Industrial Scale Nano-Aluminum Powder Manufacturing

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ABSTRACT

Producing nano-aluminum powder (n-Al) on a commercial scale places a great deal of emphasis on practical manufacturing issues. Scientists and engineers in the laboratory commonly evaluate nano-aluminum powder in the technical terms of its particle size, particle size distribution (PSD), morphology, and oxide shell thickness. The quality of nano-aluminum at the commercial scale, however, rests upon several additional parameters that emphasize manufacturing effectiveness (production rate, process reproducibility, raw material utilization, lot size and scalability) as well as product quality (powder purity, surface properties and extent of agglomeration). Balancing the practical demands of a commercially viable process with the technical needs of specialized end users has been the challenge throughout the life of Technanogy Materials Development (TMD). Today TMD stands as a company focused on the manufacture and commercialization of nano-aluminum powder and able to assist others in developing nano-aluminum applications. The issues and insights related to the scale-up of this technology during the past three years are described. The properties of nano-aluminum powder that have motivated this scale-up are also discussed.

Keywords: nano-aluminum, nanoparticle, particle size distribution, passivation, oxide layer thickness, nanomaterial

Introduction

The widely reported interest in nanotechnology and nanomaterials has brought many exciting new technologies into focus. This increased level of awareness has also brought an inevitable degree of optimism from technologists, investors and consumers alike. In contrast to the level of exuberance that nanotechnology has elicited, the commercial success of the nanotechnology industry has been modest at best. The challenges that face companies that commercialize products based on nanomaterials are nontrivial and range from practical barriers in production and processing, to end users who remain unsure of how to fully unlock the highly-touted benefits of these materials. Nanomaterials are often, in reality, very different from their more massive micron- and larger-sized equivalents. It is the combination of an ability to synthesize materials at the nanometer level and subsequently manipulate these materials to form commercially viable products that will be the real test for companies in this industry.

Technanogy Materials Development (TMD) is a small company located in Santa Ana, California that has chosen to focus on the commercialization of nano-aluminum (n-Al) powder. For the past three years TMD has had one objective, to produce the highest quality n-Al powder at affordable prices to meet the needs of a developing customer base. There are numerous methods for laboratory-scale nanoparticle production that have been well described in the literature.[1,2] Nano-aluminum has several properties that restrict its method of production. Aluminum's reactivity with oxygen, the unattractive properties of molten aluminum (corrosivity, high surface tension and solvent strength), and the thermodynamic driving force of aluminum metal to recombine into a bulk crystalline form are all challenges to the production of nanometer-sized particles of aluminum.

Inert gas condensation (IGC) is the technology favored by TMD for the production of nano-aluminum. IGC has been recognized as a route to ultrafine particles for over two decades.[3–5]

The origins of TMD's vapor phase synthesis of n-Al can be traced to the early 1990s when researchers at Los Alamos National Laboratory investigated the use of inductively heated surfaces to produce n-Al by a gas phase process. Researchers at several other laboratories within the U.S. Department of Defense were concurrently exploring similar methods for the production of n-Al. Initially, the n-Al production rate was roughly one gram per run and was limited to two grams per day. Scaling this batch process into a semi-continuous mode increased throughput to one gram per hour by early 2001. Within the next year, n-Al production rate was increased to over 40 grams per hour (one kilogram per day). By early 2003, production rate had increased to more than 300 grams per hour (over seven kilograms per day). Production capacity with current continuous operation is expandable to several times this value.

The key to scaling the vapor phase production of nano-aluminum has been the ability to base design engineering and powder handling decisions on an understanding of the n-Al product. Much of the development period focused on improving the characterization and testing procedures. This effort provided an extensive background of the physical and chemical properties of n-Al. Understanding the influence of the powder production route on the physical properties of the powder identified the important process variables for n-Al manufacturing. Tight control over the IGC production process allows production of aluminum powder with fixed and controllable diameter as well as having a fixed and controllable oxide film at the surface. Figure 1 shows the relationship between particle diameter and the percentage weight of aluminum for each particle for several fixed oxide shell thickness values. Current capabilities allow production of any practical combination of particle size and aluminum metal content.

Interest in nano-aluminum powder without any oxide coating is well founded, especially within the energetic and propellant communities. Rocket propellants, for example, are very sensitive to weight and energy density and carrying unwanted levels of unreactive oxide is undesirable. Unfortunately, it is well understood that aluminum metal is not stable in the absence of a passivating oxide layer. Since aluminum oxide is known to form at extremely low oxygen partial pressures, the formation of an oxide shell is not preventable without a robust, impermeable barrier that completely envelops the aluminum particle. In the absence of an oxide layer, aluminum nanoparticles also have a very strong tendency to agglomerate to form bulk aluminum metal. Several approaches to non-aluminum oxide coatings on aluminum nano particles have been reported including the use of inorganic and organic self-assemblies, polymeric barriers, inorganic salts and metallic coatings. Without describing the details of each process it is the belief of TMD that no other coating adequately replaces the native oxide as a reliable and robust protective layer suitable for mass production. In fact, many alternative coating technologies appear incapable of preventing oxygen from accessing the aluminum particle core resulting in oxidation and therefore both an oxide and an added coating layer.

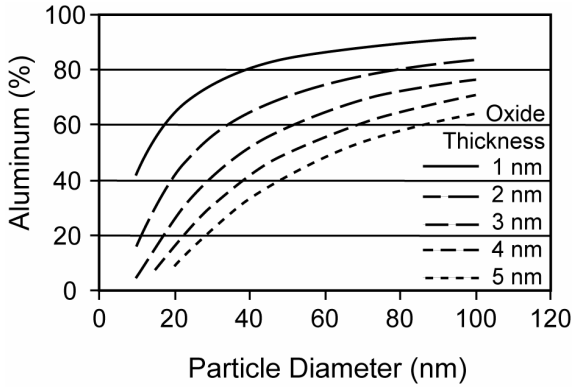


Figure 1. As the n-Al particle size increases, the weight percent of aluminum metal increases for a given oxide shell thickness (labeled in the graph). Technanogy Materials Development has independent control over both particle size and oxide shell thickness. Nano-aluminum powder can therefore be produced with any combination of size and aluminum metal content.

Control over both nano-aluminum powder size and aluminum content has been crucial to product development. Slight changes in particle size can have a dramatic effect on surface area and therefore surface area-dependent properties such as rheology, powder mixing, dispersion, surface adsorption of condensed species and bulk density. Aluminum metal content also has a large effect on nanopowder properties. The per-

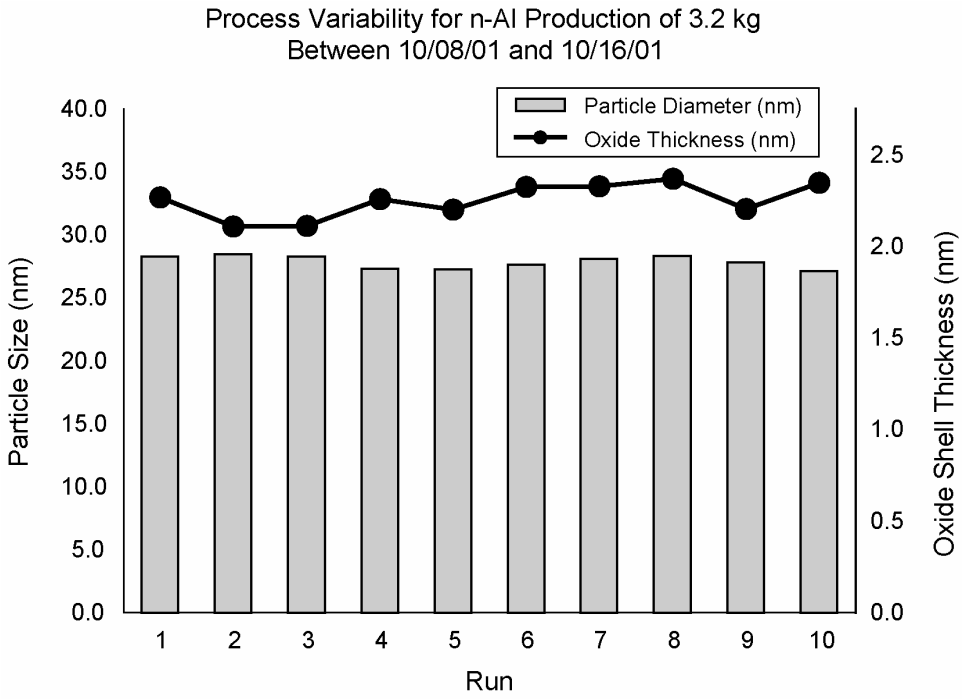


Figure 2. The reproducibility of the n-Al produced by TMD over several runs in 2001 is shown. The standard deviations of the particle size and the oxide shell thickness are 0.5 and 0.09 nm, respectively. Plotted values are calculated from surface area measurements and thermogravametric analysis as described in the text.

centage of aluminum metal is typically most critical to customers focusing on the energy release of the product. The aluminum weight percent influences particle properties such as density, reactivity, energy release rate, specific impulse and energy density as well as having implications for long-term storage and stability. Tight control over the particle size and oxide shell thickness is exhibited in the analysis of data from several runs from 2001 (Figure 2), and demonstrates the key capability necessary for any company producing nano-aluminum powder.

The Product

The nano-aluminum manufactured routinely is in the size range of 20 to 200 nm with a passivating oxide shell controllable to between 1.5 and several nanometers in thickness. The particles are discrete spheres of n-Al covered completely with an amorphous layer of aluminum oxide. As produced in the vacuum phase, the particles are free from necking, aggregation (defined in this context as the assembly of many particles held together by bonds or forces strong enough to resist breaking apart with energy input) or other permanent fusion. A scanning electron microscopy (SEM) image of n-Al produced by the IGC process is shown in Figure 3.

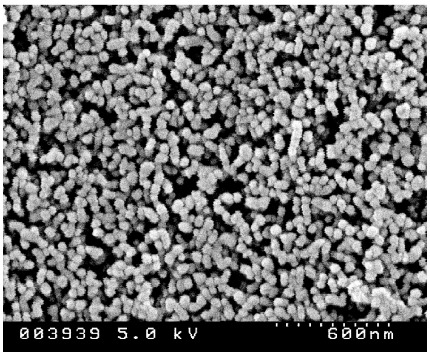


Figure 3. An SEM image of 40-nm aluminum powder produced by inert gas condensation (IGC).

The formation of soft agglomerates is unavoidable during routine powder processing and handling. The particles are agglomerated and exist as large collections of loosely associated particles upon collection in the manufacturing process, but they can be deagglomerated to yield discrete nanoparticles. As an undispersed powder in suspension, a sample of 40-nm n-Al is easily filtered using a 20-micron grade filter because the agglomerates behave more like particles of several microns. In circumstances where these agglomerates collect on the surface of a filter with much larger pores, the agglomerates create a filter with much finer pore size. Thus, the resulting network of soft agglomerates creates a "self-filter" at the nanometer scale.

Figure 4 clearly shows the inner metallic core and the amorphous oxide shell. The electron diffraction pattern from the core of a n-Al particle indicates its crystalline nature. Further, the oxide shell is consistently amorphous regardless of shell thickness or particle size, with no crystallinity apparent on any of the oxide coating locations. Elemental mapping of the nano-aluminum powder was used to confirm the presence of oxygen exclusively at the particle surface (Figure 5).

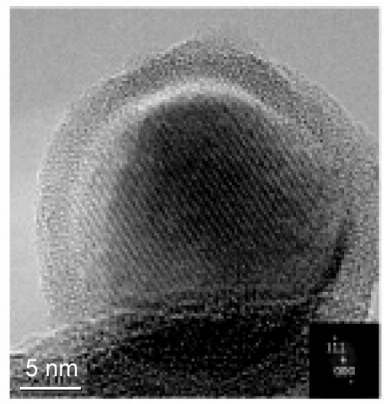


Figure 4. A transmission electron photomicrograph showing a 30-nm aluminum particle with a 3-nm oxide shell. The inset shows a selected-area diffraction pattern indicating a single-crystal and metallic aluminum core.

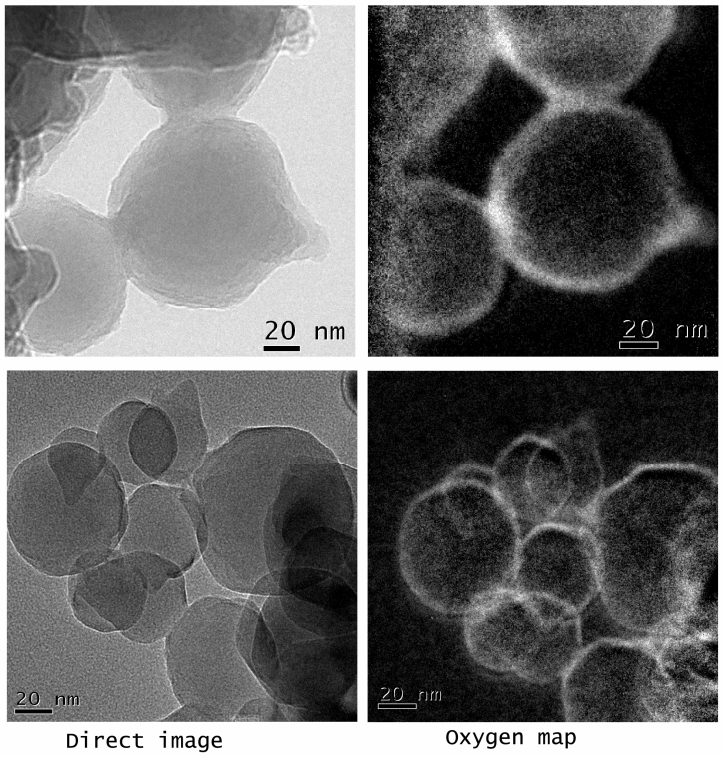


Figure 5. Elemental mapping, performed in a TEM, confirming the presence of oxygen solely in the alumina coatings of the n-Al powder.

Powder Analysis

Routine characterization is performed on every kilogram of powder produced. Analysis includes thermogravametric analysis (TGA) and particle size measurement by the gas adsorption technique and the Brunauer, Emmett and Teller (BET) calculation. The TGA and BET analyses are quantitative and well suited to quality control in a production facility where cost, maintenance and sample turn-around time of analysis results are crucial. The results from the TGA and BET analyses also provide good comparisons with the less standard electron microscopy tools. In combination these analysis tools provide a great deal of information about the physical properties of the nano-aluminum. To date an accurate methodology for measuring the particle size distribution (PSD) of n-Al produced by IGC has not been found, however, and more work is required. The specifics of particle size distribution will be discussed in more detail below. A summary of the calculation of the physical properties of n-Al from the analytical measurements follows.

Determination of Particle Size from BET

The BET surface area technique is used to calculate a mean particle size, *d*. The BET instrument introduces nitrogen gas into a test tube containing a known mass of powder and measures the volume of gas adsorbed on the surface. This value—divided by the mass of the sample—gives the specific surface area, σ, of the powder in m^2/g. Since the particles contained in the sample are spherical, combining the equations for the volume and surface area of a sphere allows the calculation of a mean particle diameter, *d*, as:

$$d = \frac{6}{\rho\sigma} \qquad (1)$$

where ρ is the density of the powder. Although the theoretical density of aluminum oxide (Al_2O_3) is 3.97 g/cm^3, pycnometry results have shown that the actual density of aluminum oxide is closer to 3.2 g/cm^3, which is the value used in all particle size calculations.

Determination of Oxide Thickness and Weight-Percent Metal from TGA

The second analysis performed on the powder is a thermogravimetric analysis or TGA. The TGA instrument measures the weight gained when the n-Al powder is heated in an atmosphere of 25% oxygen and 75% argon. The measured weight gain is then divided by the initial weight of the sample to determine the weight gain, Δm. A representative TGA curve indicating how Δm is determined is shown in Figure 6. Once Δm is known, it is used to calculate the oxide thickness and metal content of the powder as described below.

For the particle illustrated in Figure 7 the number of Al atoms in the core is:

$$\text{No. of Al atoms} = \frac{m_{Al} N_A}{A_{Al}} \qquad (2)$$

where m_{Al} is the mass of the Al core, N_A is Avogadro's number and A_{Al} is the atomic weight of aluminum. Furthermore, since the mass of the particle can be expressed in terms of its volume and density, Eq. 2 can be rewritten as:

$$\text{No. of Al atoms} = \frac{V_{Al}\rho_{Al} N_A}{A_{Al}} \qquad (3)$$

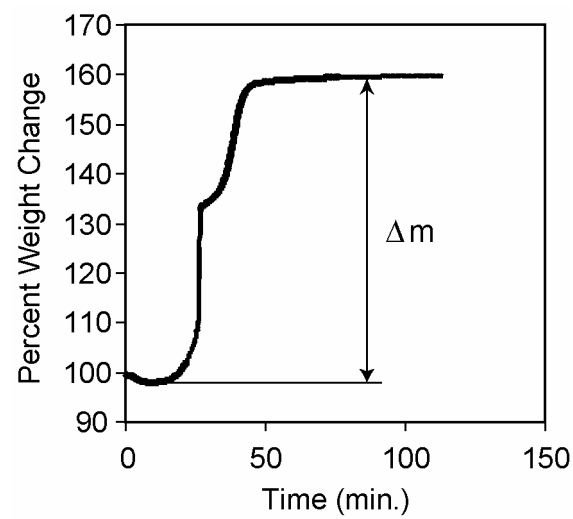


Figure 6. A representative TGA curve for a n-Al sample with the total weight gain, Δm, is shown.

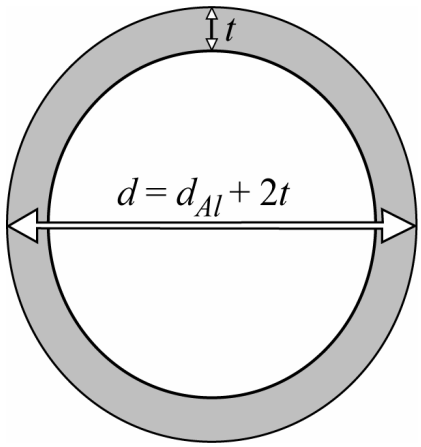


Figure 7. A spherical n-Al powder particle consists of an aluminum core with diameter equal to d_{Al}, surrounded by a thin oxide layer with a thickness of "t".

where V_{Al} is the volume of the core and ρ_{Al} is the density of Al.

The following analysis assumes that the oxide coating is stoichiometric Al_2O_3. The number of oxygen atoms, O, required to oxidize the aluminum core is 3/2 times the number of Al atoms based on the balanced equation for the oxidation of aluminum with molecular oxygen:

$$2\ Al_{(s)} + 3/2\ O_2 \rightarrow Al_2O_{3(s)}$$

$$\text{No. O atoms} = \frac{3}{2}\left(\frac{V_{Al}\rho_{Al}N_A}{A_{Al}}\right) \tag{4}$$

The added weight of these oxygen atoms is:

$$m_{ox} = \frac{3}{2}\left(\frac{V_{Al}\rho_{Al}N_A}{A_{Al}}\right)\frac{A_O}{N_A} = \frac{3A_O}{2A_{Al}}V_{Al}\rho_{Al} \tag{5}$$

Since the initial weight, w_{init}, of the particle is:

$$w_{init} = m_{Al} + m_{core} = V_{Al}\rho_{Al} + V_{ox}\rho_{ox} \tag{6}$$

the percent weight gain upon oxidation is:

$$\begin{aligned}\%\ \text{wt gain} &= \frac{m_{ox}}{w_{init}}\times 100 \\ &= \frac{\frac{3A_O}{2A_{Al}}V_{Al}\rho_{Al}}{V_{Al}\rho_{Al} + V_{ox}\rho_{ox}}\times 100 = \Delta m\end{aligned} \tag{7}$$

and Δm is the value reported by the TGA instrument. Equation 7 can be rearranged to solve for the ratio of the volume of the oxide to the volume of aluminum (β) so that:

$$\frac{V_{ox}}{V_{Al}} = \frac{\rho_{Al}}{\rho_{ox}}\left(\frac{3A_O}{2A_{Al}}\frac{100}{\Delta m} - 1\right) = \beta \tag{8}$$

The utility of Eq. 8 is that it allows the calculation of β directly from the percent weight gain as measured by the TGA, and this ratio is instrumental in calculating the particle's oxide thickness and the volume percent aluminum oxide, and other values, as described below.

For a spherical particle, Eq. 1 can be rearranged to give an expression for the specific surface area, σ, so that:

$$\sigma = \frac{6}{\rho d} \tag{9}$$

where d is the diameter of the particle as shown in Figure 7, and ρ is the density of the particle. For nano-Al particles this density is:

$$\rho = \frac{m}{V} = \frac{m_{ox} + m_{Al}}{V_{ox} + V_{Al}} = \frac{\rho_{ox}V_{ox} + \rho_{Al}V_{Al}}{V_{ox} + V_{Al}} \tag{10}$$

where V, which represents the total volume of the spherical particle, is calculated as:

$$V = \frac{\pi d^3}{6} \tag{11}$$

The total volume of a nano-Al particle is also equal to the sum of the volumes of the oxide shell, V_{ox}, and the aluminum core, V_{Al}, or:

$$V = V_{ox} + V_{Al} \tag{12}$$

Rearranging Eq. 11 to solve for the diameter of the particle and substituting in Eq. 12 gives:

$$\begin{aligned} d &= \left(\frac{6(V_{ox} + V_{Al})}{\pi}\right)^{\frac{1}{3}} \quad \text{OR} \\ d^3 &= \frac{6(\beta+1)V_{Al}}{\pi} \\ &= \frac{36\pi(1+\beta)^2}{\sigma^3(\rho_{Al} + \beta\rho_{ox})}\end{aligned} \tag{13}$$

Now, inserting Eqs. 10 and 13 into Eq. 9 allows the calculation of the specific surface area of the particle as:

$$\sigma = \frac{6\left(V_{ox}+V_{Al}\right)}{\left(\rho_{ox}V_{ox}+\rho_{Al}V_{Al}\right)\left[\frac{6(V_{ox}+V_{Al})}{\pi}\right]^{\frac{1}{3}}} = \frac{(36\pi)^{\frac{1}{3}}\left(V_{ox}+V_{Al}\right)^{\frac{2}{3}}}{\left(\rho_{ox}V_{ox}+\rho_{Al}V_{Al}\right)} \quad (14)$$

Substituting Eq. 8 into Eq. 14 and rearranging gives an expression for V_{Al} in terms of β:

$$V_{Al} = \frac{36\pi(1+\beta)^2}{\sigma^3\left(\rho_{Al}+\beta\rho_{ox}\right)} \quad (15)$$

Having an expression for V_{Al} and utilizing that expression in Eq. 11 allows the calculation of the diameter of the aluminum core, labeled d_{Al} in Figure 7 as:

$$d_{Al} = \left(\frac{6V_{Al}}{\pi}\right)^{\frac{1}{3}} = \frac{6(1+\beta)^{\frac{2}{3}}}{\sigma\left(\rho_{Al}+\beta\rho_{ox}\right)^{\frac{1}{3}}} \quad (16)$$

To determine the thickness of the oxide, the diameter of the aluminum core given in Eq. 16 must be subtracted from the total diameter given in Eq. 13. This task is simplified if both expressions are written in terms of β. Rewriting Eq. 13 in terms of β gives:

$$d = \frac{6(1+\beta)}{\sigma\left(\rho_{Al}+\beta\rho_{ox}\right)} \quad (17)$$

Now, solving for the oxide shell thickness represented by t in Figure 7:

$$t = \frac{d-d_{Al}}{2} = \frac{3(1+\beta)^{\frac{2}{3}}}{\sigma\left(\rho_{Al}+\beta\rho_{ox}\right)^{\frac{1}{3}}}\left[(1+\beta)^{\frac{1}{3}}-1\right] \quad (18)$$

The next parameter calculates the weight percent aluminum, which is related to the energy content of the particle.

$$\text{wt\% Al} = \frac{\rho_{Al}V_{Al}}{\rho_{ox}V_{ox}+\rho_{Al}V_{Al}}\times 100\% = \frac{2A_{Al}\Delta m}{3A_O} \quad (19)$$

Similarly, other values of interest can be simultaneously calculated by:

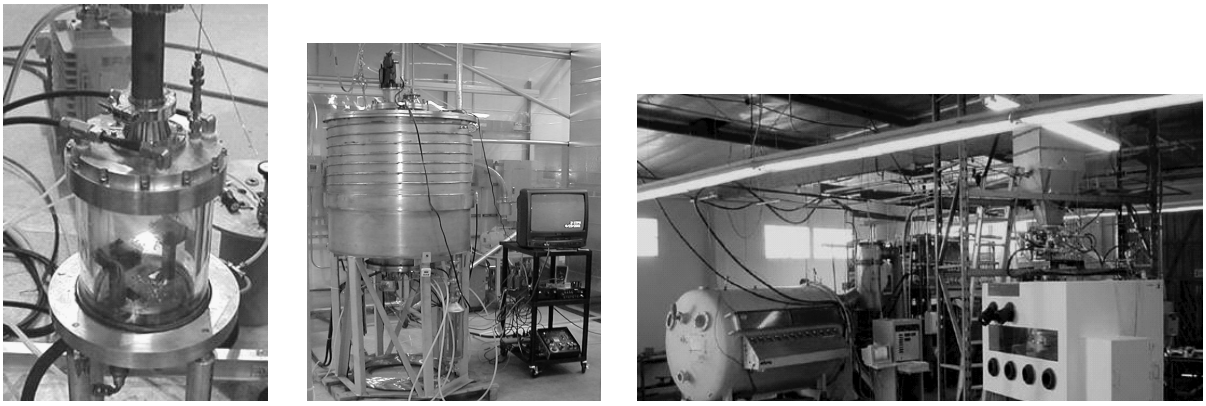
$$\text{vol\% Al} = \frac{V_{Al}}{V_{ox}+V_{Al}}\times 100\% = \frac{1}{\beta+1}\times 100\% \quad (20)$$

$$\text{vol\% aluminum oxide} = \frac{V_{ox}}{V_{ox}+V_{Al}}\times 100\% = \frac{\beta}{\beta+1}\times 100\% \quad (21)$$

$$\text{wt\% oxide} = \frac{\rho_{ox}V_{ox}}{\rho_{ox}V_{ox}+\rho_{Al}V_{Al}}\times 100\% = \left(1-\frac{2A_{Al}\Delta m}{300A_O}\right)\times 100\% \quad (22)$$

Process and Equipment

The manufacture of nano-aluminum is a vacuum process operating in the 1 to 10 torr range. High purity aluminum (grade 1199, 99.99% pure) is automatically fed into the reactor and introduced to a heated ceramic surface. The ceramic boats are resistively heated titanium diboride/boron nitride at temperatures of roughly 2000 ºC and have inert gas flowing past them. The high temperatures at and near the boat surface mandate active cooling for many of the reactor fittings and surfaces. Upon contact with the heated boat, the aluminum wire is melted and spread over a controlled portion of the boat. The boat surface temperature is kept above the melting its boiling point (2467 ºC) to yield a steady evaporation rate from the heated surface. As vapor phase aluminum molecules travel away from the heated surface, they nucleate to form multi-atom clusters that are the genesis of individual nanoparticles. Subsequent growth in the aluminum vapor leads to the formation of discrete particles in the nanometer size range. As the particles travel from the heated growth zone, they cool and crystallize. The particles are shaped during this portion of the process. Nano-aluminum particles are typically spherical due to the high surface tension acting upon the particles in the molten formation phase. The growth zone is limited to a small fraction of the distance between the heated boats and the collection apparatus. The various reactors that have been used to scale



a. **b.** **c.**

*Figure 8. Technanogy Materials Development has scaled its n-Al production from **(a)** a 1 gram per hour to **(b)** a semi-continuous 40 gram per hour level (~ 1 kg/day). TMD's latest production level **(c)** is at 300 grams per hour (> 7 kg/day) in a continuously operating reactor (c) that also integrated a conveyance and packaging system.*

n-Al production to current levels are shown in Figure 8.

An important part of the nano-aluminum production process is the method in which oxygen is introduced to the powder stream. The passivating oxide shell must be formed only after particles of the correct size have been formed but before they congeal and cluster into larger particles or aggregate clusters that will not break apart. Precise control of the level of oxygen used to passivate the powder and the location at which the powder stream is exposed to the passivating gas are keys to this process. When properly introduced, the passivating oxygen forms a thin oxide layer around each n-Al particle that prevents them from forming aggregates. The particles are cooled as they are carried in the gas stream to the collection zone. Collecting the aluminum powder on a dry filter at near-ambient temperature and low pressure tends to form soft agglomerates, but it maintains the distinct character of individual particles. When the powder is removed from the collection filters, it is sent as an agglomerated cake to a collection zone via a series of vacuum valves. A schematic of TMD's manufacturing equipment is shown in Figure 9.

Handling and transferring the n-Al powder is accomplished by one of several processes that

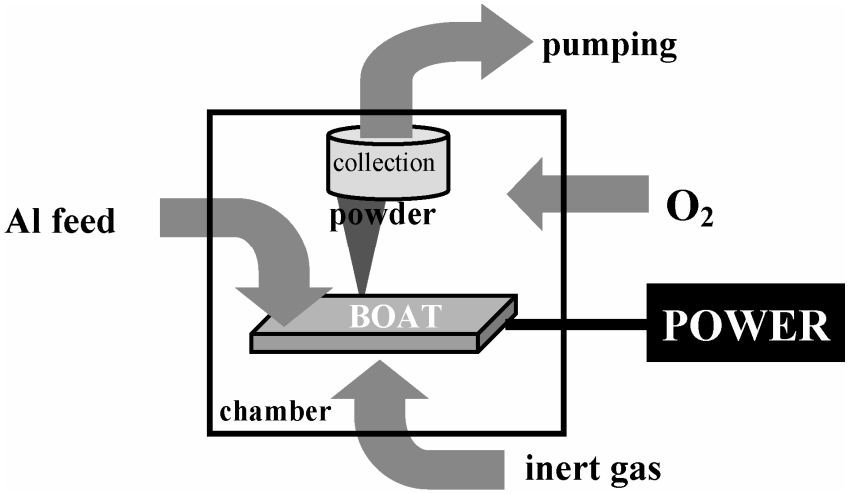


Figure 9. A schematic of TMD's nano-aluminum production process.

rely on an inert atmosphere of dry, oxygen-free purge gas. For example, the powder can be pneumatically transferred to an inert atmosphere glove box where it can be processed and packaged for shipment. In many instances the powder is still partially active due to imperfections in the passivation layer. Incomplete passivation may result from particles with incomplete oxide shells colliding and forming a zone of aluminum metal underexposed to oxygen. These clusters may resist passivation due to the inaccessibility of the active aluminum surface to oxygen. This sticking behavior is common for very small powder (< 40 nm) with a minimal oxide shell thickness (~2 nm). In such cases the level of passivation gas is low enough to lead to inhomogeneities in the powder. Under-passivation can be addressed by exposing all powder to a post-passivation process in which a batch of powder (approximately one kilogram) is mechanically agitated while being exposed to a low level of oxygen-containing gas. As the mechanical action breaks apart the particle agglomerates and exposes any under-passivated aluminum surfaces, the oxidation is carried out at a slow, controllable level. This post-passivation process is microprocessor controlled to prevent a runaway oxidation reaction. After the post-passivation treatment, the powder is fully coated with native oxide and is safe to handle. The n-Al is then sieved to clean and de-clump the material into a smooth, free flowing powder. The powder is then packaged under inert gas in metal cans with airtight lids, sampled for quality control and stored in a flammable materials cabinet.

Nano-Aluminum Powder Properties and Reactivity

Nano-aluminum powder is a broad term for aluminum with particle size in the sub-micron range. Typically, nanopowder is reserved for powders below 0.1 μm in diameter.[4] TMD focuses exclusively on n-Al powder in the size range between 20 and 200 nm. In spite of this reasonably small size range, the properties of this class of materials are amazingly dependent on both size and oxide shell thickness. The most obvious distinction between various-sized nanoscale aluminum powders is their color. Micron-sized aluminum powder is typically a light, metallic gray color. Nano-aluminum powder below 200 nm is dark gray. The color darkens as the particle size decreases. Typically, powder below roughly 40 nm is black. Figure 10 shows the color difference between >200-nm powder (gray) and 40-nm powder (black).

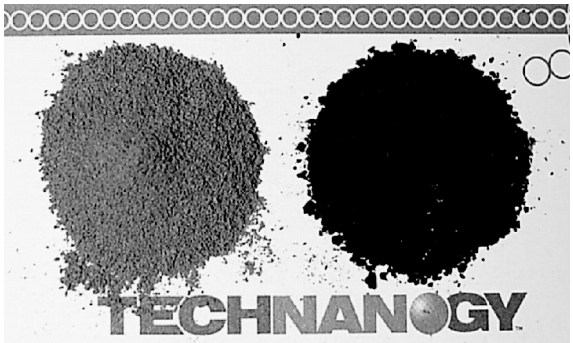


Figure 10. The color of aluminum is strongly related to particle size. Typically 200-nm powder is gray (left) and 40-nm powder is black (right).

The bulk density of aluminum powder is also strongly dependent on particle size. In general the smallest sizes of n-Al are very light and fluffy and exhibit bulk densities as low as 0.1 g/cm^3. Larger particle sizes exhibit bulk densities above 1.5 g/cm^3. The difference between micron- and nanometer-sized aluminum powders is also evident in the powder's surface area (and therefore all surface-area dependent properties such as reactivity). Figure 1 shows that the aluminum content decreases as particle size decreases for a fixed oxide shell thickness. The aluminum content of n-Al is one indicator of the large role that surface to volume ratio plays in nanopowders. A one-micron aluminum powder with a 3.0-nm oxide shell has a specific surface area of roughly 2.2 m^2/g and an aluminum metal content of 98%. A 40-nm n-Al powder with a 3.0-nm oxide shell would be only 57% aluminum metal by weight and would have a surface area of over 51 m^2/g. The high surface area of nanopowders is illustrated by considering a 100 g mass of aluminum metal, a mass roughly equivalent to the size of a golf ball. The surface area of this 100 g piece of aluminum would be 5.4×10^{-3} m^2, approximately the size of a typical 3-inch Post-It® note. When this 100 g mass of

aluminum is converted into 40-nm powder the surface area is increased to 5,500 m^2, or roughly the size of a soccer field. The single golf ball mass of aluminum would be converted into 10^{18} 40-nm n-Al particles, or roughly one particle for ever square centimeter of land on the planet Earth.

High surface areas translate to materials with very high reactivities. For example, a one-micron aluminum powder will burn only with a significant energy input (several hundred degrees of heat). In contrast, a 40-nm n-Al powder sample will burn very rapidly upon immediate exposure to an open flame. Many of the energetic applications of nano-aluminum rely on its increased reactivity directly attributed to its high surface area. Superthermites, initiators, igniters, rapid burning propellants and munition primers all capitalize on decreased diffusion distances for reactive species in contact with nano-aluminum. Another level of control over n-Al powder reactivity can be achieved by adjusting the thickness of the oxide shell on the particles. With independent control over both powder size and oxide thickness, the inert gas condensation method can deliver powders with specific energy density and energy release rate. Decreasing the oxide shell of a 40-nm n-Al powder from 3.0 to 1.5 nm increases the Al metal content in the powder from 57% to over 77%. A thin oxide layer increases the sensitivity of the powder and augments its stored energy, but this reactivity performance increase is achieved by decreasing the overall stability of the powder.

Powders with an oxide shell thickness less than 2.0 nm are generally considered unstable in the open atmosphere. Oxide shells thinner than 1.5 nm appear to be inadequate to protect nano-aluminum from pyrophoric behavior in air, or the formation of hard agglomerates during powder production. The reactivity of aluminum metal is well known, and exposed metal will reduce virtually any chemical species exposed to an unpassivated surface. The thermodynamic driving force (heat of reaction) for the oxidation of aluminum metal by molecular oxygen to form amorphous Al_2O_3 (alumina), ΔH^o, is –1676 kJ/mol.[7] Similarly, large thermodynamic driving forces also exist for the reduction of water, nitrogen, carbon dioxide and most metal oxides. A concern with aluminum powder stability is the initiation of a redox reaction that results from the exposure to either unpassivated metal or metal with a flaw in the passivating layer. Another route to chemical instability is the adsorption of moisture on the oxide surface. The hydration of the aluminum oxide surface can liberate heat (ΔH^o = 860 kJ/mol[7]) and destabilize the n-Al powder in one of several suspected routes.

One potential mechanism is that Al_2O_3 reacts with water vapor to form aluminum hydrates producing enough heat that thermal expansion of the aluminum core cracks the oxide shell. Aluminum metal thus exposed to the atmosphere would then react further with oxygen or moisture to liberate more heat as metal is converted to oxide. A single reacting particle is not a threat to destabilize an entire lot of n-Al as long as it remains an isolated event. If the exothermic oxidation energy propagates to nearby particles and is sufficient to initiate a similar oxidation event, then it is possible that a runaway reaction may proceed to completion. It is the initiation of oxidation of individual nano-aluminum particles under ambient condition, and the propagation of the heat to other particles that determines the pyrophoric behavior of n-Al. When an aluminum powder fire has initiated and the reaction is sustainable, it is nearly impossible to extinguish. The burning temperature of bulk nano-aluminum has been estimated at greater than 2500 ºC. At this temperature the aluminum metal will react with most anything including oxygen, water, nitrogen, carbon dioxide and carbonates in common class C fire extinguishers. The heat of this reaction will obviously melt most structural materials. Preventing undesired reactions is of paramount importance. Providing a n-Al product that can be safely handled in air is an important capability. Maintaining a minimum oxide shell thickness for all routine orders, post passivating the powder to quench any unpredictable reactivity, handling the powder in a controlled inert atmosphere, and packaging the powder in dry nitrogen are all important aspects of a commitment to safe handling.

The presence of adsorbed water on n-Al powder can have adverse effects even when safety is not a primary factor. Nano-aluminum powder will generally adsorb roughly five-weight percent water from the atmosphere within minutes of exposure. Moisture is liable to have adverse

effects on the end uses of the powder. Incorporating a powder containing five-weight percent water into a rocket propellant, or other pyrotechnic, may be problematic. The performance of propellants that contain reactive organics, moisture sensitive inorganic oxidizers, or water sensitive curing components may deteriorate in the presence of unintended levels of water. The formulation of n-Al into many other products may also be adversely affected by carrying unwanted water into the mixture. A high surface area power such as n-Al is well known to alter the rheology of most mixtures and can lead to increases of slurry viscosities by thousands of centipoise. Water may likely act to further affect the rheology or induce phase separation during or subsequent to the formulation process. A final detriment that surface adsorbed water may present is in the n-Al powder stability. In the presence of water the aluminum particles are liable to react, especially during processing or storage conditions that exceed room temperature or pressure. These disadvantages of surface moisture are the basis for a policy of not exposing n-Al to the open atmosphere.

To quantify the degree of powder aging, via the growth of the oxide coating over time, thermogravimetric analysis was performed repeatedly on specific lots of powder. The weight gain was translated into oxide shell thickness as discussed above and graphed versus time in Figure 11 for a specific powder lot. The trend indicates that the oxide layer will stabilize after about 2000 hours (about 3 months) of exposure to air. Several factors influence the aging behavior of n-Al powder including the atmosphere under which the powder is stored, the beginning oxide shell thickness and the particle size.

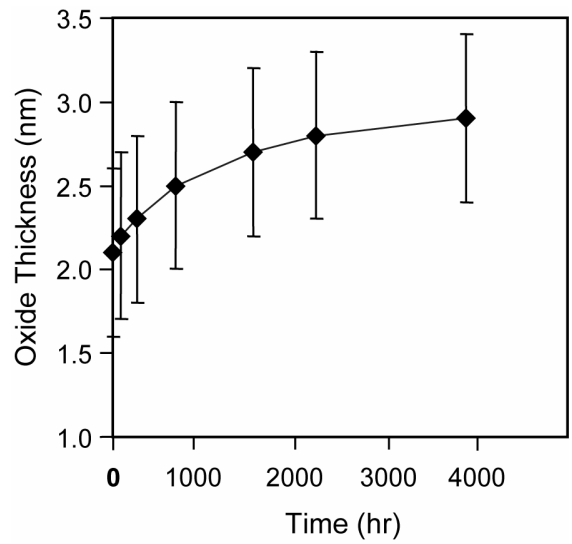


Figure 11. Plot of oxide coating thickness versus time for n-Al powder B080901B for storage in a non-air-tight clear glass vial. Note the error bar is ± 0.5 nm.

Particle Size Distribution

The particle size distribution (PSD) of powders can be measured in a variety of ways. One of the most common techniques for the analysis of ultrafine powders is the use of laser light scattering. Sophisticated instruments detect the reflected, refracted and scattered light from a laser's interaction with a suspended powder and then use complex models to compute the particle size distribution of the powder. This technology has been widely and successfully used for powders in the micron size range. Laser scattering has also been employed for various powder materials below 100 nm in size. The analysis of n-Al by laser light scattering has not been successfully accomplished to date. The most significant challenge to the use of laser light scattering for n-Al PSD appears to be the formation of stable, nonagglomerated dispersions of the material. Work continues to explore this technique for aluminum analysis. Other optical and particle counting technologies commercialized for the analysis of powders (particle counters, sieves, classifiers, etc.) are ineffective for n-Al, which is too small to be analyzed by methods that rely on mechanical techniques.

In the absence of a quantitative tool for PSD analysis the use of qualitative methods for determining size distribution information is possible. Powder color is the most obvious and the least quantitative. The use of electronic microscopy is a widely accepted tool for estimating PSD. Imaging over many fields of view with care—to accurately sample the powder—can provide an indication of PSD, but there are limitations to this approach.

Considering that one large particle in a sample of many million may skew a weighted distribution, it is important to look at many different

microscopic images of a given powder, to gain confidence in the true PSD. Imaging nanometer-sized powders intermixed with large micron-sized particles is complicated by the tendency for small particles to coat the large particles, obscuring the larger ones from the field of view. It is likely that SEM and TEM particle sizing will underestimate the mean size and the maximum particle size. BET analysis does not provide information about PSD, as it can only give the mean particle size calculated from a measurement of the specific surface area. TGA analyses also can be used to give information about PSD by studying the shape of the curve. The onset temperature of aluminum particle oxidation is dependent on particle size. Smaller particles are oxidized much more readily than larger ones and exhibit a weight gain on the TGA in an early, sharp curve. Larger particles tend to oxidize more slowly and persist at elevated temperatures in the TGA (>850 ºC) for many hours. The presence of unreacted aluminum in the later stages of a given TGA run may be used to suggest a broad PSD with large particles present. Extracting information about the size distribution of an aluminum powder sample by combining the information provided in electron microscopy, BET and TGA is possible, but it is time consuming and subject to many sources of error.

The particle size of nano-aluminum powder has been extensively evaluated using a combination of all of the techniques described above. The PSD of the n-Al is believed to be tightest at lower mean particle sizes. For example, powder with a mean particle size of 40 nm has been shown to have a very tight distribution with the vast majority of the particles below 60 nm in diameter. As the mean size of the powder increases, the PSD is believed to broaden. Powder with a mean particle size of 100 nm has a high fraction of particles that exceed 500 nm in diameter. TMD's 200-nm powder has an even higher fraction of large particles. SEM images of TMD's 200-nm powder reveal the presence of particles well above one micron in size. The physical basis for the broadening of the powder PSD as size increases is likely due to the contrasting process conditions between the production of the smallest (< 40 nm) and the largest (~200 nm) powders.

Applications

End uses for nano-aluminum were initially largely energetic and dominated by defense-related applications. Small caliber primers for defense munitions, additives for solid and hybrid rocket propellants, enhanced lethality explosives and thermite-based weapons had been widely researched and continue to be developed by government research laboratories. The interest in these applications prior to the year 2000 made them the most natural source for early commercial development, and defense and energetic applications continue to be important. Application development and collaborative research to accelerate the use of n-Al powder is ongoing with a number of public and private organizations in this area. During the last two years the non-defense energetic market for n-Al has also been explored. Private companies have probed the use of n-Al for products in pyrotechnics and fireworks, automotive inflators and airbag initiators as well as drilling and oil exploration. This sector of the market appears to rival the size of the government energetic market and is looked to as an area of expansion.

The largest growth area for nano-aluminum commercialization during the past three years has been in non-government, non-energetic applications. Recent interest in n-Al as an additive for plastics, a base material for sintering and consolidation, the formation of fully dense materials with nanoscale grain structures and the production of devices that capitalize on n-Al's special electrical properties are most notable. Unique properties and attributes of this nanomaterial continue to lead to innovative end uses for the product. The development of new products using n-Al has occurred in many different ways. In most cases customers require very little information about the material and work to produce products with little to no communication with the manufacturer. Other products are developed in close collaboration and in certain cases joint programs have been initiated that formalize relationships that draw from the strengths of one or more external collaborators.

Summary

TMD has demonstrated that it is possible to produce commercial quantities of n-Al by an inert gas condensation method. The n-Al powder is characterized by using a number of conventional analytical techniques such as TGA, BET and electron microscopy. More work is required on the important analytical challenge of n-Al particle size distribution. Energetic and non-energetic applications are being actively developed and the list of customers and applications continues to grow. Nano-aluminum powder price and quality are endless areas of development for TMD as it evolves to meet the needs of this emerging market.

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