Indispensable Refractory Metal Chlorides

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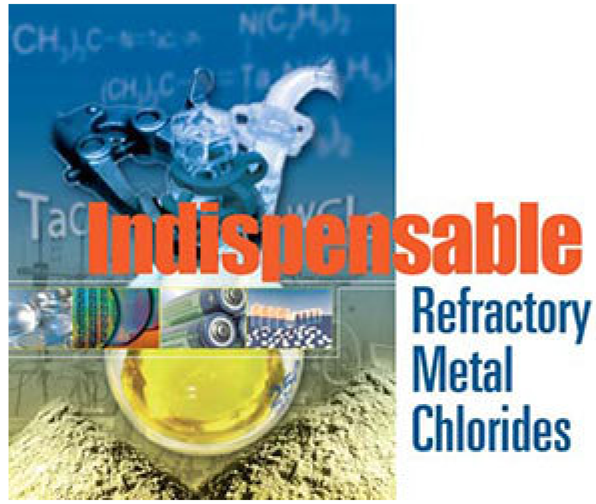

Certain materials are indispensable in our everyday lives. For example, ordinary household baking soda is a fairly simple compound that is used in a wide range of household applications; you don't necessarily have to understand how it works, but you want to make sure that you always have a sufficient supply of it. Similarly, refractory metal chlorides (RMCs)-i.e., chlorides of tantalum (Ta), niobium (Nb), tungsten (W) and molybdenum (Mo)-are simple compounds that are used in a vast number of industrial applications, ranging from raw materials for the next generation of semiconductor chemicals, to energy-related applications (batteries, fuel cells) and nanotechnology.

Production of Refractory Metal Chlorides

RMCs are inorganic powders with an octahedric structure. The pentachlorides of Nb, Mo and Ta consist of dimers, while the hexachloride of W is a monomer. Although various oxidation states exist for each of the metals (e.g., bi-, tri-, tetra-, penta- and hexa- for W and bi-, tri-, tetra- and penta- for Mo), this article will only refer to Ta-, Nb- and Mo-pentachlorides and to W-hexachloride. The chlorides are crystalline at room temperature, and reactive and volatile at moderate temperature. They decompose to their metals in the presence of hydrogen at high temperatures, are soluble in organic solvents, and possess melting points ranging from 194°C ($MoCl_5$) to

275°C (WCl_6), and boiling points from 233°C ($TaCl_5$) to 346°C (WCl_6).

RMCs can be produced in one of several ways. WCl_6 and $MoCl_5$ are produced through the chlorination of crude tungsten or molybdenum metal powder in a stream of chlorine above 600°C. A surplus of chlorine in the process is necessary to prevent the generation of the lower chlorides. With their low boiling points of 346°C (WCl_6) and 268°C ($MoCl_5$), W(VI)- and Mo(V)- chlorides are gaseous under these conditions. The gaseous chlorides are cooled and crystallized as violet (WCl_6) or dark green to black ($MoCl_5$) crystals. The chlorination takes place under a nitrogen atmosphere, due to the air sensitivity of these chlorides (see Figure 1).

$$2\ Mo + 5\ Cl_2 \rightarrow 2\ MoCl_5$$

$$W + 3\ Cl_2 \rightarrow WCl_6$$

There are two versions for the chlorination processes that produce the pentachlorides of Nb and Ta. These chlorides are also sensitive to air, so both processes must also be done under a nitrogen atmosphere. The first version is a reductive chlorination of ores and synthetic concentrates. The raw materials are palletized with coal/coke/pitch and dried. During the reaction with chlorine at 900°C, the non-volatile alkaline earth metal chlorides remain behind, while the readily volatilized $SiCl_4$, $SnCl_4$, $TiCl_4$, $TaCl_5$, $NbCl_5$ and $WOCl_4$ are distilled off and fractioned.

The second version is the more important one, because this process-namely the chlorination of ferroniobium or ferrotantalum-is much simpler and more economical. Ferroniobium and ferrotantalum are chlorinated in a melt of sodium- and iron(III)- chloride ($NaCl - FeCl_3$) at a temperature of 550-600°C. $NaFeCl_4$ is the chlorinating agent, which is regenerated by chlorine. The following reactions take place:

$FeTa/Nb + 7\ NaFeCl_4 + NaCl \rightarrow Ta/NbCl_5 + 8\ NaFeCl_3$

$2\ NaFeCl_3 + Cl_2 \rightarrow 2\ NaFeCl_4$

The volatile chlorides evaporate out of the melt, and the tetrachlorides of silicon, tin and titanium (which have boiling points between 57 and 136°C) are separated by cooling from $TaCl_5$, $NbCl_5$ and $WOCl_4$ (which have boiling points between 228 and 248°C, respectively). The chlorides of Nb and Ta are purified via a distillation process. $NbCl_5$ (yellow crystals) and $TaCl_5$ (colorless crystals) from this process are very pure. The total amount of metallic impurities is less than 50 µg/g.

Applications

A simple literature or patent database search clearly demonstrates the widespread use of RMCs in a variety of industries, including semiconductors, catalysts, energy and nanotechnology.

Semiconductors

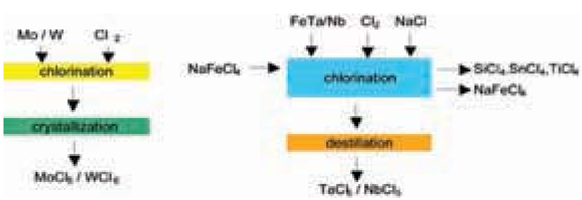

Figure 1. The chlorination processes for WCl_6 and $MoCl_5$ (left) and $NbCl_5$ and $TaCl_5$.

Due to the shrinking dimensions of integrated chips (ICs) and the increasing aspect ratios in semiconductor devices, the role of alternative deposition techniques, such as chemical vapor deposition

(CVD) and atomic layer deposition (ALD), is expected to increase. This is because the current deposition method, physical vapor deposition (PVD), has certain limitations that can be overcome by CVD and ALD. However, CVD and ALD require a new set of deposition precursors, and this is where the RMCs come into play.

Two major groups of metalorganic precursors-metal alkoxides and metal amides-currently being tested by semiconductor companies are synthesized from RMCs through reactions with alcohols and amines, respectively. The products include compounds such as Ta-ethoxide, PDMAT (pentakis dimethylamino tantalum) and TBTDET (t butylimino tris diethylamino tantalum), which can be used to generate Ta_2O_5 high-k films in memory devices (using Ta-ethoxide)[1] and TaN diffusion barriers.

Although much of the industry has focused on *chloride-derived* products for precursor development, it is worth mentioning that the chlorides themselves can be used directly as precursors in their high-purity form. As an example, U.S. patent no. 6,900,129 describes a CVD method for depositing high-quality conformal Ta and tantalum nitride (TaN_x) films from $TaCl_5$ and other inorganic tantalum pentahalide (TaX_5) precursors at 300-500°C.[2]

Catalysts

RMCs are commonly used as catalysts in numerous chemical reactions. For example, Mo-, Ta- and Nb-chlorides are used as fluorination catalysts in connection with the production of the non-ozone depleting refrigerants, namely hydrofluorocarbons (HFCs).[3] Copper spinel honeycomb catalysts are used to reduce the nitrogen oxide (NO_x) pollutants coming from motor vehicle emissions. Ta-doped catalysts that were produced by means of saturation with a $TaCl_5$ solution improve the degradation characteristics of these catalysts.[4] Additionally, ring opening metathesis polymerization (ROMP) uses tungsten and molybdenum co-catalysts, which can easily be synthesized from WCl_6 and $MoCl_5$.

Energy

The use of chlorides is spread among various energy-related applications that include the production of batteries, fuel cells and ultracapacitors. Fuel cells generate energy by a reverse electrolysis reaction, thus combining oxygen and hydrogen to create electricity, heat and water. Typically, a gas mixture containing hydrogen is used as the fuel. To increase the fuel cell's efficiency, it is necessary to separate the hydrogen from other gaseous contaminates, and this can be achieved by using hydrogen transport membranes. In one example, the transport membrane consists of a tantalum or niobium metal deposited into a porous alumina substrate.[5] The metal serves as a hydrogen-permeable layer, while the alumina serves as a support structure. This combination of materials improves the lattice match between the metal membrane and the supporting component. In this case, the tantalum/niobium layer is deposited with CVD using, among others, $TaCl_5$ and $NbCl_5$ precursors.

The use of Nb or Mo chlorides has also been described in the production of lithium secondary batteries. In one example, a high-voltage lithium secondary battery's performance is enhanced by selecting alternative materials for the positive electrode.[6] Such alternative materials include lithium-manganese oxides, in which manganese is partially substituted by, among others, Nb or Mo, for which $NbCl_5$ and $MoCl_5$, respectively, were used in the preparation.

Nanotechnology

Nanomaterials are typically materials with a particle size < 100 nm that exhibit novel and attractive properties due to their small dimensions. Although nanomaterials are not new, we are only now beginning to understand their advantages and ways to synthesize them. When it comes to the synthesis of refractory metal nanoparticles, their high melting point exhibits a problem. In the case of tantalum, which has a melting point of 2996°C, the preparation of nano-tantalum metal by physical methods is difficult, and therefore its synthesis from $TaCl_5$ is suggested.[7] According to Zhu & Sadoway, the particle size of a solid product can be reduced if the reaction takes place in a medium that is a mixed conductor (ionic and electronic).[8] This was confirmed by reacting $TaCl_5$ with sodium, each dissolved in liquid ammonia to produce ultrafine Ta powder. In another example, nanocrystalline niobium carbide (NbC) was synthesized at 550°C by co-reducing $NbCl_5$ and CCl_4. NbC can be used as an additive in the production of hard materials.[9]

Other Applications

The list of potential applications for RMCs extends beyond semiconductors, energy, catalysis and nanotechnology. Following are just a few examples:

Pulp and Paper. $TaCl_5$ has been used as a precursor material in the production of the oxide electrode $Ti/Ta_2O_5\text{-}IrO_2$ used in the oxidation of sulfides to treat waste products in the pulp and paper industry.[10]

Ceramic Matrix Composites. Precursor-polymers that were produced from refractory metal halides (such as $TaCl_5$) and organo-transition metal complexes have been used to manufacture a ceramic matrix composite (such as TaC) by means of polymer infiltration pyrolysis. The technique leads to the decomposition of the polymer, followed by the formation of refractory metal carbides or borides; the resulting material offers extremely high melting points (3880°C for TaC). Such composites could be used for multistage nozzles in rocket motors or for high-temperature coatings. This method delivers carbides with superior properties compared to those manufactured by the common chemical vapor infiltration method.[11]

Optical. Niobium is commonly used as a refractive index adjuster in optical applications. Accordingly, niobium oxide optical thin films can be generated to obtain a specific refractive index by immersing a substrate in a $NbCl_5$-containing mixture.[12] Metal alkoxides, similar to those used as CVD/ALD precursors in semiconductor applications, can also be used for optical applications, such as in optical thin film transparent layers used for electrochromic devices.[13] Additionally, the thermal management of buildings requires intelligent glass coatings. For example, thermochromic layers on glass can be prepared from tungsten doped vanadium oxide and can be deposited at atmospheric pressure using WCl_6 as a precursor for WO_3.[14]

Biomedical. According to a Japanese study, the bone-building ability (osteoconductivity) of transplants was enhanced through a chemical treatment with hydrogen peroxide solution containing tantalum chloride.[14]

RMC powders can be synthesized in various grain sizes, allowing the optimization of the desired material properties. Depending on the application, different grain sizes offer different advantages. Larger grain sizes (1-10 mm) improve flow properties and ease the material handling and its dosage, while also reducing moisture sensitivity. On the other hand, smaller grain sizes (<0.25 mm) increase the material's reactivity and solubility.

Beneficial Materials

Refractory metal chlorides are a unique group of materials used in a wide range of applications, including semiconductors, electronics and optics. Interestingly, in many of these applications, RMCs play an intermediate role, meaning that they rarely show up in the final product. They are used as additives, catalysts or perhaps as starting materials for more complex compounds. Nevertheless, these chemicals are indispensable for the industrial processes in which they are used, contributing to the efficiency, cost effectiveness and quality of the final products.

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Editor's note: References can be found with this article online at www.ceramicindustry.com.

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