Powder injection molding of a mullite–zirconia composite

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ABSTRACT

Mullite–zirconia composites have been identified as a potential material for high-temperature structural applications due to high-temperature strength, thermal shock resistance, and low coefficient of thermal expansion. In the present study, the feasibility of using powder injection molding to fabricate parts from a mullite–zirconia composite was investigated. The properties of the developed feedstock were used to simulate and identify suitable molding conditions for fabricating parts like miniature turbine stators. A test coupon was successfully injection molded from the developed feedstock. The results from the study confirm the ability of powder injection molding to fabricate complex shapes made from mullite–zirconia composites.

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1. Introduction

Mullite is a candidate for high-temperature structural applications due to high melting point, low thermal expansion coefficient, thermal shock resistance, and high-temperature strength and creep resistance \cite{1-3}. However, the fracture toughness and low temperature properties of the material are poor \cite{4}. Conversely, partially stabilized tetragonal ZrO\textsubscript{2} polycrystals exhibit high room temperature strength and fracture toughness but have inferior mechanical properties at elevated temperatures \cite{4-6}. Thus, mullite–zirconia composites have the potential to address either of the shortcomings of the monolithic materials, depending on the selected composition \cite{7}.

Improved properties have been documented for mullite–zirconia composites over a range of compositions \cite{4,7-12}. Even so, the feasibility of using the materials is nevertheless hindered by processability. Machining is difficult due to the high hardness of the composites and so a method for fabrication of near-net shapes is needed \cite{12}. Powder injection molding (PIM) is one such a method that has shown success with a variety of powder systems and geometries \cite{13}. However, the PIM of mullite–zirconia composites has not been previously reported.
The present paper investigates the feasibility of using the PIM process to fabricate components from a mullite–zirconia composite in the zirconia-rich region. Simulations are also carried out based on feedstock properties to identify suitable processing conditions for injection molding a stator for a miniature gas turbine.

2. Methods

Commercially available high-purity mullite and ceria-stabilized zirconia powders were used as starting materials. Both powders were used in as-received condition at a zirconia rich composition of ~57 vol.% zirconia and ~43 vol.% mullite. A multi-component binder system composed of polypropylene, paraffin wax, linear low-density polyethylene, and stearic acid was used in the present study. This binder blend was developed based on past binder systems that showed feasibility for PIM processing [14]. The feedstock was mixed using an Entek co-rotating 27 mm twin-screw extruder with an L/D ratio of 40. A powder loading of approximately 84 wt.% was used.

Thermogravimetric analysis (TGA) of the mixed feedstock was carried out using a Q500 (TA Instruments). TGA experiments were carried out in nitrogen atmosphere at a heating rate of 20 °C/min for 50–600 °C temperature range. Analysis was also performed in air for the same temperature range and heating rate. Differential scanning calorimetry (DSC) measurements were carried out in nitrogen atmosphere using a Q2000 (TA Instruments) calorimeter over a temperature range of 20–200 °C and at a rate of 20 °C/min. Viscosity measurements were measured in accordance with ASTM D3835 (2008) on a Goettfert Rheograph 2003 capillary rheometer. Specific heat was determined on a Perkin Elmer DSC7 calorimeter. Testing was based on ASTM E1269 (2005) and was carried out on a K-System II system in accordance with ASTM D5930 (2001). Pressure-specific volume-temperature (PVT) measurements were made using high-pressure dilatometry on a Gnomix PVT dilatometer.

Test coupons were molded on an Arburg 221M molding machine. The green parts were debound and sintered in air at 1500 °C for 4 h. Hardness measurements were made in accordance with ASTM C1327 and fracture toughness was measured using Vickers indentation [15,16]. Mold filling simulations were performed using Autodesk Moldflow 2010 software.

3. Results and discussion

TGA was used to confirm the powder-to-binder-ratio after mixing. Fig. 1 shows the results of the TGA in nitrogen (top) and air (bottom). Both results show that the final composition of the mixture is close to 84 wt.% solids content. The results also confirmed the feasibility of a multi-step debinding process with lower molecular weight components burning off first followed by the higher molecular components [16]. Furthermore, TGA experiments helped identify the temperatures at which degradation of polymers start and finish. This information will be used in selecting limits for injection molding process and also in designing debinding cycles for removing the polymers. In air, the majority of the binder components primarily degrade below 300 °C, with a peak rate at ~280 °C. However, in nitrogen, two distinct steps are seen at around ~280 °C and ~450 °C, that are attributed to the low and high molecular weight constituents in the binder mixture [16]. The differences in the results between nitrogen and air carry important implications for the debinding process, as degradation of the organics is markedly slower in nitrogen than it is in air.

The differential scanning calorimetry (DSC) results for the feedstock is shown in Fig. 2. The melting temperature of the feedstock can be identified from the plot. The plot shows a melting of lower molecular weight components at ~140 °C and the higher molecular weight components at ~60 °C. The melting point information was used in selecting temperature during injection molding process.

Fig. 3 shows the rheological results for the mullite–zirconia feedstock. Viscosity was not strongly affected by temperature presumably due to the high solids content. However, a strong correlation between viscosity and shear-rate was
observed. The viscosity was found to decrease with increasing shear rate indicating shear-thinning or pseudoplastic behavior. The pseudoplastic behavior is advantageous for injection molding as shear thickening, or dilatant, materials can experience powder-binder separation during injection molding. The rheology data suggests that it is possible to process the mullite–zirconia feedstock by PIM for shear rates above 100 s$^{-1}$, as PIM has generally proven to be successful below 1000 Pa s for shear rates between $10^2$ and $10^5$ s$^{-1}$ [17]. Further, at a temperature of 160 $^\circ$C and a shear rate of 1000 s$^{-1}$, the viscosity of the mullite–zirconia feedstock was $\sim$100 Pa s, in general correspondence to previously reported values of viscosities of ceramic feedstocks based on the wax-polymer binder systems (100–500 Pa s) under similar conditions [18,19]. The slight variations in viscosity can be attributed to differences in particle shape and solids loading in the feedstock.

The results for thermal conductivity and specific heat measurements on the mullite–zirconia feedstock are shown in Figs. 4 and 5, respectively. The amount of heat retained by the material and the rate of heat conduction are important parameters for the injection molding process. Both properties will influence the cooling time and temperature of the melt at the flow front as well as other characteristics of the molding process. It is important to know how these properties vary with temperature as the feedstock undergoes transformation from solid to the melt state and back to solid state during the molding process. The thermal conductivity of the feedstock in general increased from 0.74 W/m K to 0.93 W/m K with increase in temperature from 30 $^\circ$C to 84 $^\circ$C and decreased to 0.71 W/m K with further increase in temperature to 185 $^\circ$C. The observed trend of thermal conductivity is understood to be due to changes in crystalline and amorphous phases of the binders in the feedstock with increase in temperature. A qualitatively similar trend in the variation of thermal conductivity with temperature was observed for other ceramic–polymer mixtures [18,19]. In the case of a silicon nitride feedstock the thermal conductivity values varied between 1.43 W/m K and 1.12 W/m K at temperatures range of 62–184 $^\circ$C [18]. For an aluminum nitride feedstock, the thermal conductivity values varied between 4.26 and 2.7 W/m K at temperature range of 42–163 $^\circ$C [19].

The specific heat data showed values ranging from 685 J/kg K at 0 $^\circ$C to 902 J/kg K at 170 $^\circ$C. A qualitatively similar variation of specific heat with temperature was observed for silicon nitride and aluminum nitride feedstocks [18,19]. The specific heat for silicon nitride feedstock varied between 790 J/kg K at 0 $^\circ$C and 1160 J/kg K at 170 $^\circ$C [18]. The specific heat for aluminum nitride feedstock varied between 920 J/kg K at 10 $^\circ$C and 1210 J/kg K at 150 $^\circ$C [19].

The pressure-specific volume-temperature (PVT) characteristics of the feedstock are shown in Fig. 6. The plot shows a decrease in specific volume with increasing shear stress and with decreasing temperature. This behavior is important to understand the shrinkage behavior of the component during the packing and cooling phases of the PIM process. The plot also shows that the transition temperature increases with increasing shear stress. The sharp transition seen in each curve marks the melting temperature at the given pressure.
and clearly separates the melt and solid domains. Melting temperatures are influenced by pressure and were observed to increase from approximately 64 °C to 103 °C as pressure increased from 0 MPa to 200 MPa. The feedstock volume increased with temperature, but temperature was observed to have a relatively lower effect on volume change as pressure increased.

A multi-slotted test part (shown in Fig. 7) was successfully injection molded, debound and sintered with the developed feedstock to confirm the feasibility of the process in fabricating complex shaped parts from the mullite–zirconia composite. Sintered parts showed relative densities greater than 99% and exhibited a linear shrinkage of ~20% relative to the molded state. The sintered specimens had hardness and fracture toughness values of 11.94 ± 0.26 GPa and 4.11 ± 0.28 MPa m$^{1/2}$, respectively. A prior published study reported a relatively lower hardness (~10.5 GPa) and fracture toughness (~3.5 MPa m$^{1/2}$) for mullite–zirconia samples sintered at the same temperature and time as the present study [20]. The higher hardness and fracture toughness obtained in the present study is attributed to the higher amount of zirconia and lower porosity in the composite. The enhanced mechanical properties in the present zirconia-rich mullite composite could also be attributed to higher densification rate, higher surface compressive stresses and to residual stresses formed at the grain boundaries due to difference in thermal expansion coefficient of mullite and zirconia based on comparison with previous reports [21]. The microstructure of the sintered sample (Fig. 8) shows predominantly bright grains consistent with a zirconia-rich composition.

Fig. 9 shows the miniature turbine stator that was used for simulation studies to investigate the feasibility of PIM process to fabricate complex shaped parts from the mullite–zirconia feedstock. Initially, mold-filling behavior was investigated using the recommended molding parameters based on the measured feedstock properties (Fig. 10). The mold and melt temperature used for the simulations were 23 °C and 150 °C, respectively. Under these conditions, the mold was filled completely in 0.44 s.

After achieving evidence of the ability of the feedstock to successfully fill the mold, a molding window analysis is performed. Fig. 11 shows a slice of the molding window obtained at a mold temperature of 20 °C for the material and the stator geometry. The preferred window encompasses injection times from 0.026 to 0.46 s over a 40 °C melt temperature range. This window is similar over the entire range of valid mold temperatures (20–30 °C) for the feedstock. Part quality is affected by several process parameters such as the melt flow front

![Fig. 7 – Multi-slotted test coupon.](image)

![Fig. 8 – Microstructure of the sintered mullite–zirconia composite. The bright regions confirm the presence of a zirconia-rich composition.](image)

![Fig. 9 – Miniature turbine stator part geometry.](image)
temperature, injection pressure, cooling time, maximum shear rate, and wall shear stress. As a result, an optimization analysis of these parameters will be needed in the future to determine the best combination of injection molding settings for the Mullite–zirconia feedstock.

Future work will focus on determining the optimal injection molding parameters for the composite feedstock to fabricate the engine part. Also, the effect of varying feedstock and composite composition will be explored. In tandem, the sintering characteristics of injection-molded parts and process–property relationships will be evaluated.

4. Conclusions

A feedstock for the injection molding of a Mullite–zirconia composite was developed. A test part was successfully molded, debound and sintered from the developed feedstock. The rheological and thermal properties of the feedstock were measured and used for mold-filling simulation studies of a miniature turbine stator geometry. The simulation studies identified suitable processing conditions for the injection molding of miniature turbine stators. The results from the study confirm the ability of PIM to fabricate complex shapes made from a Mullite–zirconia composite.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES


