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Comparison between slip-casting and uniaxial pressing for the fabrication of translucent yttria ceramics

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Abstract Slip casting and uniaxial pressing were compared as first consolidation stages prior to cold isostatic pressing (CIP) to produce translucent yttria ceramics. In the first step, yttria slurries suitable for slip casting were prepared. The viscosity was optimized with respect to the starting agglomeration state, amount of dispersant, milling time, and number of milling balls. Secondly, pellets were prepared either by slip casting or uniaxial pressing and then cold-isostatically pressed. Finally, the pellets were made translucent by a combination of pre-sintering and hot isostatic pressing (HIP). Although slip-cast and pressed samples exhibited similar green-body densities after CIP and pre-sintering, the samples prepared by slip casting were more homogeneous in terms of translucency and microstructure throughout their bodies. This was attributed to the ability of slip casting to minimize density gradients during packing, and to the beneficial effect of ball-milling to remove larger agglomerates before casting. Therefore, slip casting as a first consolidation stage prior to CIP appears to be more suitable than uniaxial pressing in order to prepare homogeneous optical ceramics.

Introduction

Rare-earth metal oxides have many uses as catalysts, high-energy permanent magnets, photoluminescence materials, and high T_c superconductors [1]. In particular, yttrium oxide (yttria) is useful as a relatively inert ceramic for the casting of reactive metals like titanium [2], as translucent structural material [3], and as a solid-state laser host material [4].

In order to achieve translucent yttria by ceramic processing, many methods were developed over the course of four decades. However, all methods found in the literature employed pressing in the stage of green-body formation [3, 5–8]. In fact, starting powders were either directly consolidated by cold isostatic pressing (CIP) or by uniaxial pressing following by CIP. Ikesue [7] used an initial spray-drying step in order to enhance flow properties during compaction, but no detailed investigation on the influence of the process on optical properties was reported.

Slip casting, a common wet-forming method for ceramics, is an alternative method to dry-forming techniques like pressing. Literature claims that slip-cast ceramics exhibit more homogenous packing [9] than ceramics formed by uniaxial pressing. Uniform density in green-body compacts is a major concern for ceramics that will be sintered to transparency, since scattering centers, like pores left after firing, must be limited to low levels. CIP is known to produce green-body compacts with relatively high density and uniformity of packing. However, any further improvement in the uniformity of packing density by wet-forming methods might ease pore removal.

Nevertheless, slip casting of yttria in aqueous solution is not without its drawbacks. Yttria particles become heavily hydrated when water molecules are physisorbed onto the surface [10, 11], and it dissolves to produce trivalent yttrium cations and its hydroxo complexes. The rate of dissolution depends upon pH, and specific surface area [12]. Most commercially available yttria powders are finely divided, giving a larger surface area for hydration and dissolution to occur.

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Another obstacle to working with yttria slurries is aging. The aging process of binary suspensions of yttria-silica and of alumina has been well documented [13, 14], but aging is also observed in slurries of yttria alone. The aging phenomenon is defined as the rapid increase in slurry viscosity, and is related to the dissolution of yttria [12]. The addition of organic dispersants can help to combat aging to some extent.

In this study, ammonium poly(methacrylic acid) salt was chosen as the dispersant to produce dispersed yttria slips. While it has been proven that 2, 3-dihydroxybenzoic acid is a more effective dispersant [15] than ammonium poly(methacrylic acid) salt, the latter has the advantage of being inexpensive and commonly available.

The goal of this study was double. First, yttria slurries suitable for slip casting would be prepared. It was important to determine the preparation parameters that would yield yttria slurries with minimum viscosities, and to limit aging. Secondly, the results of green-body formation by slip casting and by uniaxial pressing prior to CIP were compared in terms of optical properties and microstructure of the final translucent yttria ceramics.

Experimental

Preparation of slurries

Two different batches of a commercial yttria powder (Superamic 39 UF, Rhodia, France) were used in this study. The first batch corresponded to the as-prepared state of the yttria powder. It showed a specific surface area of 16.2 ± 1 m^2/g. In the rest of the text, this powder is referred to as non-disagglomerated powder. The second batch had undergone an extra chemico-mechanical disagglomeration treatment by the manufacturer. The resulting disagglomerated powder had a specific surface area of 17.2 ± 1 m^2/g, which corresponds to an equivalent particle diameter of 69 nm assuming smooth monosized spherical particles. An average particle diameter of 56 nm was determined by X-ray diffraction broadening technique for this powder. This indicates that even the disagglomerated powder was somewhat agglomerated. Scanning electron microscopy confirmed the fact that the primary particles were in fact agglomerated into larger secondary particles, as it can be seen in Fig. 1.

The dispersant was a 40 wt% solution of ammonium poly(methacrylic acid) salt in water (Dispex A40, Ciba Specialty Chemicals, Switzerland) and therefore the weight percents of dispersant discussed in the study are given with respect to the weight of active substance. Dilute solutions of varying dispersant content were prepared by weighing the original 40 wt% solution into a 100 mL volumetric flask and diluting with deionized water.

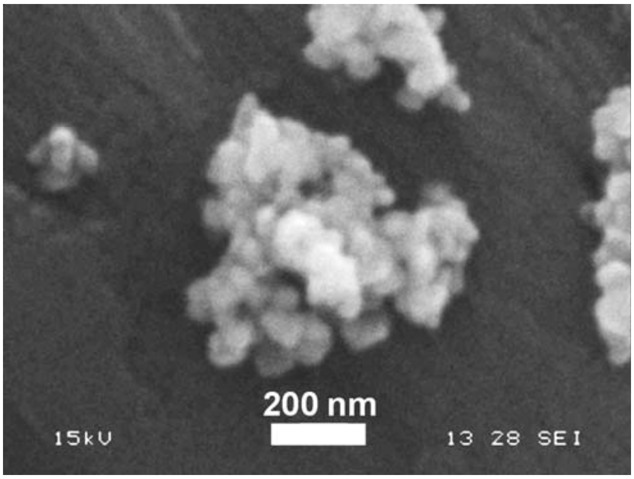

Fig. 1 Scanning electron micrograph showing typical morphology of the disagglomerated powder

Slurries of 60 wt% (23 vol%) yttria were prepared by weighing 11.535 g dilute dispersant solutions of varying concentrations (between 0.25 and 1.00 wt%) into a 30 mL Nalgene bottle and adding 16.860 g yttria powder. In all but two cases, 10 milling balls of yttria-stabilized zirconia were then added to the slurry and it was placed on a mill. The milling balls were 10 mm in diameter. In the case where 30 milling balls were added to a slurry, a 100 mL Nalgene bottle was used to accommodate the number of milling balls. In another case, a slurry was prepared and no milling balls were added before it was placed on the mill.

Slip casting, viscosity measurements, and pressing

Optimization of the rheological properties of yttria slurries was studied according to the average apparent viscosity, η_a, at a shear rate of 100 s^{-1} defined as

$$\eta_a = \gamma / \tau \qquad (1)$$

where γ and τ are the instantaneous shear stress and shear rate, respectively.

Viscosity measurements were performed using a rotational rheometer (Bohlin CVO, Malvern Instruments, UK) with a shear rate-controlled profile. Shear rate was ramped up from 0 to 100 s^{-1} for 60 s, held at 100 s^{-1} for 60 s, and finally ramped down from 100 to 0 s^{-1} for 60 s.

Pellets of 14 mm diameter were slip cast in a silicon rubber mold filled with a gypsum core according to the illustration in Fig. 2. Slurries were slip-cast at their minimum viscosities determined thereafter, i.e., after 6.5 h of milling. For comparison, some pellets of 14 mm diameter were uniaxially pressed at 10 MPa, with a double-action operating punch to be compared to slip-cast pellets. Cold

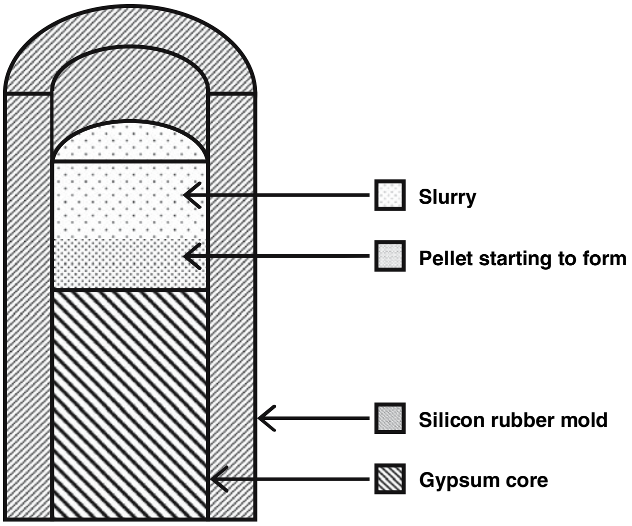

Fig. 2 Schematic cross-section of the mold used for slip casting

isostatic pressing was carried out for both slip-cast and pressed pellets, at a pressure of 200 MPa.

Burn-out procedure, sintering, and hot isostatic pressing

To determine the necessary burn-out conditions to remove the organic material introduced with the dispersant, thermogravimetry (STA 449C, Netzsch, Germany) and mass spectrometry (Aëolos, Netzsch, Germany) were run under helium flow. The burn-out itself was conducted in flowing oxygen by first ramping up the heat from 25 to 900 °C at a rate of 1 °C/min, then holding at 900 °C for 12 h, and finally ramping down from 900 to 25 °C at a rate of 1.25 °C/min.

To obtain translucent ceramics, a method developed by Mouzon et al. [16] was employed. It requires ceramics to be pre-sintered and subsequently subjected to hot isostatic pressing. Pre-sintering was conducted in air at 1,600 °C for 3 h in an alumina-lined tube furnace (DIL402C, Netzsch, Germany). Hot isostatic pressing (HIP) was conducted at 1,500 °C and 200 MPa for 2 h, using the glass canning technique.

Particle size distribution, density measurements and optical microscopy

Particle size distribution of the disagglomerated powder as-received and after milling in slurry was determined with a SediGraph 5100 (Micromeritics, Norcross, GA) particle size analyzer. To measure the equivalent spherical particle diameter, 2 g of dry powder was dispersed in 40 mL with 0.1% sodium metaphosphate. As for the slurry, a volume containing 2 g of powder was dispersed in water to reach a total volume of 40 mL. All dispersions were ultrasonicated for 2 min before measurement.

Green-body density after slip casting (or pressing) and CIP was calculated from the height, diameter, and weight of each sample. The Archimedes method in water was used to determine the density of the pre-sintered samples.

Samples after HIP were ground to a thickness of 1 mm and polished on both sides. To assess the microstructural homogeneity, optical transmission microscopy was used. Then, the samples were cut in half; one cross-section was embedded in epoxy, polished, and then etched in boiling HCl for 3 min. The revealed grains were observed by optical reflection microscopy.

Results and discussions

Viscosity and aging studies

The viscosities of six slurries of 60 wt% yttria (both disagglomerated and non-disagglomerated) and different amounts of dispersant were measured after 6.5 h of ball milling, since that is when the slurries became fluid enough to be measured. Figure 3 reports the viscosities at 100 s^{-1} for slurries based on the non-disagglomerated and disagglomerated powders as a function of dispersant content. Note the difference in scale of the *y*-axes in the two graphs. Viscosities of the disagglomerated yttria slurries are, for the most part, lower than the viscosities of the non-disagglomerated yttria slurries. For both powders, the slurry containing 0.50% dispersant had the lowest viscosity. The results show that 0.50% is the optimum amount of ammonium poly(methacrylic acid) salt for the yttria powders used in this study, both disagglomerated and non-disagglomerated.

Slurries of both powders, each containing 0.50% dispersant, were prepared in the same way and the aging of the two slurries was monitored. Figure 4 shows the aging curve of the two slurries. Both contain 10 milling balls. It should be noted that no measurements of the non-disagglomerated yttria slurry were possible for a few hours after preparation, unlike the disagglomerated yttria slurry. This is because slurries of the non-disagglomerated yttria powder were dry and paste-like upon preparation. The length of time needed for the slurries of non-disagglomerated yttria powder to reach an acceptable initial viscosity can be attributed to the agglomerated state of the powder. The slurry remains paste-like while the solution penetrates the agglomerates. Understandably, this penetration takes much less time for a powder that has already been disagglomerated.

The difference in aging times (18 h and 61 h) between the two slurries cannot be due to a difference in the powders' specific surface areas, because the specific surface areas are indistinguishable between the non-disagglomerated and

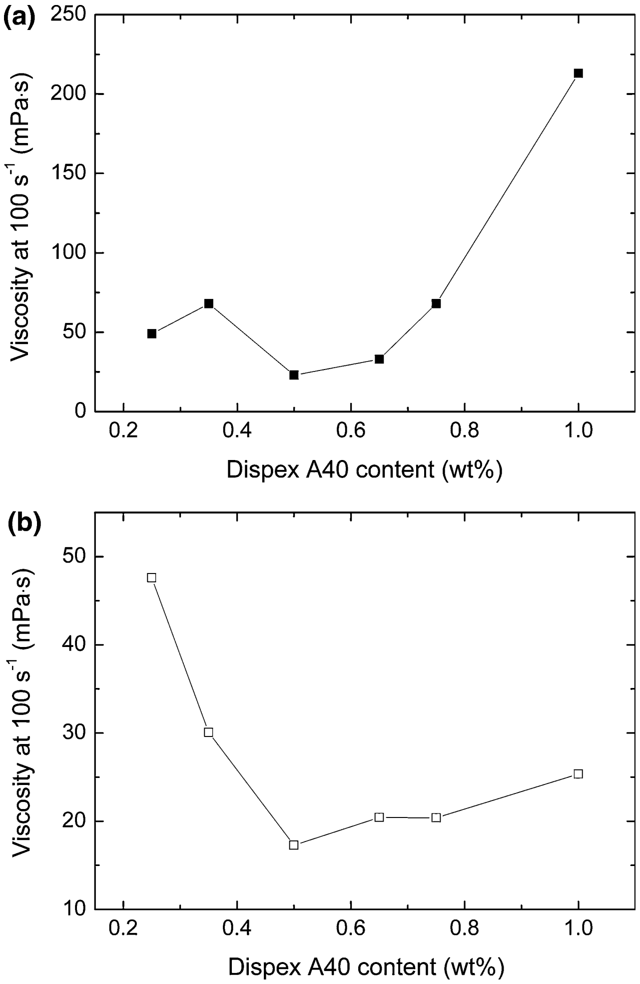

Fig. 3 Viscosity at 100 s^{-1} as a function of dispersant content for (**a**) the non-disagglomerated yttria powder, and (**b**) the disagglomerated yttria powder, after 6.5 h of ball milling

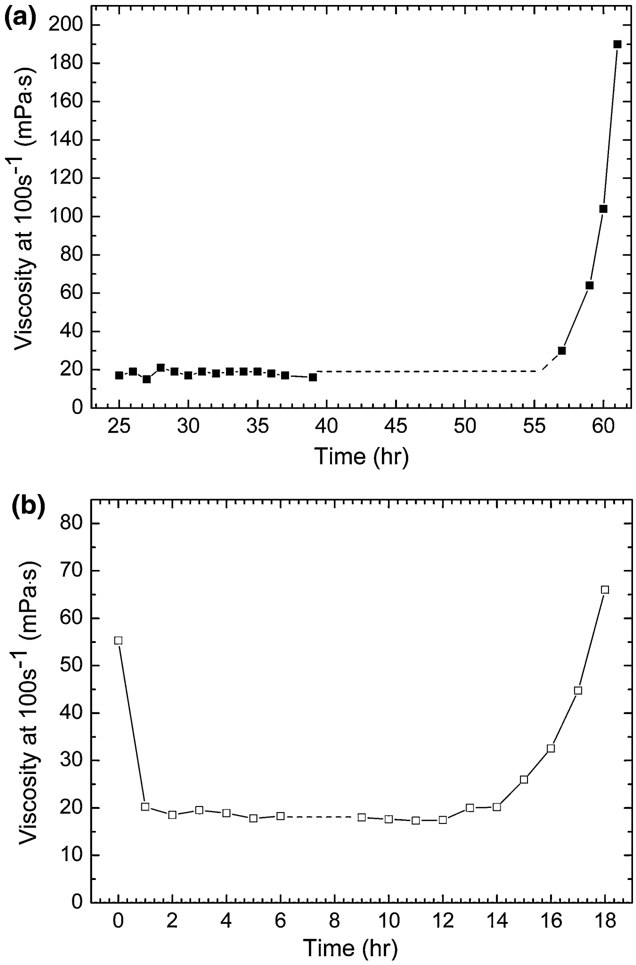

Fig. 4 Viscosity at 100 s^{-1} for a slurry of (**a**) non-disagglomerated yttria powder, and (**b**) disagglomerated yttria powder, both with 0.50% dispersant and 10 milling balls

disagglomerated yttria powders. It must be the disagglomeration treatment that is responsible for the different behaviors of the two slurries. As stated above, the more rapid penetration of the solvent in the disagglomerated powder leads to a more rapid and better coverage of the particle surface by solvent, thereby enhancing dissolution. Moreover, the disagglomeration treatment might be thought of as having changed surface chemistry and introduced surface defects by mechanical action. Since dissolution occurs at the site of defects in yttria particles [11], this might explain the differences in behavior.

Number of milling balls

The effect of the number of milling balls on aging time was also studied. Table 1 compares the aging times and minimum viscosities of three slurries of 0.50% dispersant and non-disagglomerated yttria powder, the difference between each slurry being the number of milling balls (0, 10, and 30).

The slurry with no milling balls aged the slowest, which is usually desirable. However, at its minimum, its viscosity is much higher than the minimum viscosities of the other slurries. Furthermore, there were visible agglomerates in the slurry without milling balls. A greater number of milling balls decreases viscosity by breaking the agglomerates and thereby allowing better coverage of the particle

Table 1 Aging time and minimum viscosities of 0.50% dispersant slurries of non-disagglomerated yttria powder depending on number of milling balls

Milling balls	Aging time (h)	Minimum viscosity (mPa·s)
0	264–336	1121
10	53–62	18
30	21	18

surface by solvent and dispersant. However, a too great number of milling balls increases the rate of aging, which supports the fact that an introduction of surface defects by mechanical action enhances dissolution and thus increases aging rate.

Therefore, 10 milling balls and the disagglomerated yttria powder were chosen for slip casting and all slip-cast samples forwarded on in this study were prepared with these conditions, since they showed the best and most stable rheological properties.

Decomposition study and burn-out

The temperature for burn-out was chosen according to the graph in Fig. 5, which shows thermogravimetry results for the thermal decomposition of slip cast yttria pellets containing 1 wt% of the ammonium poly(methacrylic acid) dispersant. Species that evolved during decomposition are related to the corresponding weight loss event on the first derivative of the thermogravimetry (DTG) curve.

At 900 °C, all the water and carbon-containing species have burned out, and virtually all the weight of the organic dispersant had been lost. A residual weight loss of only 0.33% remains after 900 °C. Note that the measurements were performed in helium, so that real burn-out in pure oxygen should ease the removal of organic material by decomposition into carbonic gases and water.

Among the other burn-out parameters, a slow heating rate was chosen to prevent gas entrapment. A long holding time ensures that as much organic material is removed as possible. Finally, cooling slowly prevents the brittle ceramics from undergoing thermal shock.

All samples—including the pressed pellets—were subjected to the same burn-out treatment for comparison's sake.

Density measurements

As shown in Fig. 6, there is a difference between the green body densities of slip-cast and pressed pellets as processed. Slip-cast samples show higher densities. This can be explained in terms of solid content and employed pressure for the slip-cast and pressed pellets, respectively, as explained in the following.

On one hand, the yttria slurries have a solid content of 60 wt%, which corresponds to 23 vol%. This is relatively low compared to what can be obtained with other metal oxide ceramics, but it was found to be the highest solid content allowing to keep apparent viscosity around 10 mPa s at 100 s^{-1}, which is a general rule-of-thumb for slip casting. Despite this low solid content, the slip-cast pellets reached nearly 37% densities in the green state and showed no cracks. This can be attributed to an efficient packing obtained from effectively dispersed secondary particles with the employed dispersant.

On the other hand, the low densities of pressed samples (~29%) can be explained in terms of the low pressure utilized during uniaxial pressing, i.e., 10 MPa. The role of this low pressure is only to obtain a solid compact with a desirable shape, and that can be handled for subsequent CIP.

The CIP step resulted in the same density for the two processing routes. Both the slip-cast and the pressed pellets had low densities (less than 40% theoretical density) before CIP, and therefore particle rearrangement and breakage of agglomerates was possible under the high pressure of CIP. The still relatively low densities obtained after CIP (~46%) can be attributed to the agglomeration state of the starting nanopowder, in the dry state, and in the slurry after milling. Figure 7 shows the cumulative curve of mass percentages finer over a range of equivalent spherical diameters from 0.2 to 20 µm for both the as-received powder and

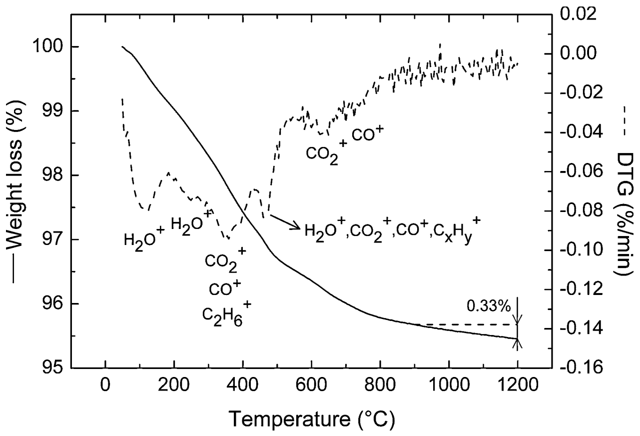

Fig. 5 Thermogravimetry/mass spectrometry curves for slip-cast yttria samples

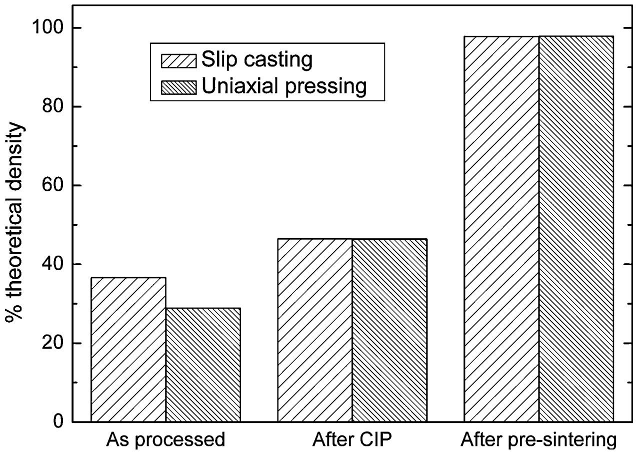

Fig. 6 Density comparison at various stages of processing

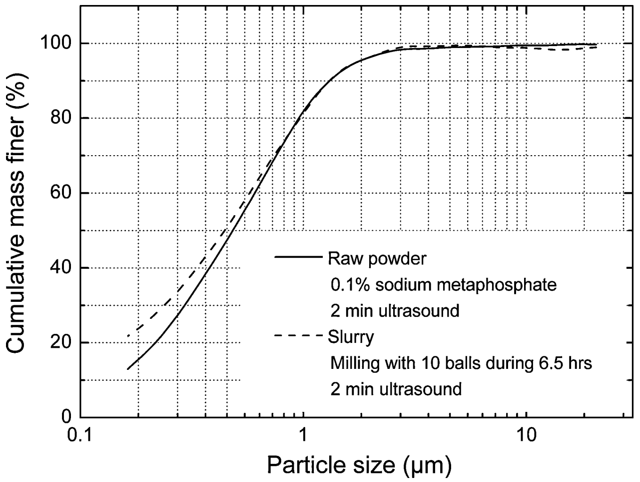

Fig. 7 Cumulative curve of mass percentages finer over a range of equivalent spherical diameters from 0.2 to 20 µm

after milling with 0.5% dispersant and 10 miling balls for 6.5 h. Both particle size distributions are fairly similar. In fact, ball milling had an effect on the population below 0.70 µm, but caused the median size to decrease only from 0.48 to 0.44 µm.

Similar pre-sintering densities were also obtained for the different processing routes, which is expected since the compared samples were prepared from a powder relatively unaffected by ball milling and exhibited the same green-body density after CIP.

Homogeneity of the final microstructure

Despite the slip-cast and pressed samples having very similar densities after CIP and pre-sintering, the homogeneity of the final microstructure after HIP differs, as can be seen in Fig. 8. In Fig. 8a, the pellet slip cast from a slurry containing 0.50% dispersant exhibits some translucency throughout the sample. In Fig. 8b, the pressed pellet exhibits excellent translucency only around the edges of the pellet, while the rest is barely translucent and dark.

Figure 9 shows the microstructures of the two pellets compared in Fig. 8, both in transmission and in reflection. Disregarding the origin and nature of optical scattering in both samples, comparison between Fig. 9a and b shows directly that the slip-cast sample is more homogeneous than the pressed sample. In fact, many macro-sized defects are present in the pressed samples, as indicated by the black arrows. They are less numerous and smaller in the slip-cast pellet. These large defects were identified as macropores and ranged between 50 and 100 µm. They must have been formed by hard agglomerates of at least this order of magnitude in size, giving rise to low-density regions during pressing. In fact, hard agglomerates in the dry powder can shield the surrounding smaller particles from pressure. Also, hard agglomerates pressed together will surround some large space, which can be seen as pores. Both types of packing inhomogeneities cause differential sintering, upon subsequent sintering, and macropores develop. Such defects are avoided in slip casting, because better mixing can be achieved in a liquid and ball milling helps break up such large agglomerates, although this cannot be ascertained in Fig. 7, since the measuring window stopped at 20 µm.

The greater microstructural homogeneity obtained by slip casting is confirmed by observation of the grain size in Fig. 9. In Fig. 9c, an average grain size of 10 µm is evenly distributed throughout the cross-section of the slip-cast sample. However, a strong gradient in grain size can be distinguished around the pressed sample in Fig. 9d and e. This gradient is contained within a layer of approximately 0.5 mm in thickness. Grain size ranges from 200 µm at the surface down to 0.5 µm in the dark part of the sample.

These microstructural inhomogeneities seem to be related to packing density. Recently, Li and Lannutti [17] demonstrated by X-ray-computed tomography that a skin with a density gradient is present around zirconia green-bodies made by uniaxial pressing and CIP, even when low pressure was used in the first step of uniaxial pressing. The zirconia powder that they employed had a close particle size

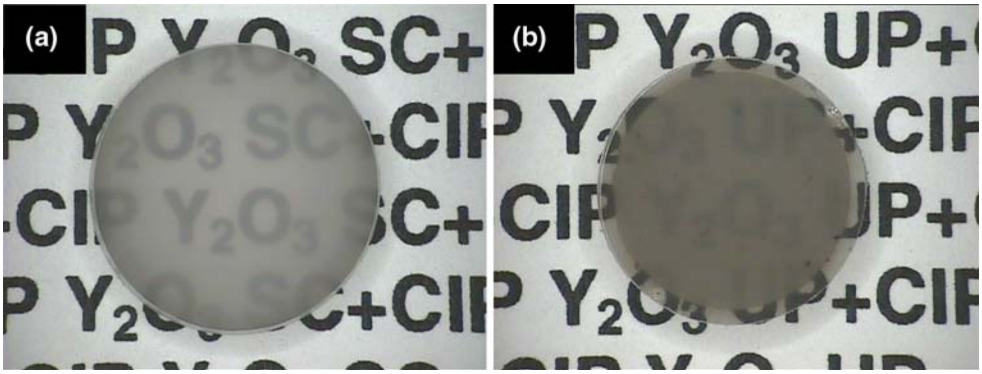

Fig. 8 Translucency comparison between 1 mm thick samples of (**a**) slip-cast yttria and (**b**) pressed yttria, after HIP

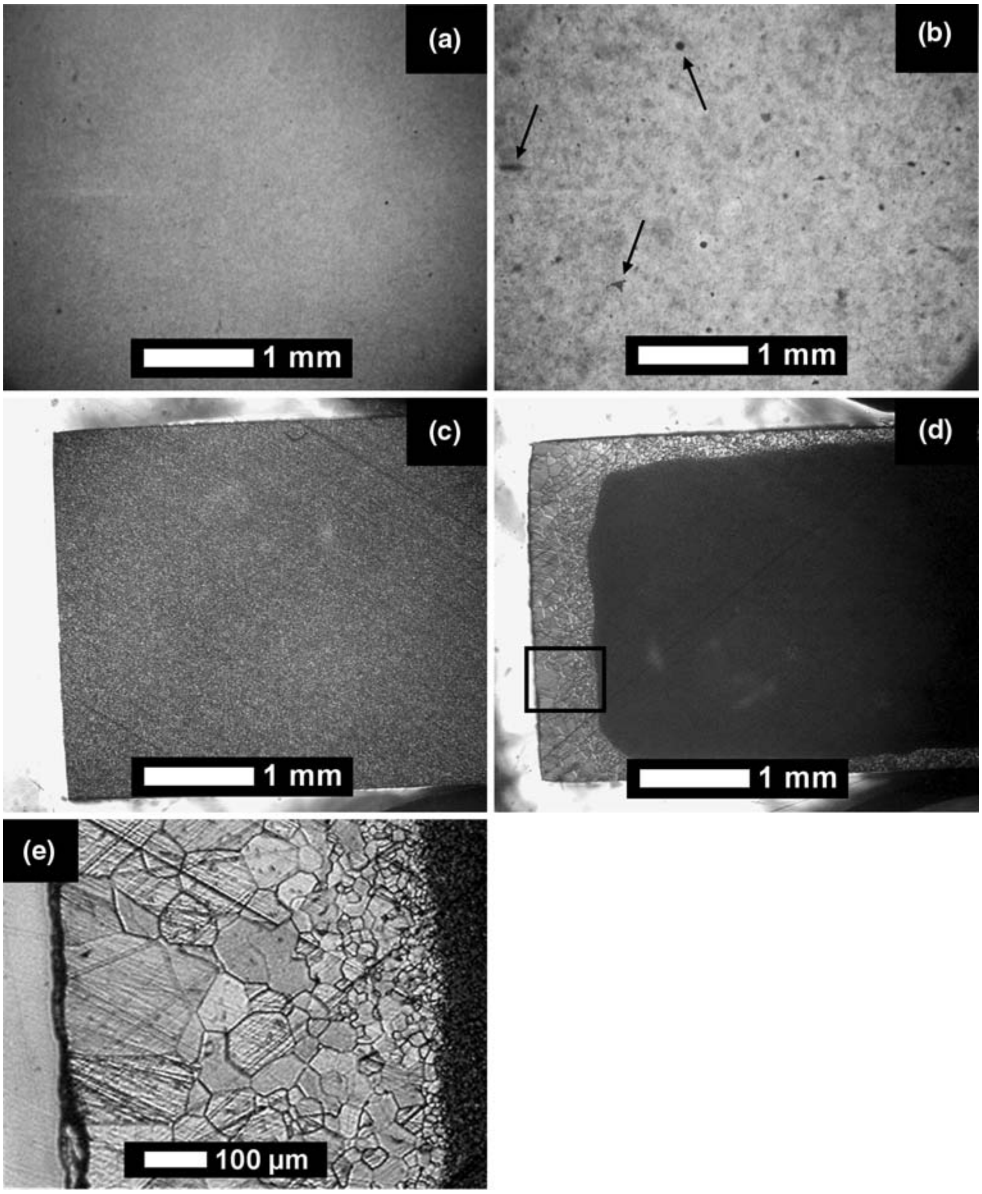

Fig. 9 Optical micrographs showing (**a**) the transmission of a pellet slip-cast from a slurry containing 0.50% Dispex, (**b**) the transmission of a pellet formed by uniaxial pressing, (**c**) the cross-sectional view of the same slip-cast pellet, (**d**) the cross-sectional view of the same pressed pellet, and (**e**) enlargement of the squared area in (**d**). *Note*: light blurry areas in the photo are due to defects in the lens system, not the samples

compared with the powder used in this work (50–100 nm). Therefore, these kinds of density variations are likely to be responsible for the observed grain size gradient, since regions with different packing densities are expected to show different sintering behaviors.

On the other hand, the homogeneity of the slip-cast pellet can be attributed to less density gradients during the compaction process, this state being conserved after CIP. Particles dispersed in a liquid can achieve a more homogenous packing arrangement in all directions during the slow process of slip casting, since they will all settle in the same way without being affected by friction against the die wall and/or pressure shielding.

Conclusion

First, this report shows that homogeneous slip-cast pellets can be obtained by using 60 wt% yttria slurries dispersed with an ammonium poly(methacrylic acid) salt dispersant. The optimum dispersant content giving minimum viscosity was found to be 0.50 wt%. The slurries showed a strong tendency to age and this was shown to increase with better disagglomeration of the starting powder. However, this problem can be handled by controlling the milling time and the number of milling balls. Increasing the latter is believed to introduce surface defects on yttria particles by mechanical action, thereby increasing dissolution and the aging rate.

Secondly, slip casting and uniaxial pressing were considered as first consolidation stages prior to CIP to produce green-body compacts for the fabrication of translucent yttria ceramics by a combination of pre-sintering and HIP. Although slip-cast and pressed samples exhibited close green-body density after CIP and pre-sintering, the samples that had been prepared by slip casting were more homogeneous in terms of translucency and microstructure throughout their bodies. This was attributed to the ability of slip casting to minimize density gradients during packing, and to the beneficial effect of ball milling to remove larger agglomerates before casting.

Therefore, slip casting as a first consolidation stage prior to CIP appears to be more suitable than uniaxial pressing for preparing homogeneous optical ceramics.

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