Improving Powders with Freeze Granulation

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Freeze granulation can help ceramic manufacturers achieve powder formulations with superior homogeneity, pressing performance and dispersibility.

Powder properties, processing procedures and requirements vary widely between industries and applications. However, all powder processing operations share a common goal—to effectively process the powder to ensure the quality and/or performance of the final product. This is especially important if the particle size of the powder is in the nano or micron range.

Advanced surface-chemical approaches and adequate technical methods and equipment are required to break up agglomerates and ensure homogeneity throughout the entire process. Traditionally, liquid-based processing methods such as sieving and spray drying have provided the best conditions for mixing and homogenizing fine powders and other additives. However, powders processed with these techniques often do not retain their homogeneity in subsequent processing steps, such as drying and compaction. Recently, a new technology called freeze granulation has emerged as a more efficient alternative to ensuring homogeneity in the final product.

Powder Granulation for Pressing

In the large-scale manufacture of technical ceramics (Al_2O_3, ZrO_2, Si_3N_4, SiC, etc.), pressing is the most widely used forming method for simple-shaped components due to its comparatively low cost. However, producing high-quality pressed parts requires a powder granulation technique that can generate larger particle clusters (granules) with the proper flow to efficiently fill a die in automatic press cycles. More than one ceramic powder and organic pressing aid is often used, and these different elements must be adequately mixed before being further processed. Effective mechanical treatment (such as ball milling) in a liquid (preferably water) and the use of an efficient stabilizing concept help ensure that the different ceramic powders are thoroughly combined, and surface-active agents (dispersants) are often added to provide repulsive forces between the particles. In some cases, polymeric pressing aids (binders and plasticizers) are added in a secondary mixing operation prior to granulation to enhance powder compaction and increase the strength of the pressed components.

Ceramic powders can be granulated by forcing the wetted powder mixture through sieves. However, this method is mainly limited to smaller-scale operations and processes that use organic solvents as the liquid medium.

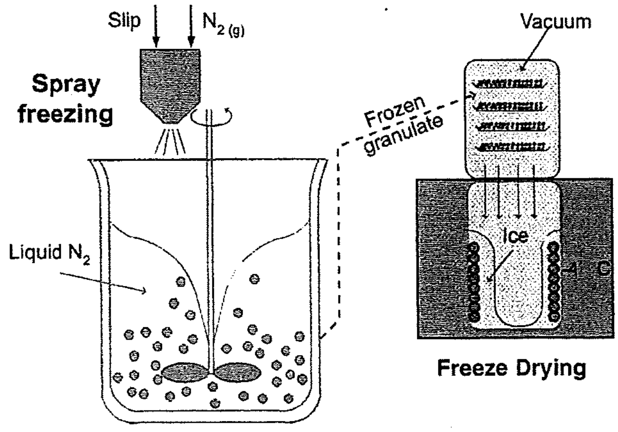

Figure 1. Schematic of the freeze granulation/freeze drying process.

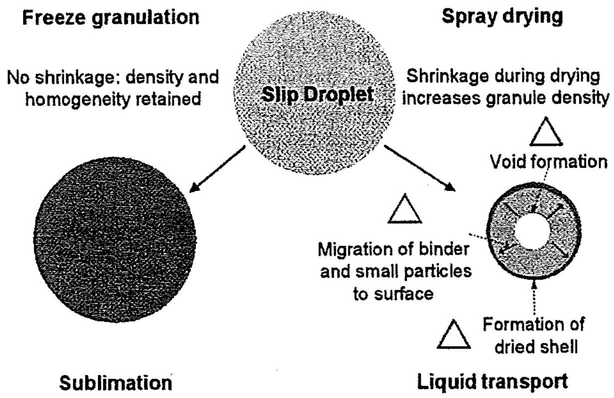

Figure 2. Comparison of the drying process in freeze granulation and spray drying.

For large-scale granulation, spray drying is the most commonly used method. In this technique, the ceramic powder suspension is pumped through an atomizing nozzle into a chamber with hot air, and the suspended droplets are rapidly transformed into dried powder granules. However, as the liquid moves through each droplet during drying, it tends to carry the polymeric additives and smaller particles with it. This phenomenon disturbs the homogeneity of the powder and creates hard granules that can be difficult to disintegrate during pressing.

The problem can be exacerbated when water is used as a dispersing medium, since hard bonds between the particles in the granules often occur when the granules are dried in air. Uncrushed granules and any migration phenomena cause inhomogeneities that can emerge in the final sintered material as strength-limiting defects. Depending on the material application, other critical properties (thermal, electrical, optical, etc.) can also deteriorate. A new granulation technique is needed to overcome these drawbacks.

Freeze Granulation for Pressing

For many powder processing applications, freeze granulation can provide an effective alternative to sieving and spray drying. In freeze granulation, a well-dis-

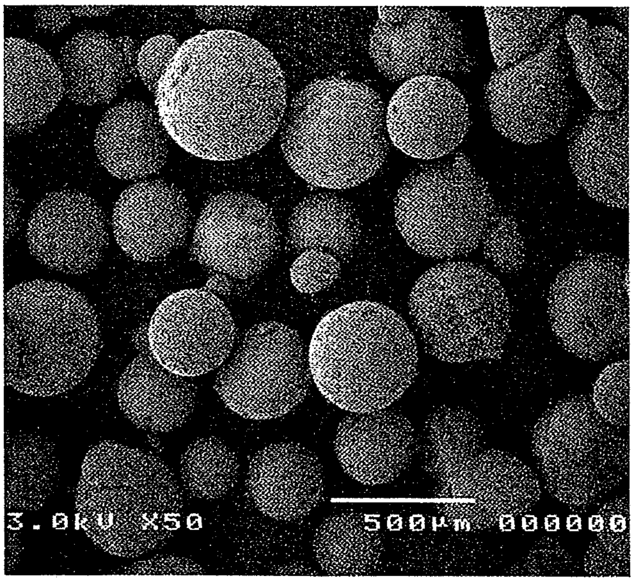

Figure 3. Granules of a multi-composite material processed with freeze granulation.

persed powder suspension is pumped through a nozzle, similar to spray drying, and is atomized into small drops by an applied gas flow. However, this operation takes place in a container with liquid nitrogen, which causes the suspension drops to freeze instantaneously (see Figure 1, p. 41). The frozen drops or granules are collected and kept frozen until drying is carried out in a freeze dryer.

During freeze drying, the solvent is removed by sublimation and changes from a solid state to a vapor without a liquid formation; as a result, many of the problems found in air drying—such as particle shrinkage, strong interparticle bonds, and the migration of additives and smaller particles to the granule's surface—are avoided (see Figure 2, p. 41). The process produces granules with a density and homogeneity that directly correspond to the characteristics of the original suspension. In subsequent pressing operations, the granules are easily broken, and the homogeneously distributed pressing aids optimally support the compaction process.

The fluidity and tap density of a freeze-granulated powder depend on the density, shape and size distribution of the individual granules. The density of a single granule is controlled by the solids loading (particle concentration) of the powder suspension and corresponds directly to this characteristic. The shape and size of the granule are controlled by the suspension rheology (viscosity profile), the suspension flow rate and the pressure of the applied gas. A lower-viscosity suspension will produce smaller granules at constant process parameters, but these results can be altered by changing the slip speed and/or gas pressure. Normally, a wide granule size distribution in the range of 50-400 µm is achieved.

When using freeze granulation, the reological properties of the powder suspension must be considered. Although a substantial variation in viscosity can exist, the suspension must exhibit a continuous shear-thinning behavior, which can be obtained by adapting the solids loading and the degree of stability with the proper type and amount of dispersant and a controlled ion (salt) concentration. With the right granulation parameters, spherical and free-flowing granules can be obtained, as shown in Figure 3. Both small and large quantities of powder suspensions can be granulated with the same granule properties. Granules can be recirculated by melting and regranulating them.

Freeze granulation and freeze drying can be used with most water-based powder suspensions. For powders that react with water, organic solvents such as cyclohexane and tert-amyl alcohol can be used. Since the solvent is collected as ice in the freeze dryer, it can be reused in future granulation processes. However, any solvents used in this process should have a freezing point in the range of -55 to +10°C. Solvents with a lower freezing point inhibit the freeze-drying process, while those with a higher freezing point can clog the spray nozzle.

Freeze granulation has been successfully used to create homogeneous powders for liquid phase sintered silicon carbide, pressed and sintered silicon nitride, and other pressed ceramic components.[1-6] Additionally, because the technology promotes homogeneity, it is especially beneficial for processing particle-, whisker- and fiber-based composites.

Creating Redispersible Powders

In addition to producing granules with excellent quality and performance for pressing applications, freeze granulation can also be used to generate low-dust submicron powder granulates that can easily be redispersed. Extensively agglomerated powders can be dispersed at a lower solids loading, freeze granulated/freeze dried, and subsequently redispersed at a significantly higher particle concentration. This process is illustrated in Figure 4, which shows the viscosity profiles of one as-received and one pre-treated Si_3N_4 powder known to be difficult to disperse to high concentrations.[7] Due to the lack of strong interparticle bonds, the granules in both suspensions are easily broken and do not immobilize the liquid medium, thereby preventing a viscosity increase. This makes it easier to reach the high solids loading that is often required to achieve adequate performance in subsequent processing steps.

Freeze granulation is especially useful for handling nanopowders, which have traditionally been considered very difficult—if not impossible—to disperse into primary particles. When freeze drying is applied in direct connection with the synthesis of the nanopowder in liquid, and the resulting frozen powder is then kept dry, the possibility to properly disperse the nanopowder rises considerably.

The mild treatment of the powders in the freeze-drying process also lessens the chance for oxidation of non-oxide particles compared to conventional drying in hot, humid air. As a result, slowed sintering and other problems caused by excessive oxidation are avoided.

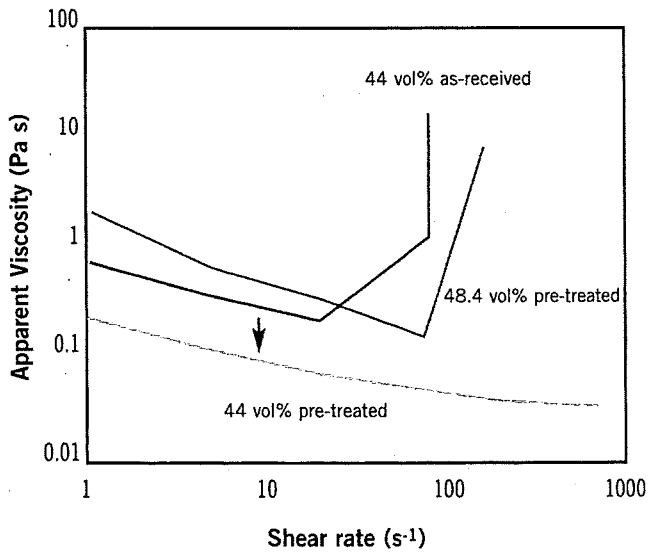

Figure 4. Viscosity profiles of Si_3N_4 slips (pH 10) based on as-received and pre-treated (de-agglomerated, freeze granulated and freeze dried) powders.[7]

Applying the Technology

Freeze granulation systems are commercially available for both laboratory and production operations. Figure 5 shows a lab-scale freeze granulator* that has a granulation capacity of two liters of suspension per hour. (For a typical ceramic powder, this corresponds to about 3 kg [6.6 lbs] of granulate.) It can also process suspensions as small as 50-100 ml with proper granulation performance. The equipment is also designed to be easy to clean, which minimizes risks of contamination when processing different materials. This system is suitable for operations ranging from lab-scale granulation to small-scale production and is especially useful for producing small batches of granules in which the composition is varied.

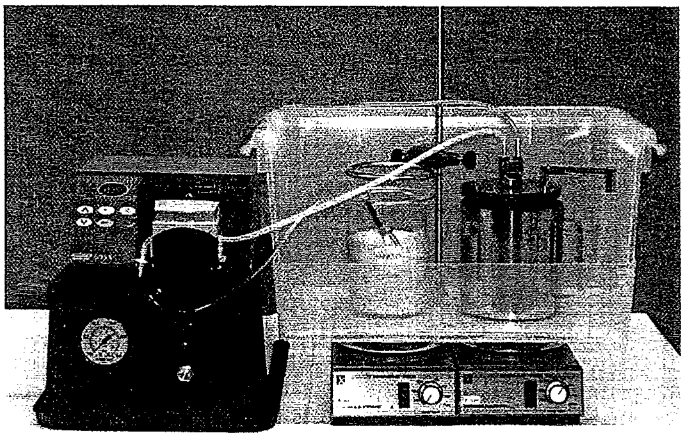

Figure 5. A lab-scale freeze granulator (the LS-2, supplied by PowderPro HB).

A system* is also available for processing larger batches of granules—up to 10 liters (~2.6 gallons) of suspension per hour. Unlike the lab unit, this system uses circulating liquid nitrogen and is therefore more efficient for production purposes.

Besides the granulator, a tray freeze dryer and a standard freezer for storing the frozen granules are required. Many commercial freeze dryers can be used with this system; however, if organic solvents are used, adaptations might be needed to improve drying and recycling control. By working closely with a qualified freeze granulation supplier, ceramic manufacturers can ensure that they select the right equipment to make freeze granulation a successful tool in their powder processing operations.

For more information about freeze granulation, contact Kent Rundgren, managing director, PowderPro HB, Skogsängsvägen 19, SE-422 47 Hisings Backa, Sweden; (46) 303-56-317; fax (46) 303-52-158; e-mail kent.rundgren@powderpro.se; or visit www.powderpro.se.

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*The LS-2 (lab) and PS-10 (production) freeze granulators are available from PowderPro HB, Hisings Backa, Sweden.