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Optimization of conditions for fabrication of a ceramic component through gel-casting technique

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Gel-casting technique has been used for the production of alumina ceramic component. It is an attractive novel ceramic forming process for making high quality complex shaped ceramic part. The optimization of the alumina loading, pH, dispersant and catalyst amount has been successfully carried out for fabrication of high strength alumina component. A high green strength of alumina component is fabricated with 55 volume% slurry, for which 220 g of alumina powder, Darvan 821A (1.0 mg/g of alumina), N-(hydroxymethyl) acrylamide, 10 wt% initiator ammonium persulfate and 10 wt% catalyst tetra-methylethylenediamine). After slurry preparation, casting and subsequent drying is done by slow heating. The green body and the component obtained after binder burn out have been characterized through scanning electron microscope and X-ray diffraction techniques.

Keywords: Alumina suspension, Ceramic, Darvan 821A, Dispersant, Gel casting

Introduction

The advances in ceramic component production have vastly expanded the application of these materials in contemporary life, and especially in the role of electronic components for energy storage, transmission, and regulation of power[1]. Advanced ceramics are typically manufactured from materials with very high purity levels and are sintered under strictly controlled profiles and conditions, unlike the more 'traditional ceramic' products. Colloidal synthesis and processing typically requires an intimate control of solution chemistry and the dispersion of particles in aqueous or non-aqueous suspensions, which can then be formed into the desired shape.

Aqueous system for preparation of stable dispersion of colloidal suspensions was developed as an environmentally friendly system[2]. Such a nontoxic system for gel-casting of ceramics was investigated using gellan gum as gelling agent[3]. More recently, a novel and simple method for gel-casting of ceramics had been developed using a nontoxic and water-soluble copolymer of isobutylene and maleic anhydride (commercially called Isobam)[4]. Such methods are more relevant for wet forming processes, where the quality of product obtained is determined primarily by the state of dispersion of the particulate matter[5].

In original gel casting formulations, gelation was obtained through polymerization of acrylamide monomers[7]. Generally, a solid loading of slurry during gel-casting is influenced by gelling system, dispersant and pH[8]. Due to the high solids content in a suspension and the generally sub-micrometric size of the added powder, the contact between suspended particles occurs frequently and the van der Waals attractive forces determine the interaction and formation of agglomerates. The use of dispersants plays a key role in preventing agglomeration by increasing the inter-particle repulsion while maintaining colloidal stability. In concentrated aqueous suspensions of alumina, the most commonly used dispersants belong to the class of the (poly)acrylic and methacrylic acid salts. The surface properties and size of the molecular chain determine these polyelectrolytes acting by the electrostatic dispersion mechanism. The common feature of polyelectrolytes is the presence of more than one ionisable surface group[9,10]. Suitable additives to effectively decrease the viscosity and have minimal impact on gelation strength were discovered from various dicarboxylic acids through investigation on

zeta potential, viscosity of suspensions, shear modulus during gelation and yield stress[11]. Commercially available Darvan 821A, Darvan C, Dolapix A88 and Dolapix CE64 were used as dispersants in various gel-casting techniques[12,13]. High solid loaded slurry having minimum viscosity achieved by adding appropriate amount of dispersing agent resulted in highest green density to the gel cast products[14]. To obtain the ceramic element of good properties, it is important to conduct the polymerization in such a way that cross-linked polymers are created. Most often used cross linking agent is N, N'-methylenebisacrylamide[15,16]. A variety of mould materials such as aluminum, stainless steel, plastic, glass and wax can be used. Properties of the mould materials coupled with the mould design play a significant role in forming of complex shapes[17,18].

Some studies have involved various casting techniques namely slip casting, injection moulding and mouldless casting[6]. The objective of the present work is to optimize the required conditions for synthesis high green strength alumina component using gel-casting method which overcomes some of the disadvantage associated with injection moulding or slip casting. In this process highly loaded but very fluid slurry consisting of alumina powder, water, dispersant and gel former was poured into a mould and subsequently gelled. Once gelation takes place, the part is strong enough to retain its shape and can be de-moulded, dried, calcined and sintered. A great advantage of the technique is that very complex shapes can be made with relative ease.

Experimental Section

Slurry preparation and casting

For 55 volume% slurry preparation, water, dispersant Darvan 821A (1.0 mg/g, dispersant : alumina) and N-(hydroxymethyl) acrylamide were taken in a 500 mL capacity polypropylene bottle containing alumina balls of 2 mm and 10 mm diameters in a way that the smaller balls fit half of the slurry and bigger balls fit the length of the bottle. Then 220 g of alumina power (A-16SG) (ALCOA, USA) with average particle size of 300 nm was added step by step to have the proper wetting. De-airing of the mixing was done in the planetary centrifugal mixer for several minutes. 10 wt% of the initiator ammonium persulfate (APS) and catalyst tetra-methylethylenediamine (TEMED) each were added finally to the slurry with vigorous stirring and then the slurry was casted carefully in the petroleum jelly coated Teflon mould at room temperature.

Drying and sintering

The mould was covered with glass plates and kept in the preheated oven at 50°C for 2 h. Cooling was done at 90% humid condition for 24 h to avoid cracking. The material was finally dried in an air-oven at 50°C for 24 h. Binder burnout was done by slow heating for the complete removal of the organics and sintering was done next to produce the ceramic component.

Characterization

The green body, binder burnout sample and the final sintered sample have been characterized through SEM (model S-3400N, Hitachi, Japan). SEM images of the surfaces of the samples have been produced by using secondary electrons and backscattered electrons produced by the interaction of an electron beam with the specimen. Secondary electrons provide information regarding the topography of the sample surfaces and backscattered electrons provide information regarding the composition. The final sintered product was also characterized through X-ray diffraction (XRD).

Results and Discussion

Rheological properties

For gel-casting, the right volume percent of alumina used was decided from the plots of the apparent viscosity and shear stress of its suspension versus its shear rate. Fig. 1 shows the slurry loaded with the highest alumina powder i.e., 55 volume% has the most suitable viscosity as well as the shear stress among various percentages of it. Hence, in all the experiments, the slurries with 55 volume% loading were considered for slurry characterization and consolidation. This most optimized slurry also has the minimum drying shrinkage and hence fits to produce a crack-free final ceramic body. As can be seen form Fig. 1, an increase of the solids loading results in a higher viscosity. A higher solid loading means that more particles are in the system per unit volume. Therefore, the mean distance between the particles will decrease. Hence, this may result in an increase in hydrodynamic interactions occurring between particles. This will lead to a stronger interaction of the electric double layer since there may be increasing electric double layer overlap of the particles. Slurries with 40-50 volume% loading were highly fluid and

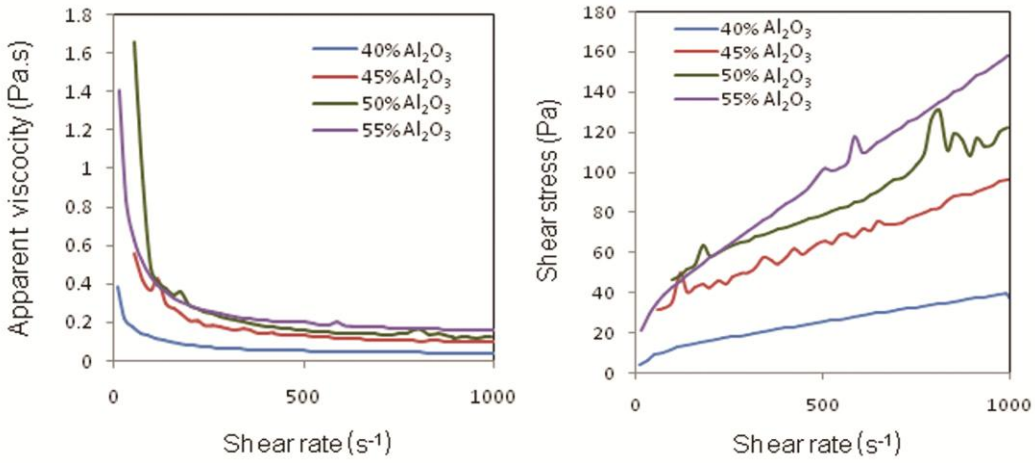


Fig. 1 — (a) Variation of apparent viscosity with shear rate and (b) shear stress with shear rate for slurry containing various volume % of alumina

bodies cast from these slurries exhibited higher drying shrinkage. Thus, slurries with 55 volume% loading were finally considered for slurry characterization and consolidation.

Optimization of dispersant dosages

Alumina dispersed in de-ionized water and monomer is highly agglomerated, which is checked by the use of a suitable dispersant. Since low viscosity is good for the gel-casting process, it is necessary to maintain the slurry fluidity and hence is important to select the proper dispersant for the powder. For complete surface coverage of alumina particles it is essential to add just exact amount of dispersant. Accurate adsorption of a dispersant on the alumina surface enables the creation of the large repulsive electric double layer, which will overcome attractive van der Waal's forces. Excess amount of dispersant is also not good because of the stabilizing barrier. Out of various dispersants, it is thus necessary to choose a suitable one along with its amount. Various methods are available to determine the optimum dispersant amount. Particle charge detector (PCD) technique was used in the present case.

The results of variation of PCD potential with different dosages of various dispersants are shown in Fig. 2. All dispersants are negatively charged and there occurs an increase in PCD potential with increasing dispersant concentration and finally maintaining a constant after reaching the plateau. At low concentration region, the adsorption of negatively charged dispersant on alumina particles render and increase the magnitude of the negative surface charge on it. The plots show that Darvan 821A is the most

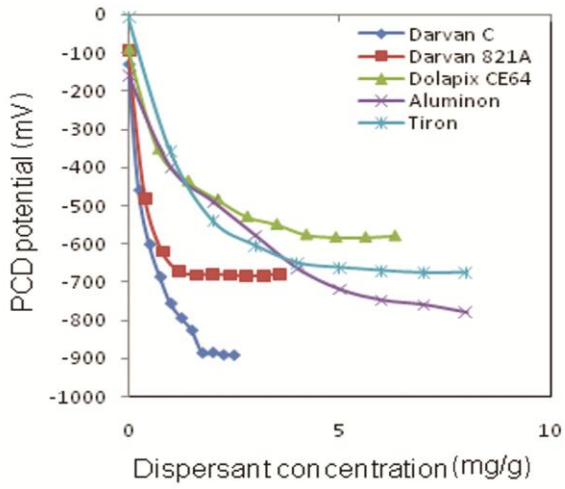


Fig. 2 — Determination of optimum dispersant dosage by PCD technique

suitable since, 1.0 mg/g (Dispersant: Alumina) concentration of it can serve the purpose of adsorption whereas more concentrations of other dispersants are required. Any amount of Darvan 821A above its optimum concentration will remain free in the aqueous phase, which can affect the viscosity of the suspensions because of the increased number of free ammonium ions in the system. Besides, the increase in the number of ammonium counter ions will lead to the compression of the electric double layer leading to particle coagulation, finally increasing the viscosity of the slurry, which is not advisable. Such a phenomenon may create difficulty in pouring and handling during the colloidal forming procedure. The reduction of the stabilizing barrier can lead to particle coagulation. This may allow for the formation of flocs

which results in an increase in the viscosity. This is not desired because it may lead to difficulty in pouring, handling and deairing during the colloidal forming procedure. Therefore, it is necessary to determine the minimal amount of Darvan 821A needed to achieve complete coverage in order to get concentrated slurry with minimum shear viscosity. After analyzing the characterization data of alumina slurry for all the dispersant, it has been decided to use Darvan 821A for further detail gel casting studies.

Gelation kinetics

Gelation process has been carried out using APS initiator and TEMED catalyst. A small variation in their amount at room temperature brings about a large change in gelation time. Higher initiator content and catalyst amount are found to complete the gelation of the slurry in a short time period (Fig. 3 and inset).

It has been found that keeping the amount of TEMED constant at 10 wt % (0.001 mL), increase in APS amount shows a decreasing trend in gelation with time. In a similar way, keeping the amount of APS constant at 10 wt % (0.01 mL), the gelation time is found to decrease with the increase in TEMED amount. The variations in both cases have been recorded up to a time period of 20.6 min. Hence, the polymerization process during gelling in presence of APS and TEMED have been carried out involving a 10 wt% of each of the component with minimal quantities, i.e. 0.25 mL and 0.025 mL, respectively.

Gelation mechanism is the polymerization and cross-linking of monomer i.e., a strong polymer - solvent gel matrix, which may be thermally induced. In gelation, the initiator and catalyst have very crucial role to start/initiate the polymerization reaction. In the present case APS is used as initiator and TEMED is used as catalyst. As its name implies, initiator initiates the polymerization process. During the casting, when the ambient temperature is increased, the initiator in the slurry is broken down into initiating radicals. The initiating radicals then react with the monomers and a monomer-free radical is produced which will react further resulting in a propagating radical.

Surface chemical properties of alumina suspension

The electro-steric (electrical double layer and steric interaction) stabilization of suspension can be achieved by manipulating electrostatic charges on the particle surface, which can be achieved by the variation of pH. Hence the surface charge is an important parameter for characterizing the dispersion behavior. On addition of Darvan 821A, a variation of

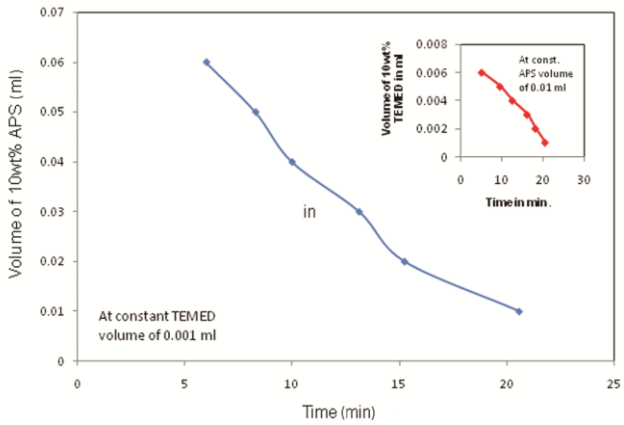


Fig. 3 — Variations of APS amount with time at constant TEMED and TEMED amount with time at constant APS (inset)

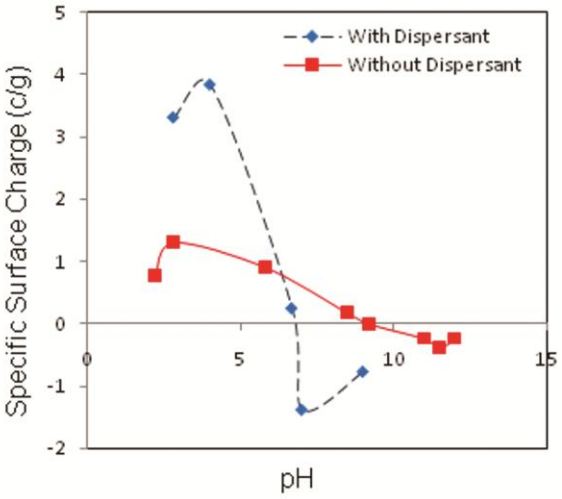


Fig. 4 — Variation of specific surface charge with pH for alumina suspension in water with and without Darvan 821A dispersant

pH value of pure alumina in aqueous medium shows a remarkable change (Fig. 4).

Alumina, being a basic oxide, has a slightly positive charge on immersion in water. Its iso-electric point (IEP) lies at a pH of 9.1. Since Darvan 821A dispersantis an anionic dispersant, the IEP shifts to a lower pH of 6.8. In other words, the surface of alumina will be sufficiently charged to have electro-stabilized suspension at acidic pH (<7) and basic pH (>9).

The surface charge of alumina particles is due to its hydrolysis in water, resulting in surface with Al-OH group. pH values below the IEP yield a positive surface charge and the solution is dominated by H^+ ions. In this region, a large number of Al-OH groups are protonated by the higher concentration of hydronium ions, resulting in a net positive surface charge. When the pH is greater than the IEP, the

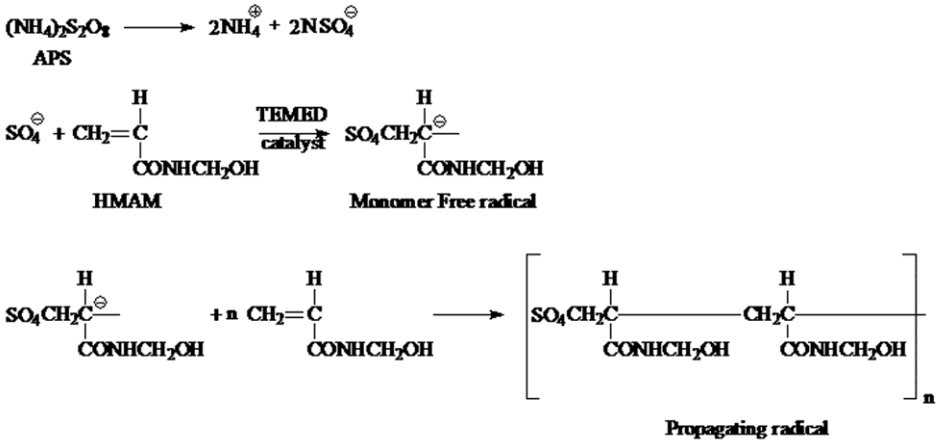
surface charge is negative. In this region, a large number of Al-OH group are deprotonated by the adsorption of hydroxyl groups onto the alumina surface. This leads to a net negative surface charge. For electrostatic repulsion, a very high magnitude of surface charge is required. This can be only accompanied by shifting the pH to acidic condition, which is not suitable for ceramic processing and manufacturing. Furthermore the compatibility of Darvan 821A to this system is compromised as in the acidic region the solubility of Darvan 821A will decrease. The IEP of Darvan 821A is between pH 2-3. Thus in this pH range, Darvan 821A will tend to aggregate out in water.

Gelation mechanism

Polymerization of HMAM in presence of APS and TEMED is a three step process, which forms a gel environment (Scheme 1), thus providing the matrix for casting of the slurry leading to the formation of green component. As shown in the Scheme 1, the first step involves the dissociation of the initiator forming thiosulphate radical, which in the next step reacts with the HMAM monomer in presence of TEMED catalyst forming the corresponding monomer radical. Finally, the monomer radical reacts with large number of monomers forming a propagating radical, which eventually gives the polymer matrix.

Drying and sintering

The green sample was dried in 90% humid atmosphere to avoid any cracking. It is necessary to completely remove the addenda such as dispersant, monomer, initiator and catalyst from the green body to ensure the production of crack free pure alumina ceramic component. The first step in the process is binder burnout and the second step is sintering. The binder burnout process involves a ramp of 2°C per minute up to 600°C followed by one hour soaking at the same temperature. Again, the temperature is raised by 3°C per minute up to 1000°C followed by one hour soaking (Fig. 5a). Sintering involves the increase in



Scheme 1 — Mechanism of gel formation

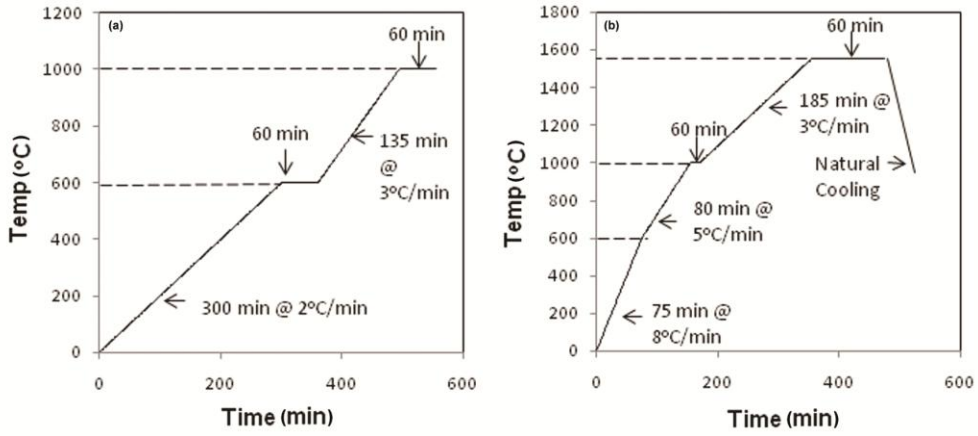


Fig. 5 — Temperature vs. time plots for (a) binder burnout and (b) sintering

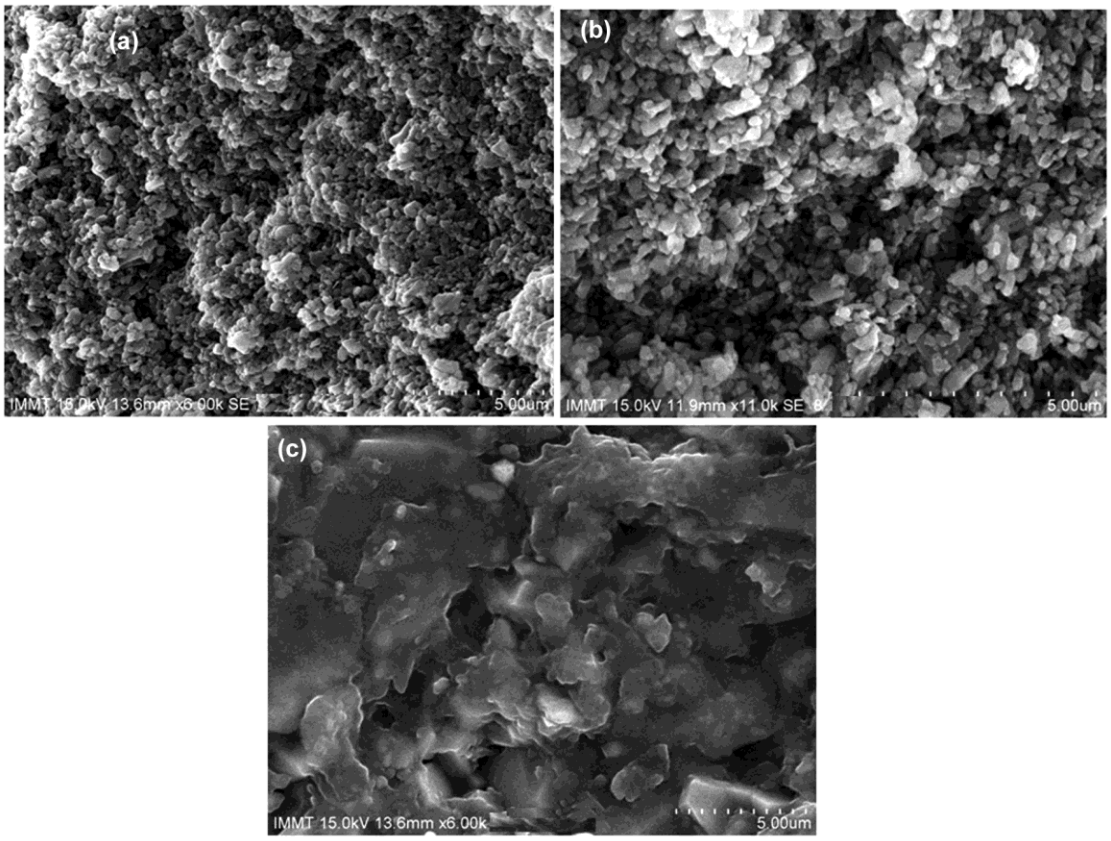


Fig. 6 — SEM images of (a) green body, (b) binder burnout sample and (c) sintered final product

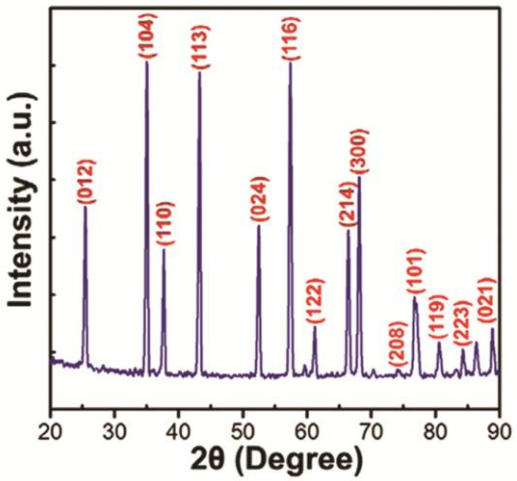


Fig. 7 — XRD pattern of final product

temperature at a higher rate of 8°C per min up to 600°C and at a subsequent rate of 5°C per minute up to 1000°C followed by 15 min soaking. Then the temperature was raised at a rate of 3°C per min up to 1550°C followed by soaking for 2 h (Fig. 5b). The plots for binder burnout and sintering processes are presented in Fig. 5.

Product analysis

The structures of green body, binder burnout sample and sintered final product have been characterized through SEM, (Fig. 6). The micrograph of green body (Fig. 6a) obtained from the mixture of alumina and monomer shows the presence of the components without any grain formation. After binder burnout due to thermal treatment, grain formation is observed in the sample (Fig. 6b). Finally, sintering process after further heat treatment leads to grain growth (Fig. 6c).

The XRD pattern (Fig. 7) of the final product shows diffraction peaks at various 2θ values corresponding (h k l) planes, which can be identified as originating from the crystalline phase α-Al_2O_3 (JCPDS-ICDD file number 46-1212). The corresponding miller indices (h k l) confirm the phase and plane present in the prepared sample. Al_2O_3 is known to have defects because of the oxygen vacancy, where an O^{2-} ion moves from a normally occupied lattice site to a vacant interstitial site, which is supposed to be prevalent defect in many oxides. Under thermal conditions, hydrogen atom interacts

Fig. 8 — Photograph of final sintered product

with the lattice oxygen of Al_2O_3 on the surface, which results in the formation of the oxygen vacancies and changes the surface properties of α-Al_2O_3. No such defects could be identified through the XRD pattern. Average crystallite size is found to be 19.91 nm as calculated using Debye-Scherrer equation. Furthermore, no additional peak or hump is seen in the XRD, which reveals that pure single phased α-Al_2O_3 is fabricated. The picture of the sintered final product is presented in Fig. 8.

Conclusion

The dispersion of fine alumina in de-ionized water and monomer is influenced by addition of exact amount of dispersant, which results in the formation of a high solid loaded, high green strength gel cast product. The slurry viscosity can be controlled by the monomer and dispersant. Through this forming process a near net shape complex ceramic component is produced. Proper drying process along with humidity control has been adopted to produce defect free gel-cast without any cracking. The method can be useful in designing sintered gel-cast components having a variety of shape and size.

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