Processing Development of Si₃N₄ Components by Injection Molding

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The development of complex-shaped ceramic components by powder injection molding has been considered as a promising technique by industry. In this study silicon nitride was used as a sample material for demonstrating the possibility of fabricating ceramic components by injection molding. An optimized process for the manufacture of components by injection molding will be presented. The effects of solid content, binder type, solvent and thermal debinding and effects of firing atmosphere will be discussed. Some promising physical and mechanical properties of sintered silicon nitride will be illustrated. Some prototypes will also be demonstrated. The developed technique could be extended for fabricating engine or functional components.
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Si$_3$N$_4$

- Oxidation and Corrosion Resistance
- Low Coefficient of Thermal Expansion
- High Toughness, Strength, Hardness
- Chemical Stability
The choice between silicon carbide, silicon nitride, and zirconia is determined mostly by the temperature and level of stress. Each material has its own domain in which it offers superior performance. Figure courtesy Asahi Glass Co., Japan.
Facing Challenge for Structural Ceramics

1. Cost Due to after Machining
2. Reliability

Figure 8.8. The energy concept in plane stress
<table>
<thead>
<tr>
<th>Composition</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon Nitride (powder)</td>
<td>81.5</td>
</tr>
<tr>
<td>Polypropylene (major binder)</td>
<td>11.2</td>
</tr>
<tr>
<td>Paraffin wax (minor binder)</td>
<td>4.8</td>
</tr>
<tr>
<td>Stearic acid (minor binder)</td>
<td>2.5</td>
</tr>
<tr>
<td>Diethyl phthalate (plasticizer)</td>
<td>trace</td>
</tr>
</tbody>
</table>

Table 3.2 Composition of injection molding blend.

Fig 3.1 Flow chart showing experimental procedure.
Fig 4.3 Viscosity - shear rate plots for silicon nitride suspension with solid contents of 55\% (O), 58\% (\Delta) and 60\% (\square) at 215\degree C.

Fig 4.2 Relative viscosity versus volume loading at a shear rate of 150\sec^{-1}.
Fig 4.6 Crack formed after solvent debinding in sample were injected at a pressure 1000 kg/cm².

Fig 2.2 Stress distribution for conventional injection molding and hold pressure of (A) 22 MPa (B) 43 MPa (C) 108 MPa. Ref: [17]
Fig 4.10 Pore distribution after solvent debinding.

Fig 4.5 Sample weight versus injection rate under various pressures.

\[ 215^\circ C, \ 550 \text{ kg/m}^2, \ 40 \text{ cm/s} \]
Fig. 4.2 TG analysis for DEP, SA, PW and PP

Fig. 1 DSC analysis of PW, SA and PP in air.
Fig. 4.17 Pore size distribution after solvent debinding and thermal debinding.

Cumulative Intrusion (mL/g)

Pore Diameter (µm)

Fig. 4.12 FTIR spectra of polymer at various debinding temperatures.

C=O: 5400
C-H: 2850
Fig. 4.10 Porosity Vs thermal debinding temperatures in three atmospheres

Fig 4.19 Model for debinding mechanism: (a) a schematic of molded body, (b) a schematic of binder distribution for solvent debinding, (c) a schematic of binder distribution at initial stage of thermal debinding and (d) a schematic of binder distribution at final stage of thermal debinding.
Table I. The density and strength of Si$_3$N$_4$ sintered under different atmospheres.

<table>
<thead>
<tr>
<th>Sintering atmosphere</th>
<th>$N_2$</th>
<th>$N_2+5%H_2$</th>
<th>air</th>
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<tbody>
<tr>
<td>Density(%TD)</td>
<td>95.5</td>
<td>94.8</td>
<td>93.5</td>
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<tr>
<td>Strength(MPa)</td>
<td>750</td>
<td>710</td>
<td>580</td>
</tr>
</tbody>
</table>
Fig 4.24 The elongated grain image of 2wt% seeding Si$_3$N$_4$ which was sintered at 1850 °C 1 hr in 10 atm N$_2$. (A) Bright field image, (B) dark field image, (C) HRTEM image of interface between A and B in (A), (D) EDS element analysis of A in (A), (E) EDS element analysis of B in (A).

Fig 4.24 Strength variation of samples with and without cold isostatic pressing.
Fig. 1: The frequency distribution of grain size in silicon nitride: (a) one-step sintered in graphite crucibles, (b) one-step sintered in BN graphite crucibles, (c) presintered at 1650°C and then sintered at 1900°C 3 h. in graphite crucibles, (d) presintered at 1650°C 1 h and then sintered at 1900°C 3 h. in BN crucibles.

Fig. 6: The normalized grain size distribution of silicon nitride sintered at 1900°C 3 h. Some samples were presintered at 1550°C, 1650°C 3 h before sintering.
Semi-infinite crack advanced, $\lambda$, through matrix compressive region toward particulate tensil region.
Fig. 3  SEM micrograph showing cross section of TiN-coated TiC.
1. Various shapes for injection molding.
Summary And Conclusions

[1] Processing for injection molding silicon nitride components was developed. Complex-shaped components with density of 97% TD and bend strength of 872 MPa were made successfully.

[2] Solvent debinding before thermal debinding substantially reduced the debinding time through the formation of open channels. A debinding model was proposed based on experimental observations.

[3] The defects were considerably reduced and strength was enhanced by cold isostatic pressing without significant dimensional changes.

[4] The debinding rate of Si₃N₄ under different atmospheres was in the order of air > N₂+5%H₂ > nitrogen. The density and strength were however, in an opposite order of nitrogen > N₂+5%H₂ > air.


[6] Properties of Si₃N₄ could be substantially enhanced through modification of microstructure, recrystallization of boundary phaser, and second-phase toughening.