HORIBA Scientific

Application Note

Optimization of High-Performance Nanostructured Powder Metallurgy Materials

AN225

Optimization of High-Performance Nanostructured Powder Metallurgy Materials with Accurate Measurements of Particle Size Distribution

Introduction

Powder metallurgy involves heating a compressed powder to a temperature below its melting point (sintering). A variety of economically important products, such as the many metal parts of modern engineering systems, are now produced by this method.

The particle size distribution (PSD) affects key characteristics of the resulting metallurgical compositions, making accurate measurements of PSD essential to the production of materials created by powder metallurgy. This is especially true for nanopowders that comprise complex and/or broad PSDs that cannot be readily measured using traditional electron microscopy or dynamic light scattering techniques.

In this note, we will briefly explore the history of powder metallurgy and then examine the importance of powder quality to the production of nanomaterials. Using a case study from the Vecchio lab at the University of California, San Diego, we will highlight the necessity of accurate particle sizing in the production of nanoparticles by spark erosion. Data from the ViewSizer 3000 (Fig. 1) indicate that particle quality and process control can be heavily reliant on capacitance charge, and that the choice of liquid dielectric has a significant impact on the resulting size distribution.

History

The production of materials from metal powders (powder metallurgy) has ancient origins. The early Egyptians and Incans utilized this technology to produce small metal objects. By 300 A.D., much larger objects were being manufactured, notably in India, but it was not until the early 19th century that powder metallurgy advanced significantly.

It was soon realized that the production of materials from powders was not restricted by the distribution of liquid and solid phases that limit alloys made by simple melting. Refinements in the blending of powders with additives led to a diversification of important industrial metal products in the early 20th century, such as the tungsten filament for incandescent lamps, exceptionally strong tungsten carbide, and porous (self-lubricating) bearings. By the latter half of the 20th century, powder metallurgy had become firmly established as the means of economically producing parts, particularly in the automotive and aerospace industries.

Figure 1. The ViewSizer® 3000

The early 21st century has seen remarkable developments in the application of powder metallurgy based on nanomaterials. Products composed of nanoscale particles can have unique electrical and magnetic properties, as well as superior strength with minimal loss in ductility. An example is the development of orthopedic weight-bearing implants.

An important aspect of powder metallurgy is the production of the powders themselves because the qualities of the starting powder often dictate mechanical, electrical, and optical properties of the final material. Historically, metal powders have been produced by mechanical attrition, such as ball milling, or by physical methods, such as atomization or gas condensation. Toward the end of the 20th century, increasingly sophisticated techniques were introduced, such as chemical vapor deposition and plasma processes. A recent focus on the production of nanoscale powders by electrical arc discharge highlights the importance of PSD and emphasizes the need for accurate particle sizing.

Advanced Powder Metallurgy Case Study

The Nanoengineering Materials Research Center (NEMRC) is a University of California San Diego-based research group under the guidance of Dr. Kenneth Vecchio. Research interests at NEMRC include processing and function of high-performance nanostructured steels, ceramics, bulk amorphous alloys, entropy-stabilized carbides, and other composites. One focus at NEMRC is on understanding and controlling the microstructural properties and development of these materials for fabrication of advanced structural applications.

Compression of powders through spark plasma sintering or high-temperature hot press, among other techniques, is used to synthesize bulk samples. Novel powder production techniques, such as spark erosion, are commonly used to produce unique nanopowders that sinter to bulk materials with enhanced mechanical properties.

Spark erosion, developed by Ami Berkowitz *et al*., is a highly versatile technique that has been used to produce powders ranging in size from a few nm to >100 μm and has been applied to materials including metals, semiconductors, and ceramics.[1-5] The process involves the breakdown of bulk samples by electric discharge in a dielectric fluid that produces a high-temperature arc (Fig. 2a). Erosion via an electric discharge is also the basis of a popular machining technique called electric discharge machining (EDM).

During the erosion process, the arc reaches temperatures as high as ~10^4 K and pressures as high as 280 MPa, which melts and vaporizes the sample material.[1-3,6,7] Both the molten droplets and the small droplets of condensed vapor are then quenched *in situ*.[3,8] These two separate mechanisms of particle formation lead to a *bimodal* powder distribution: the quenched molten droplets form larger particles and the condensed vapors form nanoscale particles (Fig. 2b,c).

The spark erosion rate and the resulting PSD are heavily dependent on both the choice of dielectric fluid and the energy parameters.[8] Higher energy sparks (>100 mJ) have been shown to produce ~1-5% by mass of nanostructured powder, whereas lower energy sparks (~9 mJ) can produce up to >60% nanostructured particles.[8] Much of the previous research in spark erosion has focused on the minimization of the occurrence of the larger particle mode to produce nanostructured powders. However, a bimodal grain distribution can be desirable when fabricating bulk metallic structures. The sintering of mixtures of powders with bimodal grain size distributions results in final samples which can show a drastic increase in strength due to Hall-Petch strengthening in the finer-grained regions, yet can maintain ductility owing to the work-hardening ability of the coarser-grained regions.

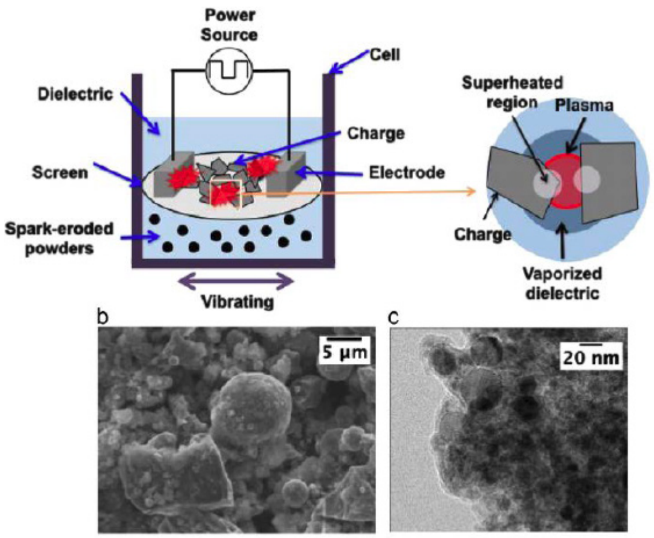

Figure 2. (a) Schematic diagram of the spark erosion process; (b) SEM and (c) TEM of spark-eroded powders.

The Importance of Particle Size Distribution Measurements

There is much interest in understanding the effect of capacitance charge and dielectric fluid on PSD. For example, by monitoring the voltage discharges occurring during the sparking process, it has been found that a 100μF nitrogen (N_2) dielectric spark has the same energy as a 120μF ethanol dielectric spark. Understanding these effects allows the process to be better tuned to produce ideal PSDs for high density, high strength, and enhanced ductility materials.

Despite spark erosion's potential to produce nanopowders, it has been challenging to accurately quantify the distribution of multiple particle sizes produced by this technique. Systems comprising heterogeneous and asymmetric particles present distinctive analytical challenges. Previous work with SEM, STEM, and TEM has highlighted the wide range of particle sizes possible, but an inability to efficiently count sufficiently large numbers of particles quickly prevents these techniques from providing a comprehensive representation of the PSD. Results produced using dynamic light scattering have been largely questionable and unreliable owing to the polydispersity of the size distribution. Therefore, in order to better understand and quantify PSD of the nanopowders, the multispectral particle analysis technique of HORIBA's ViewSizer 3000 was employed.

Test Methods

The ViewSizer 3000 characterizes nanoparticles by analyzing their Brownian motion and analyzes larger micron-sized particles by tracking their settling motion (driven by gravity). The system leverages innovative illumination and detection techniques that enable video recording of scattered light from wide-ranging sizes of individual particles simultaneously. A schematic of the ViewSizer 3000 optical system is shown in Figure 3.

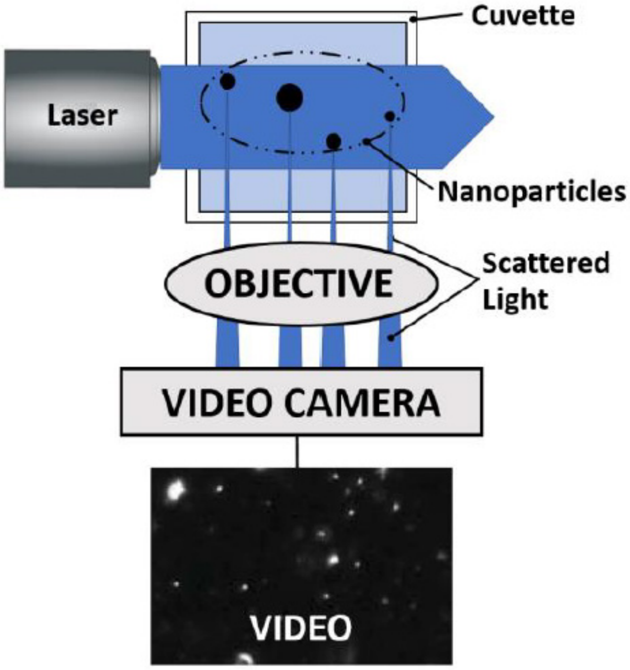

Figure 3. Schematic diagram of the ViewSizer® 3000 optical system.

A key advancement of this system is its ability to address the very large dynamic range of scattered light intensity from differently sized nanoparticles coexisting in polydisperse colloids. In other light scattering methods, the very intense scattered light from only a few larger particles overwhelms traditional detection systems and obscures the analysis of smaller particles in the sample[9]. HORIBA's ViewSizer 3000 overcomes these limitations and can quantify a wide range of particle sizes from 10 nm to 15 µm simultaneously.

The only inputs needed for the experiments using the ViewSizer 3000 are temperature, which was controlled at 22°C in this case, and liquid viscosity; the instrument automatically imputes the value for water. For each test, the instrument recorded 25 seven-second-long videos of particle motion. The sample was stirred between each video to ensure a fresh aliquot of sample is used for each video.

Sample Preparation

Powders were prepared from spark erosion performed on 316L ingots that produced a 316L nanopowder. All powders were cleansed and purified in the same manner.

Eight samples were prepared in total. Spark erosion capacitance settings of 60µF, 80µF, 100µF, and 120µF were used for nanopowders produced in both ethanol and N_2 liquid dielectrics. Powders were suspended in Xzero Type1 reference water to limit contaminants.

Nanoparticles were the main focus of this analysis so, after preparation of the suspensions, larger particles were allowed to settle before sampling from the upper portion of the suspension to ensure that the majority of the particles in the test suspension would be under 1µm.

Results

For both ethanol and N_2 liquid dielectrics, reducing capacitance clearly led to a reduction in the average particle size as well as a “smoothing” of the distribution. Lowering the capacitance also led to a lower variability in the right shoulder of the distribution (Figure 4). Likewise, a narrowing of the particle size distributions with lowered capacitance suggests that the sparking mechanism became more refined as the sparks shrank in energy and size. Thus, particle quality and process control were concluded to be heavily reliant on the chosen capacitance.

Furthermore, size distributions produced from same energy but different dielectric conditions show the dielectric has a significant impact on the size distribution produced. The average particle size produced in liquid N_2 was 80nm larger and the size distribution significantly broader than that in ethanol (Figure 5). This effect is attributed to a combination of the quenching and dielectric breakdown properties of either liquid.

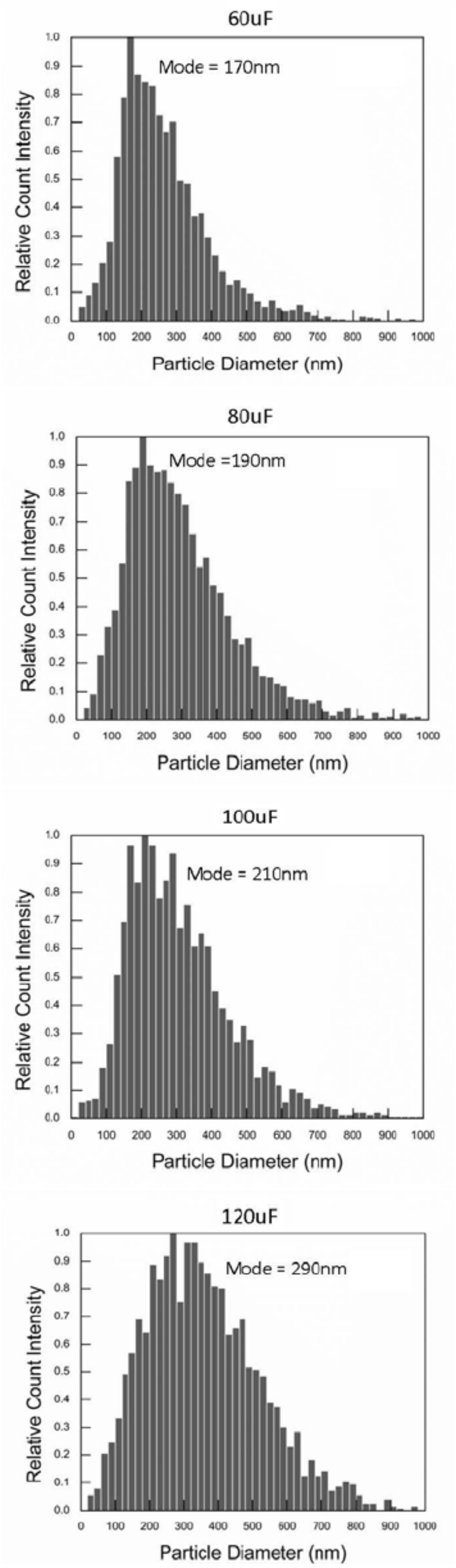

Figure 4. Size distributions of spark erosion particles produced using liquid nitrogen dielectric and under varying capacitance levels.

Summary

The optimization of high-performance nanomaterials produced by powder metallurgy requires nanopowders created with specific particle sizes. Spark erosion produces nano-powders with broad PSDs that cannot be quantified reliably using traditional sizing techniques. This has hindered optimization of the spark erosion process to fine tune the production of nanopowders.

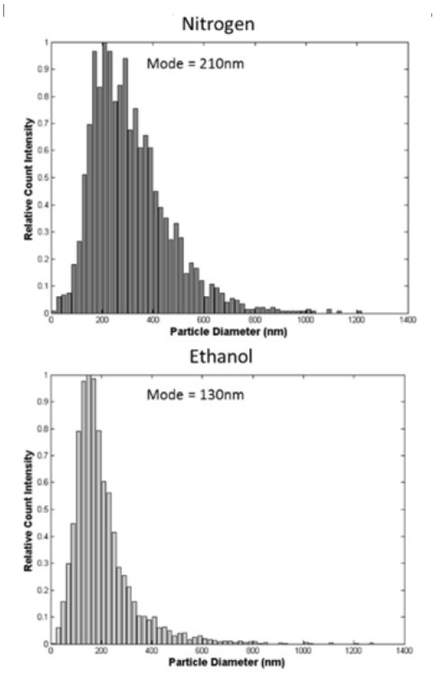

Figure 5. Results of particle size distributions extracted from same-energy sparks using different dielectric liquids.

The ViewSizer 3000 readily characterizes nanoparticles of wide-ranging sizes simultaneously, making it possible to understand the effect of dielectric fluid and capacitance charge on the PSD produced. Data from the ViewSizer® 3000 indicate that i) the liquid dielectric had a significant impact on the PSD produced, with larger average particle sizes produced in liquid N_2 than in ethanol, and ii) for a given liquid dielectric, reduced capacitance leads to a reduction in the average particle size. These results highlight the importance of accurate measurements of PSD in the production of nanopowders for powder metallurgy and show that the ViewSizer 3000 is ideal for routine use in R&D or Quality Control laboratories.

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