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GRANULATION OF CERAMIC POWDERS FOR PRESSING BY SPRAY-FREEZING AND FREEZE-DRYING

Brita Nyberg, Elis Carlström and Roger Carlsson
Swedish Ceramic Institute
Box 5403, 402 29 Göteborg, Sweden

ABSTRACT

By spraying droplets of a slurry into liquid nitrogen followed by freeze-drying of the frozen droplets, spherical free-flowing granules were formed from both water based and solvent based slurries. The structure and the homogeneity of the slip was retained in the granules. Density of granules could be controlled by changing solid concentration of the slip without adverse effect on the structure of the granules. Intergranular pores are eliminated during pressing and at lower pressures compared to high density granules. Sintering performance compared favourably to a pressing powder of high density granules.

INTRODUCTION

Many ceramic materials require processing in a solvent. Spray-drying is the most common granulation method for water based systems. Application of spray-drying to solvent based systems is expensive and requires large batches. A problem often met in spray-drying is migration of polymer (binder and lubricant) to the surface of the granules during drying resulting in hollow spheres (1, 2) and a non uniform distribution of polymer and additives. Uniform distribution of the polymer throughout the granules can be achieved by adsorption onto the primary powder particle surfaces which prevents migration (3). Mechanical granulation is a common granulation method for solvent based systems. In sintered materials made from these pressing powders strength limiting intergranular pores are often found which are remnants from not readily crushed granules during compaction. Freeze-granulation (spray-freezing with subsequent freeze-drying) is likely to give spherical and readily crushed granules with a uniform distribution of additives (polymer and sintering additive) resulting in a good microstructure of the sintered material (4, 5).

EXPERIMENTAL

Granulation

Powder granulates were made from solvent and water based slurries of silicon nitride with Y_2O_3 (6wt%) and Al_2O_3 (2wt%) as sintering additives. Two water based slurries with different ratios of binders were prepared with 28 vol% solids loading for freeze-granulation and mechanical granulation respectively. One solvent (cyclohexane) based slurry with a solids loading of 29 vol% was prepared and divided into two, one for freeze-granulation and one for mechanical granulation (Table 1). Additionally two water based slurries with different solids loading (21 and 33 vol%) and no binders were prepared for freeze-granulation and comparison of granule properties only.

Mechanical granulation was made by evaporation of the liquid in a rotary evaporator with subsequent crushing of the remaining powder cake with milling balls in a sieving machine (mesh-size 0.30 mm). A high amount of residual water was deliberately left in the powder cake giving a high moisture content of the granules made from the water based slurry. To the solvent based slurry 5 wt% of octane was added as a means to retain moisture in the granules after drying.

Spray-freezing was done by feeding the slurry into a two-fluid nozzle and spraying the droplets into a vortex of liquid nitrogen where instant freezing of the droplets (granules) takes place. Granule size could easily be controlled by slurry flow and gas flow. The capacity of the laboratory apparatus (Figure 1) is 1000 ml slurry/hour. The frozen granules then were moved into a freeze-dryer where the frozen liquid is sublimated. Granule density was measured by mercury porosimetry at atmospheric pressure where all intergranular pores (>10 µm) should be filled with mercury and no compaction forces are acting on the granules. Fill density and moisture of the granulated powders were determined prior to pressing. Cross section areas of the granules were examined by SEM.

Compaction and sintering

Green compacts with a diameter of 15 mm and a height of 10 mm were made by pressing granulated powder in a double acting die at four different pressures. Isostatic pressing of prepressed samples (prepressed at 5 MPa) was done at 225 MPa. Green density was calculated by measuring weight (± 0.001 g) and dimensions (± 0.01 mm) of compacts after burn-out of binders.

Rate-controlled burn-out of organics in N_2(g) was done at a maximum temperature of 500°C. Pressureless sintering was performed in a carbon resistance furnace at 1820°C for 3 hours in a powder bed of coarse Si_3N_4. Sintered densities were measured by water intrusion (Archimedes's method). Cross section areas of green compacts and sintered samples formed by isostatic pressing were examined by SEM.

RESULTS AND DISCUSSION

Characterization of granules

The mechanically granulated powders achieved the highest fill densities due to the dense powder cakes they were made from (Table 1). The granular shape was angular which impairs packing. The flowability was good due to the high density of the granules made by mechanical granulation. The granules of the freeze-granulated powders were spherical and free-flowing. The amount of hollow granules was sparse compared to what is generally found in spray-dried powders (Figure 2). No breakage of granules occurred and no dust from fines was observed during handling. The freeze-granulated powder made from the solvent based slurry seemed to consist of somewhat more brittle granules, when looking at cross section areas in the SEM, which may be attributed to the pressing additive (oleic acid) not giving enough contribution to green-strength.

Granule density for freeze-granulated powders was directly related to solids loading of the slurry. Solids loadings of 21 and 33 vol% yielded a granule density of 0.68 and 1.08 g/cm^3 respectively, which corresponds to the density that should be obtained if the frozen liquid was sublimated from frozen slurries in situ. Corresponding fill-densities were 0.38 and 0.58 g/cm^3 respectively.

Table 1. Characterization of freeze granulated and mechanically granulated pressing powders (Si_3N_4, Y_2O_3 (6 wt%), Al_2O_3 (2 wt%)).

System	Granulation technique	Pressing additive	(wt%)	Ratio	Solids loading (wt/ vol%)	Fill density (g/cm^3)	Moisture prior to pressing (wt%)
Water	Freeze Mechanical	PVA:Glycerol PVA:Glycerol	3 3	3:1 2:1	56/28 56/28	0.59 0.86	6 12
Cyclo-hexane	Freeze Mechanical	Oleic acid Oleic acid	2 2	--- ---	63/29 63/29	0.67 0.85	<1 1

Si_3N_4: UBE E10 (UBE Industries)
Y_2O_3: HC Starck Finest (HC Starck)
Al_2O_3: A16SG (ALCOA)

Dispersants:
Water - Lignosulphonate (0.2 wt%)
Cyclohexane - KD3 (2 wt%) (ICI)
PVA: Mowiol 4-88 (Hoechst)

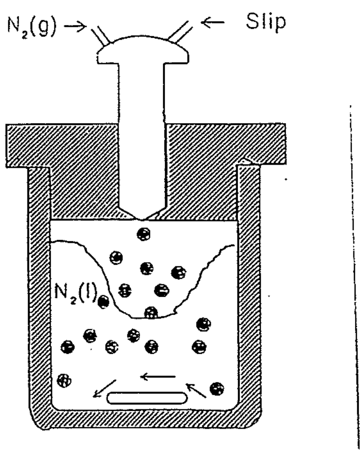


Figure 1: Spray-freezing of granules.

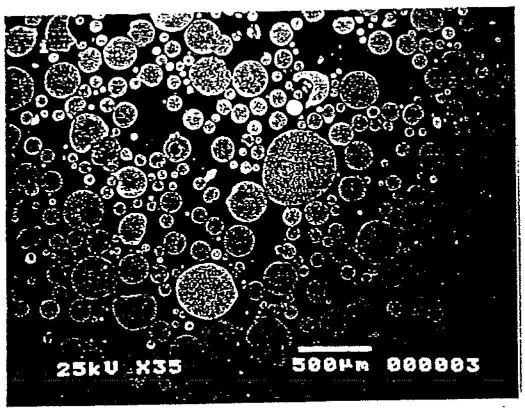


Figure 2: Freeze-granulated powder, water based system.

Compaction

Examination of green compacts (isostatically pressed at 225 MPa) by SEM showed that large intergranular pores exist in compacts pressed from the mechanically granulated powders. This accounts for not readily crushed high density granules. In compacts pressed from freeze-granulated powders these intergranular pores are eliminated during compaction due to more easily deformed low density granules. Highest density at any pressure was achieved for compacts pressed with mechanically granulated powders (Figure 3). The high densities obtained with granules made from the water based slurry is due to the high moisture content (12 wt%) of this pressing powder. Moisture acts as a plasticizer for the polyvinyl alcohol and the granules become softer (6). Despite the high moisture content intergranular pores still exist in compacts pressed from this powder. This is probably explained by the moisture not being evenly distributed in the original powder cake after evaporation. Thus, some granules become hard and some soft.

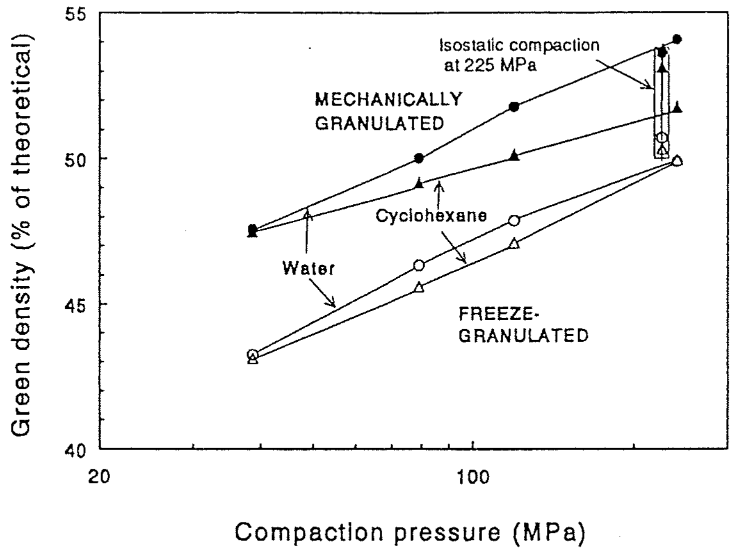


Figure 3: Compaction diagrams for mechanically granulated and freeze-granulated powders. Uniaxial compaction in a die at four different pressures. (Isostatic compaction at 225 MPa.)

Sintering

Starting from the same or even a lower green density the compacts of the freeze-granulated powders exhibited the highest sintered densities (Figure 4). The finer porosity of these compacts are more readily sintered while intergranular pores still remain in sintered compacts made from the mechanically granulated powders. This was also confirmed when examining sintered samples (isostically pressed at 225 MPa) by SEM (Figure 5). The enhanced sintering performance of compacts made from low density granules compared to compacts made from high density granules has also been confirmed by Zheng and Reed (7).

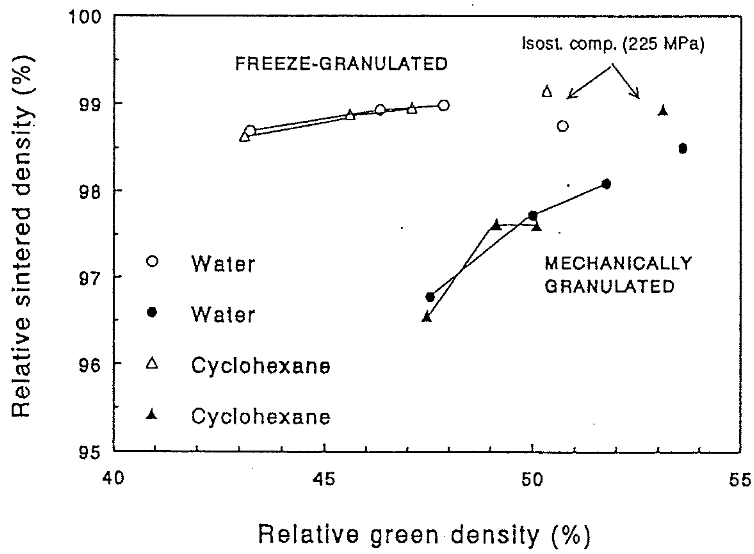
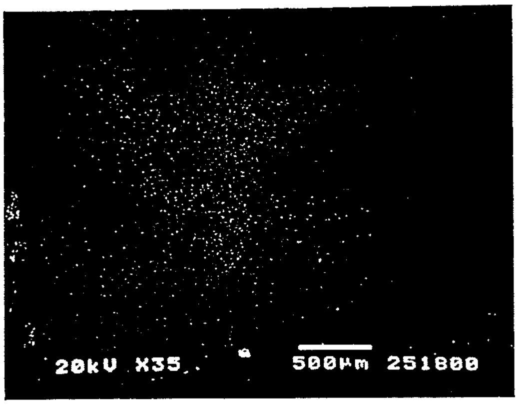


Figure 4: Sintering of compacts of different green densities at 1820°C for 3h.



A B

Figure 5: Microstructure of sintered compacts pressed with granules made from a solvent based slurry. A. Freeze-granulated. B. Mechanically granulated

CONCLUSIONS

Freeze-granulation (spray-freezing with subsequent freeze-drying) from both water and solvent based slurries gives spherical, free-flowing granules that are readily crushed during compaction. The good microstructure of the green compacts (large intergranular pores are eliminated) and the homogeneous distribution of polymer and additives enhance the sintering performance. The strength of the material is expected to be higher than for a material made from high density granules (4). The method should be well suited for composite systems where a uniform distribution of components is required.

A small laboratory equipment can be used to produce spherical, free-flowing granules in size ranges where normally large spray-dryers are demanded. Another advantage of the technique is that solvent based slurries can be used.

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