

FREEZE GRANULATION OF LIQUID PHASE SINTERED SILICON CARBIDE

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Silicon carbide was liquid phase sintered by adding Al_2O_3 (1%) and Y_2O_3 (2%). Samples were formed by uniaxial pressing. The powders were granulated using freeze granulation. A water-based slip was prepared and sprayed into liquid nitrogen. The frozen slip droplets were collected and freeze dried. The rapid freezing and drying by sublimation ensured that no demixing of the powders took place during granulation. The droplets retained their original size during the drying process and this made it possible to control the density of the granules without affecting the granule structure. The granule density and the plasticity of the binder were varied to avoid granule defects in the pressed green bodies. The pressed microstructures were evaluated by SEM studies of green bodies and by strength measurements on sintered samples. By changing the binder composition and the granule density, the sintered strength could be increased to the same level as that of slip cast materials (approximately 500 MPa in four-point bend). This strength was reached for uniaxial pressing at moderate pressures (100 MPa).

INTRODUCTION

Fine ceramic powders have to be granulated to be pressed successfully. The attractive van der Waals forces between fine powders make homogeneous filling of a pressing die impossible without granulation. Spray drying and mechanical granulation are the most commonly used methods of granulation for pressing of ceramics [1]. Mechanical granulation is done by mixing powder and liquid either as a plastic mass or in a slurry followed by pan drying. The formed powder cake is forced through a screen to form granules. In spray drying, a slip is sprayed into a drying chamber. The liquid is evaporated from the droplets by contact with the drying air, and spherical granules are formed [2].

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In mechanical granulation the contact with plastic mixing equipment and the screen is a source of metallic contamination of the granulate. The formed granules are uneven in shape which makes them flow less readily than the spherical granules produced by spray drying.

In spray drying the main problem is the inhomogeneous granules that are formed. In the early stage of drying, there is transport of liquid from the interior of the granule to the surface of the granule. During this stage there is a shrinkage of the granule. Organic binders and other soluble species are transported and concentrated at the surface of the granule. Small particles can also be preferentially transported to the surface. This migration of binders and powder particles makes the granules inhomogeneous. The binder rich surface will obstruct the later drying and sometimes cause formation of internal porosity, or if a large pore breaks to the surface, of doughnut-shaped granules. During pressing, the binder rich surface of the granules will resist breakdown and leave traces of granule boundaries in the pressed microstructure. A spray dryer has to have a spraying chamber large enough to let the granules dry before reaching the walls or other granules. If the powder has to be processed in organic solvents the drying air has to be replaced by an inert gas to avoid explosive hazards. This requires large equipment for solvent recovery that can handle the large gas volumes used for drying.

Freeze granulation comprises spraying a slurry into liquid nitrogen followed by freeze drying of the frozen granulate [3] [4]. The advantages of these methods are the homogeneity of the granulate and the small relative size of the equipment [5]. When a droplet is sprayed into liquid nitrogen the nitrogen boils around the slip droplet. The freezing is rapid and the gas bubbles forming around the droplets make it repel from both the walls of the chamber and other droplets. The chamber for spray freezing can be of a much smaller size than a spray drying chamber without problem of granules sticking to the walls.

No liquid migration takes place during freeze granulation. The droplets are rapidly frozen. The frozen liquid is then sublimated and transported away as a vapor during freeze drying. The initial size of the droplet formed in the spraying nozzle is retained throughout the process. No shrinkage and consequently no packing of the powder in the granulate takes place. In spray drying the density of a granule is controlled by the ability of the powder to pack (particle size and shape distribution) and the colloidal stability of the slip. This is analogous to the green density of a slip cast body. In freeze drying the solid content of the slip totally controls the density of the granule.

In spray drying the density of the granules cannot be controlled unless the stability of the slip is changed. This will change the structure of the granulate and decreased stability increases migration of binders during drying. In freeze granulation the granule density can be controlled by changing the solids concentrations of the slip. The structure of the granulate does not change when the solids concentration of the slip is varied. On average, lower density granules are produced by freeze drying, as no shrinkage (density increase) takes place during drying. The formation of hard agglomerates that can easily take place in drying of water-based systems is avoided by the freeze drying process due to the lower granule density.

Zheng and Reed [6] showed that low density granules are preferable during pressing. A high density granule will be pressed to a body of about the same general density as the granule density. A low density granule is pressed to a body of considerably higher density. This ensures that the low density granule will be completely broken down during pressing. A high density granule can retain its size and will often leave porosity at the granule boundaries.

Silicon carbide can be sintered by adding small amounts of Al_2O_3 and Y_2O_3 [7] [8] [9]. The additions have to be homogeneously distributed to function as sintering additives at low concentrations. This can be done by adding the oxides in the form of alkoxides [10] or by adsorption of sols [11]. In slip casting the homogeneity can be easily achieved by the homogeneity of the slip. For pressing better homogeneity can be achieved by using freeze granulation as opposed to spray drying.

EXPERIMENTAL

Slips were prepared by dispersing 600 g of powder at a solid content of 55-62 wt% in a ball mill with 1.5 kg of silicon nitride balls. SiC (UF 15, Lonza, Switzerland) was mixed in water with 1 wt% Al_2O_3 (Alcoa A16 SG, USA) and 2 wt% Y_2O_3 (Finest, HC Starck, Germany). The slip was dispersed by addition of lignosulphonate (Wargonin Extra, Lignotech, Sweden) and adjustment of the pH to 11. The binder was added after dispersion of the slip for 68 h and the slip was mixed for another 2 h. The binder was a polyvinyl alcohol (PVOH) (Mowiol 4-88, Hoechst, Germany), plasticized with either glycerol or polyethylene glycol (PEG) (PEG 400, Hoechst, Germany).

The slips were sprayed into liquid nitrogen. The nitrogen was contained in an insulated glass beaker and was stirred by a magnetic stirrer. The spraying nozzle

was a two-fluid nozzle with pressurized nitrogen (slip flow rate 10 l/h, N₂ pressure 0.015 Pa). The droplets were sprayed into the vortex of the stirred liquid nitrogen. The frozen granules were removed from the nitrogen and freeze dried in a freeze dryer at approximately 0.1 mbar.

The dried granulate was pressed uniaxially to circular plates in a double-acting die with 70 mm diameter and 5 mm thickness at 100 MPa. The binder was removed by heating slowly up to a maximum temperature of 500 °C in nitrogen. The samples were then put in a powder bed of alumina and silicon carbide powders, heated to 1600 °C for 1 h in vacuum and finally sintered in argon at 1880 °C for 4 h. Bend bars (3 x 4 mm) were cut from the sintered plate. Strength was tested by four-point bending with a 40/20 mm fixture and a cross-head speed of 1.0 mm/min.

The fracture surfaces of pressed bodies were examined in a light microscope. Green strength was tested by diametrical compression [12].

RESULTS AND DISCUSSION

Effect of plasticizer

The influence of the plasticizer was tested. PVOH:Glycerol and PVOH:PEG400 were added in 75:25 and 50:50 ratios. Glycerol evaporates during freeze drying making it difficult to control the final amount in the granulate. PEG has a much lower partial pressure at the low pressure used during freeze drying. Glycerol has a boiling point of 115 °C at 0.66 mbar that should be compared to the boiling point of >195 °C for PEG400 at 0.66 mbar. Using PVOH:PEG400 in a 50:50 ratio gave the best pressing behavior of the granules. The PVOH:PEG400 green strength was slightly reduced compared to PVOH:Glycerol in a 50:50 ratio.

The best break down of granules was observed for 50:50 PVOH:PEG400. The break down of the granules is good even at the low pressure of 100 MPa.

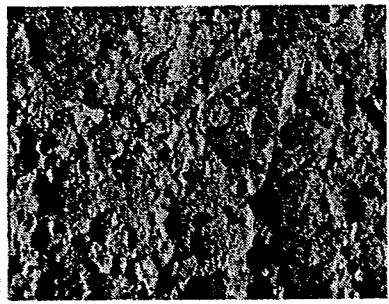
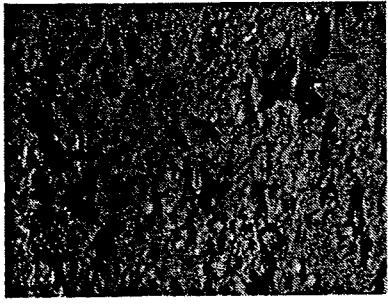
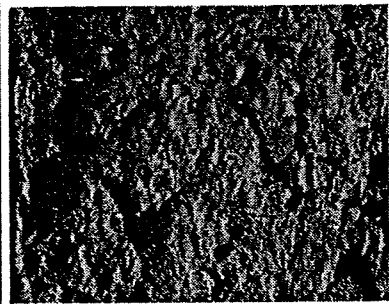
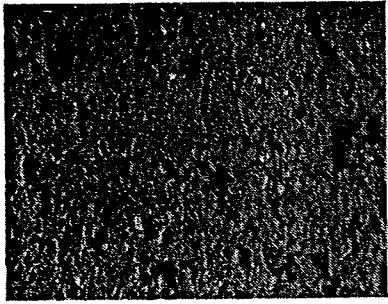
	Plasticizer: glycerol	Plasticizer: PEG 400
100 MPa		
200 MPa		
	Moisture content 0.7 wt%	Moisture content 0.7 wt%

Figure 1: Effect of plasticizer on pressed microstructure (\leftrightarrow 330 μm).

Effect of granule density

By varying the slip solid concentration the granule density could be controlled. 62 wt% and 55 wt% solids resulted in granules of 1.1 and 0.9 g/cm^3 . The decrease in granule density resulted in fewer granule residues in the pressed body and increased strength of the sintered material, as seen in Fig. 1 and Table 1.

Effect of moisture content

The moisture content after freeze drying was approximately 0.3 wt%. A granulate with PVOH and glycerol was remoisturized in a humid atmosphere to 11 wt%. When this granulate was pressed, a better breakdown of the granulate can be observed on a fracture surface of the pressed bodies, as seen in Fig. 2.

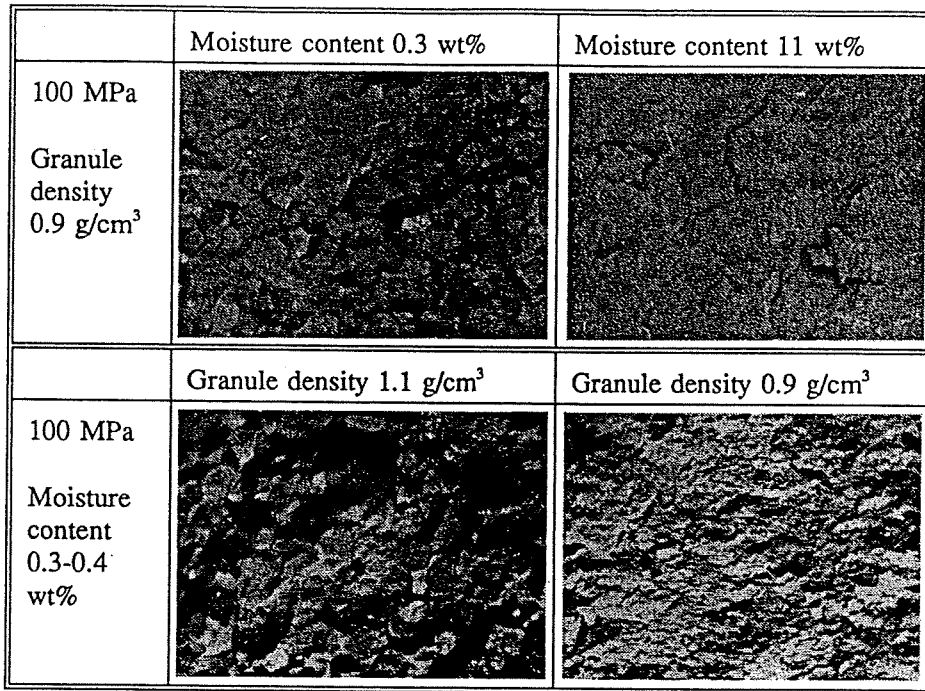


Figure 2: Effect of granule density and moisture content on pressed microstructure (\leftrightarrow 160 μ m).

Table 1. Sintered fracture strength as a function of binder system

Binder system	Binder/ plasticizer	Fracture strength MPa	Solid concentration wt%	Granule density g/cm ³
PVOH/ glycerol	75:25	339 \pm 29	62	1.1
PVOH/ glycerol	75:25	418 \pm 29	55	0.9
PVOH/ PEG400	50:50	486 \pm 52	55	0.9
Slip cast material		515 \pm 40		

CONCLUSIONS

Freeze granulation can be used to produce a free-flowing powder that can be pressed to a homogeneous green microstructure. The density of the granules can be controlled in freeze granulation. Low density granules are easily crushed during pressing and porosity due to residual granule boundaries can be avoided. The momentary freezing of droplets and the drying (sublimation) without migration of material results in homogeneous granules.

The solid concentration of the slip was reduced to get lower density granules that were crushed completely at the low pressure of 100 MPa. The binder system was made softer by substituting glycerol with a less volatile plasticizer (polyethylene glycol). The improved green microstructure resulting from these changes in processing parameters led to an improved strength in the sintered material. Pressed compacts (pressed at 100 MPa) could be fabricated with the same approximate strength as slip cast compacts.

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