Effect of whisker aspect ratio on the density and fracture toughness of SiC whisker-reinforced Si_3N_4

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Controlling the suspension properties prior to slip casting optimizes the homogeneity, density and fracture toughness of silicon carbide whisker reinforced silicon nitride (SiC_w/Si_3N_4). Further improvements in the mechanical properties are realized by combining ball milling with ultrasonic dispersion of the composite suspension. Ball milling reduces the SiCw aspect ratio from 25 to 15 which in turn increases the dispersion of the whiskers within the suspension, resulting in increases in the green and sintered density, along with the fracture toughness. In a binderless process, 20 volume% reduced aspect ratio ($r = 15$) SiC_w/ Si_3N_4 can be densified to 95% theoretical density by pressureless sintering using 8% Y_2O_3 and 2% Al_2O_3 by weight as sintering aids. These composites had measured values of fracture toughness from 9–10.5 $MPa \cdot m^{1/2}$, representing an average increase of approximately 30% over the fracture toughness for monolithic Si_3N_4 processed under identical conditions.

1. Literature review

Silicon carbide whisker reinforced silicon nitride (SiC_w/ Si_3N_4) ceramic composites have been considered important candidates for structural applications because of their high strength and fracture toughness [1]. Slip casting particulate suspensions is still the most economical shape forming method used to fabricate ceramic green bodies. However, deagglomeration of the slip is critical to the subsequent densification process because agglomerates in the suspension reduce the particle packing efficiency, producing large voids in the green bodies [2]. Colloidal processing methods have proven to be effective in reducing agglomeration in ceramic suspensions. For example, one approach is to create large surface potentials that lead to the formation of a stable double layer of charges on the particle surface [3]. The particles are then kept apart in the suspension by these electrostatic forces. Therefore, higher surface potentials lead to a greater degree of dispersion, stable suspensions and less agglomeration. Colloidal theory, particularly the use of the zeta-potential (ζ) to predict the stabilization (W) of ceramic suspension, has been extensively investigated in order to manipulate agglomeration and segregation of the various suspension components [4–12].

In the production of engineered structural ceramics, submicron powders are often used for their enhanced sinterability. However, submicron powders are generally subject to a higher degree of agglomeration in their as-received state. Unfortunately, this agglomeration cannot be removed by simply adjusting the suspension pH to change the surface potential; mechanical energy is required to reduce the degree of agglomeration. Ball milling and ultrasonic mixing have been widely used to deagglomerate ceramic suspensions. Ball milling is an effective method of reducing particle sizes as well as breaking apart hard agglomerates (aggregates). However, ball milling may encourage the formation of soft agglomerates due to particle contact along the walls of the milling vessel. Ultrasonication breaks up agglomerates by creating local, high velocity jets and pressure gradients within the suspension that are strong enough to break up weakly bonded submicron ceramic particles [13, 14]. Therefore, a processing schedule including ball milling (to reduce both the number of Si_3N_4 aggregates and the SiC_w aspect ratios) followed by ultrasonication (to remove the resulting soft agglomerates) and pH adjustment (to keep newly formed particles at a high surface potential) should yield suspensions of finely dispersed components which are relatively agglomerate free.

The effect of the whisker aspect ratio in ceramic matrix composites has been the subject of many studies [15–19]. In their model, Faber *et al*. showed that increases in aspect ratio from 3 to 12 were more effective in deflecting propagating cracks [15]. Holm *et al*. found that the sinterability of whisker reinforced ceramic composites decreased with increasing whisker aspect ratio [16]. Milewski recommended short fibers with an aspect ratio of 10 to 15 be used to maximize composite green density [17]. Shalek *et al*. reported the critical aspect ratio (r) for densification of SiC whiskers in a Si_3N_4 matrix is approximately 15 [20]. A study by Tiegs *et al*. found that the sintered density improved from 81% to 90% of theoretical density in SiC_w/Al_2O_3 composites with 20 volume% whisker loading when the whisker aspect ratio was reduced from 25 to 17 by ball milling [18]. Hoffman *et al*. achieved densities of 88.5% of theoretical using colloidal control of 20 volume% low (3.3) aspect ratio SiC whiskers in a matrix of Si_3N_4 [19].

These studies find improved densification of whisker-reinforced composites by reducing whisker aspect ratios to 15 or lower. However, this reduction in aspect ratio could simultaneously act to decrease the beneficial toughening effect of the whisker additions. This paper presents the results from a study linking the aspect ratio of SiC_w to green density, sintered density and fracture toughness of SiC_w reinforced Si_3N_4.

2. Experimental

The α-Si_3N_4 powder used in this study was type SNE10, manufactured by Ube Industries, Japan. The β-SiC whiskers, type TWS-100, were manufactured by Tokai Carbon Company, Japan. The Si_3N_4 powder has a manufacturer's reported particle size of 0.3 μm, confirmed by scanning electron microscopy. Using the Andreason pipette method, SiC_w were found to have a diameter of 0.3–0.6 μm with an aspect ratio, r of 25. This result was confirmed using transmission electron microscopy. Acoustophoretic data was collected using a MATEC 8000 system and used to calculate the suspension ζ-potential. Each suspension was prepared in 10^{-4} N KNO_3 electrolyte solution and all pH adjustments were made using either KOH or HNO_3. For these systems, KNO_3 solutions act as indifferent electrolytes while a concentration of 10^{-4} was chosen for optimal suspension stability. Fig. 1 is a plot of green density as a function of ultrasonication time for slip cast monolithic Si_3N_4. A 20% increase in green density was realized for monolithic Si_3N_4 suspensions ultrasonicated for 20 minutes. This density increase is assumed to result from a reduction in particle agglomeration within the slip. Therefore, all suspensions received 20 minutes ultrasonication to enhance green density. The Si_3N_4 powder along with sintering aids (8 wt%Y_2O_3 and 2 wt%Al_2O_3) were ball milled at pH 3, 6 or 11 in electrolyte at 50% solids loading for 24 hours, after which the SiC whiskers were added and ball milling continued for an additional 24 hour period. Continued pH adjustment is necessary during ball milling and ultrasonication due to the newly exposed surface area created during these processes.

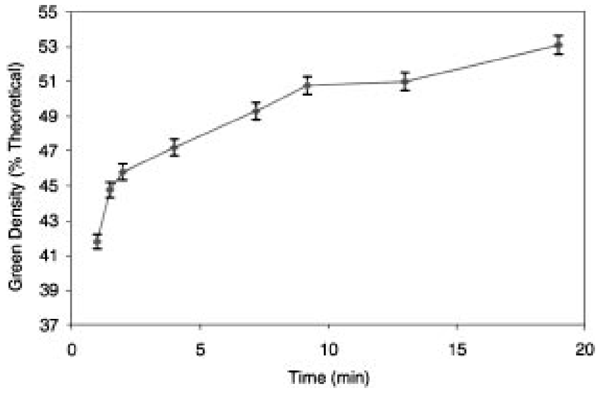

Figure 1 Green density as % of theoretical density versus ultrasonication time for Si_3N_4.

Ball milling of SiC whiskers for 24 hours resulted in a reduction in aspect ratio, r, from 25 to 15, confirmed by Scanning Electron Microscopy (SEM) evaluation. Smaller whisker aspect ratios should produce improvements in green density however, ball milling can also result in soft agglomerates. To negate possible agglomeration from ball milling, all suspensions were ultrasonicated after ball milling and the pH subsequently re-adjusted. Specimens were then slip cast in plaster molds, dried and cold isostatically pressed (CIPed) at 250 MPa.

The green slip-cast specimens were next placed in a loose powder bed of 50% Si_3N_4, 50% BN and pressureless sintered at 1800°C under flowing N_2 for 2 hours. X-ray diffraction of the sintered specimens revealed the $\alpha \rightarrow \beta$-Si_3N_4 transformation was complete after a 2-hour hold at the sintering temperature for all monolithic and composite specimens. All density values were calculated based on measurements from at least 5 samples.

The fracture toughness (K_{IC}) was estimated using an equation derived by Singh *et al*. for determining the fracture toughness of whisker reinforced Si_3N_4 from Vickers-induced cracks [21].

$$K_{IC} = 0.057H\sqrt{a}\left(\frac{E}{H}\right)^{2/5}\left(\frac{c}{a}\right)^{-3/2} \quad (1)$$

H is the material hardness (as determined from indent dimensions), a is a geometrical constant equal to 2 for a Vickers induced crack, E is the elastic modulus of the material, and c is the radial crack length. Crack lengths and indent dimensions resutling from a 200 N load were measured immediately after each indentation, 5 times on each of 5 samples per data point.

3. Results and discussion

3.1. Effect of processing pH on green density

A plot of ζ-potential as a function of pH for both Si_3N_4 and SiC_w is shown in Fig. 2. When compared to SiC_w, the Si_3N_4 has higher surface potentials at all pHs. Both materials possess similar iso-electric points (iep) at a pH of approximately 6. This data, along with the relevant material parameters, was used to calculate the stability ratio utilizing the Hogg, Healy, Fuerstenau approximation of a solution to the Poisson-Boltzmann

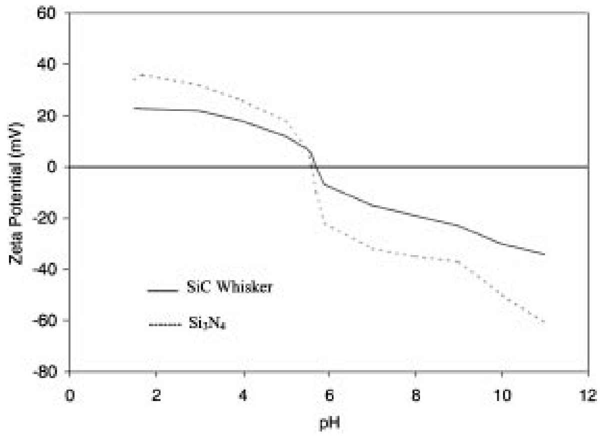

Figure 2 Zeta potential as a function of pH for SiC_w and Si_3N_4 powder at 10^{-4}N KNO_3.

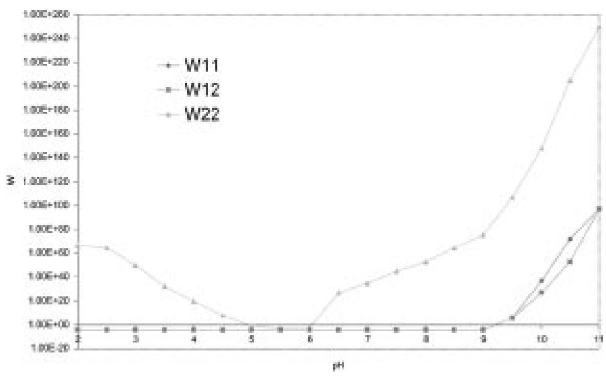

Figure 3 Log stability as a function of pH for SiC_w and Si_3N_4 powder.

equation for the repulsive interaction between 2 non-identical particles [13, 22]. Fig. 3 is a plot of the log of the stability ratio as a function of pH for homointeractions (SiC_w to SiC_w and Si_3N_4 to Si_3N_4) and heterointeractions (SiC_w to Si_3N_4). Hunter defines the behavior of colloids with stability ratio values from 1–20 as marginally stable [12]. A conservative measure of stability, defined by $\log W > 20$, was therefore chosen. The stability ratio (W) is the ratio of the total particle collisions to the number of particle collisions that result in agglomeration. Since it is desirable to create a uniform distribution of SiC_w throughout the composite, it is necessary to unagglomerate the SiC_w, and a pH > 10 ensures that $\log W > 20$. In a like manner, unagglomerated matrix particles would further maximize the distribution of reinforcing whiskers. Stability calculations show Si_3N_4 to be stable from pH 2–4 and pH > 6.5. The union of these stable pH regions for SiC_w and Si_3N_4 predicts maximum component distribution at pH > 10.

To experimentally verify these findings, monolithic Si_3N_4 samples were slip cast at pH 3, 6 and 11. The green density, as a percentage of theoretical density, is plotted as a function of pH and shown in Fig. 4, both before and after CIPing of the slip cast specimens. While CIPing increased the green density of all specimens, these increases were not enough to overcome the agglomeration created in the suspension. For example, at pH 6, both Si_3N_4 and SiC_w are predicted to have a low stability that would lead to agglomeration. Indeed, suspensions cast at pH 6 have lower green densities in comparison to samples cast at pHs 3 and 11 where stability is maximized and agglomeration is minimized. Independent studies by Lange [23] and Dynys and Halloran [24] have discussed the relationships existing between the degree of agglomeration and the green and sintered density. In a study specific to Si_3N_4, Kamiya *et al.* determined sinterability of green compacts to be a function of powder surface area and the distance between particles in the green compact [25]. Thus, improving the sinterability of Si_3N_4 should focus on fine powder sizes and green compacts with a narrow pore size distribution. Subsequently, to maximize the stability of both the Si_3N_4 and SiC_w, all suspensions were prepared at a pH of 11.

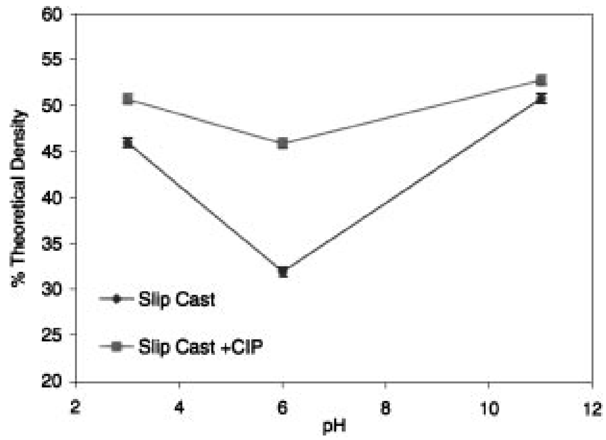

Figure 4 Theoretical density (%) versus pH for monolithic Si_3N_4.

3.2. Effect of SiC whisker aspect ratio on density

Fig. 5 is a plot of green density versus SiC whisker loading for composite specimens showing the effect of ball milling and ultrasonication ($r = 15$) and ultrasonication ($r = 25$). There are no statistically significant differences in the green density for specimens containing 10 and 20 volume% SiC whiskers at either $r = 25$ or $r = 15$. It is only at a whisker loading of 30 volume% that a minimal decrease of 2% becomes evident in the $r = 25$ samples. This difference however is exacerbated after sintering.

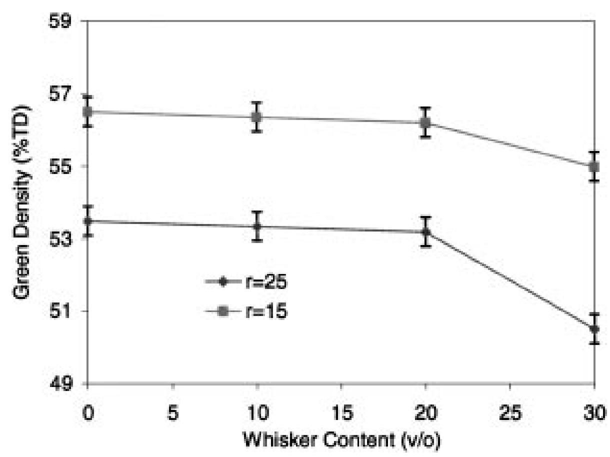

Figure 5 Green density as a function of SiC_w volume.

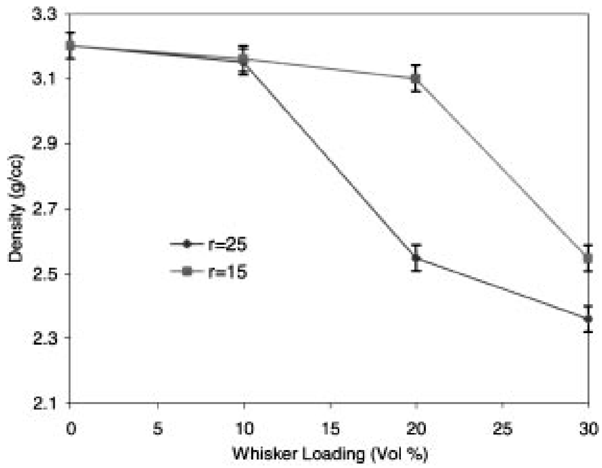

Figure 6 Sintered density as a function of SiC_w in the Si_3N_4.

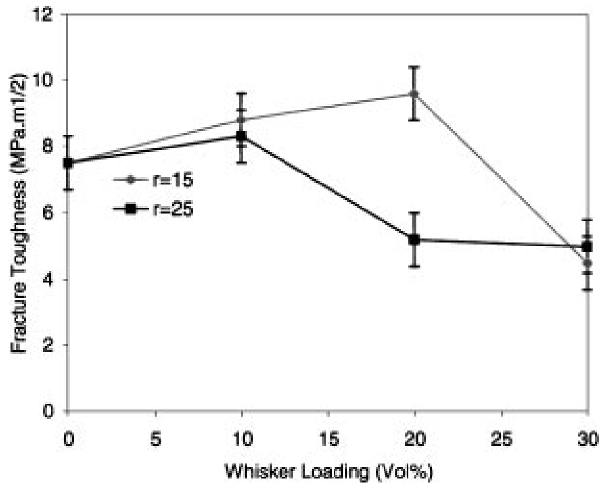

Figure 7 Fracture toughness as a function of SiC_w loading and aspect ratio.

Fig. 6 shows sintered density as a function of whisker loading for Si_3N_4 composites containing both as-received ($r = 25$) and reduced aspect ratio ($r = 15$) SiC whiskers. Densities are nearly identical for specimens up to additions of 10 volume% reduced aspect ratio SiC_w. At 20 volume%, composites reinforced with reduced aspect ratio whiskers ($r = 15$) have a density of 3.1 g/cm^3 while specimens reinforced with the as-received whisker aspect ratio ($r = 25$) having a lower density of 2.5 g/cm^3. This change in sintered density arises from the inhibiting effect of high aspect ratio additions on the matrix powder densification. In a study by Milewski [17], on the packing of fibers and spheres, as well as experimental results from Shalek *et al.* [20] and Buljan et al. [1], it was concluded that a whisker aspect ratio of $\leq$10–15 is necessary to fabricate dense whisker reinforced ceramic matrix composites. Therefore, sinterability of these composites is enhanced by ball milling which caused a reduction in whisker aspect ratio. However, while improving sinterability, smaller whisker aspect ratios may affect the fracture toughness.

3.3. Effect of SiC whisker aspect ratio on toughness

Fig. 7 is a plot of indentation fracture toughness versus whisker loading, showing the effect of whisker aspect ratio on the fracture toughness of composite specimens. Following the sintering results, higher fracture toughness values were found for the samples containing the ball milled, reduced aspect ratio whiskers. When comparing the fracture toughness of samples processed with ($r = 15$) and without ($r = 25$) ball milling, at 10 volume% whisker additions, there are only minimal differences. This was somewhat unexpected because for similar sintered densities, a longer whisker aspect ratio was expected to result in greater toughening because of increased crack deflection and component pull-out [26, 27]. However, when the aspect ratio of SiC_w is reduced by ball milling, the number of intersection sites between the whisker and the advancing crack is actually increased. While longer aspect ratios provide a greater degree of crack deflection, an equal volume percent of reduced aspect ratio whiskers provides more surface area over which crack deflection can occur. This is shown for the 20 volume% SiC_w additions where the fracture toughness of the specimens processed by ball milling ($r = 15$) showed an increase in fracture toughness, reaching 9.0–10.5 $MPa \cdot m^{1/2}$. When measured against comparable composites (see Table I), two observations become apparent. First, SiC_w additions have increased the fracture toughness when compared to identically processed monolithic Si_3N_4. Composite fracture toughness values measured in this study are in the high end of the wide range of values reported in other studies [28–32]. However, a closer look at Table I reveals that this is indeed a favorable comparison because the samples processed in this study were consolidated by *pressureless* sintering. Secondly, by decreasing the whisker aspect ratio from $r = 25$ to $r = 15$, the fracture toughness was doubled, from 4.7–5.7 to 9.0–10.5 $MPa \cdot m^{1/2}$. Specimens reinforced with

TABLE I Comparison of sintered density and fracture toughness of Si_3N_4 and SiC_w-Si_3N_4

Author	Material	Processing Method	Density (g/cm^3)	K_{IC} ($MPa \cdot m^{1/2}$)
Shih *et al.* [28]	Si_3N_4	Hot Pressing	3.29	9.9 ± 0.8
Shih *et al.* [28]	5% SiC_w-Si_3N_4	Hot Pressing	3.27	10.4 ± 1.6
Ueno *et al.* [29]	20% SiC_w-Si_3N_4	Hot Pressing	Complete	7.00
Pyzic *et al.* [30]	Si_3N_4	Pressure Sinter	Complete	8–11
Crosbie *et al.* [31]	Si_3N_4	Pressureless Sinter	3.18	N/A
Yeh [32]	Si_3N_4	Pressureless Sinter	3.25	8.0
Yeh [32]	20% SiC_w-Si_3N_4	Pressureless Sinter	3.2 ($r = 15$)	9.0–10.5
			2.5 ($r = 25$)	4.7–5.7

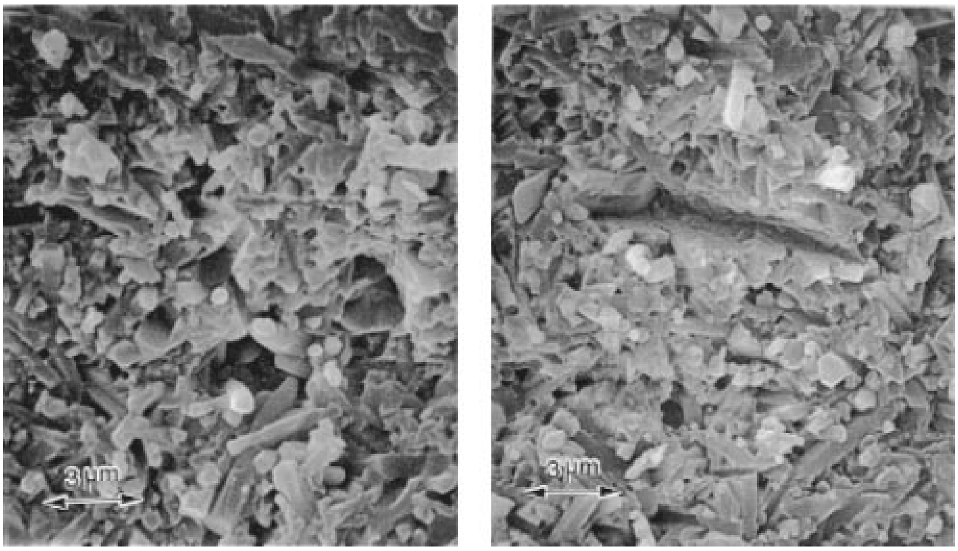

Figure 8 SEM fracture surfaces, 10 vol%, (a) $r = 25$ and (b) $r = 15$.

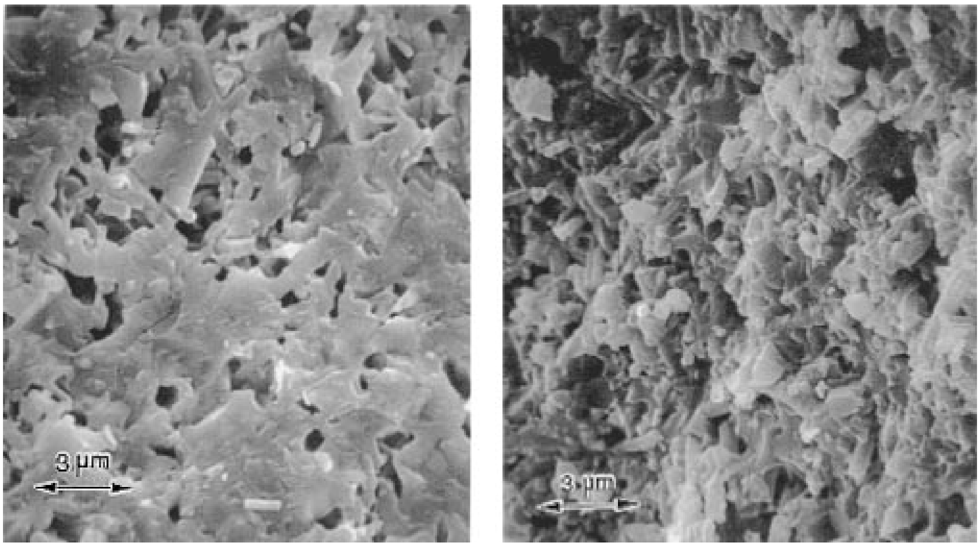

Figure 9 SEM fracture surfaces, 20 vol%, (a) $r = 25$ and (b) $r = 15$.

30 volume% as received ($r = 25$) whiskers show a significant reduction in fracture toughness. This results from incomplete consolidation of the Si_3N_4 matrix because of the inhibiting aspect ratio of the large volume fraction of SiC_w. Finally, although SiC_w additions are believed to be beneficial in terms of mechanical properties, the fracture toughness of the monolithic Si_3N_4 samples prepared by others using pressure assisted sintering is comparable to the whisker-reinforced composites.

Fig. 8 shows the SEM photomicrographs of representative fracture surfaces from specimens reinforced with 10 volume% SiC_w for samples processed with whisker aspect ratios at $r = 25$ and $r = 15$. The fracture surfaces are similar in appearance relative to grain size, porosity and frequency of grain pullout and it is therefore logical to expect similar values of fracture toughness. Fig. 9 shows the SEM micrographs of representative fracture surfaces from specimens reinforced with 20 volume% SiC_w for samples processed with whisker aspect ratios at both $r = 25$ and $r = 15$. The $r = 25$, 20 volume% SiC_w fracture surface shows significantly more porosity and a flat transgranular fracture surface. In contrast, the fracture surface of the 20 volume% SiC_w reduced aspect ratio ($r = 15$) specimens was rougher and less porous indicating a greater degree of crack deflection. Because of the relatively small average grain diameters ($<1\ \mu$m) and the acicular nature of the β-Si_3N_4 grains, it is nearly impossible to observe SiC_w in any of the SEM photomicrographs. α-SiC was, however, detected by x-ray diffraction analysis of the composite specimens. Without *in situ* observation of the fracture path, it is difficult to ascertain the role SiC_w plays in the toughening of Si_3N_4. However, in agreement with studies by Milewski [17], Shalek [20] and Tiegs *et al.* [18], the data suggest that fracture toughness increases with whisker loadings up to 20 volume% reduced aspect ratio ($r = 15$) SiC_w.

4. Conclusions

Using a binderless process, reduced aspect ratio ($r = 15$) SiC_w reinforced Si_3N_4 composites have been slip cast at pH 11, CIPed and *pressureless* sintered, achieving improvements in fracture toughness over both monolithic Si_3N_4 and SiC_w/Si_3N_4 composites fabricated with as-received ($r = 25$) whiskers. The fracture toughness of the composites fabricated by pressureless sintering was equivalent to values reported in the literature using more costly, pressure assisted consolidation techniques. Additions of 20 volume%, reduced aspect ratio SiC whisker ($r = 15$) increased the fracture toughness over that of fully dense, monolithic Si_3N_4. At 10 volume% SiC_w additions, the as-received ($r = 25$) and reduced aspect ratio ($r = 15$) composites yielded equivalent values for both density and fracture toughness with no improvements over the monolithic values. At 20 volume% whisker additions, the fracture toughness of specimens containing as-received SiC whiskers ($r = 25$) decreased because the longer whiskers decreased the sinterability resulting in a significantly more porous composite. Increases in fracture toughness from the reduced aspect ratio SiC_w are limited to additions of 20 volume%. These results are consistant with those of Buljan [1] and Shalek [20] who note that reduced aspect ratio SiC_w are necessary for complete matrix sintering. Overall, while toughening of Si_3N_4 is theoretically improved by the addition of a high aspect ratio second phase, the deleterious effects of the whisker aspect ratio on both the green consolidation and sinterability produce a decrease in the fracture toughness of the composite. Therefore, to optimize both toughness and sinterability, slip cast SiC_w/Si_3N_4 composites should be processed using SiC_w having aspect ratios <15.

Acknowledgements
We are grateful to the State of Michigan, Research Excellence Funds for financial support of this research.

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Received 10 March
and accepted 18 September 2000