Tantalum—Processing, Properties and Applications

W. Köck and P. Paschen

Tantalum—the Earth’s 49th most abundant element—is frequently produced as a by-product of tin smelting. The metal is also extracted from concentrates by reduction with sodium or fused-salt electrolysis; tantalum carbide is produced by carburization of $\text{Ta}_2\text{O}_5$ or tantalum hydride. Sintering, electric-arc melting and electron-beam melting are used to refine and purify raw tantalum. Tantalum’s unique properties make it suitable for a number of diverse applications, including capacitors, chemical equipment, hardmetal tooling and alloys. Tantalum consumption is expected to increase in the capacitor market, because of the demand for electronics equipment.

INTRODUCTION

The element tantalum was discovered in 1802 by the Swedish chemist Ekeberg.1-3 He named the new element after the figure of Greek mythology, Tantalus, to describe its resistance to acids. Tantalum is in the fifth subgroup of the periodic system and is a transition metal. The color of tantalum is silver-grey to blue-grey.

In 1824, Berzelius was the first to succeed in producing tantalum powder by reducing potassium tantalum fluoride. His powder was heavily contaminated with potassium. In 1856, Rose obtained a metal which was probably similar to that of Berzelius, through reduction with sodium. Due to their high impurity contents, the extracted metals were very hard and brittle.

In 1905, Bolten applied vacuum arc melting to tantalum powder, obtaining cold-ductile tantalum for the first time. Thus, it became possible to apply tantalum on an industrial scale for the filaments of incandescent lamps.

Due to its good chemical, physical and mechanical properties, tantalum has become an important engineering material for the chemical industry, as well as for electrical and high-temperature engineering.

RAW MATERIALS

Tantalum is found in the earth’s crust in a concentration of 2.5 ppm. It has a strong affinity for oxygen and occurs almost exclusively as an oxide in association with niobium. It frequently occurs with titanium, tin, lanthanides and uranium or thorium. The most important minerals for extraction are tantalite $(\text{Fe,Mn,Ta}_2\text{O}_5)$ and niobite $(\text{Fe,Mn,Nb}_2\text{O}_5)$; they are mainly mined in small deposits with contents of approximately $0.1\% \text{Ta}_2\text{O}_5$.

In the Western world, about one-half of all tantalum is a by-product of tin smelting. A cassiterite lattice may contain up to $4\% \text{Ta}_2\text{O}_5$, and small amounts of tantalite may also be associated with cassiterite. During the smelting of tin concentrates the slags are enriched with tantalum. The chemical compositions of these kinds of slags are given in Table 1.

The main producers of raw materials containing tantalum are Thailand, Malaysia, the Soviet Union, Canada, Brazil and Nigeria; Brazil has the largest reserves in the world, and the West produces approximately 83% of the world’s tantalum.

EXTRACTION AND PROCESSING

After crushing and grinding, tantalum ores are usually prepared in two stages. In the wet stage, a rough concentration is made through gravity separation by means of mineral jigs, spirals, sluice boxes or vibrating tables. Enrichment factors of 400 to 500 are common. Final concentration to $10-50\% \text{Ta}_2\text{O}_5$ takes place in dry processes, by magnetic or electrostatic methods.

During the preparation of tantalum-containing tin ores, which is also carried out by gravity techniques, tantalum is enriched in the tin ore concentrate during gravity separation. In rare cases, tantalum minerals are separated from the concentrate using a dry method. Most of the tantalum, however, is smelted along with tin ore concentrate and then enriched in a slag.4 Depending on the ore types, the tantalum yield may vary between 40 and 85%.

Slags with a high tantalum content of $8\% \text{Ta}_2\text{O}_5$ are digested in the same way as tantalum ore concentrates. Slags with a lower tantalum content are subjected to a preconcentration process since the costs of digestion are essentially determined by the throughput quantity. For this purpose, the tin slags are melted in an electric arc furnace under reducing conditions, with additions of iron, iron oxide or scrap. Tantalum is enriched as carbide in a ferrous alloy. Three methods are used for further processing:

- Leaching of the iron by mineral acids (possibly followed by alka-line leaching) and transformation of the carbides into acid-soluble oxides by oxidizing roasting.
- Chlorination of the ferroalloy in a NaFeCl3-melt, and separation of the chloride mixture by fraction-ated distillation.
- Remelting of the ferroalloy with the addition of oxidizing agents.$^5$

The leaching process and the remelting process yield synthetic concentrates of up to 30% $\text{Ta}_2\text{O}_5$.

The various tantalum concentrates are processed mainly by means of digestion with hydrofluoric acid. Sulfuric acid is added to increase the yield of niobium, which is usually present. After digestion, the solution is diluted with water, and the residue is separated. If this residue still contains niobium and...
tantalum, it is remelted again in the tin slag process.\textsuperscript{4,5}

The separation of tantalum and niobium from the hydrous solution usually takes place by solvent extraction with methyl isobutyl ketone. Tantalum and niobium are taken up by the organic phase; the dissolved impurities such as titanium, silicon, iron and phosphorus remain in the hydrous solution. After phase separation, niobium is re-extracted with water. After re-extraction of the tantalum-containing phase with more water, ammonia can be used to crystallize pure tantalum oxide hydrate which is then calcined, or the double fluoride (K$_2$TaF$_7$) can be crystallized by adding potassium salts. An installation of this type is shown in Figure 1.\textsuperscript{1,4-6}

Natural and synthetic concentrates may also be processed by the chlorination of raw materials. Figure 2 is a survey of processes for extracting tantalum compounds as raw materials for metal and carbide production.\textsuperscript{4}

**EXTRACTING RAW TANTALUM**

Tantalum metal can be produced by several means. Table II gives a survey of the most important industrial and semi-industrial processes.\textsuperscript{1,5,7} All processes provide metal yields of above 90% at metal grades of 99.5%, but only two processes have been successful on an industrial scale: the metallothermal extraction by reduction of K$_2$TaF$_7$ with sodium, and the fused-salt electrolysis of oxide-containing electrolytes.

**Reduction with Sodium**

The reduction of K$_2$TaF$_7$ with sodium is based on the following exothermic reaction:

\[ K_2TaF_7 + 5Na \rightarrow 2KF + 5NaF + Ta \]

It is carried out under an argon inert gas atmosphere or under vacuum at temperatures between 800 and 900°C. Different process variants are applied industrially. Figure 3 gives an overview of the process technology.\textsuperscript{4,5,8}

The reduction of K$_2$TaF$_7$ usually takes place in contact with liquid or gaseous sodium. After reduction, the mixture is either reduced discontinuously or, in modern processes, continuously in a reaction mixture with inert salts (NaCl, KCl). The reaction mixture is processed by leaching of the salts and repeated washing of the tantalum powder. The development of these reduction processes is closely connected to the development of highly capacitive tantalum powders for the manufacture of capacitors.

Highly capacitive tantalum powders are characterized by an extremely fine grain with a large surface, and a correspondingly high purity. At present, the sodium reduction is of greater technical advantage for producing tantalum powder of this fine grain size, and, additionally, within a very narrow grain size range at good metal output. An average grain size of above 1 \( \mu \text{m} \) can be produced. For the production of medium-capacitive tantalum powder as well as of all types of semifinished tantalum products, the processing technology required is the same as for powder reduced by means of fused-salt electrolysis. The increasing demand for highly capacitive tantalum powders induced many companies to decide on this metal extraction technol-