

TANTALUM AND TANTALUM COMPOUNDS

Tantalum [7440-25-7], atomic number 73, is the heaviest element in Group 5 (VA) of the Periodic Table. The element was discovered in 1802 by the Swedish chemist Ekeberg when he was examining new mineral samples found in Scandanavia (1). He named the new element “tantalum” and the mineral from which it derived “tantalite” after the Greek god, Tantalus, because of the materials’ “tantalizing” resistance to attack by mineral acids. Because Tantalus revealed the secrets of the gods to ordinary mortals, he was punished in Hades by having to stand beneath a loaded fruit tree up to his chin in water, the fruit and water retreating every time he tried to quench his hunger or thirst. Tantalus was the father of Niobe, for whom tantalum’s closely associated sister element, niobium, was named.

The chemistries of both niobium (also called “columbium”) and tantalum were subsequently investigated by Berzelius, who was a student of Ekeberg and produced the first tantalum metal, although heavily contaminated, in 1824 (2). In 1865, Marignac found that differences in the solubility of the potassium double fluoride salts of tantalum and niobium with potassium permitted a separation, and this technique was used for years as a production process to separate the elements. Dr. W. Van Bolton, in 1905, succeeded in producing a tantalum metal ductile enough to be drawn into filaments for lamp wire, but the manufacture of much cheaper tungsten wire soon displaced tantalum (3). With the passage of time and the availability of pure tantalum metal and compounds many new uses were found. By taking advantage of the metal’s unique properties of acid resistance, dielectric strength, high density, and refractory character, innovators found applications in fields as diverse as electronics, metal cutting, and chemical equipment fabrication. Perhaps the seminal discovery, however, was that of Balke and Engel, who found that a tantalum oxide film, which readily formed on the metal surface when it was made the anode in a battery-like circuit, blocked the flow of DC electric current in an electrolyte such as sulfuric acid in one direction, but not in the other. This finding led, first, to the development of the DC rectifier, millions of which were manufactured for DC radios in the 1920s and, then, to the tantalum capacitor, used in the 1930s by Western Electric in telephone circuitry (4). Today the tantalum capacitor is annually manufactured in quantities of billions, and the capacitor industry accounts for >70% of total tantalum usage.

1. Physical and Chemical Properties

Tantalum (Ta) (atomic number 73, atomic weight, 180.948) appears in Group VA of the periodic table directly below niobium. Properties of the element are summarized in Table 1 and represent the best data from several compilations (5–7).

Tantalum is readily oxidized to a +5 valence state, but is passivated by a stable, adherent oxide layer on the surface of the metal in many environments. This layer accounts for the excellent corrosion resistance of the metal in oxidizing acids, such as concentrated sulfuric, nitric, and hydrochloric below 200°C (8). Hydrofluoric acid reacts with the passive oxide film to destroy it. Thus, tantalum is readily attacked by acid solutions containing fluoride, and the reaction with HF combined with strong oxidizers is particularly aggressive. Tantalum is also attacked by hot, concentrated alkali and by halogen gases at elevated temperatures to form the

2 TANTALUM AND TANTALUM COMPOUNDS

Table 1. Physical and Mechanical Properties of Tantalum

| Property | Value |
|---|-------------------------|
| Lattice type | Body-centered cubic |
| Lattice constant, (at 20°C), nm | 0.33026 |
| Atomic volume, cm ³ /mol | 10.9 |
| Atomic radius, pm | 147 |
| Slip plane at room temperature | (110) |
| Density, g/cm ³ (20°C) | 16.62 |
| Melting point, °C | 2996 |
| Boiling point, °C | 5425 ± 100 |
| Specific heat, J/(kg) (K) ^a | 150.7 |
| Thermal conductivity, W/(m) (K) (at 20°C) | 54.4 |
| Coefficient of linear expansion, °C ⁻¹ (at 20°C) | 6.5 × 10 ⁻⁶ |
| Electrical resistivity, μΩ·cm (at 20°C) | 13.5 |
| (at 1500°) | 71 |
| Thermionic work function, eV | 4.12 |
| Magnetic susceptibility (cgs) | 0.93 × 10 ⁻⁶ |
| Tensile strength, MPa (at 20°C) ^b | 241–483 |
| (at 1000°C) | 90–117 |
| Young's modulus, GPa (at 20°C) | 186 |
| (at 1000°) | 152 |
| Poisson's ratio | 0.35 |

^aTo convert J to cal divide by 4.184.

^bTo convert MPa to atom, divide by 0.1013.

pentahalides. The metal forms compounds at elevated temperatures with other elements of groups IVA (carbon, silicon) and VA (nitrogen, phosphorous, and arsenic), but, in the absence of oxygen, is inert to most liquid metals, including sodium and potassium.

Tantalum does not have any effect on body tissues and is used in implants and biomedical devices. However, if inhaled, it has been suggested that mild fibrosis of the lungs may occur. When in a finely divided state, such as powder, tantalum burns with “white heat” if exposed to heat, flame, or an electrical arc in an oxidizing atmosphere. The reaction can be stopped only by removing or preventing exposure to the oxidizing agent.

2. Occurrence

The average tantalum content of the earth's crust has been estimated at about 1.7 parts per billion. Niobium, the sister element, is about 10 times as abundant. Free tantalum metal is unknown, and tantalum minerals are almost always found in association with those of niobium. The minerals of tantalum and niobium, called tantalates and niobates (columbates), are mainly salts of metaniobic and metatantallic acids. They are usually found as complex, oxidic materials in solid solution with other elements, such as tin, titanium, thorium, uranium, and rare earths. Table 2, summarizes the composition and refractory oxide (ie, Ta₂O₅ and Nb₂O₅) contents of the most important minerals (9).

Tantalite is the most important of these minerals. Tantalite and columbite are iron and manganese salts of metatantallic and metaniobic acids and form a continuous, isomorphous series. Microlite, likewise, is a sodium and calcium tantalate containing fluorine and is the tantalum-rich end of the isomorphous microlite–pyrochlore series. Because some of these ores contain radioactive elements, special health and safety requirements are necessary to process and contain the extraction residues. Struverite, a variation of the titanium mineral rutile,

Table 2. Chemical Compositions of Most Important Tantalum Minerals

| Mineral | Nominal composition | Ta ₂ O ₅ , % | Nb ₂ O ₅ , % | Crystal structure |
|----------------|---|------------------------------------|------------------------------------|----------------------------|
| tantalite | (Fe,Mn)Ta ₂ O ₆ | 42–84 | 1–40 | orthorhombic |
| columbite | (Fe,Mn)(Nb,Ta) ₂ O ₆ | 1–40 | 40–75 | orthorhombic |
| microlite | (Na,Ca)(Ta,Nb) ₂ O ₆ F | 60–70 | 5–10 | isometric octahedral |
| wodginite | (Ta,Nb,Sn,Mn,Fe,Mn) ₁₆ O ₃₂ | 45–56 | 3–15 | monoclinic |
| yttrotantalite | (Y,U,Ca)(Ta,Nb,Fe ³⁺) ₂ O ₆ | 14–27 | 41–56 | orthorhombic |
| struverite | (Ti,Ta,Nb,Fe) ₂ O ₄ | 7–13 | 9–14 | tetragonal, rutile type |
| fergusonite | (Y,Er,Ce,Fe ³⁺)(Nb,Ta) ₂ O ₄ | 4–43 | 14–46 | rutile type |
| tapiolite | (Fe,Mn)(Nb,Ta,Ti) ₂ O ₆ | 40–85 | 8–15 | tetragonal |
| euxenite | (Y,Ca,Ce,U,Th)(Nb,Ta,Ti) ₂ O ₆ | 1–6 | 22–30 | orthorhombic |
| samarskite | (Fe,Ca,U,Y,Ce) ₂ (Ta,Nb) ₂ O ₆ | 15–30 | 40–55 | orthorhombic |
| loparite | (Ca,Ce)(Ti,Nb,Ta) ₂ O ₆ | trace–3 | 6–11 | orthorhombic |

is a lower grade source of tantalum recovered in tin mining wastes in Southeast Asia. Since about 1970, tin smelter slags, where most of the tantalum concentrates during the smelting process, have been a significant tantalum source. Thai tin slags have been particularly rich in tantalum, whereas Bolivian slags have not. Before 1970, in Thailand, the slags were used as aggregate for road construction, but in the middle of the decade, when a tantalum raw-material shortage was evident, these same roads were dug up for tantalum values! Thai tin slags typically contain 12–15% Ta₂O₅. Although some processors extract the tantalum from slags directly, they are frequently upgraded in tantalum content to “synthetic concentrates” prior to extraction. Since the downturn in tin mining beginning in the late 1980s, however, processor usage of feed material derived from tin slags has declined, and tantalite mining as a primary product rather than a by-product has increased.

Pegmatites or their associated alluvium or eluvium have been the source of almost all commercially mined tantalites. However, since the end of the 1980s, mining of the alluvial deposits has decreased as these more easily accessible resources have been depleted. Pegmatites are a coarse variety of granite usually found in veins or dikes. Tantalite is black-brown in color, and markers frequently found as co-products with tantalite are cassiterite, beryl, spodumene, mica, and feldspar. Exploration has been assisted by aerial photography since some features of pegmatite dikes can be distinguished. Because tantalum is present in low concentrations, however, verification of economically attractive deposits is difficult. Specific-gravity measurements of particulate from alluvium or drilling test cores are useful because of tantalum’s high density, and application of X-ray spectroscopic analytic techniques has been advantageous.

Although tantalum ores are distributed throughout the world, most are low grade so that mining is limited to higher grade deposits in a relatively few countries. Estimates of world tantalum reserves have been made by the U.S. Geological Survey and are shown in Table 3 (10).

Tantalum reserves for Thailand, Malaysia, Zambia, Bolivia, China, and the Commonwealth of Independent States (CIS), all of which produce tantalum, are not included because available information is inadequate to reliably estimate output. However, the combined reserves and reserve base for Malaysia and Thailand given in a previous Mineral Survey were 9,100 and 10,900 metric tons tantalum, respectively (11). China reports an “industrial” reserve in 1992 of 32,600 metric tons (12). The grade is low ($\leq 0.016\%$ Ta₂O₅) and it is unclear what portion can be economically extracted. The CIS is also stated to have reserves as large as Australia. A country-by-country analysis of tantalum reserves and production has been published by Roskill (13). The conclusion is that on a world basis resources of tantalum are sufficient to meet projected needs.

4 TANTALUM AND TANTALUM COMPOUNDS

Table 3. World Tantalum Reserves, and Reserve Base 1999, t^a

| Country | Reserves ^b | Reserve Base ^b |
|------------------------------|-----------------------|---------------------------|
| Australia | 11,000 | NA |
| Brazil | 900 | 1,400 |
| Canada | 1,800 | 2,300 |
| Nigeria | 3,200 | 4,500 |
| United States | | negligible |
| Zaire | 1,800 | 4,500 |
| Other countries (see text) | NA | NA |
| <i>World total (rounded)</i> | <i>19,000</i> | <i>24,000</i> |

^aTantalum content, metric tons.

^bNote: Reserve base is defined as the “in-place demonstrated resource (measured plus indicated) from which reserves are estimated.” Reserves are that part of the reserve base that can be “economically extracted.”

Table 4. Tantalum Supply by Source, 2000

| Tantalum Source | Ta ₂ O ₅ Content, t |
|----------------------------|---|
| Primary mine | 1741 |
| Synthetic concentrate | 295 |
| External recycle | 540 |
| Inventory (U.S. stockpile) | 164 |
| <i>Total</i> | <i>2740</i> |

3. Tantalum Supply

Only about 50% of processor demand for tantalum is provided by primary mine production. The other sources, synthetic concentrates, scrap recycle, and inventory movement, constitute the remainder. This atypically low percentage as compared to other metal commodities is a reflection of the relatively high value of tantalum units. Therefore, processors have incentive to maximize material utilization to contain costs. Table 4 (14) summarizes estimates of the quantities of tantalum material supplied to processors for the year 2000. It should be noted that recycle includes material provided externally from users and consumers and not material which is internally recycled by the processors. Also, in recent years, tantalum inventory has been sold from the U.S. strategic defense stockpile. The inventory contribution to supply, however, excludes internal changes in processor inventory.

4. Processing

4.1. Ore Dressing

The mining of pegmatite deposits, either open-pit (Gwalia Consolidated Ltd., Greenbushes, Australia) or underground (Tantalum Mining Corporation of Canada Ltd., Tanco, Canada), is done by conventional techniques like blasting and crushing (see Minerals recovery and processing). The materials are then dressed mainly by gravity concentration. Mineral processing of tantalum and niobium ores has been described in detail, including flow sheets of the main producing plants (15).

Table 5. Enrichment of Tantalum in the Pyrometallurgical Upgrading Process

| Component | Composition, wt % | |
|--------------------------------|---------------------------------|--------------------------|
| | Slag ^a (Malaysia) | Synthetic concentrate |
| Ta ₂ O ₅ | 2 | 20.8 |
| Nb ₂ O ₅ | 2.2 | 25.6 |
| TiO ₂ | 10.5 | 25.0 |
| SnO ₂ | 1.2 | 0.1 |
| WO ₃ | 2.6 | 0.1 |
| P ₂ O ₂ | 1.2 | 0.1 |
| FeO | 15 | 8 |

^aAlso contains CaO, MgO, Al₂O₃, and SiO₂.

4.2. Upgrading of Tin Slags

The 0.2–17% Ta₂O₅-containing tin slags are upgraded in a sequence of three pyrometallurgical processing steps as outlined in Figure 1. In the first step (Fig. 1a) the slags are intensively mixed with additives like Fe₂O₃ and CaO and the mixture is continuously fed into a three-stage electric arc furnace. By adding coke and charcoal, the oxides of tantalum, niobium, tungsten, titanium and trace metals are reduced to a high carbon-containing ferroalloy with the typical composition of 10–20% Ta, 10–20% Nb, 40–60% Fe, 5–10% Ti, and 3–10% C. The ferroalloy and the slag are separated by conventional techniques like tapping. The second step (Fig. 1b) involves oxidation of the comminuted and crushed alloy by the addition of Fe₂O₃ (16) or by a roasting process. In the last processing step (Fig. 1c), the oxidized material is reduced in an electric arc furnace under strictly controlled conditions in order to collect all the impurities like tungsten, tin, and phosphorus in an alloy while tantalum and niobium form a synthetic concentrate of oxides in the furnace slag. A typical analysis of this concentrate is given in Table 5 (17).

4.3. Separation of Tantalum and Niobium

4.3.1. Solvent Extraction

The industrial separation of tantalum from niobium was carried out historically by the Marignac process of fractional crystallization of potassium heptafluorotantalate and potassium heptafluoronioate (18, 19) or the long-established Fansteel process (20), which involved the decomposition of the ore by a caustic fusion procedure. Processors have replaced these expensive processes by procedures based on solvent extraction. This technique was developed in the United States at Ames Laboratory and the U.S. Bureau of Mines (21). Figure 2 shows the flow sheet of an industrial installation for the hydrometallurgical processing of tantalum–niobium raw materials.

Tantalite and columbite, either naturally occurring or synthetically produced as concentrates from tin slags, are digested with hydrofluoric and sulfuric acid at an elevated temperature. Along with the tantalum and niobium, which both form the complex heptafluorides H₂TaF₇ and H₂NbOF₅ or H₂NbF₇, other elements, eg, Fe, Ti, and Mg, are dissolved. After filtering out the insoluble residues to remove fluorides of alkaline earth and rare earth metals, the aqueous solution of Ta–Nb in hydrofluoric acid is extracted in several continuously operating mixer–settler systems or extraction columns with an organic solvent like methyl isobutyl ketone (MIBK) (22). The complex fluorides of niobium and tantalum are extracted into the organic phase; most of the impurities, such as iron, manganese, and titanium, remain in the aqueous phase. In practice, Nb₂O₅ + Ta₂O₅ concentrations of 150–200 g/L are achieved in the organic phase. The organic phase is then scrubbed with 6–15 N H₂SO₄ and extracted with water or dilute sulfuric acid to separate the niobium from the tantalum by

6 TANTALUM AND TANTALUM COMPOUNDS

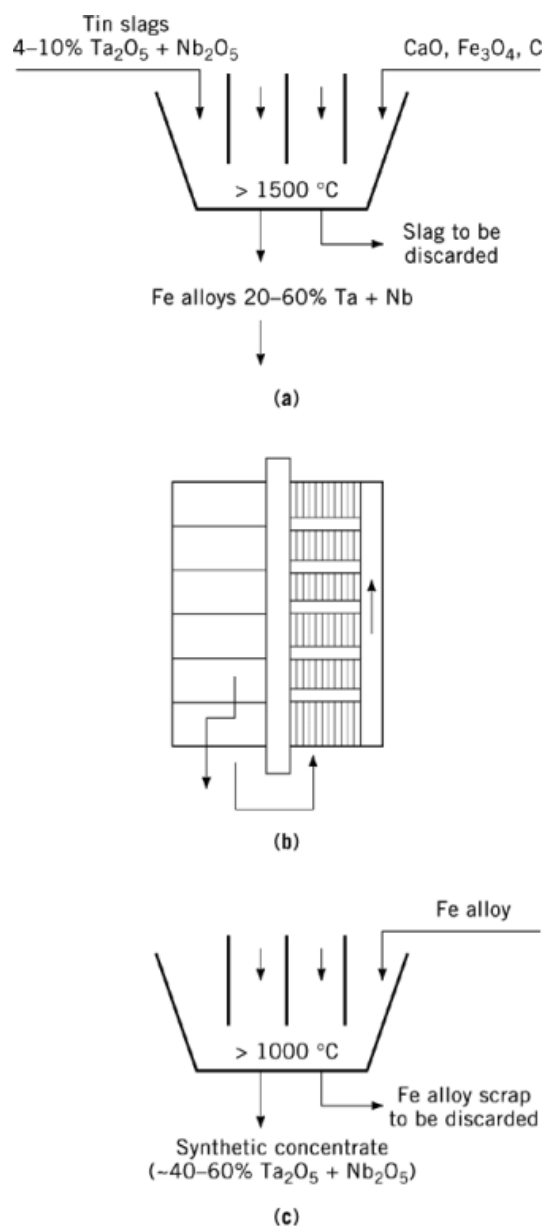


Fig. 1. The H. C. Starck pyrometallurgical upgrading process of Ta–Nb-containing tin slags where the solid vertical bars represent electrodes. The product of **(a)** electrothermic reduction of Sn slag goes to **(b)** oxidation of Fe alloy 20–60 Ta+Nb and then to **(c)** electrothermic reduction of oxidized Fe alloy. Courtesy of H. C. Starck GmbH & Co. KG.

selective stripping. The aqueous phase takes up the complex fluoroniobate and free hydrofluoric acid while the complex fluorotantalate remains dissolved in the organic phase. The aqueous niobium solution is contacted with a small amount of MIBK to remove traces of coextracted fluorotantalate. The tantalum salt is extracted from the organic phase with water (23) or dilute aqueous ammonium fluoride solution. The niobium and tantalum

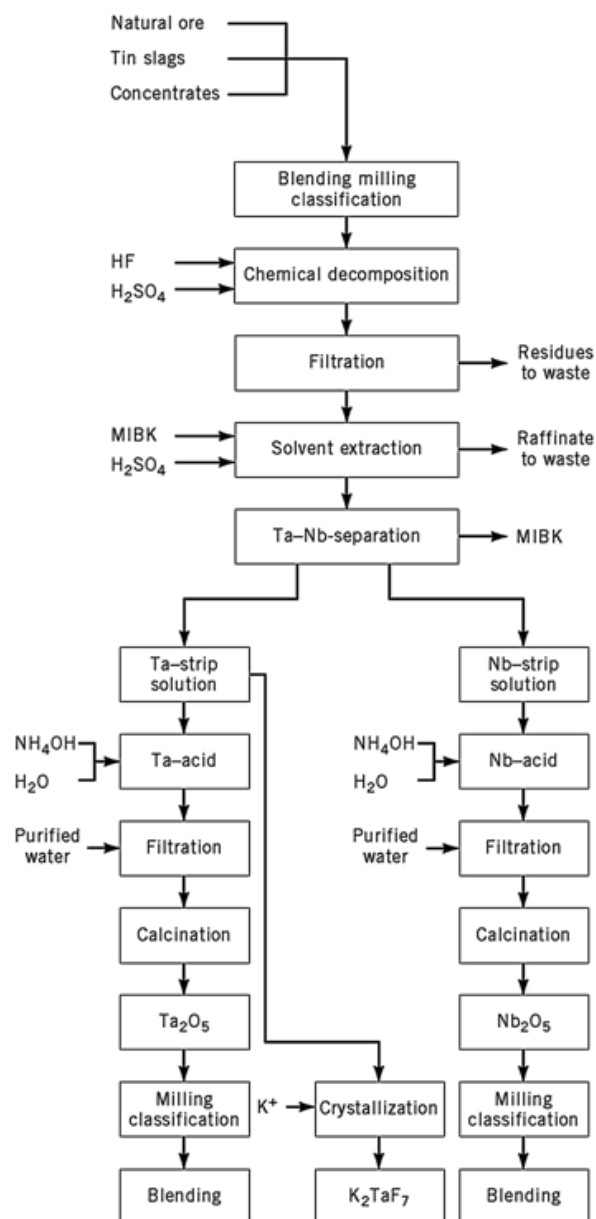


Fig. 2. The processing of Ta-Nb Raw Materials where MIBK=methyl isobutyl ketone.

salts can be produced with yields in excess of 95% and greater than 99.9% purity by using sophisticated process optimization and control.

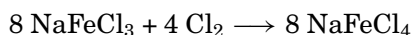
Modifications and improvements to the basic process have been made to reduce the quantity of waste products (24, 25) in the wet chemical process, to recover HF, and to economically process low Ta, high Nb containing raw materials (26). Several alternative extraction media have been reported in the literature. Most,

8 TANTALUM AND TANTALUM COMPOUNDS

except for tributylphosphate (TBP) (27) and tri-*n*-octylphosphine oxide (TOPO) (28), have never been used in industry.

4.3.2. Chlorination

The chlorination process is an alternative to solvent extraction. In reductive chlorination, the ore or concentrate is pelletized with coal or coke and pitch, dried, and then allowed to react in a stream of chlorine at 900°C. The nonvolatile alkaline earth metal chlorides remain in the bottom of the reactor while tungsten oxychloride, WOCl₄; the readily volatilized tetrachlorides of silicon, tin, titanium; and the pentachlorides NbCl₅ and TaCl₅ are distilled (29). The waste gas containing chlorine and phosgene must be rigorously controlled. The alternative chlorination of ferroalloys is much simpler and more economical (30). Ferroniobium–tantalum produced by the aluminothermic or electrothermic process is comminuted and fed together with sodium chloride into a NaCl–FeCl₃ melt. The chlorinating agent is NaFeCl₄. Chlorine is passed into the melt, continuously regenerating NaFeCl₄. The complete reaction is described by:



The reaction temperature of 500–600°C is much lower than that required for the reductive chlorination. The volatile chlorides evolve from the molten salt bath. The boiling points of NbCl₅, TaCl₅, and WOCl₄ lie between 228 and 248°C. These compounds must therefore be separated by means of a distillation column. The chlorination of ferroalloys produces very pure tantalum pentachloride in tonnage quantities. The TaCl₅ contains less than 5 μg Nb/g Ta, and other metallic impurities are only amount to 1–2 μg/g Ta.

5. Production

5.1. Tantalum Compounds

Potassium heptafluorotantalate [16924-00-8], K₂TaF₇, is the most important tantalum compound produced at plant scale. This compound is used in large quantities for tantalum metal production. The fluorotantalate is prepared by adding potassium salts such as KCl and KF to the hot aqueous tantalum solution produced by the solvent extraction process. The mixture is then allowed to cool under strictly controlled conditions to get a crystalline mass having a reproducible particle size distribution. To prevent the formation of oxyfluorides, it is necessary to start with reaction mixtures having an excess of about 5% HF on a wt/wt basis. The acid is added directly to the reaction mixture or together with the aqueous solution of the potassium compound. Potassium heptafluorotantalate is produced either in a batch process where the quantity of output is about 300–500 kg K₂TaF₇, or by a continuously operated process (31).

Tantalum pentoxide [1314-61-0], Ta₂O₅, is prepared by calcining tantalic acid or hydrated tantalum oxide [75397-94-3], Ta₂O₅·*n*H₂O, at temperatures between 800 and 1100°C. This oxide hydrate is produced by adding gaseous or aqueous ammonia to the solvent extraction produced aqueous tantalum solution in a continuous (32) or batch process.

5.2. Tantalum

Numerous methods developed to extract tantalum metal from compounds included the reduction of the oxide with carbon or calcium; the reduction of the pentachloride with magnesium, sodium, or hydrogen; and the thermal dissociation of the pentachloride (33). The only processes that ever achieved commercial significance are the electrochemical reduction of tantalum pentoxide in molten $\text{K}_2\text{TaF}_7/\text{KF}/\text{KCl}$ mixtures and the reduction of K_2TaF_7 with sodium.

5.2.1. Electrochemical Reduction

The electrochemical reduction of Ta_2O_5 in molten $\text{K}_2\text{TaF}_7/\text{KF}/\text{KCl}$ mixtures was used for many years by Fansteel Metallurgical Corporation to manufacture tantalum metal in the United States. A mixture of K_2TaF_7 , KF , and KCl was placed in an iron crucible that served as the cathode of an electrochemical cell, and the mixture was heated to above the melting point. A few percent of tantalum oxide was added to the melt, and the electrolysis was carried out using a carbon rod as the anode. Periodic additions of tantalum oxide were made to replace that consumed during the electrolysis process. The tantalum metal was recovered by crushing the cooled salt/metal mass and leaching out the salts using a mineral acid and water. The dendritic tantalum was pressed and sintered into bars and rods before conversion to sheet, wire, and powder for capacitors. The powder was quite coarse and thus not suitable for use in the tantalum capacitor applications of the 1990s.

5.2.2. Chemical Reduction

The reduction of K_2TaF_7 with sodium, used almost exclusively since 1980 to manufacture tantalum metal, was first utilized on a commercial scale by Siemens & Halske AG, Berlin, in the early 1900s. Alternate layers of the salt and small cubes of sodium were packed in a steel tube. The covered tube was heated with a gas-fired ring burner near the top of the charge to initiate the reaction that quickly propagated down the tube. The excess sodium was neutralized by adding methanol to the cooled charge. The tantalum was separated from the salt residues by leaching with hot water. The inability to mix the reactants and to control the reduction temperature seriously limited the usefulness of the process.

The demands of the solid tantalum capacitor industry for high quality, high surface area tantalum powders have driven improvements in the sodium reduction of K_2TaF_7 process since the 1960s. Powder quality and performance improved rapidly following the invention of the stirred reactor in 1960 (34). Several variations of this process have been described (35–39) but the underlying concepts have changed little. A typical reduction consists of placing the K_2TaF_7 and one or more of the diluent salts, eg, NaCl , KCl , or KF , into a reactor made of Inconel or nickel-clad Inconel. The reactor is usually 0.3–1 m in diameter and covered with a tight lid fitted with a stirrer as shown in Figure 3. The charged reactor is placed in a furnace and heated to a temperature sufficiently high to melt the salt mixture, but usually below 1000°C .

Molten sodium is injected into the retort at a prescribed rate and the temperature of the system is controlled by adjusting the furnace power or with external cooling. The variables that control the quality and physical properties of the powder are the reduction temperature and its uniformity, diluent type and concentration, sodium feed rate, and stirring efficiency. Optimizing a variable for one powder attribute can adversely affect another property. For example, a high reduction temperature tends to favor improved chemical quality but lowers the surface area of the powder.

The cooled reaction mass is extracted from the retort, crushed and leached first with dilute mineral acid, and then with water to separate the tantalum powder from the salts. After drying and classification, the primary powder is ready for processing to sheet, rod, wire, or capacitor-grade powder.

The dramatic improvements in the physical and chemical properties of tantalum powder produced by the sodium reduction process are evident in the lessening of chemical impurities (see Table 6). The much-improved chemistry reflects the many modifications to the process put in place after 1990. The dramatic reductions in

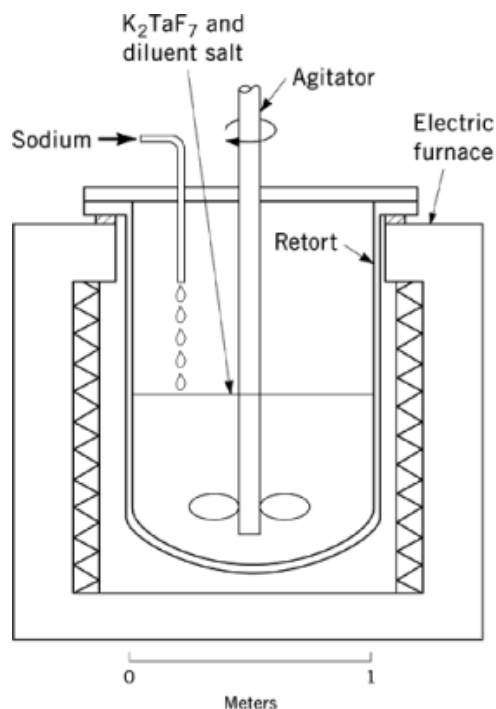


Fig. 3. Schematic of a reactor used to produce tantalum powder by the sodium reduction process.

Table 6. Comparison of Impurity Levels in Tantalum Powders

| Element | Concentration, ppm | |
|----------|-----------------------|-----------------------|
| | Powder A ^a | Powder B ^b |
| carbon | 38 | 14 |
| sodium | 12 | 2 |
| chromium | 21 | 12 |
| iron | 21 | 5 |
| nickel | 19 | 8 |

^aProcessing using 1960s technology.

^bPost-1990 processing.

alkalies and carbon concentrations have led to significant improvements in the electrical quality as measured by the performance of tantalum capacitors.

5.2.3. Post-Reduction Processing

The primary tantalum powder produced by the sodium reduction process is treated to convert the metal to a form suitable for use as capacitor-grade powder and feedstock for wire and sheet.

For use in capacitors, the primary powder is not suitable. Poor flow and pressing characteristics make it difficult to press this powder into pellets. Physical properties are improved by agglomerating the powder by vacuum sintering at a temperature in the range of 1300–1600°C. During agglomeration, the oxygen of the thermal oxide surface layer diffuses into the bulk tantalum and must be replaced to prevent uncontrolled

oxidation when the powder is exposed to the atmosphere. This is achieved after the charge has cooled by the controlled addition of small amounts of oxygen, usually as air. The resulting passivated sinter cake is milled and classified to give a powder that flows into the press die cavity and yields a pressed pellet of sufficient crush strength to withstand subsequent handling before sintering.

The consequence of the dissolution of the surface oxygen during agglomeration and its subsequent replacement is a 500–1000-ppm increase in the oxygen content of the powder. This oxygen increase, coupled with an additional increase associated with pellet sintering, can seriously degrade the electrical quality of the powder (40). The excess oxygen is removed by a deoxidation process (41); the agglomerated powder is blended with magnesium and heated for several hours at a temperature in the 900–1100°C range. The magnesium reduces the tantalum oxide on the surface and, given sufficient time, reacts with the oxygen dissolved in the metal. The cooled charge is carefully passivated, and the magnesium oxide and excess magnesium are separated from the powder by leaching with dilute mineral acid. Finally, the powder is blended into lots. More and more frequently the powder is packaged under vacuum in a plastic pouch to prevent the pick-up of oxygen over time, which can amount to several hundred parts per million in 2–3 mo.

Some powder is pressed into bars and sintered at high temperature in a vacuum furnace. The sintered compacts are then arc-melted (42) to remove impurities. The resulting tantalum ingots are hydrided to embrittle the metal (43), which is then ground to a powder, dehydrided, and classified. As seen in Figure 4, these powders are composed of fairly regular solid grains, in contrast to the capacitor-grade powders produced directly by the sodium reduction process, which consist of irregular, spongy particles. The melted powders have considerably lower surface area than the sodium-reduced powders, but higher chemical purity. They are used mostly in low specific capacitance, high voltage, high reliability applications.

Powder destined for wire is blended with high grade tantalum scrap and pressed into bars. The bars are sintered and then rolled into small-diameter rods suitable for drawing into wire with a diameter in the range of 0.2–0.8 mm. The rolling and drawing processes are interrupted periodically for annealing to reverse work hardening and the wire is carefully cleaned to remove traces of lubricant used during the drawing operation. Finally, the wire is straightened and wound on spools.

6. Uses of Tantalum Metal

The first commercial use of tantalum was as filaments in incandescent lamps but it was soon displaced by tungsten. Tantalum is used in chemical industry equipment for reaction vessels and heat exchangers in corrosive environments. It is usually the metal of choice for heating elements and shields in high temperature vacuum sintering furnaces. In 2000, over 72% of the tantalum produced in the world went into the manufacturing of over 20×10^9 solid tantalum capacitors for use in the most demanding electronic applications.

6.1. Capacitor-Grade Powder

Since 1984 about 72 percent of the tantalum metal produced annually has gone into the manufacturing of solid tantalum capacitors (STC). The principal steps in the STC manufacturing process are as follows. Tantalum powder is pressed into a pellet weighing from one to several hundred milligrams and then sintered in a vacuum at a temperature above 1300°C to give a porous compact. The pellet is formed or anodized by making it the anode of an electrochemical cell containing typically a dilute aqueous solution of phosphoric acid as the electrolyte. Upon application of a voltage, anodic tantalum oxide grows on the surface of the tantalum to a thickness proportional to the applied voltage. The resulting oxide film is an excellent electrical insulator and can serve as the dielectric in the conductor/insulator/conductor configuration of a capacitor. One conductor is the tantalum and the other conducting electrode is MnO_2 , a semiconductor, which is deposited on the anodic

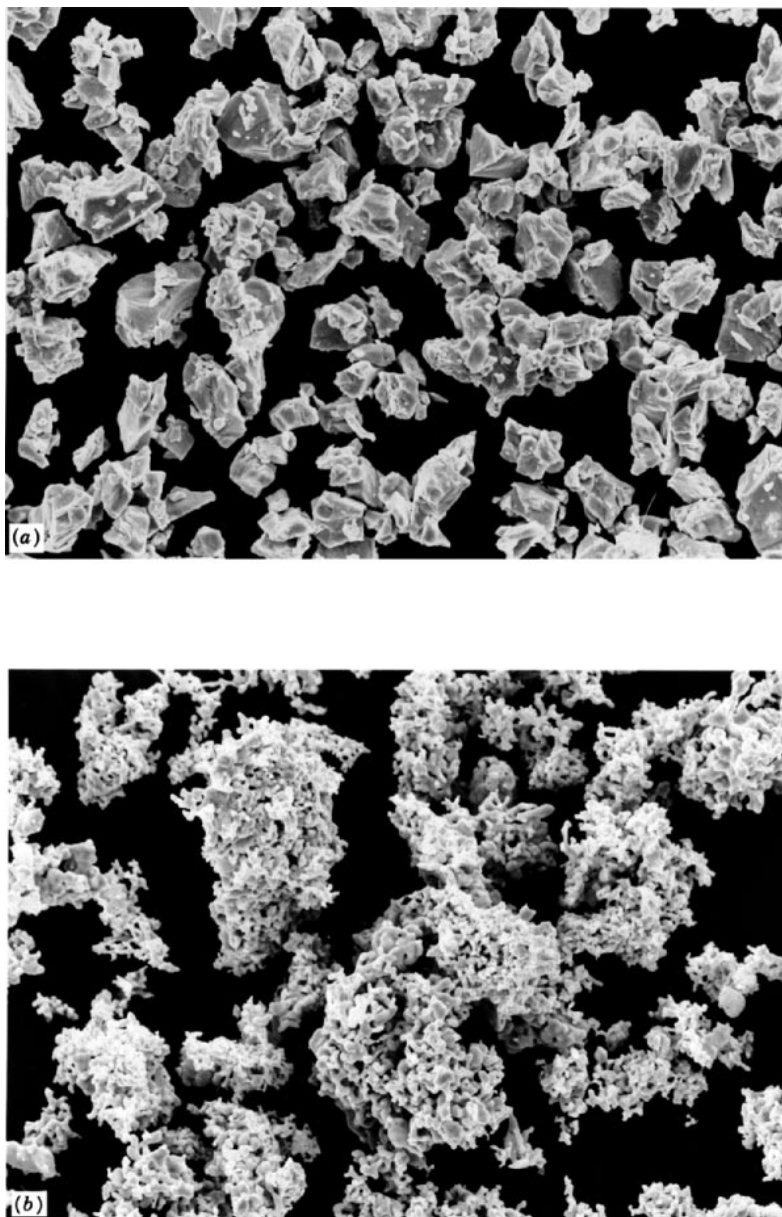


Fig. 4. The morphology of melted (a) and sodium-reduced (b) tantalum powders.

oxide by the pyrolysis of manganese nitrate. The unit is finally encapsulated usually in a variation of the surface mount chip configuration shown in Figure 5.

Solid tantalum capacitors have a high volumetric capacitance which makes them attractive for use in miniaturized electronic systems like cellular telephones, hand-held video cameras, and personal computers. The insensitivity of their capacitance to temperature and their ability to operate at temperature extremes explains why these devices are used in such harsh environments as automobile engine compartments. Solid tantalum

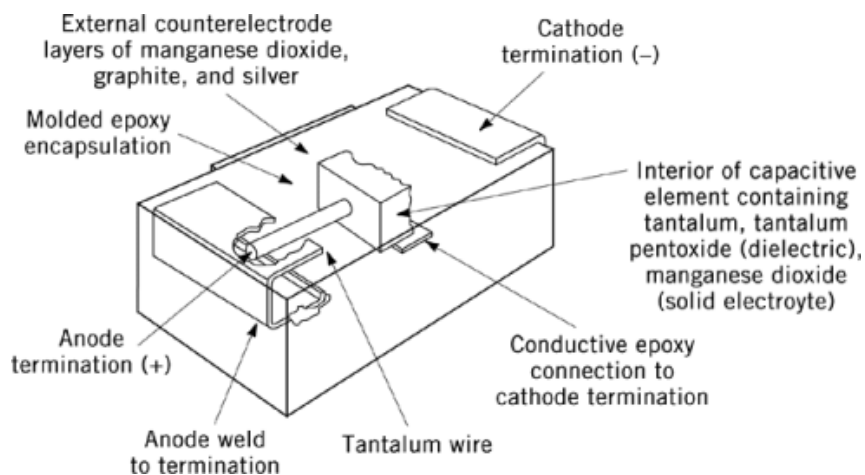


Fig. 5. A chip-type surface mount solid tantalum capacitor. Courtesy of AVX Corp.

capacitors are extremely reliable and, therefore, are often the capacitor of choice in critical applications like spacecraft electronics, pacemakers, and safety equipment.

6.2. Wire

Tantalum wire is used primarily as the anode lead wire in solid tantalum capacitors. Since the 1970s, the average weight of tantalum in a solid tantalum capacitor has dropped from several hundred milligrams to less than 50 mg; but the consumption of tantalum powder for capacitors has remained relatively constant because of the dramatic increase in the number of capacitors manufactured. The weight of wire per capacitor has remained relatively constant and thus wire consumption has increased steadily.

6.3. Fabricated Parts

The starting point for manufacturing tantalum fabricated parts is mainly high grade tantalum scrap that is converted to ingots by a combination of electron beam and arc melting. The ingots are transformed into flat stock and rod by pressing and rolling. The fabrication of functional parts uses many standard metal working techniques including turning on a lathe, cutting, bending to shape, and welding under a helium atmosphere (see Metal treatments). When specific property improvements are desired, tantalum alloys are often used: tungsten is the major alloying addition used commercially. For example, Ta/2.5% W alloy has about 50% higher tensile strength than does pure metal yet retains the corrosion resistance, ductility, and weldability of pure tantalum. Cost reductions in tantalum equipment have also been achieved by cladding the metal on a cheaper substrate, such as stainless steel by, explosive bonding.

Typical equipment made from tantalum includes heat exchangers, reaction vessels liners, thermowells, and heating elements or heat shields for high temperature vacuum sintering furnaces. Tantalum fabricated parts are found in the manufacturing of pharmaceuticals, explosives, insecticides, dyes, acidic baskets for silver cyanide barrel platers, and in hydrochloric and hydrobromic acid condensers.

Other applications occur in the defense industry where tantalum has been used in ballistics as an explosively formed projectile. The requirements for this application are rigid as to purity and metallurgical texture. Tantalum shapes (plate, heavy-walled cylinders) are also used as sputtering targets for the deposition of thin tantalum films. These films are used in a variety of applications, for example, providing corrosion and wear

14 TANTALUM AND TANTALUM COMPOUNDS

resistance to ink jet printer heads, acting as a diffusion barrier in micro-circuitry, and serving as a substrate layer to form TaN resistors in situ.

6.4. Biomedical Devices

Detailed reviews of the biomedical uses of tantalum are available (44, 45). The biocompatibility of a metal is related to its corrosion resistance and toxicity of the metal ion (46). The very low corrosion rate and inertness of tantalum make it attractive for many biomedical applications. Surgeons have used the metal as sutures, bone screws, and plates since the 1940s. Other uses include cartilage wire, nets to hold bone grafts in place, braided suture wire for skin closures and tendon repair, clips for ligation of vessels and bile ducts, mesh for abdominal wall reconstruction after hernias, plates for cranioplasty, and dental implants (see Dental materials). An undisturbed healing reaction and excellent long-term performance are found with tantalum. Mechanical performance is good and resistance to infection is high. Anodized, porous, sintered tantalum is used as nerve stimulators (47, 48). The biocompatibility of tantalum coupled with the metal's high density has led to widespread use in radiology; as powder it is used mainly for tracheography and bronchography of the respiratory tract. Tantalum for use in implants is sterilized by steam or γ -radiation (see Prosthetic and biomedical devices).

7. Anodic Oxide Films on Tantalum and Corrosion

7.1. Anodic Oxidation

The ability of tantalum to support a stable, insulating anodic oxide film accounts for the majority of tantalum powder usage (see Thin films). The film is produced or formed by making the metal, usually as a sintered porous pellet, the anode in an electrochemical cell. The electrolyte is most often a dilute aqueous solution of phosphoric acid, although high voltage applications often require substitution of some of the water with more aprotic solvents like ethylene glycol or Carbowax (49). The electrolyte temperature is between 60 and 90°C.

The thickness of the film depends on the applied voltage and is on the order of 1.6 nm/V. Film thickness is in the range of the wavelengths of visible light, and anodized tantalum has a characteristic interference color corresponding to the formation voltage. For example, a 70-V film produced at 85°C has a magenta color; a film formed to 100 V appears dark green.

7.2. Electronic Leakage

Many studies of anodic oxide films on tantalum have focused on the electrical properties. Any appreciable electronic leakage arising from a voltage applied across the oxide film degrades the quality of the dielectric and has a detrimental effect on the performance of tantalum capacitors. Considerable research has focused on work designed to explain the mechanism of electronic leakage through anodic oxide films on tantalum and similar systems. As of this writing, the pertinent literature remains contradictory and confusing.

Electronic leakage in anodic oxide films can be separated into intrinsic bulk conduction through the oxide and localized conduction at defect sites in the oxide film. Because the resistivity of stoichiometric anodic tantalum oxide is very high, on the order of $10^{15} \Omega\cdot\text{cm}$, the bulk conduction electronic current density generated by applied voltages less than necessary for ionic conduction is very low and does not contribute significantly to poor dielectric performance. The localized electronic conduction associated with chemical impurities at the surface of the tantalum and structural flaws in the anodic oxide is usually orders of magnitude greater than the electronic conduction.

Many studies (50–56) have attempted to explain bulk conduction through anodic oxide films on tantalum foils or sputtered tantalum substrates. The results of several studies were interpreted by the Poole-Frenkel

mechanism of field-assisted release of electrons from traps in the bulk of the oxide. In other studies, the Schottky mechanism of electron flow controlled by a thermionic emission over a field-lowered barrier at the counter electrode oxide interface was used to explain the conduction process. Some results suggested a space charge-limited conduction mechanism operates. The general lack of agreement between the results of various studies has been summarized (57).

Flaws in the anodic oxide film are usually the primary source of electronic conduction. These flaws are either structural or chemical in nature. The structural flaws include thermal crystalline oxide, nitrides, carbides, inclusion of foreign phases, and oxide recrystallized by an applied electric field. The roughness of the tantalum surface affects the electronic conduction and should be classified as a structural flaw (58); the correlation between electronic conduction and roughness, however, was not observed (59). Chemical impurities arise from metals alloyed with the tantalum, inclusions in the oxide of material from the formation electrolyte, and impurities on the surface of the tantalum substrate that are incorporated in the oxide during formation.

In one series of investigations (59, 60) a redox printing technique was developed that allowed direct observation of the location of sites where electronic leakage through the oxide film occurred. The presence of Fe, Ni, or C on the surface of the tantalum was shown to cause an increase in electronic conduction. A related series of studies (61–63), showed that the presence of semiconducting oxides such as Fe_2O_3 or MnO_2 on the surface of the tantalum oxide caused the electronic conduction of the film to increase when a field slightly less than the anodization field was applied. Thus, a model for the system in which oxygen vacancies are generated in the tantalum oxide film at the interface with the semiconducting oxide was proposed. These oxygen vacancies provide a source of electrons which are released by the applied field, causing the conductivity of the tantalum oxide to increase.

7.3. Heat Treatment of Anodic Oxide Film on Tantalum

One step in the manufacturing of solid tantalum capacitors is the deposition of the MnO_2 semiconductor by thermal decomposition of manganese nitrate (see Semiconductors). This requires exposing the Ta– Ta_2O_5 system to a temperature in the range between 250 and 450°C for 15 to 30 min. This heat treatment can cause an increase in the frequency, temperature, and anodic bias dependence of the capacitance, as shown in Figure 6. The source of and explanation for these effects were the subject of a significant investigation (64–67). At temperatures above 300°C, the tantalum substrate can extract oxygen atoms from the anodic oxide film, leaving behind an exponential gradient of oxygen vacancies in the oxide. These vacancies introduce *n*-type semiconduction into the oxide and, if in sufficient concentration, will cause the film to behave as a conductor. The model is shown schematically in Figure 7. The critical conductivity, σ_0 , separates the conducting from the insulating portion of the film. As the temperature increases, the level of conductivity across the film rises and the effective insulating layer becomes thinner, imparting an additional change in the capacitance besides that associated with the temperature dependence of the dielectric constant. Applying an anodic bias causes electrons trapped in the vacancies to move into the tantalum, increasing the slope of the conductivity gradient, and the thickness of the effective dielectric, thereby reducing the capacitance. The critical conductivity increases with frequency. Thus, as the circuit frequency goes up, σ_0 increases, and the intersection between conducting and nonconducting oxide shifts toward the tantalum oxide interface, which results in a lowering of the capacitance. An understanding of the effect of heat treatment structure of anodic oxide films on tantalum led to changes in the process for manufacturing solid tantalum capacitors, such as lowering the manganese nitrate pyrolysis temperature, in order to avoid the creation of a conductivity profile in the finished capacitor.

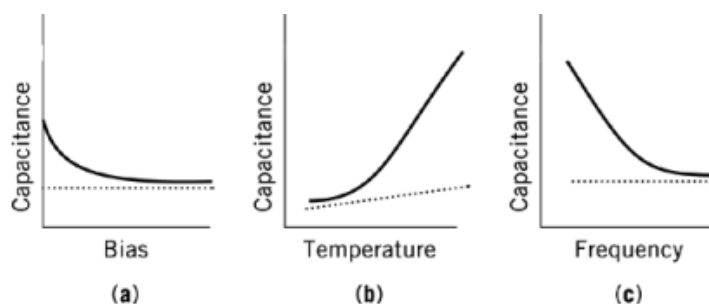


Fig. 6. Anodic oxide films on tantalum before (...) and after (—) heat treatment. Dependences of capacitance on (a) bias, (b) temperature, and (c) frequency.

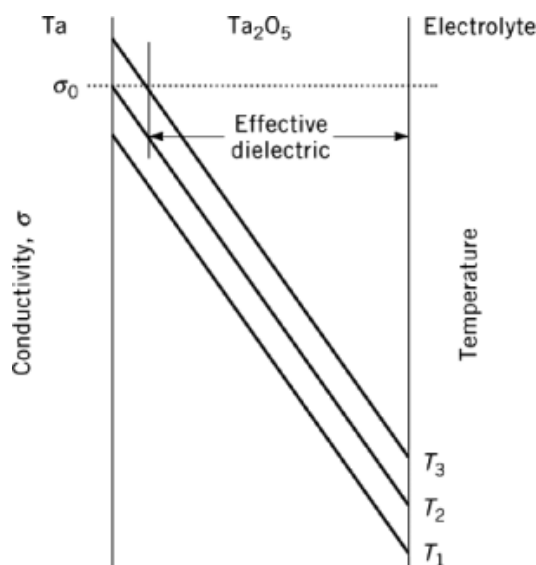


Fig. 7. Model of the conductivity profile in an anodic oxide film on tantalum after heat treatment, where $T_1 < T_2 < T_3$.

8. Corrosion of Tantalum

The corrosion behavior of tantalum is well-documented (68). Technically, the excellent corrosion resistance of the metal reflects the chemical properties of the thermal oxide always present on the surface of the metal. This very adherent oxide layer makes tantalum one of the most corrosion-resistant metals to many chemicals at temperatures below 150°C. Tantalum is not attacked by most mineral acids, including aqua regia, perchloric acid, nitric acid, and concentrated sulfuric acid below 175°C. Tantalum is inert to most organic compounds; organic acids, alcohols, ketones, esters, and phenols do not attack tantalum.

Tantalum is not resistant to substances that can react with the protective oxide layer. The most aggressive chemicals are hydrofluoric acid and acidic solutions containing fluoride. Fuming sulfuric acid, concentrated sulfuric acid above 175°C, and hot concentrated alkali solutions destroy the oxide layer and, therefore, cause the metal to corrode. In these cases, the corrosion process occurs because the passivating oxide layer is destroyed and the underlying tantalum reacts with even mild oxidizing agents present in the system.

The excellent corrosion resistance means that tantalum is often the metal of choice for processes carried out in oxidizing environments or when freedom from reactor contamination of the product or side reactions are necessary, as in food and pharmaceutical processing. Frequently, the initial investment is relatively high, but this is offset by low replacement costs owing to the durability of the metal.

9. Health and Safety

The corrosion resistance imparted to tantalum by the passivating surface thermal oxide layer makes the metal inert to most hazards associated with metals. Tantalum is noncorrosive in biological systems and consequently has a no chronic health hazard MSDS rating.

Above 300°C in air, fine tantalum powder can ignite because of the rapid oxygen diffusion through the oxide layer into the substrate. Once burning starts, a dramatic temperature rise usually occurs and the oxidation reaction can accelerate rapidly. Tantalum powder can be ignited by the localized heating associated with a static electrical discharge or contact with a hot surface.

Tantalum metal powder does not explode in the normal sense of the word, because there is no release of gas when tantalum burns. The burning of suspended tantalum powder in a confined gaseous environment containing an oxidizing agent, for example air, only produces a pressure rise associated with the heating of the gas. The potentiality of a disastrous explosion occurring exists if hot tantalum comes in contact with an oxidizing agent that reacts with the metal to produce a combustible gas. For example in the presence of water, hot tantalum reacts to produce hydrogen gas, which will then likely detonate, with tragic consequences.

A tantalum fire cannot be extinguished with the usual firefighting chemicals. The only effective way to control a tantalum fire is to smother it with a nonoxidizing chemical like sodium chloride or argon. Fire extinguishers containing sodium chloride under pressure are available for this purpose but a container of salt and a noncombustible scoop will work. Under no circumstances should burning tantalum be allowed to come in contact with water. If tantalum powder is routinely handled in a closed environment, it is prudent to design the system so that it can be flooded with argon.

Good housekeeping practices to prevent the accumulation of tantalum dust and a proper passivation procedure will prevent most tantalum fires. All equipment used to handle the powder should be properly grounded and contact with hot surfaces or flames should be avoided.

Exposure to tantalum metal dust may cause eye injury and mucous-membrane irritation. The threshold limit value (TLV) in air is 5 mg/m³, LD₅₀ is <400 mg/kg and the Occupational Safety and Health Administration (OSHA) time weighted average (TWA) exposure limit is 5 mg/m³ (69). The immediate dangerous to life or health (IDLH) concentration is 2500 mg/m³ (70). Whereas some skin injuries from tantalum have been reported, systemic industrial poisoning is apparently unknown (69).

10. Economic Aspects

10.1. Market Size

The TIC (Tantalum-Niobium International Study Center) has categorized tantalum shipments into five categories: 1) powder, 2) mill products (i.e. rod including wire, flat products, and tubing) 3) metal products comprising ingot, unwrought metal, tantalum used in alloy additions, and scrap, 4) tantalum carbide used as a toughening agent in hard metals, and 5) compounds other than TaC (see later section on Compounds). A 10-year history of usage by category, derived from *TIC Bulletins* (71), is summarized in Table 7.

Since tantalite concentrates are the main source of tantalum, prices for the other sources, as well as for tantalum products, follow concentrate pricing. The history of tantalite pricing prior to 1991 was volatile. The

18 TANTALUM AND TANTALUM COMPOUNDS

Table 7. World Shipments of Tantalum Products, metric tons Contained Ta

| Year | Powder | Mill Products | Tantalum Carbide | Metal Products | Tantalum Compounds | Total |
|-------------------|--------|---------------|------------------|----------------|--------------------|-------|
| 1991 | 391 | 175 | 174 | 109 | 59 | 908 |
| 1992 | 410 | 186 | 30 | 106 | 171 | 903 |
| 1993 | 471 | 170 | 99 | 162 | 131 | 1033 |
| 1994 | 493 | 191 | 116 | 150 | 64 | 1014 |
| 1995 | 625 | 223 | 142 | 172 | 97 | 1259 |
| 1996 | 609 | 222 | 129 | 173 | 90 | 1213 |
| 1997 | 769 | 242 | 140 | 182 | 125 | 1458 |
| 1998 | 770 | 227 | 138 | 150 | 160 | 1445 |
| 1999 | 980 | 255 | 120 | 223 | 113 | 1691 |
| 2000 ^a | 1400 | 330 | 155 | 260 | 135 | 2280 |

^aestimated

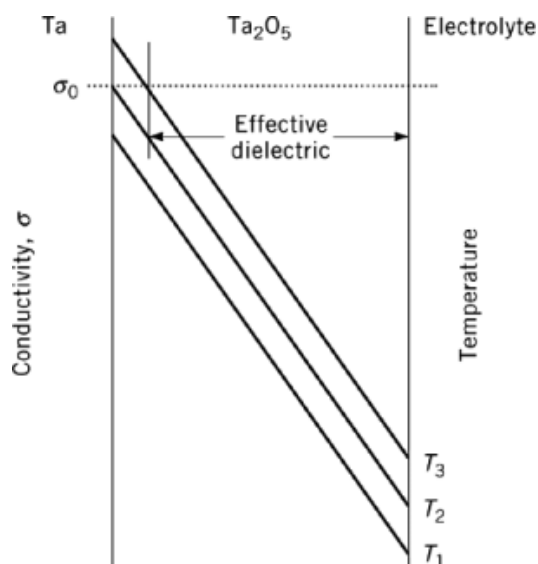


Fig. 8. Average Year-end Tantalite Pricing

signing of long-term supply contracts between major suppliers and processors succeeded in stabilizing prices for a time. However, the unprecedented demand for electronic components driven by the technology boom in computers and communications, which reached a peak in 2000, again caused a major upward price spiral. In the first half of 2001, prices have again retreated as the electronics market has softened permitting the supply/demand equation to balance. Figure 8 (72) charts the history of tantalite pricing. Producer prices are used for indexing. In 1998, the estimate of total tantalum product value based on shipments was about \$600 MM. Because of both increased shipments and prices in 2000, this value more than doubled.

10.2. Capacitors

Because of the high dependency of tantalum on capacitors, market factors affecting their usage are important. Capacitors are used in electronic circuits for: 1) coupling and decoupling, 2) filtering, 3) timing and wave shaping, and 4) oscillating. For example, decoupling capacitors are located adjacent to each integrated circuit

Table 8. Capacitor Market Consumption

| Capacitor Type | Year, billion units | | | | | Growth rate, % (Annualized) |
|--------------------|---------------------|------|------|------|-----------------|--------------------------------|
| | 1994 | 1995 | 1996 | 1997 | 2000 (est.) | |
| multilayer ceramic | 142 | 184 | 220 | 320 | 350 | 14 |
| aluminum | 76 | 83 | 60 | 66 | 120 | 8 |
| tantalum | 10 | 14 | 13 | 15 | 20 ^a | 12 |

^aValue reduced from 25 billion units reported in Ref. 14 based on industry "comments."

(IC) in digital circuits. These circuits are based on a binary determination of "1" and "0", namely, ON or OFF. Electrical pulses are supplied to determine the proper state of the circuit, and the capacitors are required to assure that the pulse is "read" precisely at the time it is applied without delay.

Several types of capacitors are used: ceramic, aluminum electrolytic, film, and tantalum. In numbers, the usage of ceramics far exceeds other types, but tantalum capacitors, although more expensive, have several advantages:

- They are available in capacitance ranging from ~ 0.1 to $> 100 \mu\text{F}$. Rated voltage varies from a nominal 6–35 V. Ceramics are designed for use at the low end of the capacitance range and aluminum-based materials, for the high.
- Tantalum capacitors are available in several designs, foil, wet electrolytic, and solid. The latter are produced leaded, where the leads are fed through holes in a circuit board and soldered, and as "chips." Chips are placed and surface mounted automatically on boards, saving both assembly time and space. Chip capacitors have by far the greatest growth rate of all tantalum designs. Although ceramics can also be surface-mounted, aluminums at this point cannot. Foil and "wet" capacitors are a small fraction of production. They are used for high voltage, high reliability devices, frequently in military applications.
- Because of the high specific capacitance (C·V/g) of tantalum powder, tantalum has the greatest volumetric efficiency. Small capacitor sizes are possible allowing miniaturization of circuit boards.
- Tantalums excel in regard to temperature stability, thus making the capacitors especially suitable for uses where exposure to heat or cold may be expected. They are also constructed to have low ESR (equivalent series resistance) resulting in minimal power losses in circuits.

The electronics "boom" has spawned major growth in the components industry, including capacitors. Market drivers for tantalum capacitors are in numerous consumer products, including cellular phones, portable computers, hard disks, and both still cameras and videocameras (73). Not only the "high tech" products but also household appliances such as vacuum cleaners, toasters, and washing machines, contain complex computing electronics. Also, a new car today supposedly contains "more computing power than the Apollo moon mission had available." Table 8, compares the capacitor production for the three major capacitor types for the years 1994 through 1997 with an estimate for 2000.

Although the growth rate for the electronic products market is expected to continue at a double-digit rate, that for tantalum materials used in capacitors will grow at a somewhat lesser rate. Because of the use of higher C·V/g powders and finer wire diameters, tantalum material usage in capacitors is forecast to have a real growth rate of 5–8% annually through 2010 (74). The major downside factor in this forecast would be a continuation of price instability for tantalum materials. When tantalum experiences price escalation, such as occurred both in 1980 and 2000, there is a tendency for circuit designers to substitute, where possible, less expensive capacitor types, with a resulting loss in market potential.

20 TANTALUM AND TANTALUM COMPOUNDS

11. Tantalum Compounds

11.1. Potassium Heptafluorotantalate

Potassium heptafluorotantalate [16924-00-8], K_2TaF_7 , crystallizes in colorless, rhombic needles. It hydrolyzes in boiling water containing no excess of hydrofluoric acid. The solubility of potassium heptafluorotantalate in hydrofluoric acid decreases from 60 g/100 mL at 100°C to 0.5 g/100 mL at room temperature. The different solubility characteristics of K_2TaF_7 and K_2NbOF_5 are the fundamental basis of the Marignac process (19). A phase diagram exists for the system K_2TaF_7 –NaCl–NaF–KCl (75). Potassium heptafluorotantalate has an LD₅₀ value of 2500 mg/kg. The recommended TWA maximum work place exposure for K_2TaF_7 in air is 2.5 mg/m³ (fluoride base) (76).

11.2. Tantalum Oxides

Tantalum pentoxide [1314-61-0], Ta_2O_5 , (mp = 1880°C, density = 8.73 g/cm³) is a white powder existing in two thermodynamically stable modifications. The orthorhombic β -phase changes at 1360°C into the tetragonal α -modification. The existence of an ϵ -modification has also been reported (77). Tantalum pentoxide reacts slowly with hot hydrofluoric acid but is insoluble in water and in most solutions of acids and alkalies. For analytical purposes, it can be dissolved by fusion with alkali hydroxides, alkali carbonates, and potassium pyrosulfate.

Tantalum(II) oxide [12035-90-4], TaO, is the only other oxide the existence of which has been confirmed. It can be prepared from Ta_2O_5 by reduction with carbon at 1900°C or with H₂ at 1100°C.

11.3. Tantalum Halides

11.3.1. Fluorides

Tantalum pentafluoride [7783-71-3], TaF_5 , (mp = 96.8°C, bp = 229.5°C) is used in petrochemistry as an isomerization and alkylation catalyst. In addition, the fluoride can be utilized as a fluorination catalyst for the production of fluorinated hydrocarbons. The pentafluoride is produced by the direct fluorination of tantalum metal or by reacting anhydrous hydrogen fluoride with the corresponding pentoxide or oxychloride in the presence of a suitable dehydrating agent (78). The ability of TaF_5 to act as a fluoride ion acceptor in anhydrous HF has been used in the preparation of salts of the AsH₄, H₃S, and PH₄ ions (79). The oxyfluorides $TaOF_3$ [20263-47-2] and TaO_2F [13597-27-8] do not find any industrial application.

11.3.2. Chlorides

Tantalum pentachloride [7721-01-9], $TaCl_5$, (mp = 216°C, bp = 242°C 242°C) forms strongly hygroscopic, needle-shaped white crystals. It is produced on an industrial scale in large tonnage by the chlorination of tantalum scrap or ferrotantalum with NaFeCl₄ or by the reductive chlorination of natural ores or synthetic raw materials. High purity $TaCl_5$ is hydrolyzed with steam and thus converted to Ta_2O_5 of the highest purity (80). The reduction of $TaCl_5$ with Mg or Al was repeatedly attempted but this thermite-type process never attained any industrial application. $TaCl_5$ is soluble in absolute alcohol, forming the corresponding alkoxides (81). The alkoxides as well as the chlorides are suitable products for the deposition of tantalum or tantalum pentoxide layers.

11.3.3. Other Halides

TaBr₅ [13451-11-1] and TaI₅ [14693-81-3] are well known but do not find industrial application. An excellent overview of the various halides, oxyhalides, and their reactions is available (82).

11.4. Tantalum Carbide

Tantalum monocarbide [12070-06-3], TaC, is a gold-colored powder produced industrially by direct reaction of carbon with either tantalum scrap or tantalum pentoxide at temperatures up to 1900°C. It is added in small amounts (0.2–2 wt %) in the form of TaC or mixed carbides like TaNbC and WTiTaC to tungsten carbide–cobalt-based cutting tools in order to reduce grain growth. Adding 2–15 wt % TaC to cemented carbides considerably increases their thermal shock resistance and their resistance to cratering and oxidation. The tantalum–carbon phase diagram shows the existence of several subcarbides (83).

11.5. Tantalum Nitrides

Tantalum nitride [12033-62-4], TaN, is produced by direct synthesis of the elements at 1100°C. Very pure TaN has been produced by spontaneous reaction of lithium amide, LiNH₂, and TaCl₅ (84). The compound is often added to cermets in 3–18 wt %. Ta₃N₅ [12033-94-2] is used as a red pigment in plastics and paints (85).

11.6. Tantallic Acid and Tantalates

Tantallic acid [75397-94-3], Ta₂O₅·*n*H₂O, is the name of the white insoluble precipitate formed by hydrolysis of alkali hydroxide or alkali carbonate fusions containing tantalum, or by adding ammonia to an acidic solution containing tantalum ions. Tantallic acid is characterized by a high surface acidity, affording it potential use as a catalyst.

Lithium tantalate [12031-66-2], LiTaO₃, is the most important tantalate. The crystal structure is related to that of perovskite. LiTaO₃ exhibits high spontaneous polarization and a high Curie temperature. For several applications in electronic devices such as surface acoustic wave (SAW) filters, second harmonic generators (SHG), and wave guides, crystals are grown by the conventional Czochralski technique from melts made of Li₂CO₃ and Ta₂O₅ (86). Similarly, other tantalates like Ba₃MgTa₂O₉ [12231-81-1] and Ba₃ZnTa₂O₉ [12231-88-8] also have the perovskite structure and are used in high frequency resonators in satellite communication systems.

11.7. Hazards of Tantalum Compounds

The toxicity of tantalum compounds depends on their solubility. Tantalum pentoxide is poorly absorbed and nontoxic perorally. The pentachloride, on the other hand, shows an LD₅₀ of 985 mg/Kg administered perorally.

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