The Effects of Nanoparticle Addition on Binder Removal from Injection Molded Aluminum Nitride

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Abstract

The effects of nanoparticle addition on the multi-step debinding of injection molded aluminum nitride (AlN) samples were studied. Experiments varying the solvent debinding conditions (time, temperature and aspect ratio) were performed on monomodal, microscale (µ) and bimodal, micro-nanoscale (µ-n) AlN samples. Variations in the solvent debinding kinetics as a result of the reduced particle size and increased powder content were examined. The bimodal µ-n AlN samples showed a slower solvent extraction of binder components compared to monomodal µ-AlN samples. The activation energy for solvent extraction estimated from diffusion coefficients (Arrhenius equation) was in close agreement with the value estimated by the master debinding curve (MDC) method. An activation value around 50 kJ/mole was estimated by both the methods for µ and µ-n AlN samples. The thermal debinding behavior of dewaxed samples was also studied and the trends correlated with the solvent debinding behavior.
1. Introduction

Binder systems play a vital role in determining the properties of the powder-polymer mixtures and their moldability [1]. Selection of an appropriate binder system is critical for the success of the powder injection molding (PIM) process [2-3]. Binder systems used in PIM comprise of multi-components with a major filler phase and minor backbone polymer along with little or no surfactants [4-11]. Following injection molding, binder removal (debinding) is required prior to the sintering stage. Various debinding techniques including solvent debinding [4-7], thermal debinding [8, 9] and catalytic debinding [10, 11] have been reported in the past. Irrespective of the techniques, the primary aim is rapid binder removal without any physical distortion of the injection molded green parts.

German had suggested a multi-step debinding process to expedite binder removal [12]. One common multi-step debinding process consists of solvent debinding followed by the thermal degradation of the remaining polymers. This initial binder removal presumably leaves interpenetrating pore channels, which allow the decomposed gas to escape during the subsequent thermal debinding step. Thus, the solvent debinding process shortens the debinding cycle significantly and has been widely accepted by the PIM industry [12, 13]. Lin et al [14] have proposed the existence of three stages of solvent debinding process. First, the solvent molecules penetrate into the binder, producing a swollen gel. When the binder-solvent interactions are strong enough, the gel gradually disintegrates into a true solution. The solution then diffuses toward the surface and thus removed. Rapid binder removal may result in defects such as cracking, distortion, and slumping [13-16]. A successful solvent debinding process thus depends on the diffusion controlling factors including the temperature [17-21], time [17-19, 21], solvent [19] and aspect ratio [17-18, 21] of the samples.

Prior studies have attempted to understand the effect of the several processing parameters on debinding kinetics [1, 17, 22]. However, little research pertaining to the effect of powder particle content and particle size distribution on the debinding kinetics is available till date. Our prior report on AlN and SiC injection molding demonstrated the use of bimodal mixtures of microscale (µ) and nanoscale (n) powders as an efficient way to improve the solids loading [23, 24]. Successful manufacturing of components
utilizing the increased solids loading greatly depends on the ability to successfully expedite removal of binders without causing defects or residual carbon content. The carbon residue formed due to improper burnout of polymer affects the thermal conductivity of polycrystalline AlN. For example, it has been shown by Tajika et al that a small amount of carbon, ≤0.3 wt. % reduces the oxygen impurity level, thus enhancing the thermal conductivity [26]. On the other hand, carbon ≥0.5 wt. % is extremely detrimental to the thermal conductivity due to a decrease in the sintered density of AlN [27].

In the current paper, the effect of nanoparticle addition on the solvent debinding kinetics of injection molded AlN samples was studied. The work was also extended to studying the variations in the residual binder content due to nanoparticle addition during the thermal debinding cycle.

2. Experimental Materials and Methods
Commercially available AlN (~1 μm and ~20 nm) and Y₂O₃ (~50 nm) were used as the starting materials in as received condition. A multi-component binder system comprising of paraffin wax (PW), polypropylene (PP), polyethylene-g-maleic anhydride (LDPE-g-MA) and stearic acid (SA) was used in the current study. The formulations and injection molding conditions for the monomodal and bimodal AlN powder-binder mixtures were discussed elsewhere [24]. In this study, bimodal μ-n AlN mixtures contained 82 wt.% larger (μ) and 18 wt. % finer (n) AlN powder. Further, 5 wt.% Y₂O₃ was added on the basis of AlN. Table 1 lists the composition of the injection molded AlN samples used in the present study. The SEM images of the starting powders used in the study are shown in Figure 1. The binder composition was chosen in such a way to facilitate a multi-step (solvent, thermal) debinding. Heptane (Fischer Scientific) was used as the solvent to dissolve the soluble binder components without any further treatment.

Injection-molded, green samples were machined to the dimensions (l×b×h in mm) of 23 × 13.2 × 7.2, 34.5 × 6.6 × 7.2 and 25 × 14 × 2, which correspond to a shape factor (ψ, volume-to-surface area ratio (V/SA) of 1.94, 1.56, and 0.82 mm, respectively. Isothermal solvent debinding experiments utilizing five specimens of each dimension were
performed in heptane at 20, 40 and 60 °C under slow and continuous stirring. The continuous solvent recycling at 2ml/min was performed to avoid concentration effect of soluble components [17, 18]. All specimens were placed together into the solvent bath and were removed at each time-point for weight loss and gravimetric analysis. The solvent debinding was monitored up to 4 h. The fraction of the soluble binder remaining ($f$) can be calculated as:

$$f = 1 - \frac{w_o - w}{f_o w_o}$$  \hspace{1cm} (1)$$

where, $f_o$ is the initial weight fraction of soluble binder, $w_o$ is the initial mass of compact, and $w$ is the instantaneous mass of compact.

To verify the specimen weight loss during solvent debinding, thermogravimetric analysis (TGA) was performed (TA instruments - Q 500) under nitrogen atmosphere (50ml/min) at a heating rate of 20 °C/min. The TGA analysis to confirm the amount of paraffin wax removed by solvent extraction was carried out by heating the solvent debound samples to 600°C. Heating the samples to 600°C results in complete burnout of residual paraffin wax from solvent debinding as well as the remaining backbone polymers. The high temperature was chosen to verify any effect of residual paraffin wax on the burnout of remaining polymers and to design appropriate thermal debinding cycles. The Furthermore, scanning electronic microscopy (SEM) (QuantaTM – FEI) images were taken on both the surface and core of the samples to examine pore evolution. Thermal debinding cycles of the solvent debound samples were performed under inert atmosphere in the CM 1212 FL furnace. TGA was once again performed on the thermally debound samples to determine the % residual binder.

3. Results and Discussion

During the solvent debinding process, heptane diffuses into the sample to dissolve paraffin wax and stearic acid. As the molecular weight of the heptane is significantly lower that the molecular weights of the binders, heptane likely diffuses into the sample faster than the paraffin wax and stearic acid diffuse out of the sample. Consequently, the rate-limiting step is assumed to be the diffusion of the dissolved paraffin wax and stearic acid molecules rather than the inward diffusion of the much smaller heptane molecules.
Zaky reported a similar observation for the removal of paraffin wax with hexane [19]. Additionally, Omar et al have determined such a trend the removal of for polyethylene glycol with water [7]. The effects of factors such as the component shape parameter, $\psi$, immersion time and temperature on the removal of binder molecules were examined in the present study.

Figures 2 and 3 show the soluble binder extracted (%) in heptane at different time-temperature combinations from AlN samples with different $\psi$ values. The bimodal $\mu$-n AlN samples showed larger fractions of soluble binder remaining compared to monomodal $\mu$-AlN samples at any given value of time, temperature and $\psi$. Further, increasing $\psi$ results in an increase in debinding times. Previously, Oliveira et al [17] and Krauss et al [18] have reported similar results for injection-molded, alumina parts. Irrespective of the $\psi$ value, the debinding rate was found to reduce with increase in the time. A similar behavior has also been reported earlier by Oliveira et al [17], Krauss et al [18] and Zaky in stainless steel molded parts [19]. With increasing solvent immersion time, the soluble components inside the samples diffuse through tortuous pathways, from inner regions to the specimen surface, leading to a reduction in the debinding rate. Increasing the solvent temperature was found to exhibit an improvement in debinding process efficiency for all specimen dimensions. This can be attributed to an increase in solubility of paraffin wax and stearic acid in heptane as function of temperature. In prior studies, Omar et al [7] and Tsai et al [15] observed similar temperature effects on the solubility of binders. No dimensional change was noticed with the samples irrespective of the solvent debinding conditions. These findings are however in variance with those of Zaky [19] and Wang et al [21] where dimensional change/swelling is reported when hexane is used as the solvent under similar conditions.

3.1. Confirmation Studies

To evaluate the total binder composition change in the samples during solvent debinding, thermogravimetric analysis (TGA) was performed. Figure 4 show the TGA curves for AlN samples with the ranges of 200–375 °C and 380–490 °C, respectively. The TGA results were in agreement with the initial proportion of binder components of the prepared feedstock. Higher limiting values of residual weight in the bimodal $\mu$-n AlN
samples reflect the higher solids loading of powder compared to the monomodal µ-AlN samples. As solvent debinding time increased, the composition varied due to a decrease in weight loss in the first degradation step, indicating the decrease in the soluble binder components. A relatively higher weight loss was observed in the 200-375°C range relative to the 380–490 °C for the bimodal µ-n AlN samples when compared to the monomodal µ-AlN samples. Oliveira et al reported similar trends for injection-molded, alumina samples [17]. After solvent debinding for 240 minutes, only the weight loss of the backbone polymer was observed in the TGA data, suggesting complete removal of soluble components.

Figures 5 and 6 shows the SEM micrographs of AlN samples at surface and core after different solvent debinding times. The micrographs prior to solvent debinding (Figures 5a, 5b, 6a, 6b) show parts filled with polymers at surface and core locations. After debinding for 15 and 30 minutes, the presence of large pores confirming the extraction of paraffin wax at the surface of the samples can be seen in both µ-AlN and µ-n AlN samples (Figures 5c, 6c). The pores at the surface of the samples are much larger in size compared to core (Figures 5d, 6d) indicating the progress of solvent extraction of paraffin from surface to the core of the sample. The micrographs after solvent debinding for 120 minutes for µ-AlN (Figures 5e, 5f) show a change in morphology of the polymer in the samples. Strands of backbone polymer can be observed in the micrographs confirming complete removal of paraffin wax. The micrographs for µ-n AlN (Figures 6e, 6f) after solvent extraction for 240 minutes showed no major change in the polymer morphology suggesting incomplete removal of paraffin wax. The observations confirm slower solvent extraction in µ-n AlN compared to µ-AlN and are in agreement with the results obtained from solvent debinding weight loss and TGA experiments.

3.2. Solvent Debinding Characteristics

From the Figures 2-3, it can be inferred that the bimodal µ-n AlN samples exhibit slower polymer removal than the monomodal ones irrespective of the debinding conditions. This can be attributed to the increase in the tortuous path to be followed by the binder components. Such behavior can be attributed to the combined effect of increased solids loading (lower % porosity) and decreased pore size via nanoparticle addition. In order to
separately analyze the effect of such nanoparticle addition from the solids loading effect, the Kozeny-Carman relation (Eq. 2) can be used to determine the permeability \( k \) [22].

\[
k = \frac{2d_p^2(1-\varepsilon)^3}{75\varepsilon^2}
\]  

(2)

where, \( \varepsilon \) is the porosity (=1-solids loading) and \( d_p \) is the average particle size. As seen in Eq. 2, the permeability is directly proportional to the square of the average particle size.

The mean particle size for the monomodal \( \mu \)-AlN is \( \sim 1 \) \( \mu \)m. In contrast, the average particle size for the bimodal \( \mu \)-n AlN can be estimated from the inverse rule of mixtures to be \( \sim 0.2 \) \( \mu \)m. Thus, addition of nano size particles has a major effect on reduction in permeability resulting in slower debinding compared to micron size monomodal samples. In the present study significantly higher permeability values were estimated for monomodal \( \mu \)-AlN compared to bimodal \( \mu \)-n AlN samples. For example at 51 vol. % solids loading, the permeability value decreased from \( 6.90 \times 10^{-15} \) cm\(^2\) to \( 0.24 \times 10^{-15} \) cm\(^2\) with the addition of nano AlN particles. It is interesting to note that in contrast to the large differences in permeability estimated by the Kozeny-Carmen relationship, the differences in solvent debinding rates for bimodal \( \mu \)-n AlN and monomodal \( \mu \)-AlN samples is relatively smaller. This indicates that despite the addition of nanoparticles and the higher solids loading, practical solvent debinding times can still be achieved without introducing defects in the samples.

At room temperature, the dissolution of paraffin wax in heptane is the likely rate limiting step in the beginning of the debinding process over a leaching time of 120 min. Polymer removal during the dissolution controlled stage is twice as fast as the removal during the diffusion limited stage at later times. As the process proceeds, longer diffusion distance through porous channels formed after initial debinding slows down the process and diffusion becomes the rate-determining step. Solvent debinding is predominantly diffusion-controlled process that can be represented as [1, 22]:

\[
\ln \left( \frac{1}{F} \right) = \frac{D_t \pi^2}{\psi^2} + K
\]  

(3)
where, $F$ is the fraction of the remaining soluble polymer, $\psi$ is the component shape parameter, $D_e$ is the inter-diffusion coefficient of polymer and solvent, $t$ is the debinding time and $K$ represents the change in the mechanism controlling the debinding behavior. The plots of $\ln (1/F)$ and $t/\psi^2$ for solvent extraction of paraffin wax at 60°C for monomodal $\mu$-AlN and bimodal $\mu$-n AlN samples used in the present study are shown in Figure 7. The figure clearly shows slower removal of paraffin wax for bimodal $\mu$-n AlN samples compared to $\mu$-AlN.

The diffusion coefficients ($D_e$) calculated from the slope of the plot $\ln (1/F)$ as a function of immersion time of the samples in the present study are summarized in Table 2. The diffusion coefficient ($D_e$) increased with increase in temperature for both $\mu$-AlN and $\mu$-n AlN samples. Higher $D_e$ values observed for increasing temperatures are possibly due to the increased solubility of the paraffin wax in heptane. Irrespective of the sample aspect ratio and solvent temperature, the bimodal $\mu$-n AlN samples showed lower $D_e$ values than the corresponding monomodal $\mu$-AlN samples. This may be due to the decreased rate of the binder-solvent interactions due to the nanoparticle inclusion. These observations require additional work using techniques like intrusion porosimetry to understand the reasons behind the experimental findings.

The diffusion coefficients ($D_e$) data was further analyzed to estimate the activation energy for the extraction of paraffin wax as:

$$D_e = D_e \exp\left(\frac{-Q}{RT}\right)$$

where, $Q$ is the activation energy for solvent extraction, $R$ is the universal gas constant and $T$ is the temperature. The activation energies for extraction of paraffin wax for $\mu$ and $\mu$-n AlN samples was estimated to be around ~ 45 +/- 5 kJ/mol.

The activation energy for solvent extraction was also estimated using the master decomposition curve (MDC) method. According to MDC concepts [25], the work for solvent extraction ($\Theta$) is related to temperature as:

$$\Theta(t,T) = \left(\frac{1}{\psi^2}\right) \int_0^t \frac{1}{T} \exp\left(\frac{-Q}{RT}\right) dt$$

Here, $\psi$ is the component shape parameter, $D_e$ is the inter-diffusion coefficient of polymer and solvent, $t$ is the debinding time and $K$ represents the change in the mechanism controlling the debinding behavior.
The value of $Q$ at which $F$ vs ln ($\theta$) for samples of different sizes merge into one curve is estimated as the activation energy of the solvent extraction process [25]. The $F$ vs ln ($\theta$) for $\mu$ and $\mu$-n AlN samples for different values of $Q$ is shown in Figure 8. The MDC analysis yielded an activation energy value of 55-60 kJ/mol for the monomodal $\mu$-AlN and bimodal $\mu$-n AlN samples respectively.

The activation energy values estimated by Arrhenius equation are slightly lower for the estimated values based on MDC method. The estimated activation energy values were also in general agreement to activation energies obtained for solvent debinding of other paraffin wax-polymer particulate systems in the literature ($\sim 42 +/- 5$ kJ/mol) [25]. The absence of significant variations in activation energies between monomodal and bimodal systems suggest that there are no fundamental mechanistic changes in binder removal during solvent debinding owing to the addition of nanoparticles, in the systems studied.

3.3. Thermal debinding of solvent debound samples

The solvent debound parts with partially open pores were subjected to thermal debinding to further remove the binders. Based on the TGA plots discussed earlier as the basis, a thermal profile for the debinding was developed. An initial heating up to 300°C at the rate of 2°C/min and a hold of 2 h was used to ensure the complete removal of the leftover filler phase from the solvent debinding step. The sample was further heated to 500 °C at the rate of 2 °C/min and kept at different hold times to remove the backbone polymers. Variations in the hold time are required to minimize the residual weight of the binder in the debound parts. As shown in the Table 3, the residual weight of bimodal $\mu$-n AlN debound sample was reduced to 0.28wt. % when held at 500 °C for 7 h. However, $\mu$- AlN samples required only 5h to attain a residual weight to 0.28 wt. %. The requirement for higher hold time in bimodal samples can be seen as the possible result of nanoparticle addition leading to more tortuous path for the degraded products to follow. Additionally, sintering studies showed lower shrinkage and densification at significantly lower temperatures for $\mu$-n AlN compared to $\mu$- AlN samples [28]. Thus, while the addition of nanoparticles assist in increasing in solids loading and achieving lower shrinkage and rapid densification on sintering, the slower debinding rate should also be taken into consideration in working with these systems.
4. Conclusions

The removal of binder by solvent extraction and thermal debinding from injection-molded monomodal and bimodal AlN samples were analyzed. The present study indicates that bimodal $\mu$-n AlN samples had relatively lower debinding rates compared to $\mu$-AlN samples. The combined effect of increased powder content and reduced average particle size via nanoparticle addition can be attributed as reasons for such behavior. However the differences in solvent debinding rates as a result of nanoparticle addition are much smaller than what permeability estimates suggest. The activation energy for solvent extraction estimated from diffusion coefficients and master decomposition curve concepts were in close agreement. No significant difference in activation energy for solvent extraction was observed for bimodal $\mu$-n AlN samples compared to monomodal $\mu$-AlN samples, indicating and absence of any major mechanistic changes in solvent debinding as a result of nanoparticle addition. The present study confirms that despite the addition of nanoparticles and the higher solids loading, practical solvent debinding times can still be achieved without introducing defects in the samples.
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<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Surface</th>
<th>Core</th>
<th>Soluble binder extracted (%)</th>
</tr>
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<tr>
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<td><img src="image6.png" alt="Image" /></td>
<td>100</td>
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</table>

**Figure 5**: SEM micrographs of μ-AlN samples ($\psi = 0.82$) after debinding in heptane at $40\,^\circ\text{C}$, as function of immersion time
Figure 6: SEM micrographs of μ-n AlN samples ($\psi = 0.82$) after debinding in heptane at 60 °C as function of immersion time
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Table 1: Composition of AlN samples tested in the current study

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solids loading (vol.%)</th>
<th>Soluble binder content (vol.%)</th>
<th>Soluble binder content (wt.%)</th>
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<tr>
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<tr>
<td>Bimodal AlN</td>
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<td>19</td>
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Table 2: Diffusion coefficients of monomodal and bimodal AlN samples.

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<th>Shape factor</th>
<th>AlN (10^{-7}cm^2/sec)</th>
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<td>µ-µ-n</td>
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<tr>
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Table 3: The effect of debinding hold time on the % residual weight of binder in AlN samples

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<th>Hold at 500°C (h)</th>
<th>% residual weight of binder in AlN</th>
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