Colloidal Processing and Slip Casting of Mullite

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Abstract: *Mullite an aluminosilicate ceramic due to its excellent refractory, mechanical and dielectric properties find wide applications as structural and high temperature ceramics as well as for electric and optical applications. Slip casting is a well established shaping or forming method to fabricate ceramic shapes having simple to reasonably complicated shapes. In the present study commercially available mullite powders were characterized for crystallographic phase purity, particle size distribution and morphology. The optimum dispersion condition of the powder in de-ionised water was studied through measurement of zeta potential as a function of pH. The mullite powder dispersed in deionised water with and without addition of MgO was slip cast in plaster mould. The slip cast samples were sintered at different temperatures to study the effect of MgO addition on the sinterability of mullite. The products were characterized for density, porosity and microstructure.*

Key Words: *Colloidal Processing, Slip Casting, Mullite.*

Introduction

Mullite [$3Al_2O_3.2SiO_2$] is an aluminosilicate, generally formed by the high temperature reaction between alumina and silica bearing materials. Mullite show excellent properties such as high melting point (1810°C), high temperature strength and creep resistance, low thermal expansion coefficient (~$3.5*10^{-6}$ /°C), good thermal and chemical stability, good thermal shock resistance, resistance to abrasion, good dielectric properties and also lower density (2.8g/cc). These properties makes mullite and its composites excellent candidate for electric, optical and high temperature structural applications (Aksay et al, 1991). Mullite is used as a matrix material in continuous fibre reinforced ceramic matrix composites (CMC), as a thermal protection systems for combustion chambers in aircraft turbine engines, heat exchanger parts, heat insulating parts, milling media, furnace tubes, refractories in the metallurgical industries, turbine engine components etc (Schneider et al, 2008). In the recent past mullite has been considered as a potential candidate material for environmental barrier coating (EBC) application on silicon based ceramics like SiC, Si_3N_4 and C_f/SiC and SiC_f/SiC composites in the hot section of gas turbine engines (Zhong Liu et al, 2015). Porous structures of mullite are widely used in several sectors such as filters for high pressure and high temperature gas flow, for fused metal filtering to remove inclusions and impurities, filters for diesel exhaust emissions, substrates for catalytic reactions, thermal insulating materials etc (Roncari et al, 2000).

Slip casting is a well established shaping or forming method to fabricate dense and porous bodies having simple to reasonably complicated shapes. The method has been applied to variety of advanced ceramics like Al_2O_3, ZrO_2, SiC, Si_3N_4, hydroxyl apatite and also to ceramic composite systems (Ramachandra Rao and Kannan, 2001 and Ramachandra Rao et al, 2001). Slip casting involves mixing of fine ceramic powders in aqueous (deionised or distilled water) or non aqueous media (eg. Isopropyl alcohol) and pouring the so formed slip or slurry into a porous mould (generally made from plaster of paris) to get the required shape. The liquid medium gets absorbed through fine pores present in the mould by capillary action, while the fine particles get assembled at the wall to form the body. The so formed green body will be removed from the mould, dried and then sintered at high temperature to result in dense product.

During the process of slip preparation the fine particles show a tendency to agglomerate because of Van der Waal's physical force of attraction which results in inhomogeneous microstructure leading to inferior properties for the sintered product. The agglomeration of fine particles can be avoided and dispersion be achieved by control or manipulation of inter particle forces. By adjusting the pH of the medium or by adding electrolytes or polyelectrolytes as dispersants, the fine particle surface will be positively or negatively charged resulting in repulsive forces overcoming the attractive Van der Waal's forces. This leads to good dispersion of the particles resulting in improved properties to the green and sintered material (Ramachandra Rao and Kannan, 2001; Ramachandra Rao et al, 1999 and 2001; Lewis, 2000). Colloidal processing and slip casting has been employed to make mullite products starting from alumina powder and colloidal silica (Burgos-Montes et al, 2007), alumina powder and kaolinite clay (Moreno and Scian, 2015) and using mullite powder (Goren et al, 2012 and Tkalcec et al, 1998) as well as alumina mullite composites (Askel, 2002) and mullite Zirconia composite ceramics (Temoche et al, 2005).

The present study deals with the slip casting of commercially available mullite powder using the optimum dispersion condition. The slip cast samples were sintered at different temperatures to study the effect of MgO addition on the sinterability of mullite. The products were characterized for density, porosity and microstructure.

2. Experimental Procedures

Two grades of commercial mullite powders, M72 and M672 (M/s Nabaltec AG, Schwan) were used for slip casting experiments. The two powders were subjected to X-ray diffraction analysis (D8 Advance, M/s Bruker, Germany) for identification of crystalline phases present and particle size analysis (Master sizer, M/s Malvern Aimil) to find out the particle size distribution of the particles. The size and morphology of the powders were evaluated through scanning electron microscopy (SEM, Leo 440, M/s Leo, England). The powders were dispersed in deionised water and the zeta potential was measured as a function of pH using zeta potential analyser (3000HSA, M/s Malvern Instruments, UK).

The mullite powders were dispersed in deionised water and the pH was adjusted to an optimum value of 10 – 10.5 and milled in polythene bottle using alumina milling media for about 16 hrs. The homogenized slip was cast in plaster moulds to give simple shapes like discs and small crucibles. The green density of slip cast samples was obtained by weight and dimensional measurements.

Slip casting was carried out using as received mullite powders and also by adding 1 and 2 wt.% of MgO as sintering additive. The slip cast samples were sintered in the temperature range 1500 to 1600°C for 1hr in a super kanthal furnace (M/s Therelek Engineers, Bangalore). The sintered samples were characterized for density by weight and volume method, apparent density and porosity by Archimedes principle, microstructure by scanning electron microscopy.

3. Results and Discussion

The X-ray diffraction patterns of the two powders are presented in Fig.1. By comparing the diffraction peak positions (2θ) and intensity with the Joint Committee on Powder Diffraction Standards (JCPDS), it is found that both the powders represent mullite with all the major peaks corresponding to orthorhombic phase (card No. 15-0776) with a small quantity of $\alpha-$ alumina (Card No. 46-1212) as the secondary phase.

The particle size distribution graphs of the two commercial mullite powders are presented in Fig.2. The particle size analysis results show that M72 powder is coarser with d_{10} = 2.29μm, d_{50} = 6.66 μm and d_{90} = 20.16 μm, while M672 powder is fine with d_{10} = 0.62μm, d_{50} = 2.00 μm and d_{90} = 10.26 μm. Also M672 show wider and bimodal size distribution as compared to M72 powder. These results are well supported by SEM photographs of these powders shown in Fig 3(a-b). The SEM photograph of M-72 powder in Fig. 3(a) show higher proportion of larger particles than those found in SEM of M-672 powder shown in Fig. 3(b).

Fig. 1 XRD Graphs of Mullite Powders; M-72 and M-672; ● = Alumina

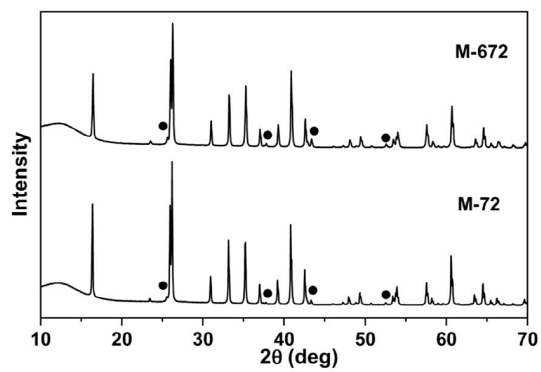


Fig.2 Particle Size Distribution of Mullite Powder (▲) M72 (o) M672

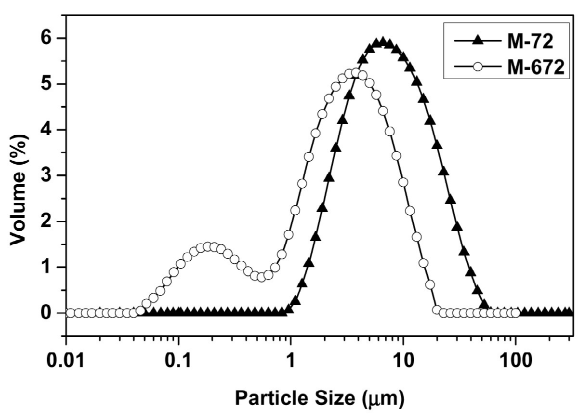
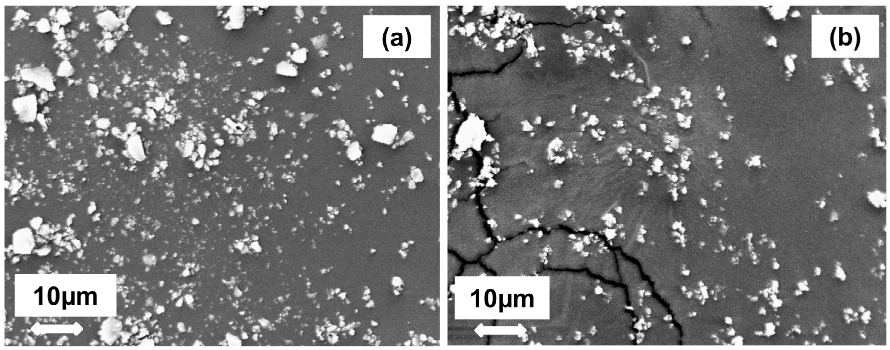
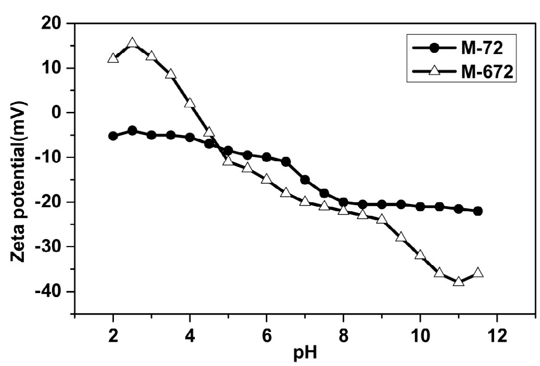


Fig.3 Scanning Electron Micrograph of Mullite Powder (a) M72 ((b) M672



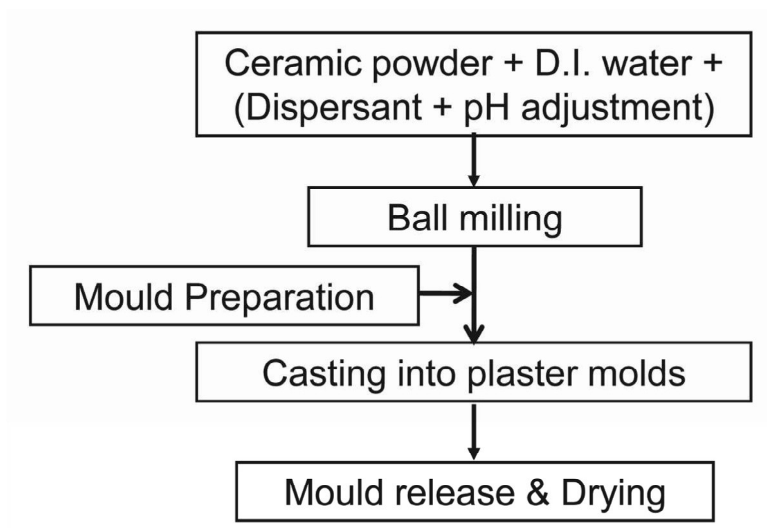
The dispersion of mullite powders in deionised water studied as a function of pH is presented in Fig 4 in terms of zeta potential. The zeta potential curve of M72 powder shows that the powder surface is negatively charged in the entire pH range while it is more negative in the alkaline pH as compared to acidic pH. This behavior is similar to that of silica and hence indicates that the powder surface behaves mostly as silica. On the other hand the Zeta potential of M672 powder is positive in the pH range 2 to 4 and negative above the isoelectric point 4.2. The high zeta potential of about 36mV at pH of 10 to 11 indicates high surface charge resulting in repulsion between the particles and hence good dispersion. Hence the pH of the mullite slurry was adjusted to pH 10 to 10.5 for slip casting experiments.

Fig.4. Zeta Potential of Mullite as a Function of pH



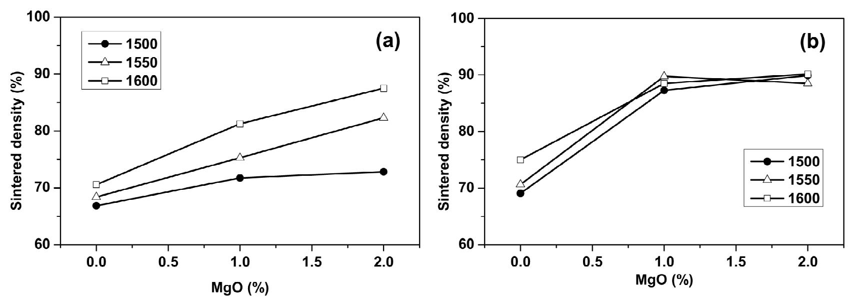
The slip casting of two commercial mullite powders were carried out in deionised water with controlled pH condition to give optimum dispersion and high solid loading of about 80 Wt.% (55 Vol.%). The flow chart of the slip casting process is given in Fig. 5. The green density of slip cast samples of M72 and M672 with and without MgO additions was 62 ± 2%. This high green density indicates that the dispersion of the particles in the liquid medium is optimum leading to good packing of fine particles.

Fig.5. Flow Chart of the Slip Casting Process



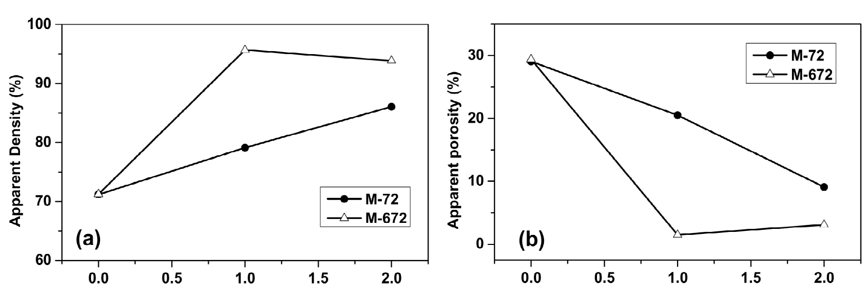
The slip cast samples are sintered in the temperature range of 1500°C to 1600°C for 1 hr. The densities measured through mass by volume method for samples sintered at different temperatures are plotted in Fig. 6 as a function of sintering additive. The apparent density and apparent porosity of M-72 and M-672 samples sintered at 1550°C measured by Archimedes principle are presented in Fig. 7 as a function of percentage of sintering additive added.

Fig.6. Sintered Density at Different Temperatures for (a) M-72 and (b) M-672 Powders as Function of Percentage of Sintering Additive



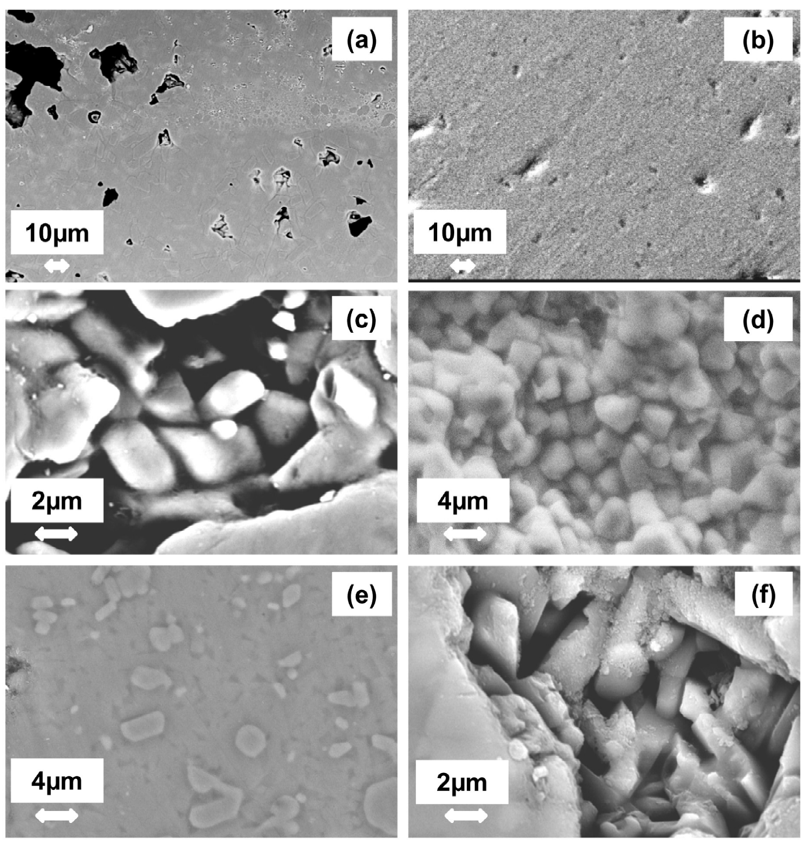
From the Fig. 6 it can be found that the density of slip cast mullite samples without the sintering aid increases marginally with the increase in sintering temperature from 1500 to 1600°C (67 to 71% for M-72 and 69 to 75% for M-672). On the contrary, the samples with doping of MgO show increased density of 72 to 88% for M-72 and 87 to 90% for M-672 powders in the temperature range of 1500 to 1600°C. The enhanced density is attributed to the influence of sintering additive on densification. The higher densification in case of M-672 as compared to M-72 at the entire temperature range studied could be attributed to the finer particle size of the powder.

Fig.7. (a) Apparent Density and (b) Apparent Porosity of M-72 and M-672 Samples Sintered at 1550°C as a Function of Percentage of Sintering Additive



The apparent porosity of M-72 and M-672 samples sintered at 1550°C presented in Fig.7(b) decreases with increase in sintering additive in correlation with the increase in sintered density [Fig 7(a)]. Among the two powders M-672 show highest density of 95.5 ± 0.5% and lowest porosity of 1.5 ± 0.2% on sintering at 1550°C, while M-72 powder reaches highest density of 94 ± 0.5% and porosity of 3 ± 0.3% at 1600°C . These results indicate that M-672 powder is superior to M-72 powder with respect to sinterability.

Fig.8. SEM Micrographs of Polished and Acid Etched Sintered Slip Cast Mullite Samples. (a) M-672 (b) M-672-1Mg (c) M-672 (d) M-672-1Mg (e) M-672-2Mg (f) M-72-2Mg



The representative SEM micrographs of polished and acid etched (Dilute acetic acid) samples of slip cast mullite with and without sintering aids sintered at 1550°C are presented in Fig. 8. The SEM micrograph of M-672 sample presented in Fig. 8(a) show considerable open porosity in correlation with the 29% porosity presented in Fig 7. The dense surface feature shown in Fig 8(b) for M-672 with 1% addition of MgO (M-672-1Mg) represents the highest density achieved at 1550°C. The SEM in Fig 8(c) reveals the porosity and grain structure of the M-672 sample at higher magnification, where as the dense microstructure is observed for M-672 doped with 1% MgO (M-672-1Mg) in Fig 8(d). The SEM in Fig 8(e) and (d) reveals the dense microstructures of 2% MgO doped M-672 and M-72 respectively.

4. Conclusion

Two commercial mullite powders M-72 and M-672 used in the present study were found to show X-ray pure mullite phase and their particle size distributions were in the range of 2.3μm to 20.0μm and 0.6μm to 10.3μm respectively. Both the powders show higher zeta potential values in the alkaline pH range of 10 to 11 indicating high surface charge leading to good dispersion. The slurry prepared from these powders in aqueous media at pH = 10.0 to 10.5 could be slip cast to give green body having density of 62 ± 1%. On sintering in the temperature range of 1500 to 1600°C, M-672 powder having finer particle size resulted in higher density as compared to M-72 powder. The addition of MgO as sintering aid has resulted in increased density and decreased porosity for both M-72 and M-672 powders as compared to non doped samples. M-672 powder having 1% MgO as sintering aid resulted in highest density of 95.5 ± 0.5% and lowest porosity of 1.5 ± 0.2% on sintering at 1550°C for 1 hr. The microstructural observations correlate well with the density and porosity results.

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