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Ceramic domes fabricated by a combination of tape casting and vacuum forming

Xuesong Lu[a], Julian R.G. Evans[a,*], Steve N. Heavens[b]

[a] Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK
[b] Ionotec Ltd., 14 Berkeley Court, Manor Park, Runcorn, Cheshire WA7 1TQ, UK

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Abstract

Tape casting is a low cost fabrication process for flat ceramic sheet and this paper demonstrates how it can be combined with vacuum forming to make α-alumina domes of 250–300 μm sintered thickness. The suspension formulation makes use of systems of double plasticizers and double solvents in a poly(methyl methacrylate) binder to provide plastic ceramic films by tape casting from which preforms for vacuum forming were cut. In order to retain the shape of vacuum formed domes during debinding and sintering, an initial low temperature anneal is needed. The study indicates that the ratio of plasticizers to binder and the particle size are two dominant parameters in influencing the elongational flow. The whole process provides a novel method to make thin ceramic domes.

Keywords: Tape casting; Shaping; Electron microscopy; Al_2O_3

1. Introduction

Vacuum forming is widely used for forming plastics in different industries such as automotive manufacturing,[1] antenna fabrication,[2] lens fabrication[3] and for some laminated articles[4] and it is widely used in packaging. A great advantage of vacuum forming is that it is a low-cost method of producing materials because it can be automated and the mould can be made of light-weight construction because it has to withstand only atmospheric pressure.[5] The auxiliary equipment is very simple, consisting of only a heater, clamping device and a vacuum pump with reservoir and valve.[5] Generally the vacuum forming process uses thermoplastic sheets heated above the glass transition temperature of the material and then formed into a part by biaxial stretching over a mould. The part is then cooled and removed from the mould after it becomes rigid enough to support itself.

One of the big problems for vacuum formed bodies is non-uniform thickness distribution which is caused by inappropriate mould design and processing conditions and much effort has been directed to solving these problems. Liu[6] developed a novel viscoelastic model with eight node overlay iso-parametric elements to simulate the vacuum forming of filled isotactic polypropylene. Taylor et al.[7] examined the influence of process variables on final thickness distributions for vacuum-formed thermoplastic parts. The process variables investigated included air evacuation rate, sheet surface temperature, mould temperature, and material slip over the mould surface. The part thickness distribution for uniform initial sheet surface temperature was found to be insensitive to variations in the surface temperature, the rate at which the sheet was stretched into the cavity and the mould-surface temperature.[7] However, the boundary conditions imposed on the sheet had a definite influence on the thickness distribution inside the cavity. When the sheet was free to stretch and slide over the top mould surface, additional material entered the cavity resulting in an overall increase in the final part thickness in comparison with the case in which the material was restrained from stretching and sliding into the cavity.

Pin-array moulds have been developed that can be adjusted to give many shapes. Kleespies et al.[8] demonstrated a method for producing prototypes of compound curved surfaces with a variable configuration mould composed of an array of discrete pins and a rubber interpolation sheet. This made it possible to conduct a multi-parameter design study involving theoretical, numerical and experimental methods to explore the feasibility of

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* Corresponding author. Tel.: +44 20 7679 4689.
E-mail address: j.r.g.evans@ucl.ac.uk (J.R.G. Evans).

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Table 1
Physical properties of materials.

Materials	Particle size (μm)	Density ($kg\,m^{-3}$)	Type	Function	Source
α-Al_2O_3	4.2	3980	99.9%	Powder	Ionotec Ltd., UK
α-Al_2O_3	0.3	3980	99.99%	Powder	Condea Vista, USA
Poly(methyl methacrylate) (PMMA)	–	1170	Mw: 350,000	Binder	Sigma–Aldrich, UK
Poly(ethylene glycol) (PEG)	–	1128	Mw: 570–670	Plasticizer	Sigma–Aldrich, UK
Dibutyl phthalate (DBP)	–	1050		Plasticizer	VWR, UK
Ethanol	–	789	99.7–100%	Solvent	VWR, UK
Methyl ethyl ketone (MEK)	–	804		Solvent	VWR, UK

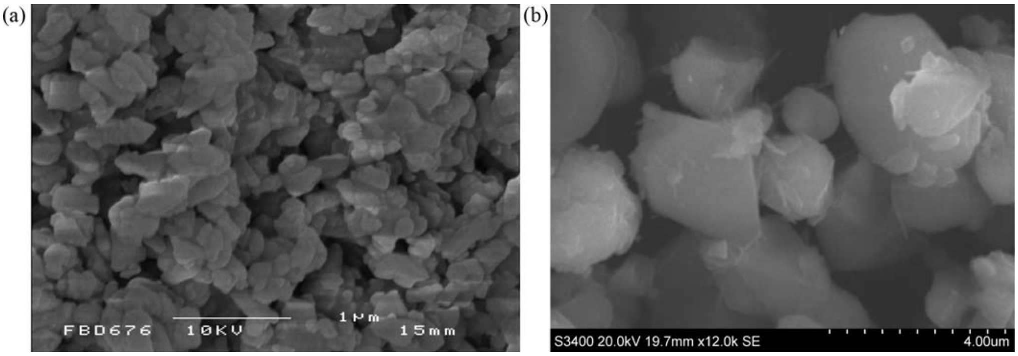

Fig. 1. SEM images of α-alumina powder: (a) 0.3 μm α-alumina; (b) 4.2 μm α-alumina.

building prototype surface parts in a variable moulding process. Wang et al.[9] developed a design for screw-pin tooling (SPT) again allowing a multitude of curvatures to be prototyped from one mould and investigated it for producing vacuum formed components.

The first time that vacuum forming was applied in the fabrication of ceramic bodies was by Haunton et al.[10] using thin sheet made from 50–60 vol.% ceramic powder and a thermoplastic polymer to make sintered alumina shapes by vacuum forming. The sheets for vacuum forming were made by continuous extrusion in a twin screw compounding extruder. Very thin, flat ceramic sheets can also be made by the tubular film blowing.[11] In this paper, our aim is to make vacuum formed α-alumina domes using ceramic film produced by tape casting which is a cost-effective and widely practiced ceramic forming method. Until now, the tape casting of sheet suitable for vacuum forming has not been reported.

2. Experimental details

The sources and relevant details for the materials are shown in Table 1. Two α-alumina powders were used differing in average particle size by a factor of ten. SEM images of particles are shown in Fig. 1. The fine powder was milled by a Dyno-mill (Type KDL A, W.A. Bachofen AG, Maschinenfabrik Basel, Switzerland) to break down agglomerates. The preparation of suspensions is based on the formulation reported in Table 2 and the sequence follows this order of mixing. First, the α-alumina powder was added to the solvent which was a mixture of ethanol and MEK and dispersed by ultrasonic probe (U200S, IKA Labortechnik, Stanfen, Germany) for 1 h. The binder (PMMA) was then added to the mixture of solvents and powder and the ultrasonic probe was applied for more than 2 h to dissolve the polymer fully and continue powder dispersion. Then the plasticizers were added while mixing under the ultrasonic probe for a further hour. Finally, the suspension was stored in a glass or polyethylene bottle and put on a roller mixer to prevent sedimentation while awaiting use. Before tape casting, the suspension was degassed.

These suspensions were cast using a double-doctor blade with independent blade adjustment on the tape casting bench shown in Fig. 2. The size of the blade was 250 mm wide × 100 mm high with a bevel of 45°. The substrate was glass plate of dimensions 350 mm wide × 1700 mm long. During tape casting, the gap between the substrate and the blade was 1.7 mm. Displacement is obtained by pneumatic actuation in a spark-free chamber. The velocity of casting was controlled to be equal to the liquid flow rate. During drying, the rate of diffusion of solvent in the

Table 2
Formulation for tape casting of α-Al_2O_3 for vacuum forming.

Materials	α-Al_2O_3	PMMA	PEG	DBP	Ethanol	MEK
Function	Ceramic	Binder	Plasticizer	Plasticizer	Solvent	Solvent
Vol. fraction	9.75%	7.5%	1.5%	0.75%	26.83%	53.67%

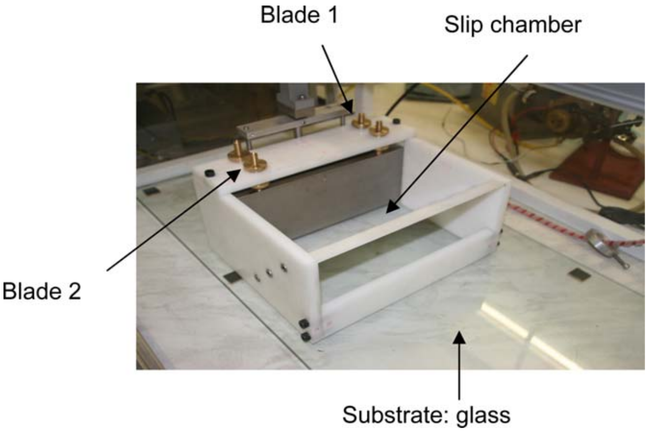

Fig. 2. Tape casting assembly.

tape should approximate to the solvent evaporation rate and to control the solvent evaporation rate, the atmosphere was partially buffered by introducing solvent in the tape casting chamber and partially covering the tape with a transparent box. After 12 h, the tape could be removed easily from the glass.

The vacuum forming chamber is shown in Fig. 3. The internal diameter of the chamber is 80 mm and its internal height is 30 mm. Pre-forms of 100 mm diameter were cut from the tape. These discs are rigid at ambient temperature and there were no cracks or other defects on the surface. The outer diameter of the flange was 125 mm. The flange, containing upper and lower ‘O’ rings is held by four sprung screws, equally spaced. The vacuum was provided by a venturi vacuum pump via a 200 L evacuated reservoir. A dome-shaped mould ($d = 72$ mm, $h = 22$mm) as shown in Fig. 3 was made of plaster. Heating was provided by a hot air blower situated on the top of the chamber. At first, the tape-cast sheet was fixed on the top of the chamber by the flange and the air blower was used to heat the sheet to a temperature of 85 °C. Then the vacuum valve was opened gradually until the sheet started to fall from the center. With the assistance of heating, the sheet was finally drawn on the mould. When cooled, the dome so-formed could be separated from the mould and removed from the vacuum chamber. The debinding procedure involved heating at 1 °C/min with dwells at 150, 200, 250, 300 and 400 °C, this being a cautious unoptimized schedule. The sintering conditions were 1540 °C for 2 h in air.

3. Results and discussion

3.1. Tape casting

The preparation of tape for vacuum forming differs somewhat from conventional ceramic tape casting because the thermoplastic sheet must sustain elongational flow when heated during forming and then become relatively rigid on cooling. When cooled, it must be able to support the shape during mould release and subsequent handling. Traditional tape casting tends to produce elastic and flexible sheet. Other requirements are the same: the ceramic solid fraction should be as high as possible with uniform distribution of ceramic and organic material and the tape should be free from defects, such as cracks. However, the solid fraction is slightly lower, for a given powder, than the maximum in conventional tape casting in order to promote elongational flow. A system of dual plasticizers and dual solvents was selected because it can prevent a polymer skin forming during drying. Table 2 gives the formulation that was arrived at for tape casting α-alumina suitable for vacuum forming.

The experimental results showed that the plasticizer content heavily influences the quality of as-cast tape for vacuum forming. Generally, the ratio of plasticizers (PEG and DBP together) to binder (PMMA) should be less than or equal to 33 vol.% but more than 23 vol.%. If more than 33%, the cast sheet is very soft and cannot retain its shape after vacuum forming. If less than 23%, the sheet is adherent to the glass and cannot be peeled from the substrate without losing integrity. The ratio of PEG to DBP can be decreased to 2:1 but should be more than 1:1. With more PEG in the plasticizer, the sheet tends to become very brittle and unsuitable for vacuum forming. With low PEG in the plasticizer mixture, the cast sheet adheres to the glass. These ratios control the balance of tape cohesion and adhesion to the substrate. The ideal volume fraction of PMMA was 7–7.5% and experiments for both powders showed that when the PMMA volume fraction was more than 7.5%, the suspension was viscous and could retain air, producing bubbles as it is poured into the casting chamber which then appear in the tape. When the PMMA volume fraction was less than 7%, the suspension flowed and spread out uncontrollably over the casting route.

When the tape with the coarser powder (particle size of 4.2 μm) was nearly, but not fully dried, the tape could be peeled from the glass substrate easily and allowed to dry fully. However when using the fine powder (particle size 0.3 μm), the tape must

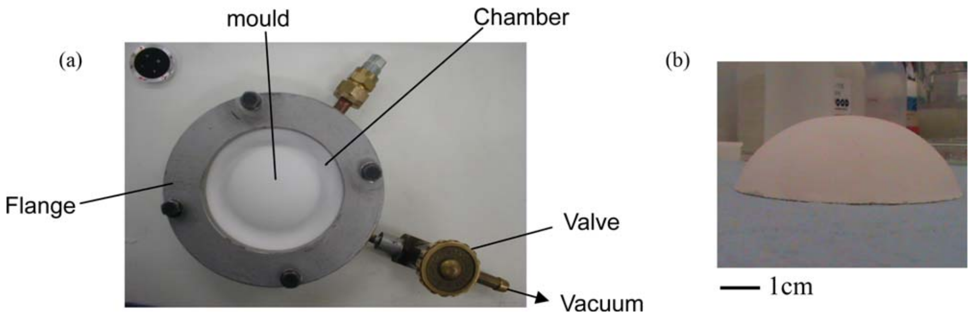

Fig. 3. Vacuum forming chamber and plaster mould.

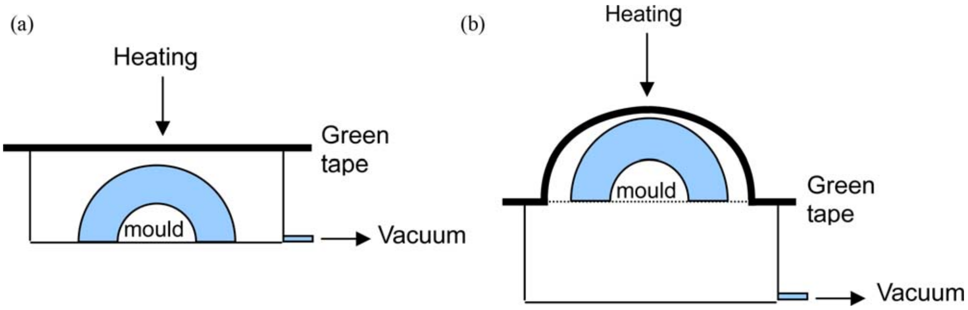

Fig. 4. Set-up for vacuum forming processes: (a) process 1; (b) process 2 before applying vacuum.

be removed after drying for 12 h while partially covered and the atmosphere inside the box buffered by solvent. At this stage, the tape was still wet but if the cast sheet was allowed to dry totally *in situ*, it could not be removed from the glass.

The sheet thinning after drying was 77% for the tape with 4.2 μm alumina powder and 71% for the tape with 0.3 μm alumina powder referenced to the doctor blade height of 1.7 mm. This large shrinkage includes thinning by lateral flow on the casting bench as the suspension is drawn under the doctor blade and solvent loss with particle rearrangement during drying.

3.2. *Vacuum forming*

Vacuum forming is one of the biaxial elongational flow processes that can be used for ceramics[12] and involves three stages: heating, biaxial deformation with vacuum applied on one side and cooling. Heating raises the temperature of the preformed disc above the glass transition temperature of the polymer and confers flexibility whereupon the applied vacuum causes biaxial deformation. Cooling brings the temperature below the glass transition temperature (T_g) returning the sheet to a rigid state so it can support its shape. This traps molecular orientation which relaxes for entropic reasons if the vacuum forming is subsequently reheated resulting in loss of shape. Below T_g, glass-forming systems undergo very slow relaxation towards the equilibrium state and this process is responsible for changes of enthalpy, volume or mechanical properties[13] but if reheated above T_g relaxation strains are pronounced and the vacuum formed shape is lost.

Vacuum forming was conducted using two processes distinguished by the initial mould position in relation to the pre-form: In process 1 as shown in Fig. 4(a), the mould is lower than the pre-form. Hot air heating of the pre-form is applied from the top and then air is removed from the lower chamber which is connected to a vacuum reservoir. The tape falls and is drawn into the mould as the vacuum is slowly increased. Process 2 is shown in Fig. 4(b): the mould is higher than the pre-form and again heat is applied to the tape from above. When the pre-form becomes soft, the flange is clamped and vacuum is applied to the chamber.

The maximum tape extension under vacuum that could be tolerated before melt fracture was different for the different ceramic powders each of which had the same powder volume fraction. Depending on whether the particle size was 4.2 μm or 0.3 μm, the vacuum forming was performed in different ways. Generally, the tape with coarse powder was suitable for either vacuum forming process but the as-cast tape with fine powder was suitable only for vacuum forming using process 2 and when the first process was used, the pre-form tended to fracture because the tape could not sustain high elongation. Fig. 5(a) shows vacuum formed domes made by the sheet and Fig. 5(b) and (c) shows the trimmed products.

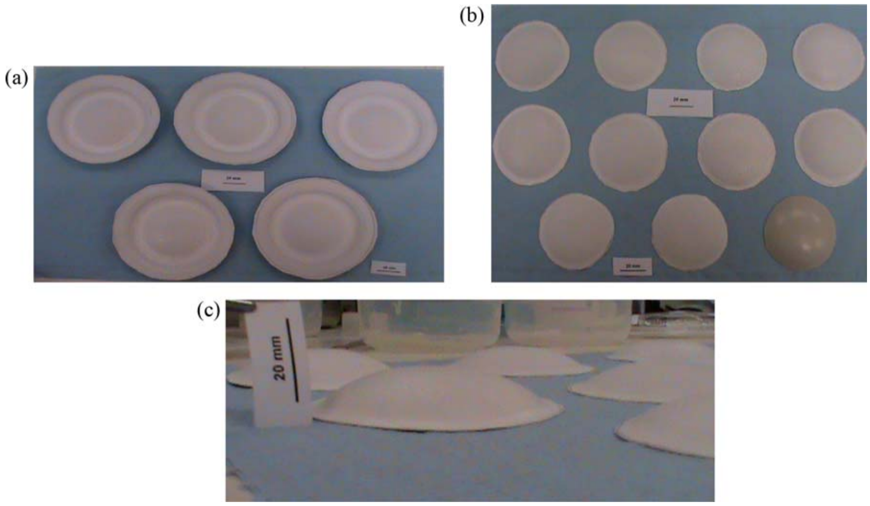

Fig. 5. Vacuum forming and formed domes: (a) as-formed domes; (b and c) edge trimmed.

3.3. Low temperature anneal, debinding and sintering

The vacuum formed dome with coarse powder was subjected to a low temperature anneal before the debinding process to induce constrained polymer relaxation otherwise the dome disappears and the shape reverts to the original flat as a result of entropic relaxation when the polymer is heated. Annealing of polymers can be divided into three categories: (1) annealing below the glass transition temperature; (2) annealing above the glass transition temperature; (3) annealing by chemical processes. Annealing of amorphous polymers below the glass transition temperature produces changes in many physical properties such as density, complex permittivity, enthalpy, complex mechanical modulus and creep compliance.[14] Annealing above the glass transition temperature permits the relaxation of chain extended polymer coils and involves associated strains. Annealing by chemical processes such as oxidation or photodegradation leads to the breaking of chemical bonds.[15] In these experiments, the annealing temperature is much higher than the glass transition temperature, and eventually heating extends into the range where chemical bonds are broken and plasticizer is lost as the temperature is raised to remove the organic binder.

In the procedure described by Fig. 6(a), the reversed dome is placed in a coarse alumina powder bed and a mould is placed in the dome. The sheet is constrained by the mould and relaxes while the shape is retained during heating at 180–200 °C for 4 h, a conservative schedule that has not been optimized in this work. If the vacuum formed domes made with fine powder do not go through this heat treatment before debinding, the dome only partially retains its shape. Its resistance to complete collapse can be attributed to polymer immobilization on the higher surface area powder. For subsequent debinding and sintering, the dome was put on coarse alumina as shown in Fig. 6(b). Without the low temperature anneal, the domes made with coarse powder can collapse fully after debinding because the coarse powder is less able to resist polymer relaxation.

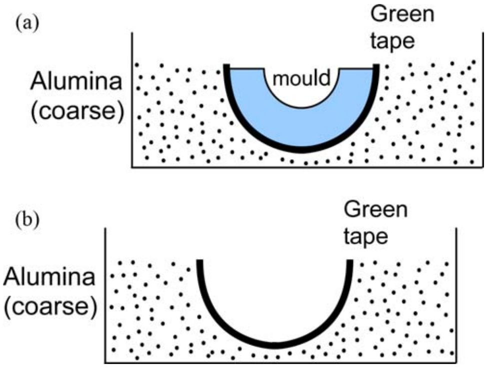

Fig. 6. (a) Setting the vacuum-formed tape before debinding and (b) the arrangement for sintering.

Fig. 7(a) shows the unfired vacuum formed dome with coarse powder made by tape casting and vacuum forming. The solid fraction in the dried green tape is 50 vol.%. Fig. 7(b) shows the sintered dome which has been annealed under low temperature. The diametral linear shrinkage from the dried state to the sintered state was 12% and the height was retained at approximately 9 mm. These shrinkages are low because of the restraint imposed during the early stages of reheating by embedding the form in powder with the mould placed on top. SEM images of the sintered sample showing the fracture surface and the upper surface are shown in Fig. 7(c) and (d) respectively. The thickness of the

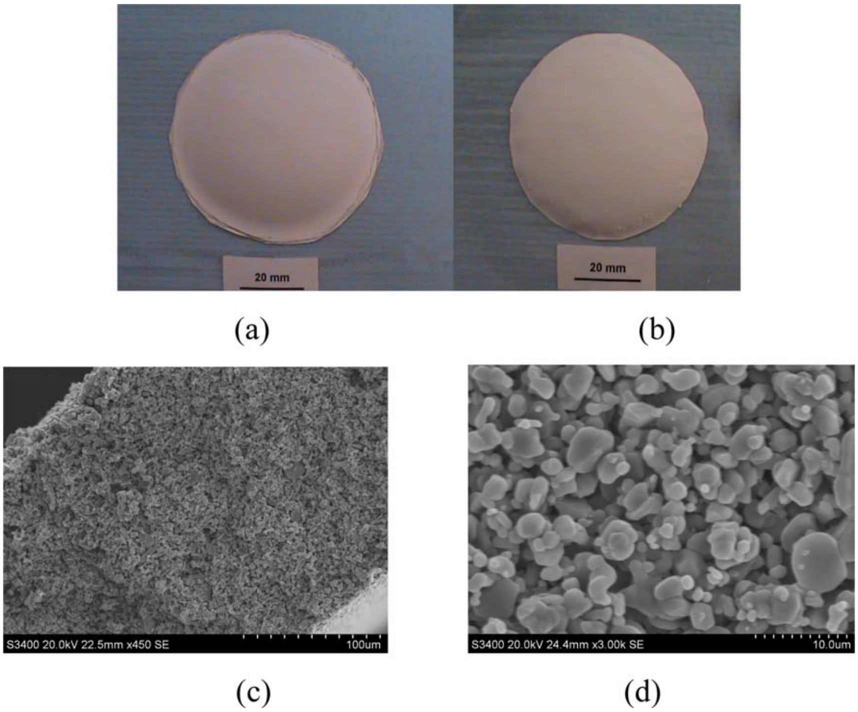

Fig. 7. Vacuum formed and sintered domes (particle size: 4.2 μm): (a) vacuum formed dome; (b) sintered dome; (c) fracture surface (SEM); (d) sintered surface (higher magnification SEM).

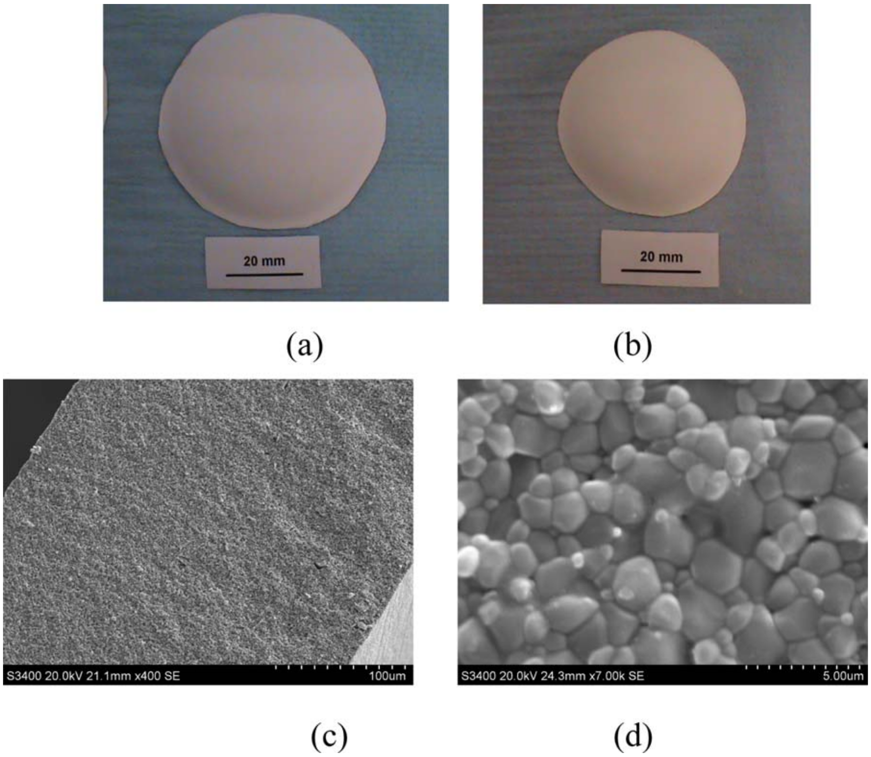

Fig. 8. Vacuum formed and sintered domes made from fine powder (particle size: 0.3 μm): (a) vacuum formed green dome; (b) sintered dome; (c) fracture surface (SEM); (d) sintered surface (higher magnification SEM).

sintered sample is 250 μm and linear shrinkage in the thickness direction is 38% based on the thickness of dry tape (0.4 mm). This shrinkage is not restrained and includes loss of residual solvent, loss of polymer and sintering.

When the alumina particle size was changed from 4.2 μm to 0.3 μm, although the sintered dome partially retained its shape without the low temperature anneal, this additional restraining process during the early stages of reheating was still necessary. Fig. 8 shows the vacuum formed and sintered domes made with the fine powder. The solid fraction in the dried tape was also 50 vol.%. The diametral shrinkage was 19%, higher than that for the coarse powder and the ceramic shell is nearer to full density as shown in Fig. 8(c) and (d). The thickness of the sintered samples was 300 μm and the linear shrinkage in the thickness direction was 40% based on the thickness of the dry tape. The sintering at 1540 °C produced a density of $3684 \pm 74\,\mathrm{kg\,m^{-3}}$ as measured on 12 sintered domes made from the fine powder by Archimedes method (the error is 95% CL). This corresponds to 92% relative density for a theoretical density of $3987\,\mathrm{kg\,m^{-3}}$ and suggests that a higher sintering temperature of ∼1600 °C is preferable. The coarse powder retained open porosity at this sintering temperature.

4. Conclusions

A sequence of operations for combined tape casting and vacuum forming of coarse and fine alumina powders was established. For the formulation of suspensions, a system with double plasticizers and double solvents was selected. The binder was PMMA and the ratio of plasticizers to binder should be less than 1:2 but more than 3:10 (i.e. between 23% and 33% by weight).

During tape casting, in order to reduce the incidence of defects such as cracks on the surface of the sheet, drying rate was moderated by partially covering the tape in an attempt to control solvent evaporation rate which should ideally be kept the same as the internal solvent diffusion flux.

The vacuum forming can be performed in two ways: with the mould initially above or below the pre-form in the vacuum forming chamber. The procedure selected depended on whether the powder was coarse or fine; it is likely that the fine powder hinders polymer mobility and changes the susceptibility of the polymer–ceramic system to melt fracture.

Before debinding and sintering, the vacuum formed domes are given a low temperature anneal, inverted and with the mould placed in the dome in order for the complete polymer relaxation without shape recovery. Without this, the dome collapses and the green shape reverts to the flat sheet during heating in the debinding schedule.

Through the process sequence described above, ceramic domes have been achieved by a new method that potentially allows for mass production of ceramic domes at modest cost.

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