

Bimodal powder mixtures for the powder injection molding of SiC and AlN

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ABSTRACT

In this paper, we studied the effect of nanoparticles addition on the green density and sintering of injection molded SiC and AlN. Using a bimodal powder mixture increased the solids loading for SiC and AlN systems, respectively. The nanoparticles addition also improved the sinterability of SiC and AlN by reducing the liquid phase formation to 1800 and 1500 °C, respectively. Around 99.3% density is obtained for bimodal μ -n AlN system when pressureless sintered at 1650 °C.

Keywords: SiC, AlN, bimodal, PIM, sintering

1 INTRODUCTION

Silicon carbide (SiC) and aluminum nitride (AlN) exhibit thermal and mechanical properties (**Table 1**) of relevance to applications in electronics, aerospace, defense and automotive industries [1-4]. A successful translation of these properties into final applications depends on the fabrication of these ceramics into fully dense microstructures.

Table 1: Properties of sintered SiC and AlN ceramics

Property	SiC	AlN
Density (g/cc)	3.2	3.26
Thermal Conductivity (W/m.K)	120	170
CTE ($10^{-6}/^{\circ}\text{C}$)	4	4.5
Vicker's Hardness (GPa)	22	10.4
Fracture Toughness ($\text{MPa}\cdot\text{m}^{0.5}$)	4.5	2.6
Flexural Strength (MPa)	450	320
Volume Resistivity ($\Omega\cdot\text{cm}$)	10^{14}	$>10^{14}$

High sintered densities are required for attaining preferred values of thermal and mechanical properties. For example, She and Ueno studied the effect of varying the amount of $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ as the sintering aids over the % porosity [5]. Similarly, Sciti and Bellosi compared the combinations of $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ and $\text{La}_2\text{O}_3\text{-Y}_2\text{O}_3$, as the sintering aids for the SiC densification [6]. Sintering temperature and hold time were the commonly studied process parameters in the past. For example, Junior and Shanafield [4] and She and Ueno [5] reported the increase in the sintered density with the increase in the sintering temperature. On the other hand, Rodriguez et al [7] and Izhevskiy et al [8] noticed an increase in the sintered density with higher hold time at the sintering temperature.

In this paper, we tried to improve the green density of the feedstock by blending two different particle sizes [9, 10]. Such a bimodal mixture was selected in such a way that the smaller particles fit into the interstitial spaces between the larger particles without forcing them apart. In the present work, bimodal μ -n SiC and AlN were mixed in different ratios along with their sintering aids. The effect of varying the nanoparticle content over the solids loading was studied and composition providing the maximum solids loading was thus chosen. The formulations were then scaled up and injection molded to provide the “green” samples. Powder injection molding (PIM) was chosen as the net-shaping technique so as to fabricate complex part geometries at a higher production rate. Following the molding cycle, the polymer was removed by solvent and thermal debinding. The debound “brown” samples were then sintered and measured for densities and weight loss.

2 EXPERIMENTAL SECTION

2.1. Materials

Commercially available α -SiC, AlN, Y_2O_3 were used as the starting materials as received. Multi-component binder system comprising of paraffin wax, polypropylene, polyethylene and stearic acid was used in the current study. The binder composition was chosen in such a way to facilitate a multi-step (solvent, thermal) debinding.

2.2. Instrumentation

Torque rheometry (Intelli-Torque Plasticorder - Brabender) was performed to determine the composition (critical solids loading) of SiC and AlN feedstocks. The formulations determined were scale-up with a co-rotating twin-screw extruder (Entek Extruders, OR). Thermogravimetric analysis (TGA) (TA-Q 500) and differential scanning calorimetry (DSC) (TA-Q 1000) were done to shortlist the molding temperatures. Arburg 221M injection molding machine was used to shape the “green” SiC and AlN samples. All sintering experiments were conducted in the CPF-tube furnace systems (Thermal Technology LLC) with no external pressure. The sintered densities were measured via Archimedes apparatus. The micrographs of the samples were taken with the QuantaTM -FEG (FEI) dual beam electron microscope.

3 RESULTS AND DISCUSSION

3.1 Feedstock Formulation and Scale-Up

Torque rheometry was performed to determine the powder fractions required to achieve a homogenous bimodal powder-polymer mixtures. The binder components were melted first at 160 °C and bimodal powders premixed with the sintering aids were then slowly added.

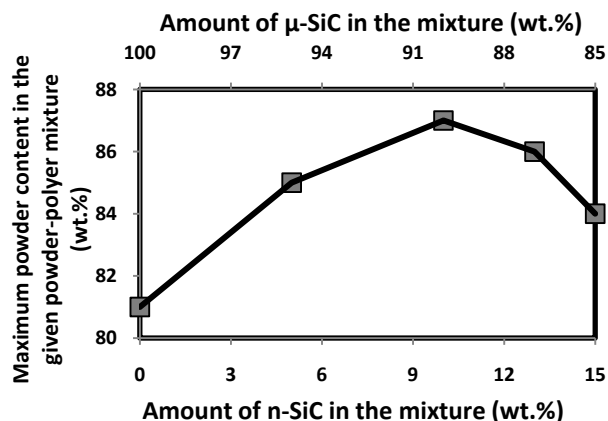


Figure 1a: Effect of n-SiC addition to μ-SiC on the maximum powder fraction in the powder-polymer mixture

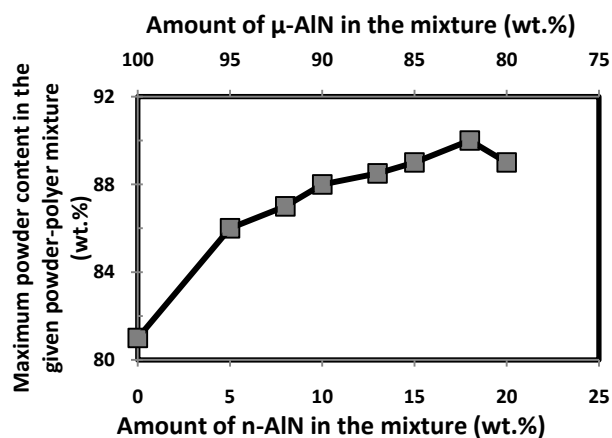


Figure 1b: Effect of n-AlN addition to μ-AlN on the maximum powder fraction in the powder-polymer mixture

There is an upper limit to powder content that is possible in a powder-polymer mixture for any particle size distribution. The particle size distribution was varied by adding nanoparticles to the μ-sized powders. The fraction of n-particles in the bimodal μ-n powder mixture was plotted against the maximum powder content in the resulting powder-polymer mixtures as shown in the **Figures 1a** and **1b**. In both the SiC and AlN systems, a maximum limit to increasing the packing fraction of the particles in the powder-polymer mixture by nanoparticle additions was observed. Thus, a maximum powder content of 87 wt. % (65.5 vol.%) in the powder-polymer mixture was achieved with a bimodal mixture containing 90 wt.% μ- SiC and 10 wt.% n-SiC (**Figure 1a**). Similarly, a maximum powder

content of 90 wt. % (71 vol.%) in the powder-polymer mixture was achieved for the bimodal AlN mixture containing 82 wt.% μ- AlN and 18 wt.% n-AlN (**Figure 1b**). A comparative experiment involving a monomodal 100 wt.% μ-SiC and μ-AlN, resulted in a maximum powder content of only 81 wt. % (53 vol.% - SiC and 52 vol.% - AlN) in the powder-polymer mixture. In addition to the increment in the solids loading, an increase in the torque (directly proportional to the mixture viscosity) is noticed with the nanoparticle addition.

With their tendency to agglomerate, nanoparticles exhibit poor packing density [10, 11]. Hence, the current finding of increase in the powder content (solids loading) with the nanoparticle addition proves to be novel and could result in a possible change in the sintering behavior of SiC and AlN. From the critical solids loading obtained, an optimal solids loading of 59 vol.% (82 wt.%) and 64 vol.% (5 wt.%) were selected for scale up of bimodal μ-n SiC and AlN feedstocks, respectively.

3.2 Feedstock Characterization

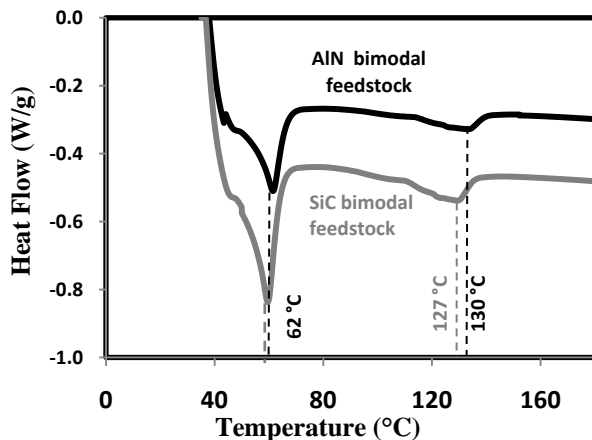


Figure 2: DSC of extruded SiC and AlN feedstocks showing two melting peaks at 62 and 130 °C

The thermal properties of the extruded feedstocks provide basic guidelines for the subsequent PIM steps. **Figure 6** shows the DSC of the feedstocks where two endothermic peaks at 62± 2 °C and 130±3 °C are observed during heating. These peaks indicate the melting of PW and SA at 62 °C and backbone polymers at 130±3 °C [12]. It can thus be inferred that the melt temperatures for injection molding should be higher than 135 °C.

From the TGA plot (**Figure 3**), the AlN bimodal feedstock composition can be finalized as 84.7± 0.2 wt.% powder and 15.7 ± 0.2 wt.% binder. Similarly, it is 81.7± 0.3 wt.% powder and 18.7± 0.3 wt.% binder for the SiC bimodal feedstock. The two stage degradation reveals the degradation of the filler phase from 175-400°C and backbone polymers from 450-525°C. These pyrolysis data can be used for establishing the upper limit for the injection molding temperatures and thermal debinding profiles [12].

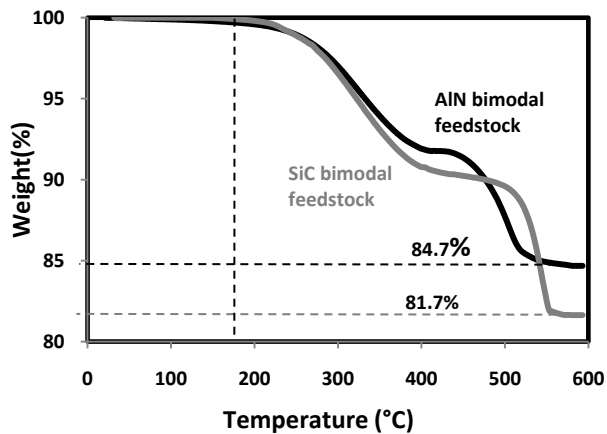


Figure 3: TGA confirming the composition of the bimodal SiC and AlN feedstocks along with their thermal profiles.

3.3 Injection Molding and Debinding

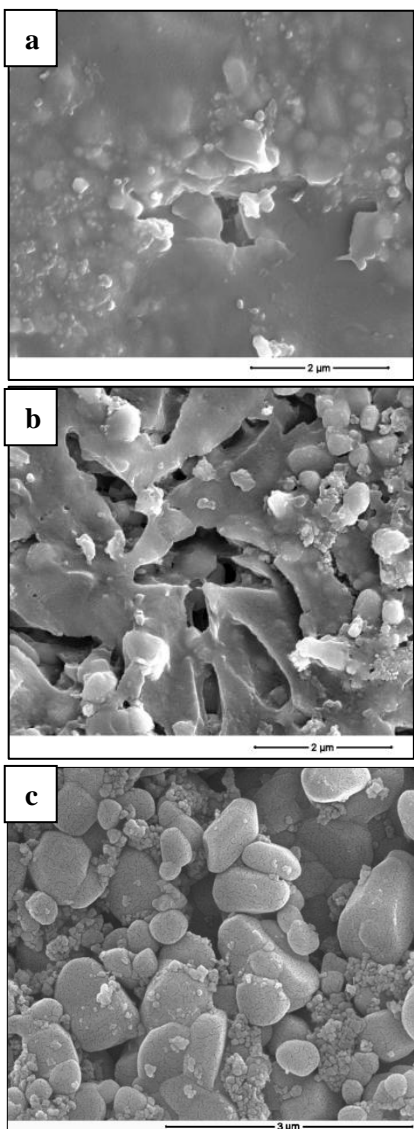


Figure 4: Microstructure of μ -n AlN sample after, (a) injection molding, (b) solvent and (c) thermal debinding

From the TGA and DSC measurements, injection molding temperature window is found to be between 135 to 170 °C. To harness the pseudoplastic behavior of the binder mixture, molten feedstock pellets were injected at 165 °C to produce the “green” samples. The binder’s role of providing fluidity and shape to the green parts is complete after injection molding and is thus subjected to removal. Initially, the green samples were immersed in heptane to remove soluble binder components. A large amount of open pores, after solvent debinding, allows the degraded products to diffuse to the surface easily. Consequently, the thermal removal of insoluble binder components will be finished in a much shorter period without endangering the integrity of the resulting “brown” sample [13]. Micrographs in the **figures 4 a-c** represent the solvent and thermal debinding of injection molded AlN samples. Absence of prior studies and importance of the successful debinding necessitates a future work on studying the effect of material (particle size, solids loading and part geometry) and process parameters (solvent type, immersion time, temperature, heating rate and hold time) on the debinding kinetics.

3.4 Sintering

Figure 5 plots the effect of sintering temperature over the % relative densities of bimodal AlN and SiC samples. Around 99.3% relative density was achieved for bimodal AlN at 1650 °C. This is around 100 °C less than what is reported prior for pressureless sintering of AlN [4, 14]. The drastic decrease in the sintering temperature suggests the reaction between Y_2O_3 and Al_2O_3 from the n-AlN to form the yttrium aluminum garnet (YAG) liquid phase. The above argument is once again confirmed with the SEM micrographs revealing liquid phase formation at 1500 °C (**Figure 6a**) and densification at 1650 °C (**Figure 6b**). Prior reports by Molisani et al [14] and Watari et al [15] involving μ - Y_2O_3 and μ -AlN mentioned that the least temperature require for eutectic is 1690 °C. Thus, the reduced sintering temperature in our work can be inferred as the outcome of employing a bimodal powder mixture along with a nanosized sintering aid.

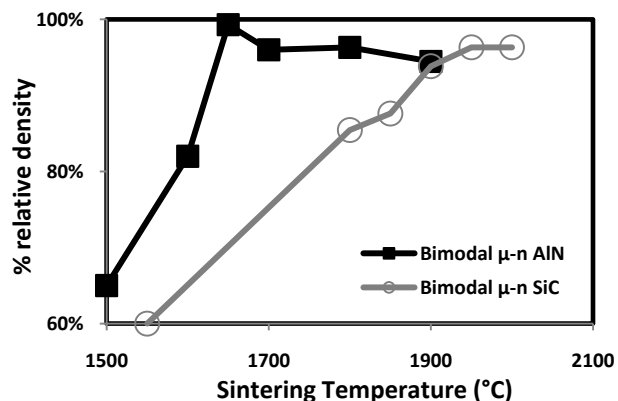


Figure 5: Effect of sintering temperature on the densification of bimodal μ -N SiC and AlN samples

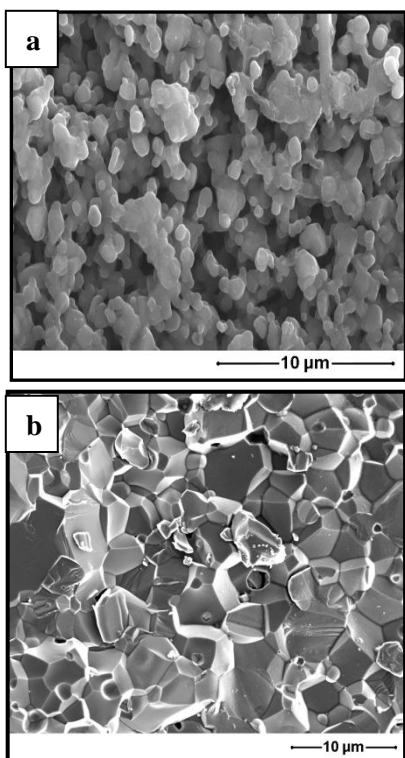


Figure 6: SEM micrographs of bimodal μ -n AlN revealing liquid phase formation at 1500 °C (a) and 99.3% relative density at 1650 °C (b).

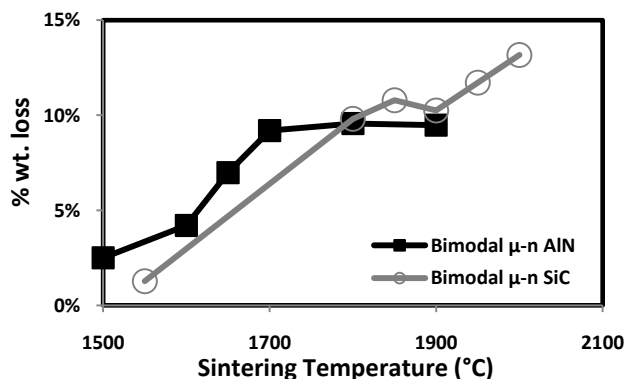


Figure 7: Effect of sintering temperature over the % wt. loss experienced during the densification of bimodal SiC and AlN samples

The bimodal SiC on contrary exhibited a steady increase in the relative density with increase in sintering temperature with the maximum being 97% at 1950 °C. Similar results in SiC were noticed in the past by She and Ueno [5] and Herrmann et al [18]. Achieving around 85% densification at 1800 °C however confirms the formation of liquid phase below 1800 °C. Employing higher hold time at this temperature might further help in understanding the sintering behavior. The inability to reach the maximum densification in SiC and decrease in the AlN density with temperature might be correlated to the % weight loss experienced in both the systems during sintering. **Figure 7** plots the effect of sintering temperature over the % wt. loss

experienced by these bimodal systems. She and Ueno [5], and Molisani et al [16] have reported similar weight loss behavior exhibited by SiC and AlN during sintering. The immediate future work in these systems will involve studying the effect of sintered density and microstructure over the mechanical and thermal properties.

4 CONCLUSIONS

Higher solids loading of 65 and 71 vol.% were obtained for SiC and AlN feedstocks by employing bimodal powder mixtures. With the addition of AlN and SiC nanoparticles, the onset of sintering was brought down to 1500 and 1800 °C, respectively. In addition to the above results, pressureless densification at relatively low temperatures (1650 °C for AlN) suggests the use of bimodal μ -n powder mixtures as a potential approach to process a broad range of difficult-to-sinter ceramic and metal powders.

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