Abstract

The present work is an effort at understanding the rheological behaviour of aqueous ceramic slurries and development of techniques for forming dense and highly porous ceramic shapes and structures. The work is divided into two major parts – forming of dense and highly porous ceramics. The first part of the work involved preparation of highly loaded gelcasting alumina slurries, studies on rheological behaviour of the freshly prepared and aged slurries and development of processes for gelcasting of dense alumina ceramics. The second part of the work involved development of a simple process for fabrication of porous ceramics by direct foaming of slurries and identification of interrelationships between rheology of slurries, microstructure and mechanical properties of porous ceramics.

The rheological studies centered around understanding the effect of nature and amount of two dispersants - Darvan 821 A (ammonium polyacrylate) and DBAC (dibasic ammonium citrate) - on the thixotropy and aging behaviour of alumina gelcasting slurries. Initial studies involved optimization of the two dispersant amounts based on achievement of lowest viscosity for 55-volume % alumina slurries. Once optimum amount for the two dispersants was determined, all rheological studies were carried out for slurries prepared with three different amounts of each of the dispersant – lower than optimum, optimum and higher than optimum.

The slurries were subjected to two different aging treatments over a period of 48 hours – static aging where the slurries were stored undisturbed and dynamic aging where the slurries were kept rolling after slurry preparation step had been completed. Slurries with dispersant amount lower than optimum exhibited greatest change in slurry viscosity as a result of the aging treatments. DBAC based slurries experienced a greater percentage increase in viscosity than Darvan based slurries during static aging. All slurries, except the one with

below optimum amount of DBAC, exhibited a decrease in viscosity after 48 hours of dynamic aging. The extent of thixotropy for the freshly prepared alumina slurries was greatest for slurries with dispersant amount below optimum and least for slurries with optimum amount of dispersant. Thixotropic behavior of aged slurries followed similar trends as exhibited by the changes in viscosity. Slurries that experienced an increase in viscosity also showed pronounced thixotropic behavior following aging.

Studies on gelcasting of dense alumina ceramics were based on use of slurries prepared from an aqueous premix of monomer (methacrylamide - MAM) and crosslinker (methylene bisacrylamide - MBAM) system as reported in the research literature. The study considered the critical aspects that had a significant influence on the quality of gelcast parts. The critical aspects considered include deairing of slurries, mold materials and mold design, casting, gelation and drying procedure of gelcast parts. The most effective deairing approach was seen to be roll milling of slurry with 1-octanol as an antifoaming agent in the absence of milling media followed by keeping the slurry at rest to ensure gradual rise and collapse of air bubbles. The effectiveness of the successful deairing treatments was demonstrated by comparison of the flexural strength of green samples produced from the as-milled (without deairing) and well-deaired slurries. Proper mixing of initiator and catalyst was essential, prior to casting, to prevent local coagulation in the slurries. The potential of the gelcasting process in fabrication of a range of simple and complex dense ceramic components was also demonstrated. For casting of complex shapes, wax molds were successfully used which could be easily dissolved away. For rigid metallic or plastic molds use of split design was found to be beneficial for easy release of cast parts.

A novel and innovative use of egg white (ovalbumin) as a gel forming material, as proposed in the present work, provided an environment friendly alternative for forming of dense ceramic compacts. Temperature induced gelation was carried out by heating the ovalbumin based alumina slurries in a

water bath at 80°C. A special ovalbumin based slurry composition was successfully employed in forming of alumina tapes as thin as 50 – 60 μm in the sintered state. The natural tendency of ovalbumin to foam and consequential presence of air bubbles as defects in cast samples was countered by addition of 1-octanol to the mix prior to milling. Even then some air bubbles were present in the as-milled slurries, which were retained in the dried green body.

The tendency of ovalbumin to foam combined with its excellent binding action has been utilized in development of a simple process for fabrication of ceramic foams. The process involves fabrication of ceramic foams by direct foaming of aqueous ovalbumin based ceramic slurries. Slurries with different alumina loading and ovalbumin-water ratios were prepared. Initial experiments demonstrated that the as cast foams were extremely sensitive to drying. The as cast foams usually collapsed when dried slowly over long periods and cracked when dried fast. This sensitivity of the as cast foams to drying conditions was addressed by use of special setting procedures.

Setting of ceramic foams was achieved through coagulation of ovalbumin by addition of concentrated nitric acid. For foams with alumina loading below 20 volume %, acid addition resulted in excessive shrinkage causing cracking of foams. Addition of sucrose to the slurries resulted in highly stable foams that had nearly zero shrinkage. With addition of sucrose defect free foam samples exceeding 95 % porosity could be prepared. The sucrose containing samples could be set and dried simultaneously at 50°C, thus reducing the total cycle time significantly in comparison to the acid coagulated samples. With use of sucrose, defect free samples could be made consistently while with acid addition the fabrication of defect free samples was a little unpredictable. Overall porosity and microstructure of ceramic foams could be controlled through ceramic loading, ovalbumin-water ratio, foaming time, sucrose amount and sintering temperature. The ceramic foams, even with

porosity exceeding 95 %, fabricated by the above process were strong enough to be machined in the green state.

Foaming of aqueous alumina slurries and the resulting foam microstructure was seen to be a strong function of slurry rheology. The extent of foaming decreased with increase in slurry viscosity. The total porosity in sintered ceramic foams correlated to the extent of foaming of the slurries. The total porosity and cell size was always lower in case of foams made from slurries with higher viscosity. The extent of interconnection between the cells was seen to be a function of the extent of foaming, the ovalbumin volume percent, and the solids loading. The interconnection area between the cells in sintered foams decreased as the cell walls in the green ceramic foams became stronger with increase in ovalbumin content. The percent open porosity increased linearly with increase in total porosity in sintered ceramic foams.

As expected, the crushing and flexural strength of sintered ceramic foams decreased with increase in porosity. For a fixed alumina loading, the strength of sintered samples increased with increase in ovalbumin content. Similarly, for a fixed ovalbumin content, the strength of sintered ceramic foams increased with increase in alumina loading.

The above observations indicated that the microstructure and properties of sintered ceramic foams could be tailored to suit specific applications by controlling the slurry compositions.