Characterization of Low-Level, Oversize Particles in Abrasive Powders

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Abstract

Abrasive powders are used in fine grinding and polishing applications many of which require defect-free surfaces. Scratching is a primary defect that can be caused by very low levels (less than 10 ppm) of large, oversize particles in the powders. Powders containing low levels of oversize particles can escape the scrutiny of quality control efforts because particle size analysis techniques have detection and sensing limits that prevent detection and quantification. This paper describes several common size analysis techniques with special regard to the limits of detecting oversize particles. Recommendations are described for measuring and quantifying low levels of oversize particles in powder size ranges of greater than and less than 10 microns.

Key words: Diamond, Abrasives, Powders, Size analysis, Oversize

1. Introduction

Many of the abrasive powders that are used for grinding, lapping or polishing are derived from crushing and/or milling larger particles into finer sizes. These powders include silicon carbide, aluminum oxide, boron carbide, cubic boron nitride and diamond. Fine abrasives are usually manufactured by crushing and grinding; followed by size classification methods that include screening, air classification or some form of sedimentation. Although the size reduction operation is important for obtaining the finer sizes from a coarser feed material, it is the size classification process that creates the narrow size fractions that are important for proper performance of abrasive grains in a surface modification application such as lapping or polishing. If the surface modification requires a surface finish that is free of scratching, i.e., no obviously large, deep grooves created by substantially larger particles in a set of narrowly graded particles, then special care must be taken to ensure that these particles are not present in the powder. Scratching is a serious visual and technical defect in applications like gem or crystal glass polishing, chemical mechanical planarization (CMP) of micro-electronic circuitry, precision wire sawing of semiconductor ingots and in computer hard drive media. Unfortunately, the inherent nature of oversize particles is that the concentration needed to cause serious damage to a surface is well below the detection limits or capability of most modern size analysis methods.

On the fine side of the size distribution curve, it is equally possible to have low levels of fine-size particles that suffer from the same detection limitations as those on the coarse side. If present in low levels, these particles usually have no effect on the performance of the abrasive. When present in larger quantities, and depending on the relative fineness of the size, undersize particles can have greater impact on characteristics like dispersion, tendency of forming agglomerates or packing behavior.

Another important factor is particle shape. The effect of particle shape on polishing performance is not as well understood as size effects. Many size measurement techniques are sensitive to shape and particles having very high aspect ratios or have a plate-like shape can appear as oversize particles. However, in many applications using abrasive particles for lapping or polishing, the high aspect ratio or plate-like particles will behave differently from oversize particles with more equi-axial or blocky shapes. In general, the
blocky oversize particles tend to be more problematic because they resist breakage under load and survive longer than those with irregular shapes. This paper will focus on the effects of oversize particles only.

A number of processes are used for reducing or eliminating oversize particles in powders or slurries. These include: sieving, filtration, elutriation, sedimentation and various forms and modifications of these. However, in order for any process to be controlled with confidence, it is necessary to measure the attribute that one is classifying or modifying. In the case of oversize particles, this becomes quite difficult because of the difficulty in measuring them. A number of size standards exist for defining various grades of abrasive powders; for example in the diamond abrasive industry: Federation Europeenne des Fabricants de Produits Abrasifs (FEPA)\(^4\), American National Standards Institute (ANSI)\(^5\) and Industrial Diamond Association (IDA)\(^6\).

There are two factors that make it difficult to control the level of oversize particles in a powder where the term oversize refers to particles substantially coarser than the median size of the powder. The first is the ability of detecting the particles with a certain degree of certainty. The second factor is applying the proper metric that adequately quantifies the level of oversize particles in a powder. The size attributes of powders are normally measured using particle size analysis techniques such as sieves, microscopic methods, sedimentation, electrical or optical sensing zone, laser light scattering techniques and others. Although each of these techniques employ different definitions of particle size, the distribution of sizes within a powder are measured and quantified using statistical terms such as the mean, median or mode size, standard deviation or percentile points on a cumulative curve of the total size data. These metrics serve quite well for describing the bulk properties and general performance of powders. However, these metrics are not useful for describing low levels, on the order of a few parts per million or even parts per billion, of oversize particles that can cause severe problems in surface modification processes.

This paper will describe the limitations that are associated with most of the modern techniques used for measuring the bulk size characteristics of powders. Additionally, semi-qualitative techniques are described which allow evaluation of oversized particles for very fine powders that are the most difficult to quantify by other techniques.

2. Effect of Oversize Particles

In applications that use abrasives for 2 or 3-body lapping or polishing, the ideal mode of operation is that uniformly sized particles are spread onto a lapping plate or polishing cloth using a liquid carrier. When the substrate being lapped or polished is placed in contact with the slurry on the plate, the particles are forced into a single layer between the plate and substrate (See Fig. 1). Only those particles that contact the workpiece and lapping plate provide the action that abrades or polishes the substrate. Where more compliant lapping surfaces are used, like polymeric films or cloths, there is more particle contact with the workpiece, but the pressures exerted by larger particles can exceed those of the smaller ones that are not pushed as far into the lapping cloth. In either case, narrow particle size distributions provide the highest level of particle contact, uniformly support the load placed on the substrate and polish or abrade with the highest material removal rate and best (defect free) resulting surface finish.

When oversize particles are present within a powder, even at levels that are not detected by most size analysis techniques, a considerable amount of surface damage can be caused from the lapping and polishing process. Fig. 2 shows the effect of a few large particles among millions of smaller narrow-sized particles. When the large particles are between the lapping plate and substrate, the particles resist breakage under load and survive longer than those with irregular shapes. This paper will focus on the effects of oversize particles only.

Fig. 1 Schematic of graded particles in a lapping or polishing application showing how uniformly sized particles bear the applied load.
plate and substrate, they will support a disproportionate amount of the load placed on the workpiece. The smaller particles around the large particle will bear no load and therefore be rendered useless. If the oversize particles support the pressure placed upon them without fracturing, the result will be relatively deep scratches on the workpiece.

3. Definition of Oversize Particles

The concept of an “oversize” particle has the most relevance with relationship to a “narrow” size distribution. In powders having broad size distributions, the definition and effect of oversize is more vague and less pronounced and for purposes of this discussion, we will limit the definition to narrowly graded powders or those having a median size to standard deviation ratio of 5 or larger (for example a powder having a median size of 15 microns and standard deviation of 2.5 microns will have a ratio of 6).

There are two magnitudes of oversize particles that can exist within a set of particles: Near-oversize refers to solid particles which are present in a distribution with a high degree of statistical probability and occur with enough frequency that they are detected and accounted for within a size distribution. These are the particles that make up the coarse “shoulder” of a distribution curve (see Fig. 3) and are generally 1.5 to 2 times larger than the median and are represented within the 90th to the 99th percentiles on a number
basis. For narrowly graded powders, these particles do not generally lead to scratching problems.

Gross-oversize particles that may be present in a distribution usually occur as rogue particles that were not removed from the powder due to process inefficiencies or contamination during handling or storage. In this case, gross-oversize particles are defined as solid particles whose size lies above the coarse shoulder of the particle size distribution curve and are statistical outliers from the rest of the population. Gross-oversize particles are generally 2 to 5 or more times larger than the median size. As little as 0.25 mg of 10 micron particles in as much as 80 kg of 1 micron mean size powder may be enough to allow one 10 micron particle to be included in as little as 60 mg of the bulk powder. Because it is the very largest particles in a powder that cause the scratching problems described in the introduction, for the remainder of this discussion, we will refer to gross-oversize particles as oversize particles.

In many cases, agglomerates of individual median-sized or near-sized particles will behave as oversize particles. The extent with which they can scratch or cause defects depends upon how tightly bound the individual particles are within an agglomerate. Tightly bound agglomerates, that occur with more frequency as the median size of a powder decreases, can behave as solid particles. Agglomerates that are held together with less cohesive force may behave as solid particles initially, then break apart under the applied load.

4. Characterization of Oversize Particles

The common size analysis techniques used for measuring particle size distributions of powders are: sieving, sensing zone methods (electrical and optical), laser light scattering, sedimentation, photon-correlation spectroscopy and microscopy. Each of these methods is based on fundamental principles that are well understood and each technique has advantages over others in specific size ranges, materials and applications. When employed properly, the size analysis techniques generate statistically significant size data for the bulk of the population of powders or particles that are being measured. Bulk size properties include mean, median, standard deviation, skewness factors, and percentiles that are statistically significant.

Table 1 lists the features of the common size analysis techniques with respect to their ability for detecting and quantifying oversize particles. The techniques are listed with respect to the lower detection limit. As can be seen by the table, the sieving technique, which actually performs a physical separation of the particles based on sieve-size, has a tremendous capacity for “measuring” billions of particles in relatively short timeframes. Given that the sieving time is sufficiently long enough to provide each particle with opportunity to fall through the sieve mesh or be retained, the process of determining whether a particle is above or below the sieve size has a high degree of resolution.
In the case of using a sieve for detecting oversize particles, a single sieve is employed rather than nesting a series of sieves. The sieve is chosen so that the size of the openings represents an arbitrary definition of oversize so that any particles retained on the sieve would be classified as such. Although no detailed size information is obtained on the bulk of the distribution, the particles that are retained on the sieve can be easily quantified by counting or weighing or other means. The added bonus of using sieves for measuring oversize particles is that these particles are actually removed from the powder and a value-added function has been performed.

Although sieving seems like the ideal method for measuring and detecting oversize particles, there are practical limitations for its use across all products and sizes. With the development of ultrasonic sieving technology, the ability of sieving powders through very fine mesh sizes has improved significantly. Wire mesh screens are made as fine as 635 mesh (20 microns) and electroformed screens as fine as a few microns. Electroformed sieves finer than 10 microns are expensive and fragile. At this size, it becomes difficult and time consuming for even ultrasonic energy to encourage the fine particles to fall through the sieve openings. Therefore 10 microns is near the practical limit of the sieving technique. Other concerns with using the sieving technique are the selection of sieve size with respect to the coarse shoulder of the distribution: if the sieve size is too close to the shoulder, many “near-size” particles will be present on the sieve cloth (see Fig. 3). These particles require long sieving times to orient and fall through the sieve and can cause the sieve cloth to blind. If the sieve is much coarser than the coarse shoulder of the distribution, the powder will fall through more easily, but oversize particles that are near the sieve size, and fall through, would not be accounted for. Given that sieves are usually available only in standard size ranges, there may be little flexibility in matching the sieve size based on the coarse shoulder of the size distribution. Finally, sieves must always be thoroughly inspected for holes or tears before being used for size analysis.

Another popular technique for measuring particle size distributions is the electrical sensing zone or optical sensing zone. Particles are sampled into these devices in dilute suspensions so that they can pass through the sensing zone one at a time and are therefore counted individually. As the particles enter into or through a zone, they trigger or disrupt either an electric current or a light beam. A sensor detects, quantifies the intensity of the signal and records the data in a size channel. The resolution of the “size” that is measured is a function of the sensitivity of the sensors, which in modern electronic systems are quite good.

In principle, it would seem that the sensing zone techniques are ideal for measuring and detecting oversize particles. In practice however, this technique is limited by several factors for the ability of measuring oversize crystals. In the case of electrical sensing zone methods, particles suspended in an electrolyte are drawn through an orifice. Particles can only be detected and measured if they pass through the orifice. This of course, requires that the orifice be larger than the coarsest particles in the sample. If there are particles in the sample that are coarser than the orifice, they will not be detected and can also cause plugging of the orifice. Another significant limitation of the sensing zone techniques is the counting statistics related to measuring dilute samples. For electrical sensing zone techniques the count rate is controlled by the concentration of particles in suspension and the suction applied through the aperture. An optimum count rate exists whereby too low of a rate results in inefficient use of time and exacerbation of background noise, whereas too many particles can result in coincidence effects; two or more particles entering the sensing zone simultaneously. When this happens, the analyzer detects these as single, larger particles. In practice, an optimum count rate is approximately 50,000 particles per minute. If oversize particles are present in concentrations of several parts per million, then it is possible that one oversize particle may be present in the population that is sampled in one or more minutes of analysis time.

Other limitations with electrical sensing zone technique occur from the background “noise” that is generated from the electrolyte solution. There are two forms of “noise” that are generated from the electrolyte: the first is a high frequency noise that usually occurs in the finest size channels and is more prevalent as the aperture size decreases. This noise can be accounted for by making an analysis of clear electrolyte having no particles in suspension and subtracting these background counts from the data obtained with the particles. The biggest effect of this noise is that it limits the use of the electrical sensing zone technique to sizes down to about 2 to 5 microns. The second form of noise is low frequency noise that can occur randomly in any size channel. Small bubbles, suspended contamination, particle build-up near the aperture inside the orifice tube, voltage fluctuations or electrical interruptions caused from loose electr-
cal connections or the stirring motor, etc. Fig. 4 shows the effect of 'noise' that resulted from analyzing a 40 micron mean sized powder that had been sieved three times through a 270 mesh (53 um) sieve to remove any oversize particles. As can be seen, counts still occurred in the coarser channels. Filtering the electrolyte and keeping connections clean can reduce this form of noise, but it cannot be completely eliminated. Both high frequency and low frequency forms of noise can result in counts that appear as coarse particles.

In general, electrical sensing zone techniques are suitable for measuring oversize particles only when the oversize particles are smaller than the aperture size, when the analysis is performed with minimal coincidence effects and when no low frequency noise is present during the analysis. Even when all of these criteria are met, the technique is best suited for powders with mean sizes greater than 5 microns.

Microscopy techniques performed either manually or coupled with digital image analysis equipment, are popular size analysis methods that can also reveal information on particle shape, composition and other features not possible with higher speed analysis techniques. As Table 1 describes, size analysis using optical microscopy methods is applicable for sizes down to about 1 micron and electron microscopes are suitable for sizes down to about 0.05 microns. Although the resolution associated with microscopy is excellent, the trade-off is that the data collection schemes are considerably slower than other size analysis methods resulting in poorer counting statistics for a given analysis time. When used for measuring bulk powder attributes, especially for narrow size distributions, the data from several thousand particles is usually adequate. However, for detecting and measuring oversize particles, especially those that exist in the parts per million ranges, the microscopy techniques do not lend themselves to scanning millions and millions of particles. Despite the quantitative limitations, the practice of scanning prepared slides of particles under a microscope looking for rogue oversize particles is quite common.

Laser light scattering size analysis methods, based on forward and right angle light diffraction principles are very popular for measuring size distributions. These methods are very appealing because they cover wide size ranges (0.1 to 1000 microns), require small sample quantities (less than 1 gram), generate reproducible data, and are fast and easy to operate. Commercially available systems can analyze powders dispersed in a liquid (usually water) or dry powders that have been aerosolized. In either case, the laser beam passes through a field of particles to a detector or series of detectors. The light passing through the field of particles is scattered at various angles and...
forms a diffraction pattern that is unique to the size distribution of the powder. The detectors are arranged at fixed angles that relate to a given size or size channel and the intensity of scattered light that falls onto each detector determines the percentage (typically by volume) of those particles in the distribution. The sensitivity of these detectors is such that it requires the cumulative amount of light scattered from many particles simultaneously to achieve the minimum level of light that the detectors can sense. It is the sensitivity limit of the light detectors that limits the ability of this technique for measuring oversize particles in a powder.

A few oversize particles dispersed among millions of particles are simply undetectable by this technique. Fig. 5 describes this effect. In example A, a 1 micron mean size powder contains less than 0.01 percent by mass of oversize particles generally in the 10 micron or coarser size range. This powder produces an extremely poor surface finish when used for lapping or polishing glass substrates. In spite of the obvious presence of oversize crystals, the laser light scattering technique did not detect these. In fact, example B shows a powder with essentially the same size distribution as example A, but the sample B powder does not contain any oversize particles and performs as expected.

Sedimentation methods of particle size analysis can be performed using homogeneous suspensions in either a gravitational or centrifugal field. In either case, particle size is based on the differential settling rates of particles based on Stokes’ Law. The determi-
nation of weight or volume fraction of particles within a size range is made in several ways: by physically collecting a sample of suspension and weighing the solids, by measuring the attenuation of an x-ray source through the suspension or by measuring the attenuation of a light or laser beam. If employing the cumulative weight measurement method, the ability of the sedimentation technique for detecting oversize particles is very limited simply because the weight of even a few oversize particles is well below the sensitivity of most weighing balances. If using radiation attenuation, the technique is limited in the same way that laser light scattering techniques are: by the lack of sensitivity of the detectors.

Photon correlation size analysis techniques are applicable to particles in the size range of 0.005 to 1 micron. Particle size is based on the response of a laser beam to particles vibrating in a liquid. Although the physics of the laser response to the particles is somewhat different than in laser light scattering systems, the basic limitations for detecting low-level oversize particles are essentially the same: the detectors simply do not have the sensitivity of detecting the response of a few larger particles within the field of on-size particles.

5. Oversize Measurement Recommendations

For powders with mean sizes coarser than 10 microns, sieving is clearly the preferred and most reliable method of measuring and detecting low levels of oversize particles. If the bulk size distribution of the powder is known, then a single sieve with sieve openings that are above the coarse tail of the distribution can be selected. Depending on the size of the powder, a known quantity of powder can be placed on top of a clean sieve (having been pre-inspected for holes and tears), and vibration and/or ultrasonic energy can be used for sieving the material through the openings. Sieving is complete after some point in time such that: 1.) No material resides on the sieve cloth or, 2.) A steady amount of residual material resides on the sieve cloth for a fixed period of time. As an added measure of accuracy, any residual material on the sieve cloth and sidewalls of the sieve can be washed through the sieve with water or alcohol.

If residue is present on the sieve, and it represents enough material for accurate weighing, then the residue can be carefully transferred to weighing paper and weighed. In some cases, there may not be a sufficient amount of material for weighing, then, a visual inspection of the sieve cloth under a stereo microscope would allow an estimate of the number of oversize particles retained. Microscopic analyses of this residue would also allow an estimate of the size of the oversize particles. The visual analysis of retained particles on a sieve cloth is aided by using smaller diameter sieves, such as a 3-inch diameter sieve. Smaller sieves help concentrate any oversize particles that may be present in a smaller area. Using this technique, it is indeed possible to find and measure a single oversize particle in a relatively large quantity (representing billions of particles) of powder.

For particles in the 0.1 to 10 micron mean size range, sieving techniques become less practical unless one knows beforehand that the oversize particles are larger than the sieve size that would retain them. Because of the limitations described above for the sensing zone techniques, these methods are not reliable for detecting low levels of oversize particles primarily because one cannot know with any certainty if counts that occur above the 99th percentile of a distribution are coincidence effects, noise or, in fact, real particles.

One technique that can be used for isolating and ultimately quantifying oversize particles in this size range is a modified sedimentation technique. As discussed above, the resolution of sedimentation technique is not suitable for detecting low levels of oversize particles when measuring a full distribution of particles and when using on-line radiation attenuation techniques. However, it is possible to utilize the technique for repeatedly fractionating a suspension at a single Stokes’ diameter that would be chosen based on the known size distribution of the powder. In this technique, a known amount of powder is weighed and dispersed into a suspension at 1 to 5 weight percent solids. The dispersion technique would normally employ de-ionized water containing 0.1 to 0.5% of a surfactant in addition to pH adjustments so that the zeta potential of the dispersed solids is sufficiently high that adequate stability of the suspension is achieved. A combination of mechanical and ultrasonic agitation usually provides enough energy for breaking up any agglomerates that may act as oversize particles. For the very finest size powders, i.e., those less than 0.5 microns, longer agitation times will usually be required.

For powders with mean sizes greater than 1 micron, the sedimentation fractionation technique can be performed using gravity settling in a clean glass beaker. Using Stokes’ Law, one can calculate the settling time required for the finest oversize particle to settle from the top of the liquid level to the bottom (or
near the bottom) of the beaker. When the suspension is thoroughly mixed and dispersed, the beaker is allowed to stand for the calculated time while the particles settle. At the designated time, a pipette or pump is used for withdrawing the suspension down to a level near the bottom of the beaker. The withdrawn suspension can be saved or discarded, but is not required for further analysis. As the sediment always includes all of the oversize plus some of the bulk material, several decantation cycles must be performed. Therefore, after the first decantation, the beaker is filled again with “clean” de-ionized water that has been treated with surfactant and pH modifier. The retained suspension, which is now more dilute, is stirred and ultrasonically agitated. The suspension is then allowed to stand again for the calculated time until the oversize particles settle to the bottom and the suspension is decanted again. The process of diluting and decanting is repeated until the settled suspension contains a minimum level of on-size particles. The number of cycles required for isolating any oversize particles will also depend on the concentration of the initial solids loading in the suspension. For example, for the oversize particles to be more than 50% of the sediment, you would need 10 decantation cycles if the oversize particles are twice the median size and 4 cycles at 5 times the median, for 1 ppm oversize. For 1 ppb, it comes out to about 15 cycles and 6 cycles.

When the fractionation process is completed and if residue is present at the bottom of the beaker, and it represents enough material for accurate weighing, then the residue can be carefully dried, transferred to weighing paper and weighed. In some cases, there may not be a sufficient amount of material for weighing, then, a visual inspection of the settled particles under a stereo microscope would allow an estimate of the number of oversize particles in the powder. Microscopic analyses of this residue would also allow an estimate of the size of the oversize particles.

In powders having a mean size less than 1 micron, the same process as described above can be used however, centrifugal sedimentation can reduce the settling times. Whether one uses gravitational or centrifugal sedimentation, it is imperative that one minimizes the risk of external contamination of particles from mixers, probes, decant tubes, etc. In the case of gravity settling, the process can generally be scaled up to accommodate larger quantities of powder if necessary.

6. Summary

Levels of oversize particles may exist within narrowly graded abrasive powders at levels that are in the parts-per-million to parts-per-billion range. The presence of these particles can have a serious and deleterious effect on the performance of these powders especially in abrasive lapping, polishing and precision wire sawing applications. Although abrasive powders are manufactured to stringent size controls for the bulk distribution and measurement techniques are quite effective at characterizing the bulk of the distribution, the ability of detecting the low-levels of oversize particles remains a challenge. These low levels of particles are below the detection limit of most modern, high-speed size analysis techniques. The limitations of some of the most popular techniques are described with respect to their ability for detecting rogue oversize particles.

For powders with mean sizes at or above 10 microns, a sieve analysis technique is described that can be used for detecting and quantifying oversize particles with considerable resolution. For powders that are finer in size, a sedimentation technique can be used for isolating any oversize particles that may be present. The sedimentation method can be performed using either gravity or centrifugal sedimentation techniques.

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**Author’s short biography**

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Dr. Timothy F. Dumm graduated from the Pennsylvania State University in 1989 with a degree in Mining Engineering and doctorate in Mineral Processing. He has worked with the industrial diamond division of the General Electric Co. and Diamond Innovations Co. in Worthington, OH for the past 16 years. He has developed milling, classification and characterization techniques for fine diamond and other superabrasive powders. He is currently involved in developing new applications for diamond in a broad range of industries including oil & gas drilling, electronics, plastics, glass, paints & coatings, ceramics and semiconductors.