prospect Resources	Arcadia	Zimbabwe	2.74	0.01	Planning
Birimian	Boougouni (Goulamina)	Mali	3.50	−	Planning
Premier African Mins	Zulu	Zimbabwe	2.62	0.01	Planning
Perilya	Moblan	Canada	3.48	−	Planning
Bacanora	Zinnwald	Germany	1.94	−	Planning
Novo Litio	Sepeda(Romano)	Portugal	2.47	<0.01	Planning
Ardiden	North Aubry	Canada	3.57	−	Planning
Lithium Australia	Sadisdorf	Germany	1.11	−	Planning
Lepidico	Alvarroes	Portugal	2.72	−	Planning
American Pacific	Fort Cady	USA	1.99	−	Planning
Plymouth Minerals	San Jose	Spain	1.45	−	Scoping
Savanah Resources	Mina de Barroso	Portugal	2.47	−	Exploring
Frontier	PAK	Canada	3.86	0.01	Feasibility

1−Lithium carbonate equivalent (contained Li X 5.323); 2−Ta_2O_5 basis recovery of tantalum is likely to be only 10% of total tantalum consumption [20]. The secondary resources of Ta can be divided into two groups: the pre-consumer scrap, which was generated during the manufacture of Ta-containing electronic components, and the consumer scrap (post-use scrap of related tantalum products) [31].

It is reported that around 8% of Ta loss occurs in the manufacturing of capacitors, and the loss is even higher when preparing sputtered targets [72]. GILLE and MEIER [73] listed the current material streams of tantalum (primary and secondary), in which the proportion of pre-consumer scraps of total tantalum demand is 30%. Another report shows that the recycling of pre-consumer scrap of tantalum processing accounts for approximately 20%−25% [74]. However, these data can only represent the situation in developed countries, which have large numbers of Ta refineries. Tantalum consumer scraps are mainly recovered from cemented carbide and superalloy scrap nowadays [75], and their recoveries are approximately 60% and 90%, respectively [19]. 70% of these recycled superalloy scraps are remelted to regain the same alloys, 20% are processed into low-grade materials (down-cycling), and the rest (10%) are delivered to nickel refineries [76]. Table 2 summarizes available recovery information on tantalum in USA, Japan, etc.

Table 2 Available tantalum recovery information

Year	Country/ Region	Recovery amount/t	Recovery rate/%	Ref.
1998	USA	210	21	[76]
2021	USA	−	30	[31]
2012	Worldwide	250−700	−	[77]
2014	Worldwide	990	35	[37]
2012	USA, Japan	−	25	[78−80]

According to Table 2, the tantalum scrap processing started early in developed countries, such as USA and Japan, and in developing countries is still small [37]. Figure 10 shows the import of tantalum scrap in different countries [81].

As shown in Fig. 10, tantalum recycling in the world showed an increasing trend from 2003 to 2012, and this is influenced by the global awareness of sustainability and the development of tantalum recycling technologies. The importing of Ta scrap decreased between 2012 and 2019, which was mainly influenced by the regulations in different countries, and the trading of Ta containing materials was under supervision.

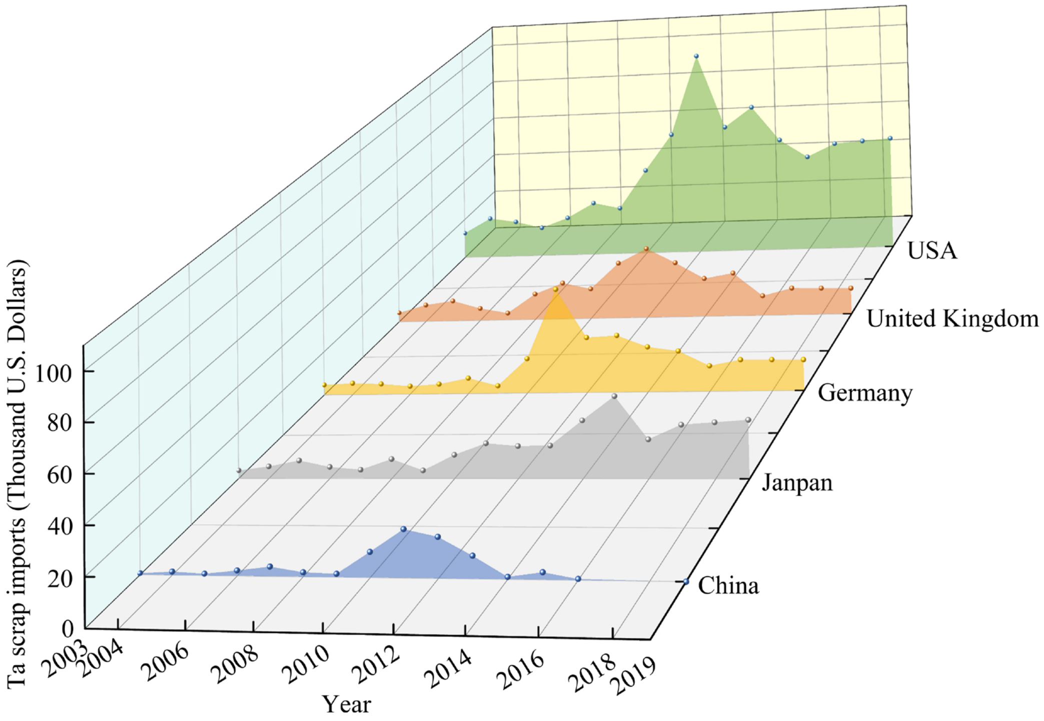

Fig. 10 Annual imports of tantalum scrap in some countries

4 Primary tantalum production

The extraction of tantalum from ores and other resources has been studied in many research [47,82]. The process consists of several sequential steps, involving tantalum and niobium leaching, solution purification and intermediate compound reduction [83]. The tantalum production processes practised in major plants in the world are listed in Table 3 [84]. And Fig. 11 shows various processes for tantalum production [57,85,86].

Table 3 Technologies for tantalum and niobium production in world

Country	Company	Technology	Solvent
USA	Cabot	Hydrometallurgy	MIBK
Germany	H. C. Starck	Hydrometallurgy	MIBK
Russia	Solikamsk	Chlorination process	−
China	Ningxia orient tantalum industry	Hydrometallurgy	MIBK
Brazil	CBNN	Direct reduction	−
Uzbekistan	Erba Metallurgical Plant	Hydrometallurgy	MIBK
Brazil	AMG Brasil	Direct reduction	−
Janpan	Mitsui Minning & Smelting	Hydrometallurgy	MIBK

4.1 Decomposition of tantalum concentrate

Owing to the refractory nature of tantalum minerals, Ta concentrates are usually treated with strong alkali/acid, or at high temperatures. The approaches that are applied in the industry are caustic fusion, alkaline solution leaching, acid leaching, chlorination roasting and carbothermal reducing [87]. The chemical reactions involved in these decomposition processes are shown in Supporting Materials. The key parameters of these methods are listed in Table 4.

The caustic fusion was the first used method to decompose tantalum−niobium concentrates [88], but it has been phased out due to economic and environmental disadvantages [89]. Compared to the caustic fusion method, the alkaline solution leaching greatly reduces the reagent consumption. But the investment in industrialization is too high [91]. Acid leaching is currently the dominant decomposition process, and hydrofluoric acid (HF) has been proven to be an effective leaching agent [94,95]. The main reactions involved during the HF decomposition are as follows [94−101]:

$$\mathrm{(Fe,Mn)(Ta,Nb)_2O_6+18HF=2H_2(Ta,Nb)F_7+H_2(Fe,Mn)F_4+6H_2O},\quad 20\%\le C_{\mathrm{HF}}\le 40\% \tag{1}$$

$$\mathrm{(Fe,Mn)(Ta,Nb)_2O_6+14HF=2H(Ta,Nb)F_6+H_2(Fe,Mn)F_4+6H_2O},\ 40\%<C_{\mathrm{HF}} \tag{2}$$

$$\mathrm{TiO_2+6HF=H_2TiF_6+2H_2O} \tag{3}$$

$$\mathrm{SiO_2+6HF=H_2SiF_6+2H_2} \tag{4}$$

However, HF is only suitable for the high-grade tantalum−niobium concentrates. The low-grade tantalum−niobium concentrates are usually leached with sulphuric acid, but the process and conditions are different to control [96,97]. Another concern is the pollution caused by fluorine containing wastewater, gases and hazardous wastes in the process [98,99]. About 6%−7% HF is lost during the decomposition process due to its high volatility and the decomposed residual acid cannot be fully recovered and utilized [100,101]. POLYAKOV and POLYAKOVA [104] began to study the regeneration of HF in the tantalum decomposition process to reduce the production costs in 1994. Unfortunately, no further industrial applications and cost-effectiveness of the relevant studies have been reported. However, 4 t of solid waste, of which 500 kg is radioactive waste, is generated when producing 1 t $\mathrm{Ta_2O_5}$ [101,105]. Due to the harmful environmental effects of HF, several alternative processes have been tried to leach Ta. Table 5 gives the research development in the decomposition of tantalum concentrates, and the chemical reactions involved in the new decomposing processes are shown in Supporting Materials.

It is common in the Chinese industry to use a mixed acid of HF and $\mathrm{H_2SO_4}$ in the decomposition process of Ta concentrate. The improved method is more effective than the single usage of HF, and the addition of sulphuric acid can reduce the volatilisation loss of HF and the total acid consumption [95]. Furthermore, pyrometallurgical treatment of tantalum concentrates has also attracted concerns. Chlorination roasting is an efficient way, which can treat complex tantalum−niobium concentrates and tin slags [92,113]. In the early 1960s, a chlorination roasting process was designed by CIBA in Switzerland, and it was

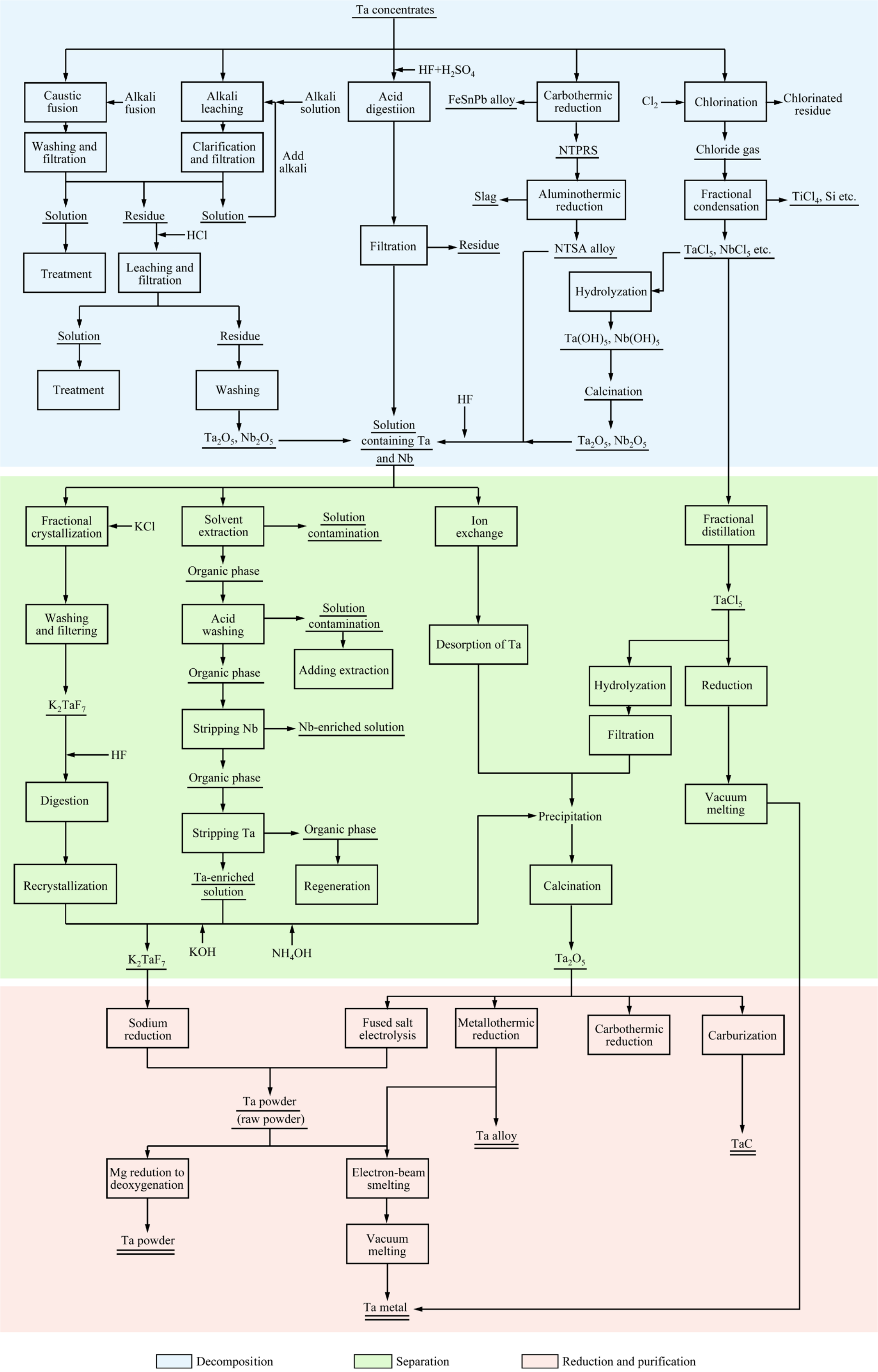

Fig. 11 Extractive metallurgy of tantalum

Table 4 Key parameters of tantalum concentrate decomposition

Method	Reagent	Reagent consumption/ [kg·kg (concentrate)$^{-1}$]	Temperature/ °C	Time	Decomposition rate/%	Other	Ref.
Caustic fusion	NaOH, KOH	3	800	20−30 min	80	Melt alkali at 400−500 °C	[88−90]
Alkaline solution leaching	NaOH, KOH (35%−45%)	0.5	150−200	2−3 h	−	High pressure	[91−93]
Acid leaching	HF (60%−70%)	4	90−100	4 h	66−81	HF volatilization rate 6%−8%	[94−101]
Chlorination roasting	Cl_2+C	−	400−800	−	−	−	[102]
Carbothermal reducing	C	−	−	−	−	−	[103]

Table 5 Progress in research on decomposition of tantalum−niobium concentrates

Method	Reagent consumption	Temperature/ °C	Time/ min	Decomposition rate/%	Ref.
KOH sub-molten salt decomposition	7:1	300	60	96	[106]
KOH roasting−leaching	2:1	400	60	94	[107]
Microwave-assisted decomposition	1:1 ($NaHCO_3$)	400−700	−	−	[108]
High-pressure HF leaching	0.049:1 (HF)	220	80	80	[109]
NH_4HF_2 decomposition	30:1	250	180	98.52−98.66	[110,111]
High-pressure CCl_4 decomposition	1g:6 mL	250−525	120	97	[102,112]

successfully implemented in the industry [114]. However, it is seldom used in industry nowadays, because of serious equipment corrosion, environmental pollution, poor operating conditions and high energy consumption. The reduction of columbite concentrate by coal makes it possible to obtain an iron alloy that contains tin and lead, in addition to a niobium−tantalum "pre-reduction" slag (NTPRS). The slag is subjected to alumthermic reduction to obtain a NbTaFe alloy (NTSA), a commercial product of the Brazilian company Paranapanema [103].

4.2 Separation of tantalum and niobium

Nb and Ta are related elements in minerals, and Ta(V) and Nb(V) have an almost identical ionic radius (64 pm for CN=6) due to the lanthanide contraction [114−116]. This particular situation determines that the separation of these two metals by chemical processes is really difficult. The separation methods of tantalum and niobium include fractional crystallisation, solvent extraction and ion exchange. Fractional crystallisation [117], which is based on the difference in the solubility between potassium fluotantalum (K_2TaF_7) and potassium niobium oxyfluoride (K_2NbOF_5), was the first method used for the large-scale preparation of pure tantalum compounds [118]. However, the tantalum pentoxide produced contains high content of niobium (0.1−0.3 wt.%), iron (0.2 wt.%), silicon (0.3 wt.%) and titanium (0.01 wt.%) [119]. Therefore, this process was replaced by solvent extraction after 1957. The ion exchange method allows for the efficient separation of tantalum and niobium. However, the chemical behavior of tantalum and niobium is characterized by an extreme tendency to hydrolysis, which limits the development of the ion exchange [120]. Solvent extraction is widely used in industry with the advantages of being flexible, effective and simple [109]. There are five main extractants, which are used in industry, and they are methyl isobutyl ketone (MIBK), tributyl phosphate (TBP), cyclohexanone (CHN), 2-octanols (2-OCL) and ethanamide (A101), and the chemical reactions for extraction of tantalum−niobium with various extractants are shown in Supporting Materials [120,121−123]. Figure 12 shows the properties and separation of the extractants, with MIBK being widely used due to better extraction results [57,124,125]. The main reactions involved during the solvent extraction of Ta and Nb with MIBK are as follows [125]:

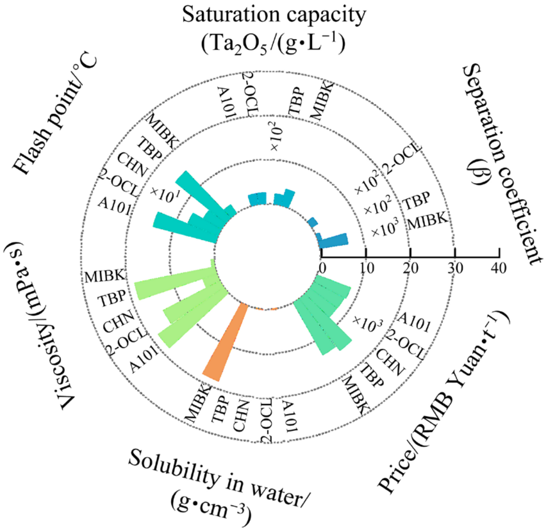

Fig. 12 Properties and performances of different extractants

$$H_2TaF_7+nH_2O+2C_6H_{12}O=(H\cdot nH_2O\cdot C_6H_{12}O)_2TaF_7 \quad (5)$$

$$HTaF_6+nH_2O+C_6H_{12}O=(H\cdot nH_2O\cdot C_6H_{12}O)TaF_6 \quad (6)$$

$$H_2NbF_7+nH_2O+2C_6H_{12}O=(H\cdot nH_2O\cdot C_6H_{12}O)_2NbF_7 \quad (7)$$

$$HNbF_6+nH_2O+C_6H_{12}O=(H\cdot nH_2O\cdot C_6H_{12}O)NbF_6 \quad (8)$$

$$H_2NbOF_5+nH_2O+2C_6H_{12}O=(H\cdot nH_2O\cdot C_6H_{12}O)_2NbOF_5 \quad (9)$$

The probable reactions involved during the stripping of Nb and Ta from MIBK are as follows:

$$(H\cdot nH_2O\cdot C_6H_{12}O)_2NbF_7+H_2SO_4=H_2NbF_7+(H\cdot nH_2O\cdot C_6H_{12}O)_2SO_4 \quad (10)$$

$$(H\cdot nH_2O\cdot C_6H_{12}O)_2TaF_7+2NH_4F=(NH_4)_2TaF_7+(H\cdot nH_2O\cdot C_6H_{12}O)_2F_2 \quad (11)$$

The main reactions involved during the processing of stripped Ta solution are as follows:

$$H_2TaF_7+12NH_4OH=(NH_4)_2Ta_2O_6\cdot H_2O+10NH_4F+5H_2O \quad (12)$$

$$H_2TaF_7+2KCl=K_2TaF_7+2HCl \quad (13)$$

$$K_2TaF_7+12NH_4OH=(NH_4)_2Ta_2O_6\cdot H_2O+4KF+10NH_4F+5H_2O \quad (14)$$

All solvent extraction processes are carried out in the presence of F$^-$, which is confronted with a great environmental challenge [120]. There is an urgent need for tantalum metallurgy to develop processes, which can run under low or fluorine-free conditions with increasingly stringent environmental requirements. The MIBK pulp extraction method [126,127] reduces the concentration of hydrofluoric acid used from 6 to 1.6 mol/L. However, running the process with low hydrofluoric acid concentration may cause emulsification of the extractant. YANG et al [128] used ultrasound to eliminate emulsification and achieved a recovery of 96.21% of tantalum. NIKOLAEV et al [129] reduced the concentration of hydrofluoric acid in solutions containing tantalum and niobium by diluting, evaporating and precipitating insoluble metal fluorides. The development of new extractants and systems is another viable point to solve the problem of fluorine contamination. The phosphonic acid functionalised ionic liquids (TSILs) provide efficient extraction of tantalum−niobium with HF concentrations of 1 mol/L [130]. Tertiaryamines, such as Alamine 336, are also promising extractants for the extraction of tantalum and niobium from oxalic acid solutions at low HF concentrations or in the absence of HF [131]. The separation of niobium and tantalum was successfully achieved by using Alamine 336 as the extraction solvent, and the recoveries of tantalum−niobium were 99.3% and 88.2%, respectively [132]. DUTTA et al [133] developed a solvent extraction process based on Alamine 336 (TOA). The process eliminated the adverse effects of fluoride during the extraction process, which prepared niobium and tantalum with purity of 98.88% and 98.08%, respectively. Although amine extractants have great potential, their application on an industrial scale has not yet been reported. The extraction system still requires further study to unravel the extraction mechanism, identify the optimum conditions and to find solutions to the problem of third-phase generation.

4.3 Preparation of tantalum

Though tantalum metal can be produced by several means, only two processes, namely sodium reduction of K$_2$TaF$_7$ and salt electrolysis of K$_2$TaF$_7$ in the presence of oxide, have been successful on an industrial scale [134]. Nearly 90% of world tantalum is obtained by sodium reduction of K$_2$TaF$_7$ [88]. Nowadays, with wide application of tantalum, the reduction process presents diversified development oriented by product demand.

4.3.1 Thermal reduction method

Reduction processes for tantalum compounds by metal reductants, such as magnesium, calcium, and aluminium, have been well studied. In addition, some non-metal reductants, such as carbon, silicon and hydrogen, also receive attention. Table 6 gives some parameters for the various reducing processes, and the chemical reactions involved in the reduction process are shown in Supporting Materials.

The sodium-thermal reduction of potassium tantalum fluoride, K_2TaF_7, where metallic sodium is used as the reductant, is one of the earliest technologies, but still in use, full-scale technologies [135]. The reduction reaction of K_2TaF_7 with sodium produces 3 MJ/kg of mixed reactants approximately, which is sufficient to sustain the reaction [118]. All commercial tantalum powders have been prepared by this method due to low energy consumption from 1953 [145]. However, the potassium fluorotantalate is costly and corrosive, and the reduction process tends to produce large amounts of toxic gases [146]. The oxygen content of obtained tantalum powder is high, which subsequently requires deoxygenating by magnesium reduction or multiple electron beam melting [147].

The specific surface area of tantalum powder prepared by magnesium reduction of tantalum oxide can reach 15 m^2/g [136], making it suitable for the application in tantalum capacitors [148]. Therefore, magnesium reduction of tantalum oxide is considered to be the most promising method for preparing cap-grade tantalum powder. Magnesium vapor reduction and self-propagation reduction are two different magnesium reduction processes. Table 7 provides salient features of these two processes.

Some difficulties, such as contaminations and non-uniformity of the reaction, have hindered the industrialization of the Mg reduction process. The magnesium vapour reduction process prevents impurities in the reducing agent from contaminating the tantalum powder. However, tantalum powder was also found to be susceptible to impurities in the reaction vessel. OKABE et al [151] developed a new process, in which feedstock preforms were used to avoid contamination of the reaction vessel. YUAN and OKABE [152] further reduced Ni contamination in the reaction vessel by using an Mg−Ag alloy as a reducing agent based on the raw material preform process. Figure 13 shows a schematic diagram of the two improved processes.

The diffusion process of magnesium vapour in the tantalum oxide phase is difficult to control and the homogeneity of the product needs to be improved [149]. To avoid these problems, the self-propagating reduction of Ta_2O_5 and Mg has been investigated. The self-propagation reduction is an energy-efficient method, where the reaction temperature and reaction rate can be controlled by adjusting the amount of magnesium. However, the

Table 6 Some parameters of tantalum compound reducing process

Reductant	Compound	Temperature/°C	Particle size	Oxygen content/10^{-6}	Ref.
Na	K_2TaF_7	800	2−3 μm	1500−300	[134,135]
Mg	Ta_2O_5	800−1459	50−300 nm	13000	[136,137]
Ca	Ta_2O_5	~3000	Lump	5660−6100	[119,135,138]
Al	Ta_2O_5	~3000	Lump	−	[139,140]
C	Ta_2O_5	1900−2000	30−40 μm	300−500	[141]
Si	Ta_2O_5	1150−1600	−	−	[142]
H_2	$TaCl_5$	1000−1400	50− 100 nm	6000−6900	[143,144]

Table 7 Comparison of magnesium vapor reduction and self-propagation reaction processes

Reduction process	Advantage	Disadvantage	Ref.
Magnesium vapor reduction	Low reductant contamination, and controllable morphology	Long time, high vapor consumption, high energy consumption, and uneven reaction	[148,149]
Self-spreading reaction	Rapid reaction, low energy consumption, and uniform reaction	Susceptible contamination and formation of magnesium tantalate	[150]

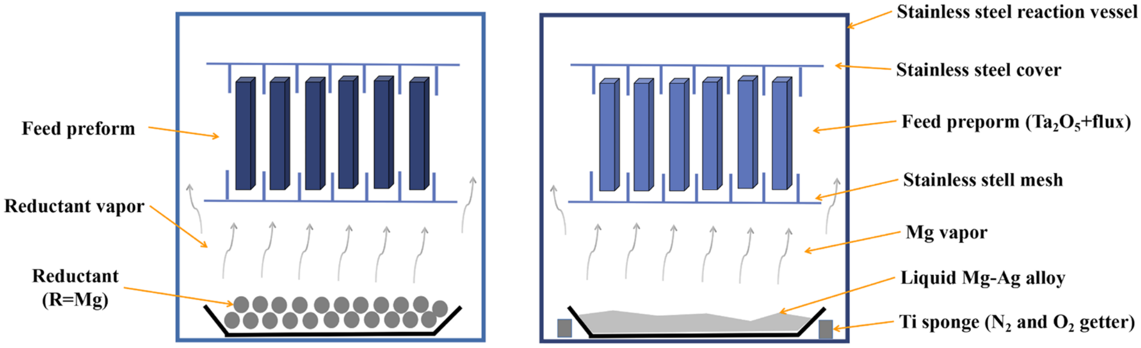

Fig. 13 Experimental set-up [153,154]

process tends to produce by-product of $Mg_4Ta_2O_9$, and this affects the quality of the tantalum powder. Some studies have shown that the addition of NaCl to the reactants can inhibit the formation of magnesium tantalate by-products [153,154]. NERSISYAN et al [153] proposed an MSA-CS (molten salt assisted high-temperature synthesis) method, in which the mixture of Ta_2O_5 and Mg was diluted with NaCl, and then reacted at high temperature in argon gas. Spherical ultrafine tantalum powder with good dispersion was obtained, but its low specific surface of it is not suitable for capacitors. WON et al [155] used Ta_2O_5 $(5+m)Mg-kNaCl$ to synthesis Ta powders with homogeneous coral shapes by SHS method, which has promising applications in the tantalum capacitors. NERSISYAN et al [156] prepared tantalum powders with individual particle sizes between 50 and 700 nm in a $Ta_2O_5 + kMg$ system with controlling temperature via liquid magnesium. Tantalum powder can be used for preparation of ultra-high-capacity tantalum anodes [157,158]. Tantalum powders containing large amounts of magnesium tantalate by-products have also been investigated for secondary reduction treatment or pre-prepared precursors of magnesium tantalate followed by reduction. ORLOV and KRYZHANOV [159] re-treated tantalum powder, which contained 30% magnesium tantalate, with magnesium, and obtained a tantalum powder with an increased specific surface. Another study showed that nano-porous tantalum powders with specific surface areas well above 30 m^2/g were prepared using materials with high Mg, Ta and O contents as precursors [137]. And the tantalum powder with a specific surface area of 65 m^2/g (calculated particle size of 6 nm) was synthesised by the reduction of $MgTa_2O_6$ and $Mg_4Ta_2O_9$ with magnesium vapor [7]. In addition, the mechanisms involved in the reduction of tantalum oxide by magnesium have been investigated. MÜLLER et al [8] have found that tantalum oxide powders and magnesium form complex interpenetrating morphologies after vapor reduction. Nanoscale flake and rod-like morphologies were formed early in the reaction, and this regular structure decomposed and coarsened in further annealing. By leaching the magnesium oxide, porous tantalum with a large specific surface area is finally obtained. HWANG et al [160] conducted a kinetic study of reduction behavior of tantalum oxide using different initial particle sizes (0.3 and 1.2 μm). The results showed that the reduction activation energies of the 0.3 and 1.2 μm powders were 5.234 and 8.695 kJ/mol, respectively.

The tantalum powder obtained by calcium thermal reduction with a small specific surface and high oxygen content (0.566−0.610 wt.%) [118], which makes it unsuitable for use in capacitors. However, the tantalum powder can be cold-rolled into various products such as rods after electron beam melting. A recent study has found that calcium reduction of Ta_2O_5 in molten $CaCl_2$ allows preparing fine tantalum powders in the form of cauliflowers. The tantalum powders have high potential for improving capacitor performance, as they have a greater capacitance compared to conventional powders with the same surface area [135]. Studies on the mechanism show the formation of cauliflower-like tantalum powder, which is more likely to form in the area with a high concentration of CaO [138].

Tantalum in bulk form can be prepared by thermal reduction with aluminium, which often has a high content of impurities and requires further purification [139,140]. In addition, the temperature of the process is above 3000 °C, which greatly increases energy consumption and operational difficulties. Several researchers have developed a range of processes to reduce the temperature of thermal reduction of aluminium. NAIR et al [140] reduced the reduction temperature to 800 °C with an applied electric field, but the electrolyte contained fluoride, increasing the economic cost and environmental pressure. Another method is to add excess aluminium and iron oxide to form an alloy to generate additional heat for replenishment, which decreased the reduction temperature by 350−500 °C. Calcium oxide is added to lower the melting temperature and promote slag and metal separation [140]. MUNTER et al [161] studied the simultaneous reduction of tantalum pentoxide and iron oxide in a series of melting processes. The alloy obtained was a dense ingot with good phase separation and a reduction reaction starting temperature of 960−970 °C.

Additionally, it is possible to reduce tantalum oxide by non-metallic elements such as carbon and silicon. Carbon reduction of tantalum oxide has low costs and production cycles. The tantalum powder obtained by this method has a high content of C and N impurities, which makes it difficult to meet the requirements of industrial tantalum powder [141]. Ta−Si−O alloy can be obtained after silicon-thermal reduction of tantalum oxide, which subsequently needs to be purified by high-temperature thermal vacuum treatment [142]. Some researchers have also focused on the hydrogen reduction of $TaCl_5$. The plasma hydrogen reduction tantalum chloride method proposed by the Japanese company Cabot can produce uniformly dispersed tantalum powders of 50−100 nm, but high equipment requirements and energy consumption keep it in the laboratory stage [135]. Some related studies include hydrogen reduction of gaseous tantalum−niobium chloride processes [143], conversion and crystallinity of reduced tantalum powders [144].

4.3.2 Electrolysis of molten salts

As graphite crucible and cathodes are used in the fused salt electrowinning of tantalum, the contamination of carbon in the cathode deposits of tantalum powder to the extent of 1%−1.5% is very common [57]. Therefore, traditional molten salt electrolysis is gradually being phased out in the preparation of capacitor-grade tantalum powder. However, molten salt electrolysis is still an important method for the preparation of tantalum coatings [162].

The FFC method [163], where metal oxides can be reduced to metal in an electrolytic cell containing molten $CaCl_2$ with the metal oxide as the cathode and graphite as the anode, has been shown to reduce tantalum oxide to tantalum metal [164]. The advantages of the FFC method are fluorine-free environment, and no need for expensive sodium metal and energy savings. WU et al [164] have shown that Ta_2O_5 can be reduced to fine Ta powder particles in molten $CaCl_2$ by FFC. The oxygen content can be reduced to about 0.12 wt.%, but a significant problem is that the carbon content of the product is still too high. BARNETT et al [165] decreased the content of C in Ta powder by using SnO_2 as the anode via FFC-Cambridge. AHMADI and SUZUKI [166] performed the electrochemical reduction of TaS_2 in molten $CaCl_2 \cdot xCaS$ (x=0.1, 0.5 mol%) at 900 °C, which greatly reduced the C and O content of the tantalum powder. In the case of mechanism, SONG et al [167] showed that Ta_2O_5 underwent three intermediate stages at 1123 K in reduction: $Ta_2O_5 \cdot 0.5CaO$, $Ta_2O_5 \cdot 2CaO$ and $Ta_2O_5 \cdot 4CaO$. Another significant disadvantage of the FFC method is the low process efficiency. The reason is that the voltage applied during electrolysis must be lower than the decomposition voltage of the molten salt, which leads to slow reaction rates and side reactions. To improve current efficiency, researchers have proposed the electrochemical reduction of Ta_2O_5 in molten Mg−NaCl−KCl or LiCl−Li_2O molten salt systems [168,169].

4.3.3 Other methods

Some new methods of Ta_2O_5 reduction have emerged in recent years, such as the solid oxide−oxygen ion conductive film method (SOM) [170] and the electron dielectric method (EMR) [9,171]. The principle of the SOM method is the direct dissociation of tantalum oxide minerals by applying an electrical potential. Oxygen ions are oxidised at the anode through a membrane (SOM) and reduced at the cathode to give Ta metal. This process allows the efficient production of tantalum metal without the need for expensive decomposition of raw materials and generation of harmful by-products. Compared to the tantalum powder produced by metallic thermal reduction, the EMR method allows for a finer tantalum powder to be produced without the need for raw material reductant contact, largely avoiding the contamination of the reduction product by the reductant. YOON et al [171] also used a combined MR−EMR process to increase the recovery of tantalum powder from 65% to 74%.

5 Tantalum production from secondary materials

The high demand for Ta and the depletion of Ta resources have redirected the industrial community to think about the recovery of tantalum from secondary materials [172]. The Covid-19 crisis has revealed the instability of the global supply chain. It is urgent to develop new secondary sources. Indeed, there are no further potential findings for the recycling of pre-consumer scrap, other than to improve efficiency. The circular economy can be a long-term strategy to mitigate the risks of tantalum supply [173]. Tantalum, with a current end-of-life recycling rate of less than 1%, has been intermittently discussed [70].

Industrial-scale tantalum recycling is usually based on input material with high purity such as production scrap, cemented carbide and superalloy scrap. The unoxidized tantalum scrap can be remelted in an electron beam furnace or dehydrogenated in a vacuum furnace to produce tantalum powder, while oxidised tantalum material is roasted and then treated with nitric or hydrochloric acid [174]. Interestingly, unexplored supply route is the recovery of Ta from capacitors, particularly from end-of-life products. The Global E-waste Monitor reported that 44.7×10^6 t of e-waste were generated in 2016, with an annual growth rate of 5%−10%. The grade of valuable metals in this e-waste is 10−100 times higher than that in the ore in question, and the energy consumed to extract it can be saved by 20%−95% [175]. Currently, 20% of e-waste is recycled, but tantalum accounts for 1% of the total [130,176]. More than 60% of tantalum is used in the electronics industry [35]. Unfortunately, current technology does not realize the effective recovery of tantalum from used scrap in electronic equipment [177]. The reason is a conflict of interest in the recovery of tantalum and other valuable metals in WEEE. In the traditional process of recovering copper from WPCB, tantalum mainly enters into the slag phase with other impurities, making it difficult to recover [178,179]. At the same time, the continued miniaturization of electronic equipment also increases the difficulty of tantalum recycling [73,75]. Based on the minor Ta content in WEEE (1.72×10^{-2} wt.%), it can be concluded that a recovery of this refractory metal is uneconomical due to the dissipative distribution in the wastes [179].

Recycling of tantalum from WEEE is not practiced yet, but some investigations on recycling methods for tantalum capacitors have been studied. Table 8 lists the various methods used to recover tantalum from used capacitors.

Table 8 Recycling methods for used tantalum capacitors

Step	Aim	Method	Property	Ref.
Identification and liberation	Enrichment of tantalum capacitor	Artificial treatment	High accuracy and high cost	[180]
		Automatic disassembly	High efficiency, and low accuracy	[181]
Physical processing	Separation of resin and tantalum anode	Mechanical processing	Simple operation and low separation rate	[180, 182]
		Pyrolysis	High separation effect, and high energy consumption	[183]
		High temperature oxidation	High energy consumption and complex operation	[184]
		Ionic liquids treatment	High energy consumption and high equipment requirements	[185]
		Supercritical water processing	Harsh experimental conditions	[186]
Metallurgical processing	Purification of tantalum and its compounds	Hydrometallurgy	Long process, and high product purity	[187]
		Pyrometallurgy	Short process, and high energy consumption	[188]

In order to improve the recovery of tantalum from WEEE, it is necessary to divert tantalum-containing equipment for dedicated recovery of tantalum early in the recycling process [189]. There are a large number of tantalum capacitors separated from printed circuit boards for recycling [189]. The automatic identification and dismantling of tantalum capacitors have been studied and have proven to be feasible [190]. In addition, the manufacturers should take recycling into account when designing their products [191]. Mechanical treatment and pyrolysis are common methods to separate the tantalum anode from the epoxy resin shell. Ordinary mechanical treatment is often inefficient. Cryogenic mechanical treatment is promising in terms of improving crushing efficiency while avoiding the liberation of exhaust gas [192]. Pyrolysis is another commonly-used method, including pyrolysis under molten alkali and alkali vapour, which reduces the pyrolysis temperature and fixes the halogens [193]. In the case of the purification of tantalum, both hydro-metallurgical and pyrometallurgical methods have their advantages and disadvantages, and the combination of the two often produces better results [194]. Moreover, the value-added utilization of waste tantalum capacitors is another issue that requires ongoing attention [195]. In conclusion, the separation and recycling of tantalum from used electronic waste remain the key to further research and development.

6 Conclusions

Based on the above literature survey, the global production of tantalum concentrates is expected to remain high in the future, but the proportion of artisanal mining in Central Africa is likely to decline and conventional mining will increase. The supply of tantalum from tin slag is expected to remain at current levels and the supply of tantalum from lithium-making processes is expected to increase. At the same time, the recovery rate of tantalum scrap is expected to increase slightly due to the structural transformation of the tantalum consumption side and the current emphasis on sustainable development. Based on these data and projections, mitigation strategies such as long-term offtake agreements and the development of a diversified tantalum supply chain, diversified geographic supply locations or an increased share of tantalum recovered from scrap are recommended to minimise the risk of supply shortages and price increases and to ensure a secure and sustainable supply of tantalum to the world.

At present, hydrometallurgy has dominated in the production of tantalum in the world, in which MIBK is the most common extractant. And metallurgical plants are eschewing the classical scheme for tantalum and niobium production. The use of new raw materials and the development of new tantalum and niobium separation processes other than the hydrofluoric acid system, are important efforts for tantalum and niobium metallurgy. Ta industry requires new and efficient value-added metallurgical techniques to meet the demands of modern technological developments for functional materials.

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Supporting Materials

Supporting Materials in this paper can be found at: http://tnmsc.csu.edu.cn/download/19-p3132-2022-0976-Supporting_Materials.pdf.

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钽资源及其生产综述

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摘 要：钽(Ta)是一种关键高科技金属，在电工电子、航空航天等战略新兴产业中都有重要应用。当前尚无钽的替代材料，近 20 年来全球钽供应危机不断加剧。本工作对钽资源及其生产进行全面综述。地壳中已查明 Ta 储量不足 300 kt，钽的提取以钽精矿为主要原料，此外，锡冶炼渣、锂矿石、废钽产品也能生产约 37%的金属钽。钽的生产是一个高耗能过程，HF 浸出−溶剂萃取−K_2TaF_7还原工艺是工业上制 Ta 最常用的工艺，但较高的生产成本和大量废弃物的产生是制约该方法可持续发展的重要因素。钽的清洁生产及高效回收将受到持续关注。

关键词：钽；应用；资源；生产；回收

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