POWDER INJECTION MOLDING OF MULLITE[1]

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Abstract
Mullite has be identified as a potential material for manufacturing gas turbine engine parts due to its properties like high temperature strength, good thermal shock resistance and low thermal coefficient of expansion. In the present study, the potential of using powder injection molding to fabricate parts from mullite 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 part 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.
Key words: Mullite; Powder injection molding; Miniature gas turbine.

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1 I\INTRODUCTION

Mullite is recognized as an excellent candidate for high temperature structural components due to its high-temperature strength, excellent creep resistance, good thermal shock resistance, and low thermal expansion coefficient properties. However, the low fracture toughness of mullite (~ 2.2 MPa·m$^{1/2}$) limits the use of the material in these types of applications.(1) Prior research study has showed that the fracture toughness of mullite is increased significantly with addition of partially stabilized zirconia [1]. The fracture toughness of partially stabilized zirconia obtained by addition of MgO, Y_2O_3, or CeO_2 is in the range of 6-9 MPa·m$^{1/2}$. This increase in fracture toughness is achieved due to a stress-induced martensitic phase transformation.(2)
Machining of mullite is difficult due to its inherent high hardness. Thus application of mullite to fabricate components depends on the ability to manufacture net shape parts requiring minimal machining. Powder injection molding (PIM) has a potential to fabricate parts from mullite due its ability to economically manufacture high volume, near net shape, complex parts. The present paper reports a study carried to understand the feasibly of using injection molding process to fabricate parts from mullite. Simulations were carried out based on the feedstock properties to identify suitable processing conditions for injection molding parts like miniature turbine stators.

2 MATERIALS AND METHODOLOGY

Commercially available high-purity mullite and ceria-stabilized zirconia powders were used as starting materials. Both powders were used in as-received condition. 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.(3)
The composition of the powder-binder mixture was determined by torque rheometry using an Intelli-Torque Plasticorder (CW Brabender). Scale up was done by extrusion using an Entek co-rotating 27 mm twin-screw extruder with an L/D ratio of 40. Thermogravimetric analysis (TGA) of the extruded 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°C-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°C-200°C and at a rate of 20°C/min. Viscosity measurements were measured in accordance with ASTM D3835(4) on a Goettfert Rheograph 2003 capillary rheometer. Specific heat was determined on a Perkin Elmer DSC7 calorimeter. Testing was based on ASTM E1269(5) and was carried out in a nitrogen atmosphere at 20°C/min. Thermal conductivity was measured on a K-System II system in accordance with ASTM D 5930.(6) Pressure-specific volume-temperature (PVT) measurements were made using high-pressure on a Gnomix PVT dilatometer. Mold filling simulations were performed using Autodesk Moldflow 2010 software.

3 RESULTS AND DISCUSSION

The results from torque rheometry are shown in Figure 1. The results show a rapid increase in torque with addition of powder to the powder-binder mixture. Torque equilibrates at a lower value after each addition until the critical solids loading condition is reached (88 wt% powder content in this case), past which the torque drops to zero. This zero torque condition indicates an excess of powder in the mixture inhibiting development of homogenous mix. The results from the torque rheometry can be used to identify the composition of powder-binder mixture for injection molding.

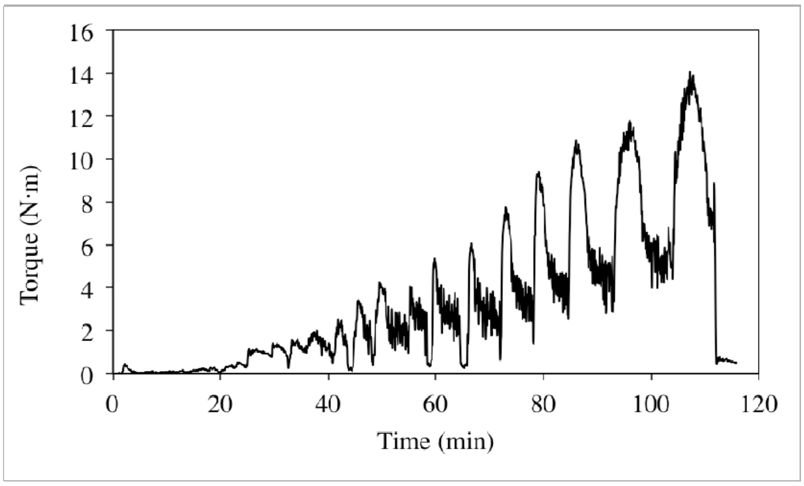

Figure 1. Torque rheometry plot for mullite powder-binder mixture.

The powder-to-binder ratio should be high in order to avoid slumping of the part upon debinding.(7) Figure 2 shows that the torque (which is proportional to the viscosity) increases exponentially as the powder content is increased highlighting sensitivity of small changes in powder content on the ability to process the material as the solids loading approaches critical. Thus, the optimal solids loading for injection molding is typically below the critical composition.(7) A feedstock with around 85 wt% powder content was targeted for scale-up by twin-screw extrusion based on the observed results.

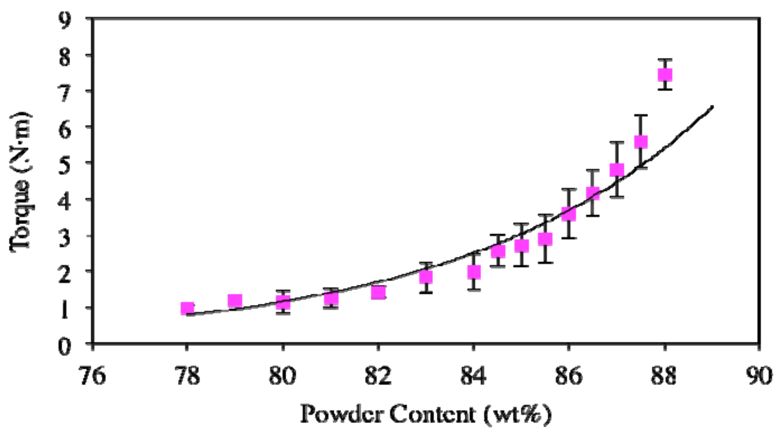

Figure 2. Effect of powder content on mixing torque behavior for mullite powder-binder mixture.

Thermogravametric analysis (TGA) was used to confirm the powder-to-binder-ratio after extrusion. Figure 3 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 multi-step debinding process with lower molecular weight components burning off first followed by the higher molecular components.[8] 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. 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.

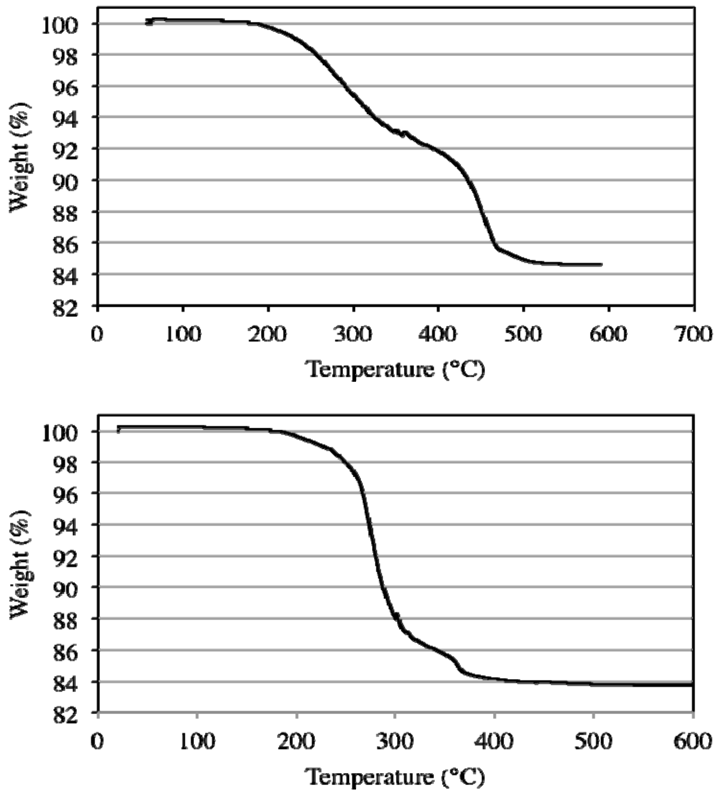

Figure 3. TGA of mullite feedstock in nitrogen (top) and in air (bottom).

The differential scanning calorimetey (DSC) results for the feedstock is shown in Figure 4. The melting temperature of the feedstock can be identified from the plot. The plot shows a melting of lower molecular weight components around 60°C and the higher molecular weight components at approximately 140°C. The melting point information was used in selecting temperature during injection molding process.

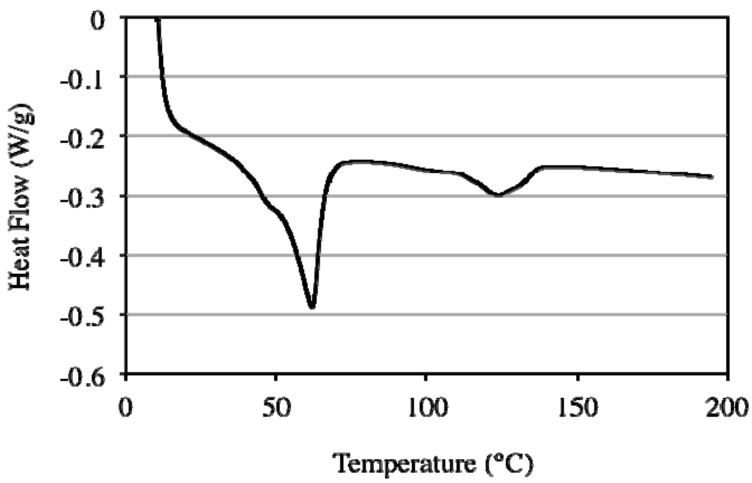

Figure 4. DSC of mullite feedstock.

Figure 5 shows the rheological results for the mullite 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 data shows that it is possible to process the mullite feedstock by powder injection molding for shear rates above 130 s^{-1}, as PIM has generally proven to be successful below 1.000 Pa·s for shear rates between 10^2-10^5 s^{-1}.[8]

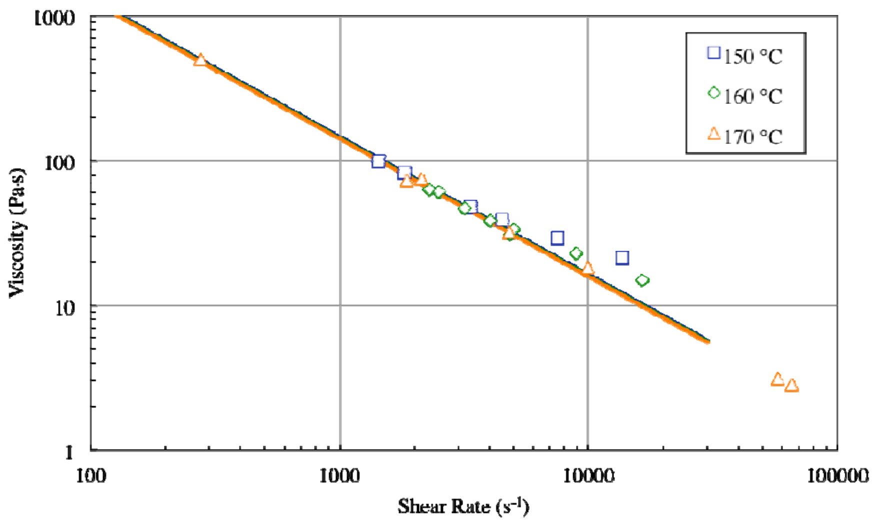

Figure 5. Rheological behavior of mullite feedstock.

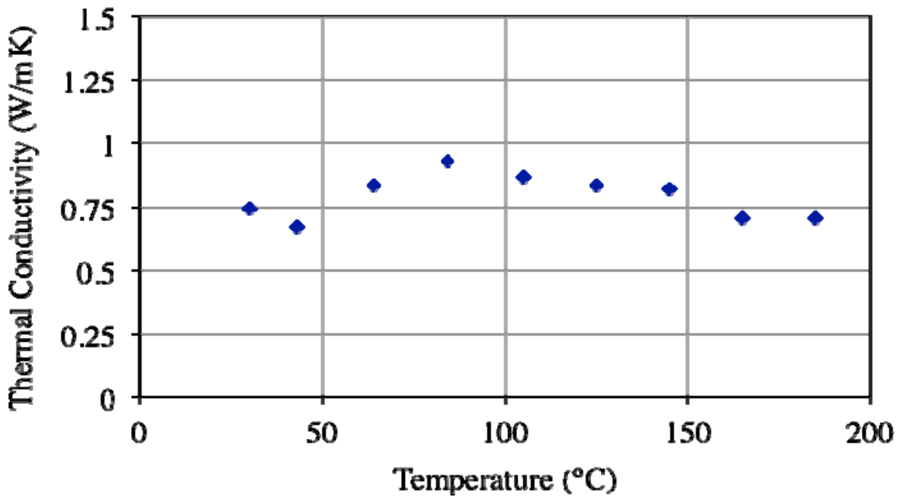

Figure 6. Thermal conductivity of the mullite feedstock.

The results for thermal conductivity and specific heat measurements on the feedstock are shown in Figures 6 and 7, 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.

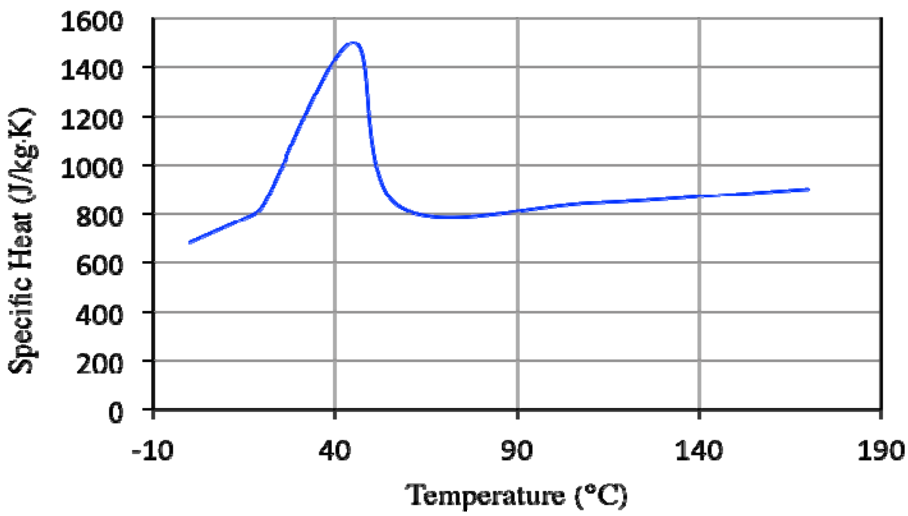

Figure 7. Specific heat capacity of the mullite feedstock.

The pressure-specific volume-temperature (PVT) characteristic of the feedstock is shown in Figure 8. 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.

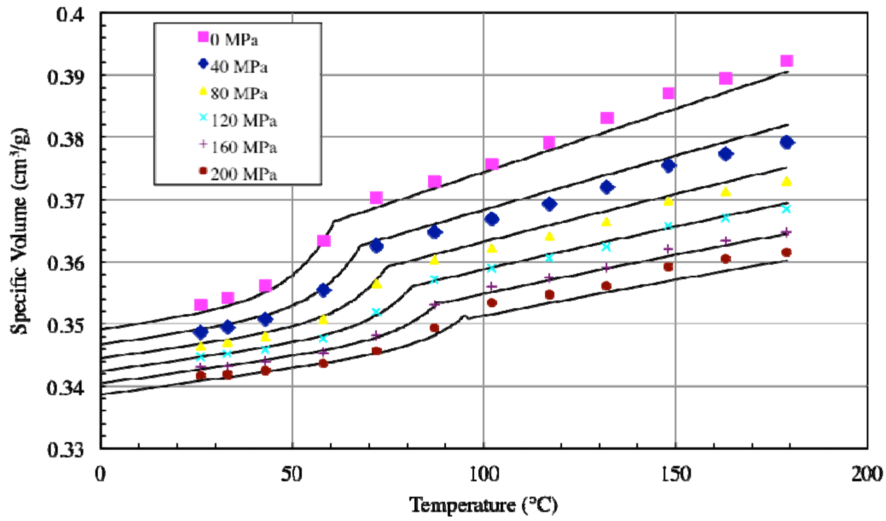

Figure 8. PVT behavior of the mullite feedstock.

A multi-slotted test part (Figure 9) was successfully injection molded, debound and sintered with the developed feedstock to confirm the feasibility of the process in fabricating complex shaped parts from mullite.

Figure 9. Multi-slotted test part.

Figure 10 shows the miniature turbine stator that was used for simulation studies to investigate the feasibility of powder injection molding process to fabricate complex shaped parts from mullite feedstock. Initially, mold-filling behavior was investigated using the recommended molding parameters based on the measured feedstock properties (Figure 11). 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.

Figure 10. Miniature turbine stator part geometry.

After achieving evidence of the ability of the feedstock to successfully fill the mold, a molding window analysis is performed. Figure 12 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 0.02 s to 0.46 s over a 40°C melt temperature range. This window is similar over the entire range of valid mold temperatures (20°C-29°C) for the feedstock.

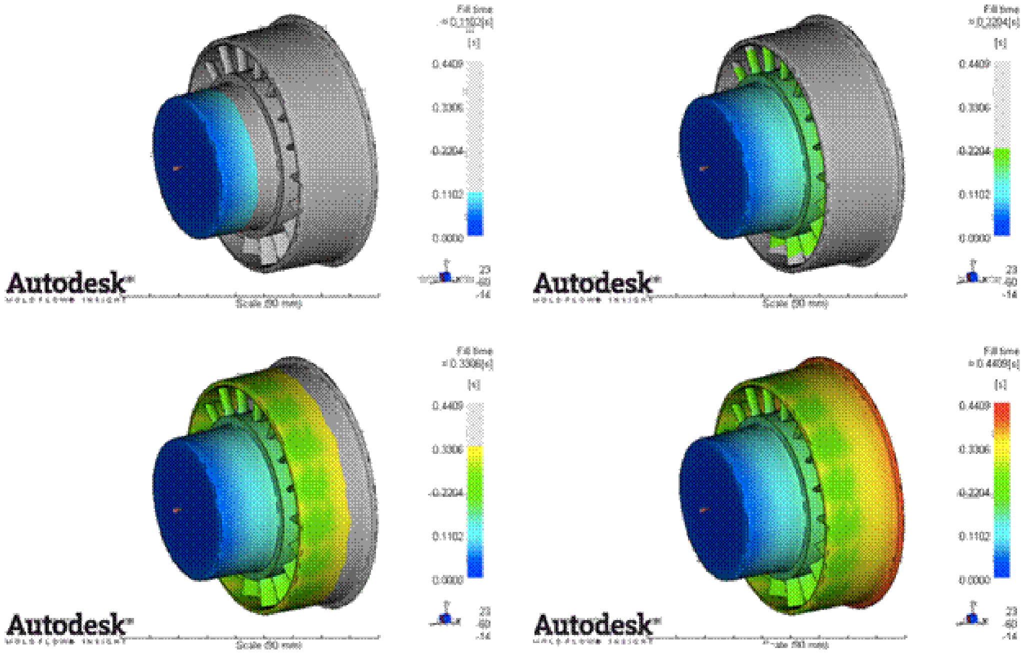

Figure 11. Progressive mold-filling behavior of mullite feedstock.

Quality plots of the molded part were also generated for the molding window (Figure 13). The plots give a measure of the overall part quality over the range of selected molding parameters (e.g. melt temperature). The plots are based on the quality indicators like flow front temperature, injection pressure, cooling time, shear rate, and shear stress. As part quality is a function of multiple parameters, an optimization analysis of these parameters will be needed to determine the best injection molding settings for the mullite feedstock.

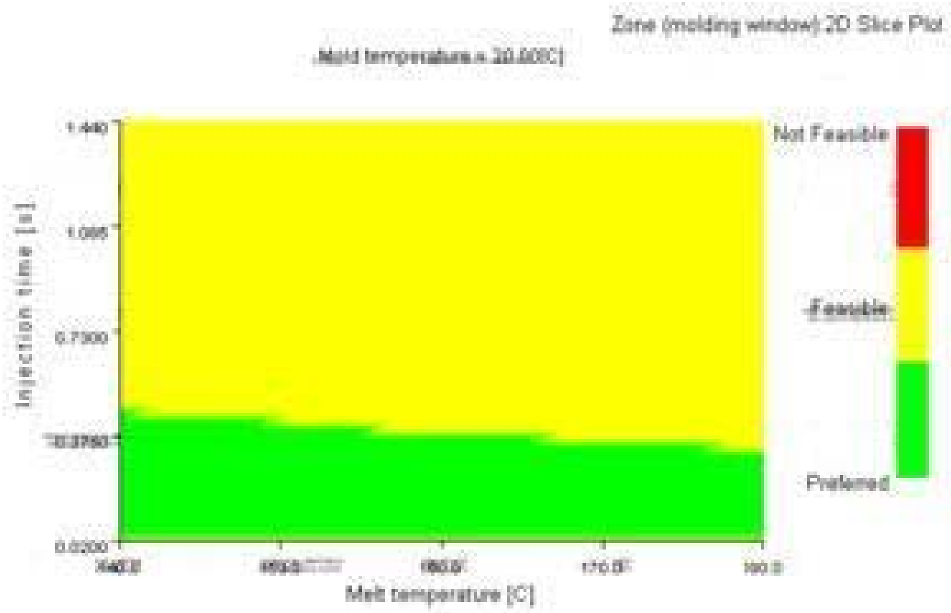

Figure 12. Molding window slice plot at a mold temperature of 20°C.

Future work will focus on determining the optimal injection molding parameters of mullite feedstock to fabricate the engine part. The sintering characteristics and mechanical properties of injection-molded part will also be evaluated.

5 CONCLUSIONS

A feedstock for injection molding mullite 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 simulation studies of PIM of gas turbine stators. The simulation studies identified suitable processing conditions for injection molding gas turbine stators. The results from the study confirm the ability of powder injection molding to fabricate complex shapes made from mullite.

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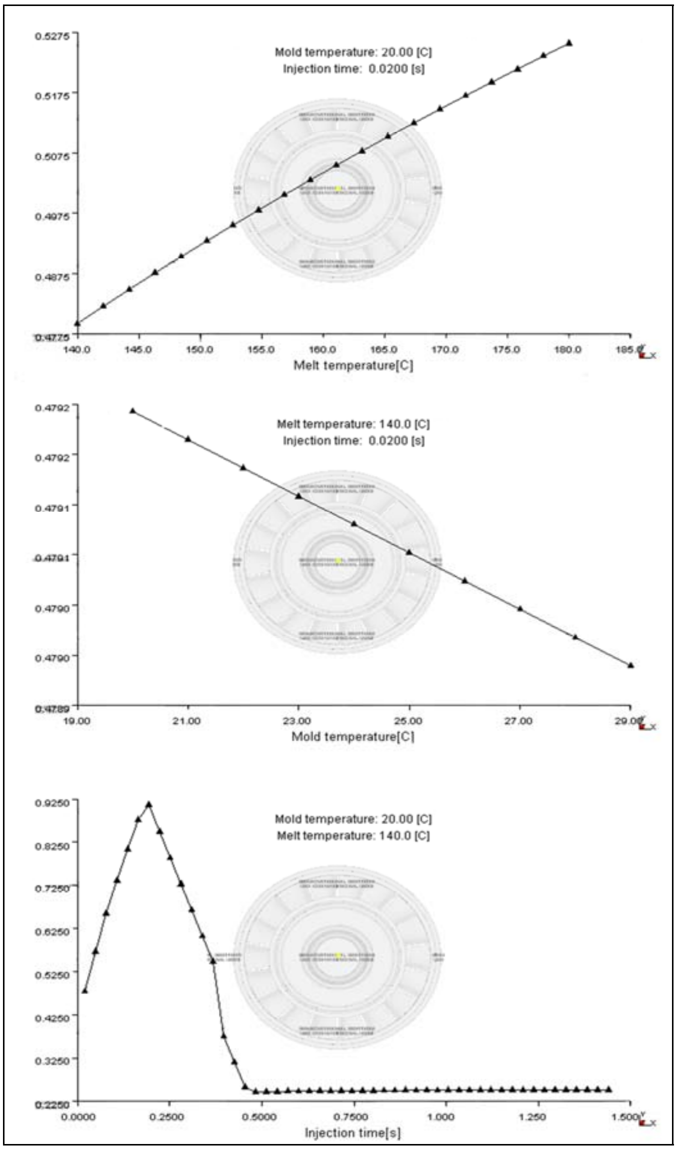

Figure 13. Part quality as a function of melt temperature (top), mold temperature (middle), and injection time (bottom).

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