Alumina Slurries Inclusion in Freeze Casting

Pramod Fauzdar
Department of Mechanical Engineering
Vivekananda Global University, Jaipur
Email ID: pramod_kumar@vgu.ac.in

Abstract: Using aqueous slurries to mould alumina parts, freeze-drying techniques were used to press less slip moulding. Glycerol has been used to eliminate defects associated with expansion and ceramic surface rejection during the freezing of water as a water solidification agent. Castable alumina slurries with solids up to 60 per cent loading were prepared and characterised using viscosity and zeta-potential measurements with and without glycerol additions. In order to achieve highly dense alumina bodies with a uniform microstructure, frozen sections were dried under vacuum by ice sublimation to obtain a net shape of green bodies. The combined effects of high solids loading slurries, less than 56.4 % volume and glycerol additions were essential for freeze casting. The feasibility of complex formation was demonstrated by using Freezing principles and aqueous alumina slurries with high mixing of solids. This led to freeze formed samples were processed with a uniform microstructure in the absence of ice formation related defects.

Keywords: freeze casting, alumina slurries, glycerol, ceramic, microstructure, surface rejection.

INTRODUCTION

Over the past decade, technical ceramics have experienced tremendous development, requiring more versatility and durability in the forming techniques. Much work has been carried out in the field of modern, complex-shape-forming techniques due to the complexity of shaping ceramics in the sintered state [1]. To form complex-shaped advanced ceramics in non-porous moulds, various techniques have been developed. Injection molding has been used as a ceramic forming method for many years, but the extremely high organic content results in difficult removal of binder and highly viscous slurries that involve high-pressure metal forming systems. However new low pressure, low-organics, and freeze injection molding methods have been under development, the costly and complex equipment used by these methods will discourage industry.

Gel casting is a modern forming technique involving the polymerization of a monomer into a solid, ceramic-loaded body that can be machined in a green state or directly formed into a complex mould in an aqueous or non-aqueous solvent. While this method is very effective, problems such as additive toxicity, comprehensive drying processes and troubled polymerization reactions have proved difficult to overcome in many ceramic systems [2]. Freeze casting of ceramic parts has the potential to be a simpler approach to the manufacture of complex ceramic parts. Freeze casting involves preparing a ceramic slip poured into a mould that is then frozen and vacuum-dried to sublimate the solvent. This technique enables the frozen solvent, given the inherent strength of frozen solvents, to temporarily act as a binder to hold the part together for demoulding. This minimizes, thus, the concentration of additives for better solid purity and shorter binder burnout periods. The removal of the solvent by sublimation also avoids drying stresses and shrinkage that can lead to cracks and warping during the normal drying process of a solvent-saturated body, as shown by the drying of frozen sol-gel ceramics [3]. The goal of this investigation is to develop the use of water and glycerol as viable freeze-casting solvents for processing castable slurries of high loading solids that generate highly dense parts after sintering [4].

METHODOLOGY

Experimental procedure:

- *Materials*

As-received alumina powder has been used for all tests, having a nominal particle size of 0.35 mm and a surface area of 9.3 m^2/g. Watery freezing slurries were made using an anionic ammonium polymethacrylate dispersant, acrylic emulsion binder, ethoxylated acetylene diol surfactant, and glycerol cryoprotectant [5]. The use of ammonium polymethacrylate dispersants has been well reported in stabilizing high solid loading, 60% volume, and alumina slurries. Darvan C consists of ammonium polymethacrylate, Mw= 10 000, suspended in an aqueous solution of 24 %. In a 50% water solution, the B-1001 acrylic emulsion binder is suspended and has a viscosity of; 250 mPa*s. Dynol 604 surfactant is used to improve water wetting characteristics and can reduce water dynamic surface tension at concentrations of 0.25 wt percent from 71 to 24 mN / m at 23 °C. Glycerol is primarily used to prevent the growth of large ice crystals and water crystallization-related freezing defects [6].

- *Procedure:*

The flow chart for freeze-casting is shown in figure 1. In order to characterize the effect of solid loading on viscosity, green density, sintered density, and microstructure, alumina slurries were prepared at 44, 46.5, 49.5, 52, 54.5, 57, 59.5 and 62 volume percent. Glycerol additions were made using an original water-glycerol premix directly applied to the ball-milling tub where the slurries were mixed (250 mL high-density polyethylene (HDPE)). The effect of additions to glycerol was tested using 10, 15, 20, 25, and 30 wt percent water glycerol. Based on the total weight of alumina powder, these slurries used 1.2% wt dispersant and 2% wt binder. The surfactant content of Dynol was 0.25 wt percent of the slurry's water weight.

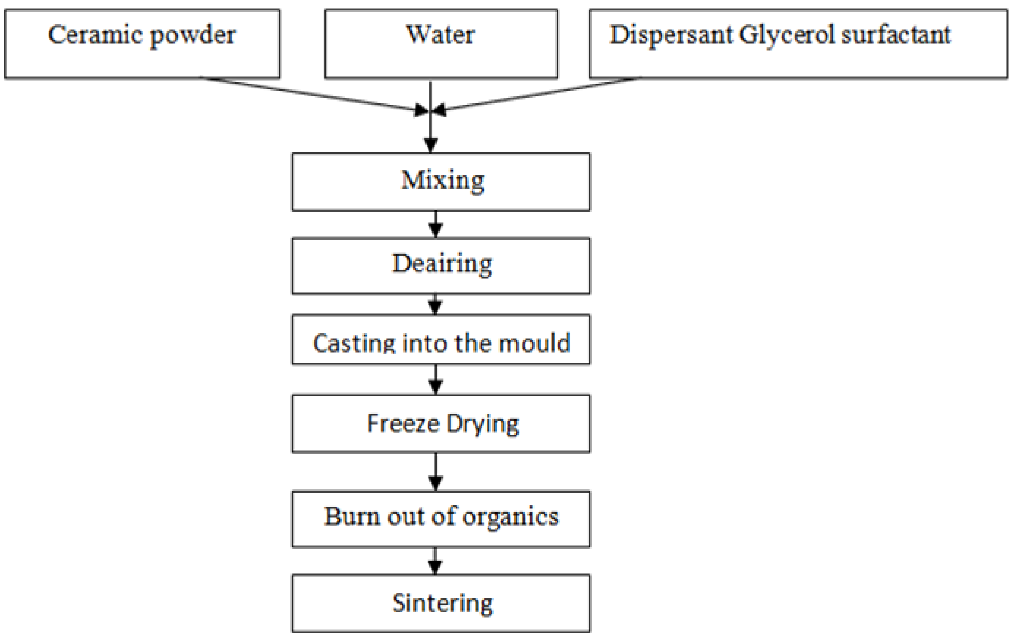

Fig.1 Free Casting Flow Chart

- *Characterization:*

The viscosity of the slurries was measured at a shear rate between 0 and 100 S^{-1} at 24^0 c using a rotating concentrate cylinder viscometer. An electro-acoustic analyzer was used to perform zeta-potential measurements. This device calculated the electro kinetic sonic amplitude of oscillating charged particles in an alternating electrical field of 1 MHz. Known solvent and solid properties were used to measure the zeta-potential. Green and sintered densities were calculated by measuring the sample size and weight and given as relative densities based on the theoretical alumina density of 3.98 g/cm^3. All data points are the sum of five measurements of density. On fracture surface of samples, the micro structural growth of sintered parts was observed using electron microscopy scanning. The binder burnout behavior of green bodies was measured at a heating rate of 5^0 C/min at a maximum temperature of 600^0 C using thermal gravimetric analysis [6].

RESULTS AND DISCUSSION

Density and microstructure:

The freeze casting of aqueous slurries is correlated with various complications, such as solidification volu me expansion of water, creation of large ice crystals, and rejection of suspended particle on the solidification front. Displays a deviation from linearity due to water expansion during solidification (9 percent of volume) [8]. Lower loading of solids leads to less water in the slurries and thus less overall expansion, resulting in higher green densities. However, reveals much lower than expected values. Considering the fine alumina powder used and a sintering temperature of 1650 ° C, highly dense sintered samples were expected to be provided by samples with green densities of 50%.Sample micro structural evolution ranging from 45 percent to 60 percent by volume [9]. The observed micro structural differences arise from changes in the loading of solids as the freezing rate for all samples remained constant. The distribution of pore size has a significant effect on the sintered microstructure, which may result in the observed non-uniform sample densification [10]. As the material densifies, large pores that are thermodynamically stable appear to combine with smaller pores and thus isolate tiny alumina pockets from bulk. Pores (less than 25–50 mm, in size), are sufficiently large to be able to achieve full densification through the diffusion of the solid state

CONCLUSION

Using freeze-drying principles and high solid loading aqueous alumina slurries, complex-shape forming feasibility has been expressed. In order to freeze monolithic structures, highly condensed water-based slurries were not suitable, as large volumetric expansion and solidification deficiencies resulted in micro structural voids in green bodies during freezing. Glycerol was added as a cryoprotectant to distributed slurries (up to 20 percent of the quantity of water) to modify the crystallization behaviour of the water. This led to freeze-formed samples being addressed in the absence of ice formation-related defects with a uniform microstructure. Glycerol also greatly decreased the viscosity of ammonium polymethacrylate dispersant stabilized condensed slurries, enabling the preparation of high-solids-loading slurries. A 40 percent reduction in viscosity with a load of 60 percent of volume solids when glycerol was added was obtained for alumina slurries. Enhanced steric stabilization effects have been due to the possible development of micelles between glycerol and adsorbed dispersant molecules.

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