Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 6115–6121

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Diametral deformation behavior and machinability of methyl cellulose thermal gel cast processed alumina ceramics

P. Biswas, M. Swathi, P. Ramavath, K. Rajeswari, M. Buchi Suresh, Roy Johnson*

Center for Ceramic Processing, International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), Balapur, Hyderabad 500005, AP, India

Received 18 January 2012; received in revised form 20 April 2012; accepted 21 April 2012
Available online 9 May 2012

Abstract

Thermally induced gelation of methyl cellulose as the networking additive has been demonstrated for consolidating alumina from slurry of 70–72 wt% solid loading. Concentration as low as 0.2 wt% of methylcellulose had been found to be sufficient to form a uniform network in ceramics with enhanced machinability even with the conventional tools. Cast and machined samples could be sintered close to theoretical densities without any warpage or visible cracks with very fast heating rates of 3 °C/min. Low failure stress and high compression distance exhibited by the thermal gel cast samples in comparison to the compacted samples during diametral tests compliments the observed machinability.

Keywords: B. Failure analysis; Ceramics; Gel cast; Machinability

1. Introduction

Colloidal processing of ceramics is a common and practical pathway for defect free complex shaping and densification [1–5]. Among the most commonly employed techniques, gel casting based on in-situ polymerization of acryl amide based monomers offers major advantages of high solid loading (50–55 vol%), high green strength and uniform green microstructure enabling green machining [6–9]. However, the wide spread commercial use of acrylamide based gel casting process has been limited as it suffers from the serious drawback of being toxic. The need for an environmentally benign non-toxic polymeric agent has led to the emergence of relatively low toxic gel casting systems based on organic monomers like, 2-hydroxyethyl methacrylate (HEMA) [10,11], methylene bisacrylamide and methacrylamide [12], etc. Cross linkable binder systems like, epoxy resins, ethylene glycol diglycidyl ether (EGDGE), glycerol polyglycidyl ether (GPGE) [13,14], and polyvinyl alcohol (PVA) [15–17], have been evaluated alternatively for casting of ceramics. Gelling agents like gelatin [18,19], alignic acid salt and hydroxyl aluminum diacetate (HADA) [20], boehmite and acrylic acid [21,22], were also employed successfully for casting. Nevertheless, the time consuming drying and binder removal schedules are still considered to be bottle necks in commercial production. Further, the hazardous emissions as a result of pyrolysis of the incorporated organic polymers are also of environmental concerns.

Methyl cellulose, a water-soluble organic compound is widely used in shaping of ceramics and metallic parts by injection molding and extrusion [23]. The use of polysaccharides as consolidating agents has been successfully demonstrated earlier for fabrication of ceramic and metallic components [24–25]. Injection molding of articles from metallic powders by employing thermal gelation of methyl cellulose in the presence of glycerin and boric acid as modifiers has been patented by Rivers as early as 1976 [23]. The gelling ability of starch in water has been successfully utilized for the development of porous ceramics by Lyckfeldt and Ferreira [24]. Simple and very complex shapes with ultimate porosities in the range of 23–70% were reported. Gel casting of alumina bodies exploiting the

*Corresponding author. Tel.: +914024443169; fax: +914024442699.
E-mail addresses: royjohnson@arci.res.in, suresh@arci.res.in (R. Johnson).

0272-8842/$36.00 © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.04.059

synergetic effect of agar and galactomann was demonstrated as a low cost, non-toxic technique for colloidal forming of ceramics [25]. It has been long known that aqueous solutions of methylcellulose (MC) undergo thermally induced gelation at temperatures $> 50\ ^{\circ}C$ due to the intermolecular association of the hydrophobic groups as a function of temperature [26–28]. The dissolution of methyl cellulose in water at room temperature or lower than room temperature is reported to be due to the enclosure of hydrophobic moieties by water molecules. It is generally agreed that heating causes dehydration of hydrated methoxyl groups, which then undergo hydrophobic association giving rise to the formation of the network, i.e., gel. This thermal gelation characteristic of methyl cellulose solution has recently been exploited successfully for the colloidal forming of ceramic suspensions. An aqueous gel casting process has been reported using methyl cellulose as the gelation agent for γ-$LiAlO_2$ ceramics [26]. Use of 1% methyl cellulose solution in the slurry could lead to green bodies of γ-$LiAlO_2$. However, the density achieved was relatively poor (80% TD). More recently, the authors have reported the fabrication of dense alumina bodies employing very low concentrations of methyl cellulose as the networking additive [28]. Authors have also demonstrated the use of this environmentally benign process to achieve close to theoretical densities. In the present study, the thermally gel cast samples were subjected to diametral deformation testing and machinability studies were carried out and compared with a compaction processed samples.

2. Experimental procedure

2.1. Characterization of alumina powder

Alumina powder (M/s. ACC Ltd., Mumbai, India) was characterized for its physicochemical properties such as phase by XRD (D8-Bruker, Germany), morphology and particle size using Scanning Electron Microscope (FEG SEM, Hitachi, Japan), BET surface area was estimated using nitrogen adsorption technique (Micromeritics Instrument Corp.) and particle size distribution by dynamic light scattering (Zetasizer, Malvern Instruments, UK).

2.2. Methyl cellulose gelation studies

In order to study adaptability of the methyl cellulose (MC) gelation phenomena for the ceramic shaping, varying concentrations of aqueous MC (0.08–0.5 wt%) solutions were prepared. The solutions were subjected to rheological measurements with a controlled stress rheometer (Model: MCR 51, Anton Paar, Austria) with a heating rate of $1\ ^{\circ}C$/min. The complex viscosity measurements have been made using parallel plate and the curves were recorded under oscillated shear mode in the viscoelastic regime.

2.3. Processing of compacts

Compacts were prepared using compaction and thermal gel casting as discussed below. Compaction processing was carried out by wet milling alumina under aqueous medium with 0.5 wt% methyl cellulose as binder for 6 h in polypropylene bottles in a pot jar mill. Grinding balls of 1 mm diameter at 1:1 charge to ball ratio were used to ensure proper mixing. The homogeneous slurry was oven dried at $80\ ^{\circ}C$ and then subsequently sieved to form granules which are further compacted using hydraulic press to achieve green density of $> 50\%$.

Alumina powder was made into an aqueous slurry in deionised water using Darvan 821 A (R. T. Vanderbilt Co., Inc., Norwalk, CT, USA) as a dispersant. The suspension was then milled for 6 h in polypropylene bottles in a pot jar mill using alumina balls of 1 mm diameter at 1:1 charge to balls ratio to achieve solid loading of alumina in the range of 75–78 wt%. The slurry after de-airing was mixed further with 0.2 wt% of methyl cellulose (Dow chemical company). Rheological behavior of the slurries was measured at varying shear rates (MCR 51, Anton Paar, Austria) to determine the flow properties. The variation in viscosity as a function of temperature was also studied at low shear rates of $10\ s^{-1}$ in the temperature range of 25–75 $^{\circ}C$ at the rate of $1\ ^{\circ}C$/min till a sharp raise in viscosity is obtained, indicating the thermal gelation. The slurry was casted into prefabricated teflon molds of rectangular and circular geometries. The samples of circular geometries of 30 mm diameter produced were subjected to diametrical testing as per the standard procedure and the rectangular samples of bigger dimensions were subjected to machining and sintering studies as discussed below. The mold was designed with proper tapering to facilitate easy release and petroleum jelly was applied for lubricity. The slurry was poured into the mold and the temperature was increased up to the gelation temperature and held at that temperature till the cast samples got released from the mold. The samples thus obtained were further dried at $80\ ^{\circ}C$ in a hot air oven for 24 h and are characterized for their green densities.

2.4. Characterization of compacts

Compacts were dried till they exhibited a constant weight and were machined to a uniform dimensions and the green densities were determined. The compacts were subjected to diametral-compression test and a comparison of failure stresses within the compacts with respect to processing conditions was studied. The tests were carried out at Stable Micro Systems, UK, using a texture analyzer. This test is carried out by a procedure similar to that often used to assess the crushing strength of compacts, i.e., diametral compression between two flat platens (Fig. 1(a) and (b)). The determination of tensile strength from this procedure depends upon the correct state of stress developing within a specimen of known shape and dimensions. Tensile, compressive and shear stresses distributions within a cylindrical compact placed between the

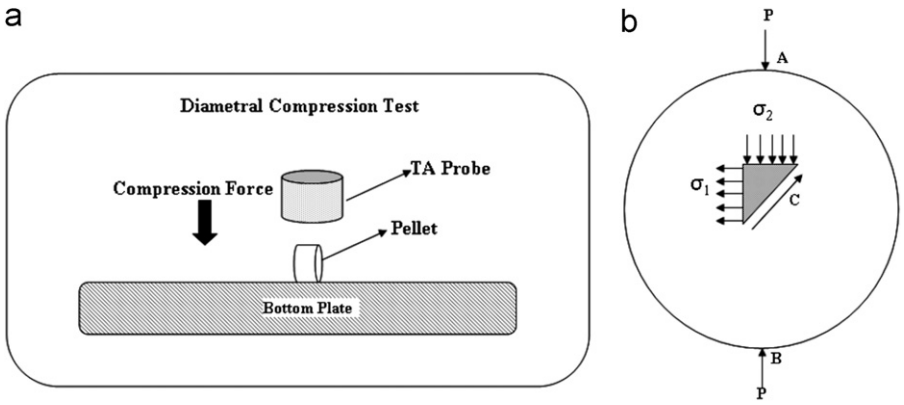

Fig. 1. (a) and (b) Diametral-compression test (schematic) and stress distribution across loaded diameter for a compact between two points of loading A and B.

platens of the texture analyzer can be calculated by elastic theory under the conditions of ideal line loading as illustrated in Fig. 1(a) and (b). The instrument also measures the failure forces and the distance that the probe traveled once in contact with the sample. The instrument software further calculates the failure stresses based on the sample dimensions. The fractured samples were also subjected to fractography to evaluate the fracture behavior.

2.5. Machining and sintering of thermal gel cast specimens

Green thermal gel cast alumina samples were subjected to two machining operations such as drilling and milling. Drilling of samples was carried out using HSS tools in a workshop with a hand drilling machine. During milling the material came out in the form of long agglomerates rather than the powder formation observed with green ceramics. The dried and machined samples were heated till 500 °C at a heating rate of 180 °C/h to ensure the removal of organics in the samples followed by heating to the peak sintering temperature of 1500 °C in a PID controlled Muffle furnace (Nabertherm, Bremen, Germany) at the rate of 300 °C/h. The sintered samples were characterized for their density using Archimedes' principle and microstructural analysis of polished and thermally etched samples was carried out using SEM (Hitachi 3200S, FE SEM, Japan). The specimens were also subjected to hardness evaluation by Vickers Indentation (Leica, Germany) at 10 kg load.

3. Results and discussions

3.1. Characterization of alumina powder

XRD pattern of the alumina powder shown in Fig. 2(a) confirms corundum as the major phase. Particle size analysis by laser diffraction has shown an average particle size of < 1 μm. Fig. 2(b) presents the SEM micrograph of the powder. BET surface area of the powder is found to be 6 M^2/g. The result is in good agreement with particle size measurement and exhibited morphology of irregular shapes with occasional agglomeration which is typical characteristic of industrial grade powders.

3.2. Thermal gelation of aqueous methyl cellulose and alumina slurry

Fig. 3(a)–(c) shows the effect of MC concentration on the gelation behavior when subjected to heating rate of 1 °C/min. It is evident that all aqueous methyl cellulose solutions behave identical with incipient gelation at 55 ± 5 °C, while subjected to heating. However, the rise in viscosity values was minimal of 16 Pa s for 0.08 wt% MC and 60 Pa s for 0.2 wt% MC and 1000 Pa s for concentration of 0.5 wt% of MC in the temperature range of 70–75 °C. It is observed that a simultaneous occurrence of gelation and precipitation with 0.5 wt% methyl cellulose leads to agglomerations instead of network formation.

The plot of temperature versus complex viscosity for the alumina slurry containing 0.2 wt% MC is shown in Fig. 4. It is evident that the trend in the viscosity is almost similar to that of the MC solution. However, the incipient gel point has reduced to 30 °C in comparison to 55 ± 5 °C for aqueous MC solutions. The premature gelation observed with the slurry can be attributed to the enhanced hydrophobic interactions in the presence of alumina powders.

3.3. Characterization of compacts

A typical force versus distance curve recorded for compacted sample shown in Fig. 5 has exhibited a gradual raise of force with the highest failure stress of 794 kPa. Dimensions and green densities of the compacts processed through compaction and thermal gel cast processing techniques along with their compression distance and failure stress of the diametral compression tested samples are shown in Table 1. Thermal gel cast sample exhibited the maximum failure stress of 462 kPa with a measured compression distance of 0.22 mm. The high failure stress observed in the case of compaction processed sample can be attributed to the mechanical inter-locking of the particles in combination with

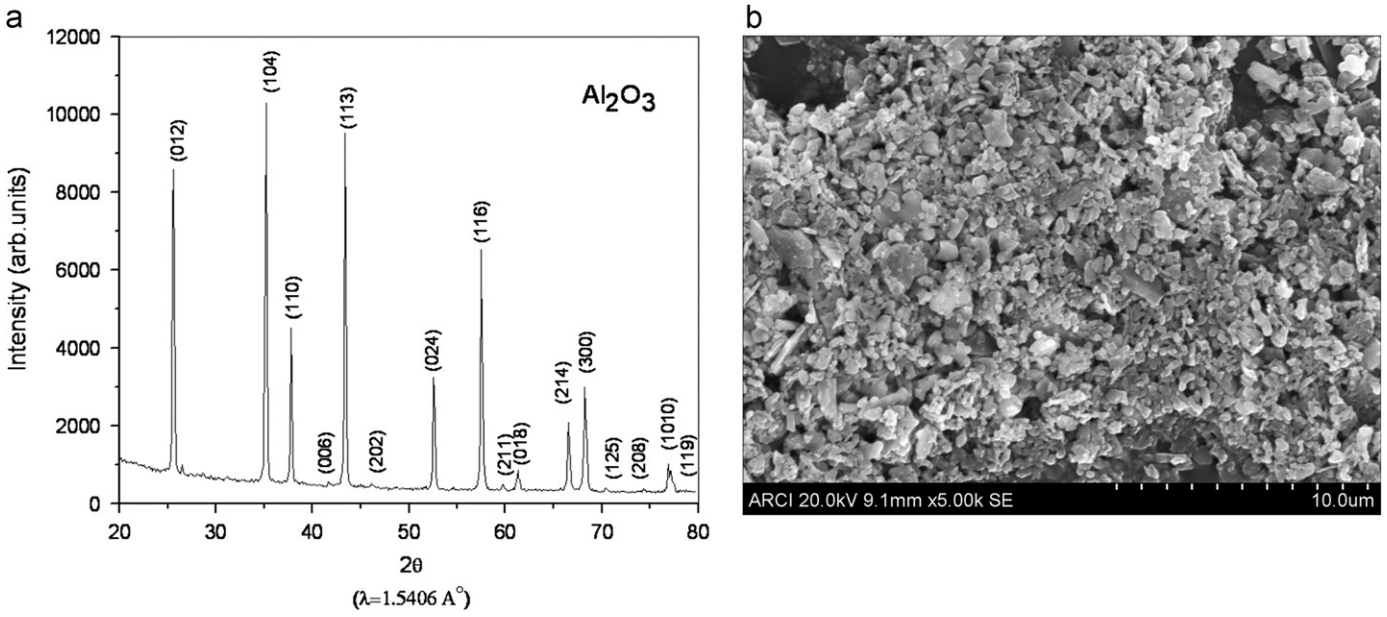

Fig. 2. (a) XRD pattern of ACC alumina powder and (b) morphology of ACC alumina powder.

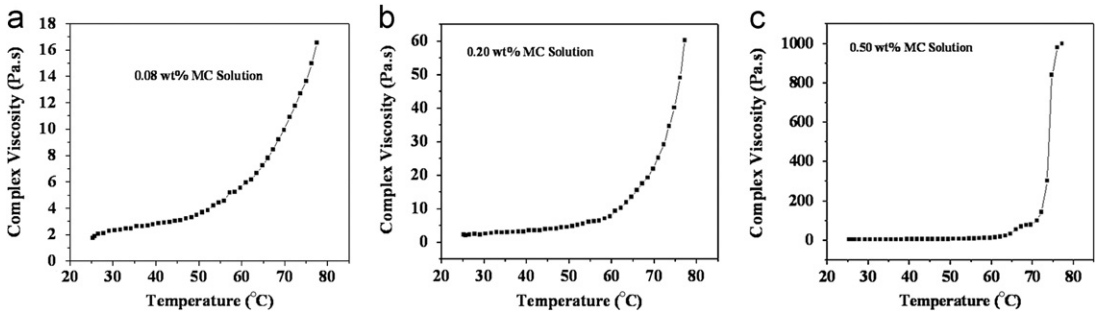

Fig. 3. (a) Effect of methyl cellulose concentration (0.08 wt% MC) on gelation behavior, (b) effect of methyl cellulose concentration (0.2 wt% MC) on gelation behavior and (c) effect of methyl cellulose concentration (0.5 wt% MC) on gelation behavior.

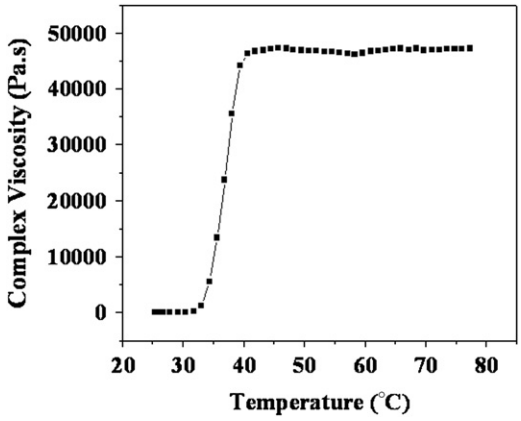

Fig. 4. Complex viscosity variation with temperature for the alumina slurry.

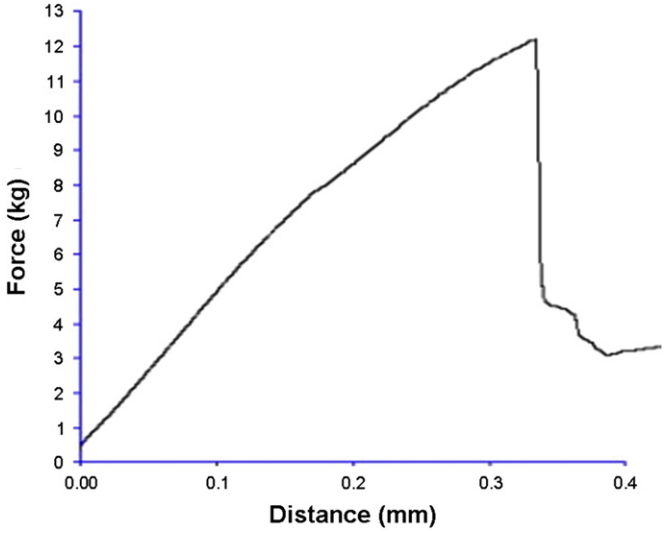

Fig. 5. Force versus displacement curve for a diametrical test specimen (compaction).

the van der Waals forces. A higher compression distance with a lower failure stress in thermal gel cast sample in comparison to compacted sample shows more compressive deformability which in turn indicates a high machinability.

The mechanical properties of the pellets and uniformity within the pellets are the two major factors those determine the stress distribution within the specimens. The load applied will spread from the contact points, preventing line loading which in turn reduces the shear and compressive stresses, prevails the tensile stresses leading to failure. Samples processed through thermal gel casting have resulted in the predominant tensile failure splitting of the pellet into two halves along the loaded diameter. Fig. 6(a) shows typical fractured pellets processed through thermal gel casting diametral compression showing the predominant tensile failure. However, the samples processed through compaction process exhibited fractures in an irregular manner representing predominant compression and/or shear failure as shown in Fig. 6(b).

Table 1
Dimensions, densities, compression distance and failure stress of the diametral-compression tested samples.

Serial no.	Observation	Compaction	Thermal gel casting
1	Diameter (mm)	30.605	24.755
2	Width (mm)	6.165	6.545
3	Green density (gm/cc)	2.05	1.92
4	Theoretical density (%)	51.4	48.2
5	Compression distance (mm)	0.191	0.22
6	Failure stress (kPa)	793.7	462.3
7	R2 of stiffness	0.9945	0.997

3.4. Fractography

SEM fractographs obtained from the specimens tested till failure under diametral-compression test are shown in Fig. 7(a) and (b) for compaction and gel cast samples, respectively. Though large numbers of fractographs at different magnifications are obtained in each of the conditions, for the sake of clarity only one representative fractograph for each condition is shown. It is evident from the micrographs that compacted samples exhibit hard agglomerates even after achieving a green density, $>55\%$ of TD. These agglomerates slide over one another during rearrangement under compaction pressure and are difficult to remove by deformation or fracture. Application of higher pressures is found to result in laminations due to spring back effect.

However, in the case of colloidal processed thermal gel cast specimens, such kind of hard agglomerates are absent and a uniform distribution of particles is observed. The difference in the pore size distribution and the degree of densification in gel cast bodies also visualized by microstructural observations, as shown in Fig. 7(b). Application of thermal gel

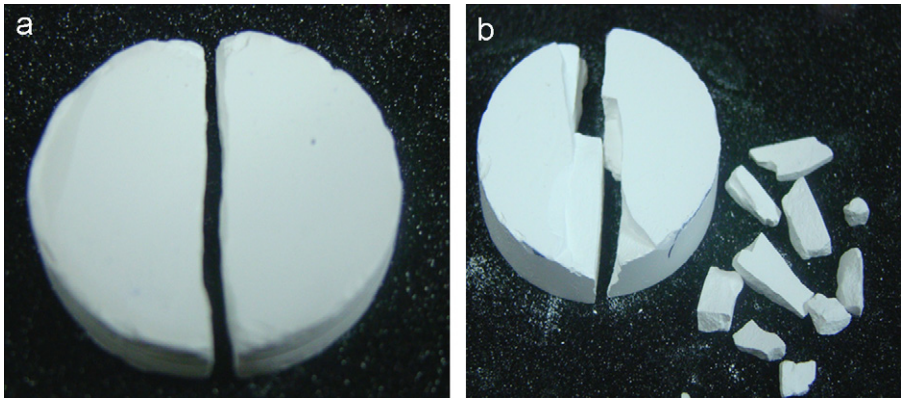

Fig. 6. (a) Fractured pellets processed through methyl cellulose thermal gel casting (after diametral compression test) and (b) fractured pellets processed through compaction (after diametral compression test).

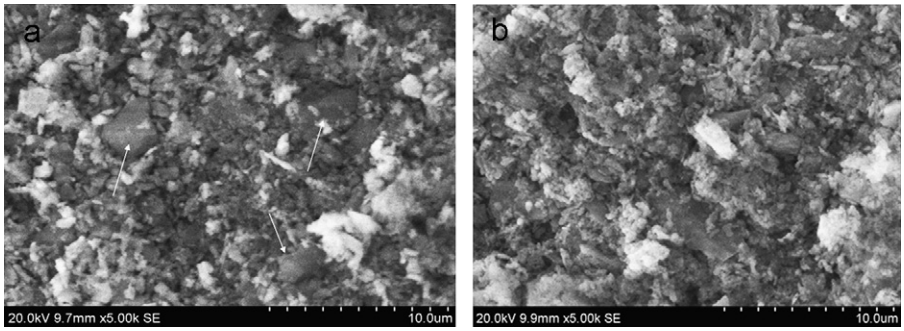

Fig.7. Fractographs of (a) compaction and (b) methyl cellulose based thermal gel casting.

casting significantly improved homogeneity and minimization of defects in the green body, though lower green density is observed. In the case of compacted green samples, the fracture origin can be of coarse agglomerates and hence non-uniform distribution of densities. However, a high fracture stress is exhibited because of the high mechanical interlocking of the particles under high compaction pressures.

3.5. Machinability and sintering of thermal gel cast specimens

Fig. 8 shows the green thermal gel cast samples after machining indicating the machinability of green samples. Samples are even machined with conventional tool and conventional equipments. No visible cracks were developed in the samples with sharp edge milling and drilling tools and also exhibited very good surface finish. Ceramic green machining has many advantages over direct machining of sintered ceramics, which not only results in exorbitant cost, but also introducing subsurface cracks. All the samples produced in this study were strong enough to be machinable and no visible cracks were observed.

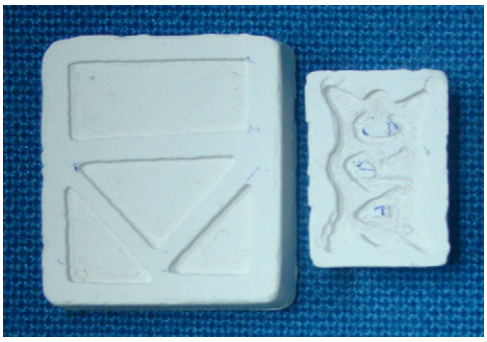

Fig. 8. Green thermal gel cast samples after milling and drilling.

In the present study machined samples were sintered at a ramp rate of 3 °C/min to the peak temperature of 1500 °C. The actually machined and sintered samples are shown in Fig. 9. The samples could be sintered to $>99\%$ of TD and no visible micro-cracks were seen, indicating the absence of even subsurface cracks which generally occur during machining. Samples have shown shrinkage of 17–18% and could be sintered to 99% of TD. Further the samples have shown no visible cracks. The micrographs of the fractured surfaces of the sintered samples processed through compaction and thermal gel cast techniques are shown in Fig. 10(a) and (b). Both the microstructures of the samples reveals a dense grains and the hardness in the range of 1700–1800 kg/mm^2, for both the samples.

4. Conclusions

Thermally induced methyl cellulose gel casting process has successfully employed for shaping of alumina ceramics

Fig. 9. Sintered thermal gel cast samples after milling and drilling.

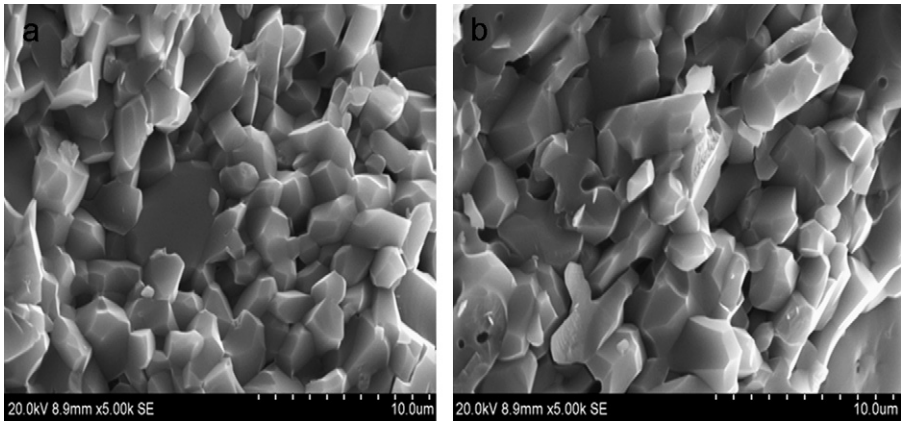

Fig. 10. (a) and (b) Morphology of fractured surfaces of compacted and thermal gel cast samples.

with enhanced machinability under conventional machining process with no visible cracks. Studies on diametral deformation behavior in thermal gel cast samples exhibited low failure stress and high compression distance with a better machinability in comparison to compacted samples. Elucidation of green microstructure revealed improved uniformity without any hard agglomeration in the case of thermal gel cast samples. Low concentration of methyl cellulose in the cast and machined samples permits faster binder removal and sintering of samples close to theoretical densities without any warpage.

Acknowledgments

Authors are thankful to Dr. Guy Jones, Stable Microsystems, U.K., for their help in carrying out diametrical deformation tests on the samples.

References

[1] F.F. Lange, Powder processing science and technology for increased reliability, Journal of the American Ceramic Society 72 (1989) 3–15.
[2] W.M. Sigmund, N.S. Bell, L. Bergstrom, Novel powder-processing methods for advanced ceramics, Journal of the American Ceramic Society 83 (2000) 1557–1574.
[3] R. Janssen, S. Scheppokat, N. Claussen, Tailor made ceramics based components—advantages of reactive processing and advanced shaping techniques, Journal of the European Ceramic Society 28 (2008) 1369–1379.
[4] J.A. Lewis, Colloidal processing of ceramics, Journal of the American Ceramic Society 83 (2000) 2341–2359.
[5] A. Krell, P. Blank, The influence of shaping method on the grain size dependence of strength in dense submicrometre alumina, Journal of the European Ceramic Society 16 (1996) 1189–1200.
[6] C. Young, O.O. Omatete, M.A. Janney, P.A. Menchhofer, Gelcasting of alumina, Journal of the American Ceramic Society 74 (1991) 612–618.
[7] O.O. Omatete, M.A. Janney, R.A. Strehlow, Gel casting—a new ceramic forming process, American Ceramic Society Bulletin 70 (1991) 1641–1649.
[8] S. Dhara, R.K. Kamboj, M. Pradhan, P. Bhargava, Shape forming of ceramics via gel casting of aqueous particulate slurries, Bulletin of Materials Science 25 (2002) 565–568.
[9] A. Krell, P. Blank, H. Ma, T. Hutzler, M.P.B. van Bruggen, R. Apetz, Transparent sintered corundum with high hardness and strength, Journal of the American Ceramic Society 86 (2008) 12–18.
[10] K. Cai, Y. Huang, J.L. Yang, A synergistic low toxicity gel casting system by using HEMA and PVP, Journal of the American Ceramic Society 88 (2005) 3332–3337.
[11] K. Cai, Y. Huang, J.L. Yang, Alumina gelcasting by using HEMA system, Journal of the European Ceramic Society 25 (2005) 1089–1093.
[12] M.A. Janney, O.O. Omatete, C.A. Walls, S.D. Nunn, R.J. Ogle, G. Westmoreland, Development of low-toxicity gelcasting systems, Journal of the American Ceramic Society 81 (1998) 581–591.
[13] X.J. Mao, S.Z. Shimai, M.J. Dong, S.W. Wang, Gelcasting of alumina using epoxy resin as a gelling agent, Journal of the American Ceramic Society 90 (2007) 986–988.
[14] X.J. Mao, S. Shimai, M.J. Dong, S.W. Wang, Investigation of new epoxy resins for the gel casting of ceramics, Journal of the American Ceramic Society 91 (2008) 1354–1356.
[15] F. Chabert, D.E. Dunstan, G.V. Franks, Cross-linked polyvinyl alcohol as a binder for gelcasting and green machining, Journal of the American Ceramic Society 91 (2008) 3138–3146.
[16] S.L. Morissette, J.A. Lewis, J. Cesarano, D.B. Dimos, T.Y. Baer, Solid freeform fabrication of aqueous alumina–poly (vinyl alcohol) gelcasting suspensions, Journal of the American Ceramic Society 83 (2000) 2016–2409.
[17] S.L. Morissette, J.A. Lewis, Chemorheology of aqueous-based alumina–poly (vinyl alcohol) gelcasting suspensions, Journal of the American Ceramic Society 82 (1999) 521–528.
[18] M. Lombardi, V. Naglieri, J.M. Tulliani, L. Montanaro, Gelcasting of dense and porous ceramics by using a natural gelatine, Journal of Porous Materials 16 (2009) 393–400.
[19] Y.L. Chen, P. Xie, J.L. Yang, Y. Huang, Alumina casting based on gelation of gelatine, Journal of the European Ceramic Society 19 (1999) 271–275.
[20] R. Studart, V.C. Pandolfell, E. Tervoort, L.J. Gauckler, Gelling of alumina suspensions using alginic acid salt and hydroxyaluminum diacetate, Journal of the American Ceramic Society 85 (2002) 2711–2718.
[21] K. Prabhakaran, C. Pavithran, Gelcasting of alumina from acidic aqueous medium using acrylic acid, Journal of the European Ceramic Society 20 (2000) 1115–1119.
[22] K. Prabhakaran, S. Ananthakumar, C. Pavithran, Gel casting of alumina using boehmite as a binder, Journal of the European Ceramic Society 19 (1999) 2875–2881.
[23] R.D. Rivers, Method of Injection Molding Powder Metal Parts, US Patent no. 4113480, 1978.
[24] O. Lyckfeldt, J.M.F. Ferreira, Processing of porous ceramics by starch consolidation, Journal of the European Ceramic Society 18 (1998) 131–140.
[25] S.M. Olhero, G. Tari, M.A. Coimbra, J.M.F. Ferreira, Synergy of polysaccharide mixtures in gel casting of alumina, Journal of the European Ceramic Society 20 (2000) 423–429.
[26] X. Xu, Z. Wen, J. Lin, N. Li, X. Wu, An aqueous gel-casting process for γ-$LiAlO_2$ ceramics, Ceramics International 36 (2010) 187–191.
[27] N. Sarkar, Jr.G.K. Greminger, Methyl cellulose polymers as multifunctional processing aids in ceramics, American Ceramic Society Bulletin 62 (1983) 1280–1284.
[28] U.S. Hareesh, R. Anantharaju, P. Biswas, K. Rajeswari, R. Johnson, Colloidal shaping of alumina ceramics by thermally induced gelation of methyl cellulose, Journal of the American Ceramic Society 94 (2011) 749–753.