Production of High Surface Area Oxygen Sensitive Powders by Na Flame Synthesis

L.A. Mann*, A. Rai**, J. Koenitzer***, R.L. Axelbaum****

*Cabot Corporation, Billerica, MA, USA, larry_mann@cabot-corp.com
**Cabot Corporation, Billerica, MA, USA, ashish_rai@cabot-corp.com
*** Cabot Corporation, Billerica, MA, USA, john_koenitzer@cabot-corp.com
***Washington University, St. Louis, MO, USA, axelbaum@wustl.edu

ABSTRACT

Cabot Corporation is developing a new particle generation platform that is ideally suited for the production of oxygen sensitive nano-scale powders. The Na Flame Synthesis process is based on the hypergolic vapor phase reaction between the metal-halide(s) of the desired element(s) and sodium in an inert atmosphere, such as argon. Provided that the sodium/metal halide ratio is maintained at or above the stoichiometric value, and the temperature is maintained sufficiently low, the conversion of halide is nearly 100%. The process produces high purity nano-scale particles, encapsulated in the sodium halide salt byproduct. The salt encapsulation aids in the collection and handling of particles that would otherwise be highly oxygen reactive, and the salt can be removed in subsequent process steps. The process is capable of producing particles composed of pure metals, metal alloys, intermetallics, metal-matrix composites, and non-oxide ceramics. Cabot's initial focus for this new platform is the production of high surface area tantalum powders for high-performance capacitors needed by the electronics industry, but many other applications are envisioned. These include materials that enable more efficient energy generation and storage, and materials with improved physical, thermal, and mechanical properties for advanced structural, aerospace, thermal management, and wear applications.

Keywords: tantalum, flame synthesis, sodium, nano-scale powders, oxygen sensitive

1 BACKGROUND

Cabot Corporation is well known as a leading producer of carbon black and fumed silica performance materials, with 39 manufacturing facilities operating in 21 different countries. Both materials are produced using flame-based processes at large scale. A single carbon black reactor is capable of producing more than 50,000 tons/year of carbon black, and a single fumed silica reactor more than 5,000 tons/year of fumed silica. The Supermetals Division of Cabot Corporation is a leading producer of capacitor grade tantalum powder for use in the electronics industry, with plants in Boyertown, PA (USA) and Kawahigashi-machi, Fukushima Prefecture (Japan).

High-purity tantalum powders are traditionally produced in a molten-salt batch process in which sodium is used to reduce potassium fluorotantalate to form pure tantalum powders, commonly referred to as the KSalt Process. (1) The KSalt process has been used for over 30 years to produce tantalum powders, which are essential to the manufacture of tantalum capacitors. These highly-stable capacitors are ubiquitous in many consumer and industrial electronics, such as computers, smartphones, and automobiles. Key quality characteristics of tantalum powders in electronic capacitor applications include:

1. **Specific Surface Area** (m^2/g)- Capacitance is proportional to surface area, and therefore higher specific surface area enables more capacitance per unit weight (and per unit volume).
2. **Purity**- The dielectric layer in tantalum capacitors is formed by electrochemically growing a thin layer of tantalum pentoxide (Ta_2O_5) on a porous anode formed by pressing and sintering tantalum powder. Impurities in the tantalum powder can result in defects in the dielectric layer, degrading the performance of the capacitor.
3. **Powder Morphology**- The bulk density (g/cm^3), primary particle size, and aggregate/agglomerate size, shape, and pore structure all have significant influence on capacitor manufacturing yield and capacitor performance/reliability.

Capacitor grade tantalum powders are currently being produced by the KSalt process with specific surface areas as high as 5 m^2/g (capacitance of approximately 250,000 μFV/g). (1) The morphology of a typical capacitor grade tantalum powder produced by the KSalt process is shown in the SEM micrograph in Figure 1.

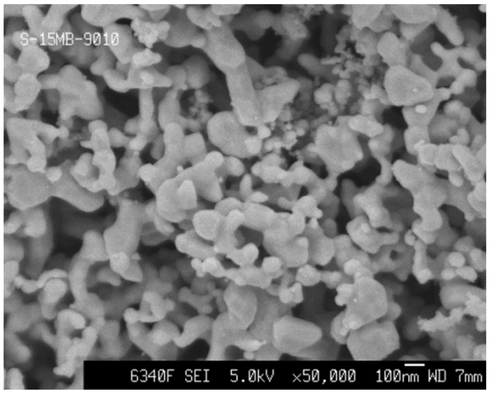

Figure 1. 3 m^2/g Ta powder produced by KSalt Process

In the KSalt process, smaller primary particle size, and hence higher surface area, is achieved by reducing the concentration of KSalt in the molten salt reactor. Thus, the quantity of tantalum powder produced during a single batch reaction declines as target specific surface area increases. The lower productivity and increased costs associated with using more diluent salts (typically KCl and KF) per unit of tantalum produced results in rapidly increasing costs for producing tantalum powders with specific surface areas greater than about 5 m^2/g. It is therefore desirable to find a new method for producing tantalum powders with high specific surface areas that is economically viable on a commercial scale.

2 THE SODIUM FLAME SYNTHESIS PROCESS

The Na Flame Synthesis process was initially developed by R.L. Axelbaum, D.P. DuFaux and L.J. Rosen, at Washington University. (2) (3) Exclusive rights to the foundational patents for the Na Flame Synthesis process were licensed to Cabot Corporation in 2007. Several types of powders have been produced using the Na Flame Synthesis process, including pure titanium, tantalum, niobium, and aluminum. (4) (5) Multi-component particles have also been produced, including titanium diboride, aluminum nitride and niobium coated iron particles. (6) (7) (8) (9) Depending on the elements of interest and the operating conditions of the reactor, multi-component particles may consist of alloys, homogeneous or segregated mixtures, or core-shell layered structures. (10)

Figure 2 is a schematic diagram of a Na Flame Synthesis burner/reactor system, as described in the original patents. It consists of a feed system for each of the metal halide streams (a bubbler, sublimer or an evaporator may be used), a feed system for the sodium (usually a vaporizer), a burner, a reactor, and a particle collection system.

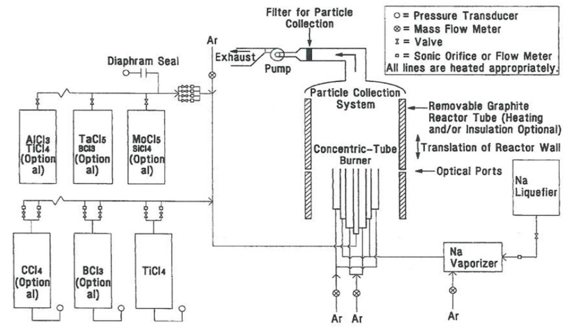

Figure2. Schematic of Sodium Flame Synthesis Process

The design of the feed, burner, reactor, and particle collection systems is critical to the operability of Na Flame Synthesis process. The feed system must be capable of providing tightly controlled flow rates of metal halide and sodium. If the ratio of metal halide to sodium falls below the stoichiometric value, the conversion of metal halide to metal will be incomplete, and corrosion of the system may occur. On the other hand, sodium in excess of the stoichiometric value presents several challenges. Excess sodium may deposit in the collection system along with the product, posing risks to product quality, or it may pass through the collection system, in which case a remediation process to remove it will be necessary. The excess sodium also presents several safety challenges. The design of the burner and reactor is also critical. The metal halide and sodium streams must be kept separate until they are downstream of the burner, in order to prevent product deposition on the burner. The geometry of the burner, the flow rates of the reactant and inert streams, and the geometry of the reactor all have strong influence on the mixing rates, and therefore the size, shape, and nature of the reaction zone (flame), which may be laminar, turbulent, or transitional. They also influence the temperature profile in the system.

The structure of the particles produced by the Na Flame Synthesis process depends on the properties of the material produced (especially the melting point) and the operating conditions of the burner and reactor (concentrations, velocities, temperature profiles, and residence time). As in all flame processes, nuclei form in the mantle of the flame, grow, collide, coalesce, and sinter. In the Na Flame process, at a point downstream of the flame where the temperature has decreased sufficiently, the sodium halide byproduct of the flame reaction (typically sodium chloride) condenses onto the particles that have formed previously. As further cooling occurs, the salt freezes, encapsulating the metal particles. Because of the Kelvin effect, condensation of the sodium chloride occurs on the larger particles/aggregates, and smaller particles may not be encapsulated. (The smaller particles may, however, subsequently be scavenged by the salt particles.) Figure 3 provides a schematic of the particle formation processes.

NSTI-Nanotech 2011, www.nsti.org, ISBN 978-1-4398-7142-3 Vol. 1, 2011

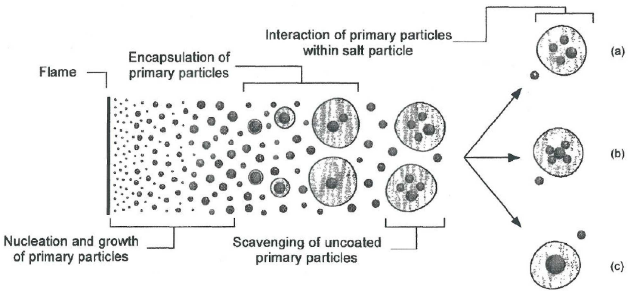

Figure 3. Schematic of particle formation process

3 TANTALUM POWDERS PRODUCED BY THE SODIUM FLAME SYNTHESIS PROCESS

Tantalum has a very high melting point (3017 C), and therefore tantalum particles produced by the Na Flame Synthesis process are typically submicron to micron size aggregates with primary particles that are on the order of 10-50 nm in diameter. Such particles are found to have specific surface areas of 2-20 m^2/g. A TEM photomicrograph of salt encapsulated Ta particles is shown in Figure 4, and an SEM photomicrograph of Ta particles with the salt removed is shown in Figure 5.

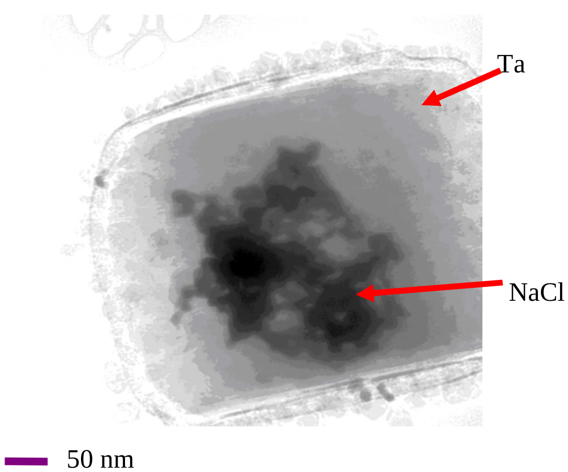

Figure 4. Salt encapsulated Ta particles

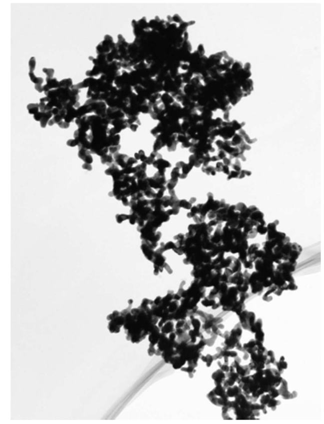

Figure 5. Ta particles with salt removed

The tantalum particles produced by the Na Flame Synthesis process are found to be of high purity, provided the sodium to metal halide ratio is maintained at or above the stoichiometric value at all times, and steps are taken to prevent moisture and oxygen from entering the reactor. Tantalum powders with surface areas as high as 20 m^2/g have been produced using the Na Flame Synthesis process. The “as produced” powders have surprisingly good flow properties, but the bulk densities are lower than desired for the manufacture of high performance capacitors (typically less than 1 g/cm^3, as compared to target values of 1.5-2.5 g/cm^3). The bulk density of “as produced” Na Flame Synthesis powders can be increased to the target values using proprietary powder processing methods.

4 CONCLUSIONS

Cabot has been sampling high surface area tantalum powders produced by the Na Flame Synthesis process to its capacitor manufacturing customers, with encouraging results. It is believed that the Na Flame Synthesis platform will be capable of providing several new generations of high performance tantalum powders to the capacitor industry, thereby enabling the continued miniaturization of these essential electronic components. Cabot is also exploring opportunities to produce other high value nano-scaled powders using the Na Flame Synthesis process.

REFERENCES

1. Bergman, R.M. and C.M., Mosheim. 4,684,399 United States, 1987.
2. Axelbaum, R.L., DuFaux, D.P. and Rosen, L.J. 5,498,446 United States, 1996.
3. Rosen, L.J., et al., et al. 7,442,227 United States, 2008.
4. Processing of Salt Encapsulated Tantalum Particles for High Purity, Ultra High Surface Area Applications. Barr, J.L., Axelbaum, R.L. and Macias, M.E. 2006, J. Nanopart. Res., 8(1), pp. 11-22.
5. Synthesis of Stable Metal and Non-Oxide Ceramic Nanoparticles in Sodium/Halide Flames. Axelbaum, R.L. 2000, Powder Metall., 43(40), pp. 323-325.
6. Gas-phase Combustion Synthesis of Aluminum Nitride Powder. Axelbaum, R.L., et al., 1996, Proc. Combust. Instit., 26(2), pp. 1891-1897.
7. Nano-phase W and W-Ti Composite via Gas-Phase Combustion Synthesis. Axelbaum, R.L., et al.,. 1996, Mater. Manuf. Processes, 11(6), pp. 1043-1053.
8. Gas-phase Combustion Synthesis of Titanium Diboride (TiB2) Nanocrystals. Axelbaum, R.L., et al., 1996, J. Mater. Res., 11(40), pp. 948-954.
9. A Flame Process for Synthesis of Unagglomerated, Low-Oxygen Nanoparticles: Application to Ti and TiB2. Axelbaum, R.L., et al., 1997, Metall. Mater. Trans. B, 28(6), pp. 1199-1211.
10. Flame Synthesis of Superparamagnetic Fe/Nb Nanocomposites for Biomedical Applications. Nuetzel, J.A., et al., 2009, Proc. Combus. Instit., 32(2), pp. 1871-1877.