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Investigation of whisker orientation in SiC whisker-reinforced alumina composites using neutron diffraction

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Abstract

Alumina composites with 10, 20 and 30 vol.% SiC whiskers were fabricated using colloidal processing methods followed by uniaxial hot pressing. Orientation of whiskers was quantified using neutron diffraction methods that allow one to probe the bulk of the composite samples. The results indicate that significant whisker alignment was present even in the green samples and that hot pressing further enhanced this alignment but not to a substantial extent. Although slightly enhanced whisker rotation was observed with increase in whisker content in the alumina matrix, the overall degree of whisker alignment in the final products was not strongly dependent on pH of the slurry and whisker volume fraction.

Keywords: Ceramic matrix composite; Whiskers; Al_2O_3/SiC; Neutron diffraction

1. Introduction

In recent years, a considerable body of studies have been done on oxide matrices reinforced with SiC whiskers.[1–12] The Al_2O_3–SiC whisker system is probably one of the most important systems because both the matrix and reinforcement phases have been well studied. It has been known that alumina has excellent high temperature stability and low oxygen permeability and that SiC has good resistance to high temperature oxidation because of the formation of a protective film of silica.[2] The addition of SiC whiskers into alumina has resulted in substantial improvement of mechanical properties, for instance, fracture toughness,[1] flexure strength, resistance to thermal shock, fatigue, and creep deformation.[3–11]

As uniaxial hot pressing is commonly employed to fabricate the composites, the whiskers tend to align with their axes perpendicular to the hot pressing axis (HPA). Therefore, the mechanical properties of the composites are expected to be dependent on sample orientation with respect to the HPA. If the elastic loading of whiskers as a whole is an important factor of the creep response, a different creep response is expected for different loading directions.[11,12] Indeed, Lipetzky et al.[9] demonstrated during creep of 33% whisker-reinforced alumina that when the four-point flexure loading direction is parallel to the HPA, a higher creep rate was observed than in the case of the loading direction and tensile axis both perpendicular to the HPA.

This report presents the effect of slurry pH on the composite microstructure and the development of whisker texture at various conditions. Neutron diffraction methods, which reveal the bulk properties of solids rather than surface properties, can be used to quantify the orientation of whiskers in the alumina matrix.

2. Ceramic powder processing

To understand the effect of whisker network structure and orientation on the creep response, composites with large differences in whisker alignment were desired. This was essentially approached through adjusting pH and solids loading of the slurry. Fig. 1 shows the measured zeta potential as a function of pH for suspensions of alumina and SiC whisker[d]. As shown,

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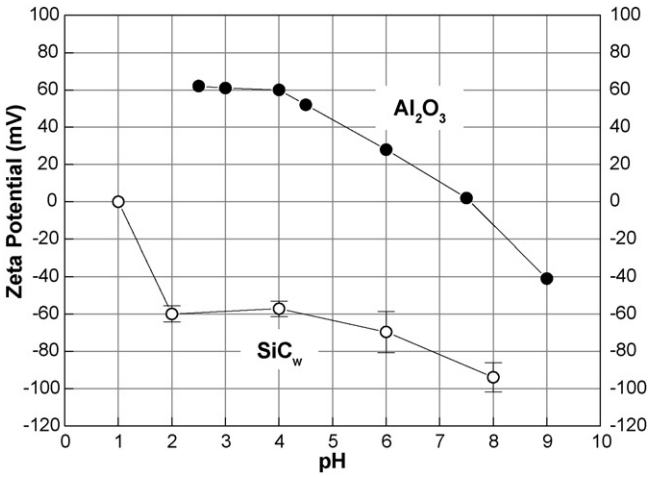

Fig. 1. Zeta potential as a function of pH for SiC and alumina suspensions.

the alumina suspension showed an IEP of ∼8, which is towards the lower end of the range of the data that have been reported in the literature.[13–15] However, the SiC suspension exhibited an IEP of about 1 which is close to that reported for SiO_2, i.e. ∼2.[15] It appears that heteroflocculation can occur over a wide range of pH value between 2 and 7. Considering the much smaller size of the alumina particles it is likely that the heteroflocculation will draw the fine alumina particles onto the surface of the whiskers. If each single whisker is well coated with fine alumina particles, it would behave like a positively charged large alumina particle. Indeed, during the electrophoresis analysis on Al_2O_3–SiC_w suspension under pH 2 SiC whiskers were observed to move in the same direction as Al_2O_3 particles,[11] which might suggest heterointeraction between the two particles. Therefore, if the pH at which the alumina particles are well dispersed also enables a strong heteroflocculation, the suspension should exhibit good stability. To see the effect of pH on the stability of a composite suspension, several slurries (solid loading ∼20%) were prepared for settling experiments with the pH in the range of 2–10. Fig. 2 shows the measured relative heights of the sediment cake after about 6 months. In general, dense sediments were observed at low pH while lose flocculation occurred at high pH resulting

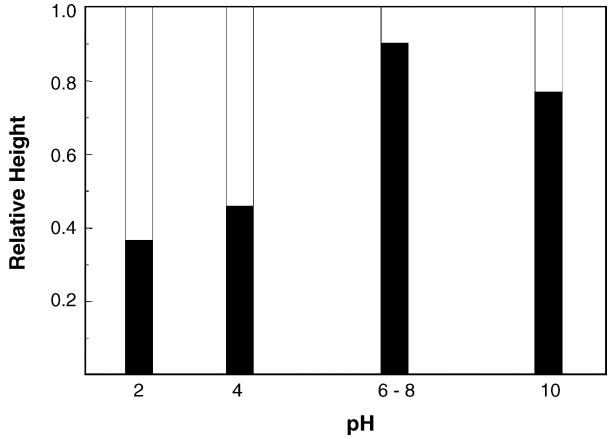

Fig. 2. Sedimentation of composite slurry at different pH values after about 6 months.

Table 1
The experimental schemes for green body formation

Composite	SiC (vol.%)	pH	Solid loading (vol.%)
S302 (C302)	30	2	15–30
S202 (C202)	20	2	35–40
S102 (C102)	10	2	45–50
S306 (C306)	30	6	15
Alumina	0	2	50

C stands for green sample and S for hot pressed sample.

in sediments with much lower density. As shown, the height of solid is the lowest at pH 2 which corresponds to the highest stability. This suggests that the formation of whisker clusters is most limited at pH 2, resulting in the highest packing efficiency of the mixed particles. However, at high pH (≥6) it is likely that the strong flocculation of alumina particles would leave SiC whiskers rejected and hence clustered. During sedimentation, well-dispersed whiskers would tend to align with their axes perpendicular to the direction of gravity, while the clustered whiskers would maintain their orientation within the clumps. As a result, different whisker distributions may be expected within a green body and the subsequent hot pressing might inherit this difference in spite of the overall increase in whisker alignment. In light of this hypothesis, slurries were prepared using pH 2 and pH 6, in an attempt to produce composites with well-aligned whiskers and randomly oriented whiskers, respectively. Table 1 shows the recipes for preparation of slurries and consolidation methods. It was found that the viscosity increased with increasing pH for a given solid loading. Therefore, the solid loading was necessarily lowered with increasing pH, which enabled an appropriate viscosity for slip casting. The optimum solid loading should be a compromise between castability of the slurry and low shrinkage during the drying cycle.

3. Microstructure of hot pressed composites

As the presence of whiskers raises the sintering pressure, relatively high sintering temperatures and loads were needed to achieve full densification. Before being loaded into the graphite die for hot pressing, the dried green sample was mechanically ground so as to smooth the sample surfaces and fit into the die. Thin graphite foil was used to wrap the samples completely, which facilitated sample removal after hot pressing. The final densification was performed at the temperature range of 1700–1850 °C under ∼50 MPa. Fig. 3(a) shows a typical SEM micrograph taken from an as hot pressed sample with 30 vol.% whiskers where the surface is parallel to the HPA. Here, the overall uniform distribution of whiskers is noted although locally they are often seen in close contact with each other. It appears that those whisker concentrated areas are associated with more extensive pores, indicating their susceptibility to thermal etching. It is also noteworthy that most whiskers are located at grain boundaries and junctions, especially at triple grain junctions. In addition, a fine and uniform matrix grain size is evident from the micrograph. Fig. 3(b) shows a SEM micrograph taken from the same sample but with the surface perpendicular to the HPA. Note that most alumina matrix grains have been removed from the

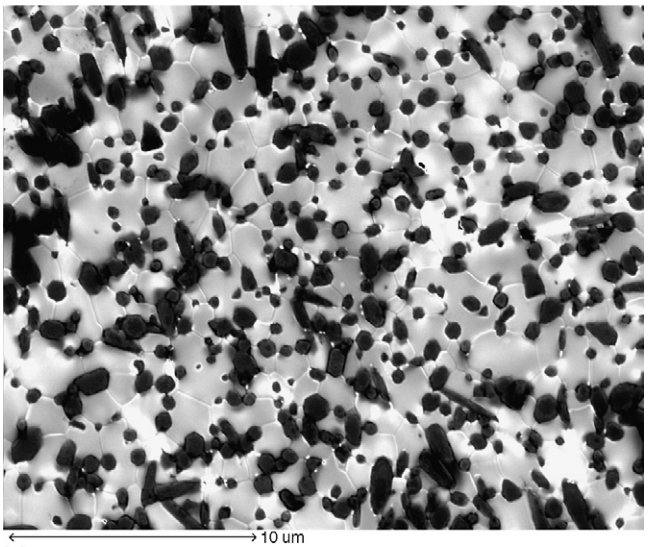

Fig. 3. (a) A SEM micrograph of S302 with the surface parallel to HPA. The scale bar equals 10 μm. Thermal etching caused the surface porosities, especially within whisker clusters. The polished surface was thermally etched at 1350 °C for 1 h. (b) A SEM micrograph of S302 with sample surface perpendicular to HPA. The scale bar equals 20 μm. The surface was thermally etched at 1400 °C for 2 h.

sample surface by deep thermal etching, leaving only whiskers at the surface. Given such a high number density, these whiskers have already formed an interconnecting network.

4. Characterisation of whisker orientation

Texture measurements were carried out in the E3 beamline attached to the NRU reactor at Chalk River Laboratory (CRL). Texture measurement by neutron diffraction has been treated in detail by Brockmeier.[16] Fig. 4 illustrates the sample coordinate system and angles defined for texture measurements. Details on instrumentation can be found elsewhere.[11]

In order to characterise the whisker orientation, the crystal structure of the SiC whiskers was studied by diffraction methods and transmission electron microscopy. The results indicate that they are essentially single crystals of cubic β-SiC phase (3C) with highly populated planar defects along the whisker axis which corresponds to one of the four <1 1 1> directions.[11,17] In theory, unlike with the hexagonal crystal structure, for the cubic crystal structure there is no reflection whose intensity at a given sample orientation can be uniquely related to the volume fraction of the whiskers possessing the same orientation[e]. However, the presence of high density planar defects in SiC whiskers led to a simplification based on the following observation. In aluminum matrices reinforced by well-aligned SiC whiskers[f] along the extrusion axis, Root and Rack[18] were able to distinguish the variants of {1 1 1} that are not parallel to the whisker axis by systematically orienting the sample. They recorded a weak broad off-axis {1 1 1} peak located at a smaller scattering angle than the major on-axis (1 1 1) peak. This result suggests that for whiskers that are not unidirectionally aligned if a measured {1 1 1} peak is the sum of all variants with considerable contribution from the off-axis {1 1 1} reflections, it will develop significant asymmetry. However, this was not observed in the peaks recorded in our study; hence it was concluded that the contribution from the off-axis {1 1 1} reflections is insignificant and, thus, can be ignored. It should be emphasized that this approximation can be made only because of the loss of long-range periodicity along the other three off-axis <1 1 1> directions, which is not true for the well-grown crystals with cubic structure.

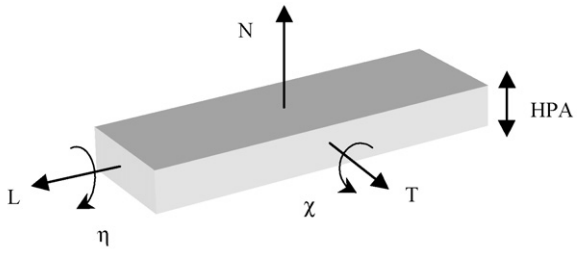

Fig. 4. A schematic of the sample coordinate system and angles defined for neutron diffraction measurements.

As there is no preferred orientation around the long axis of the whisker, the orientation of a single whisker within a sample can be described by two independent parameters, χ and η. As shown in Fig. 4, the former is the angle between the HPA, **N** and the long axis of whisker and the latter the angle around the transverse direction, **T**. If the normalized intensities are averaged for η for a given χ, the volume fraction of whiskers can be mapped as a function of φ, that is the angle between the long axis of whisker and HPA (**N**).

Angular distribution of whiskers with respect to the axis of interest was quantified by the following approach. First, the (1 1 1) SiC pole figure is constructed from the raw neutron diffraction data using the in-house computer programs developed in CRL, in such a way that the center of the pole figure is

[e] Here we do not consider the rotational freedom with respect to the whisker axis.

[f] Provided by the same supplier as those used in the present study.

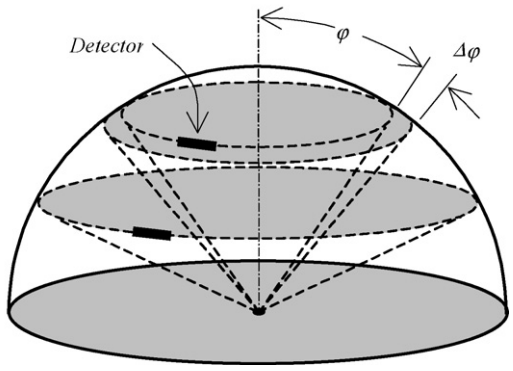

Fig. 5. The geometry for measuring angular volume fraction of whiskers.

coincident with the HPA. Suppose $\langle I \rangle$ is the normalized average intensity around the HPA for the angular range of $(\varphi, \varphi + \Delta\varphi)$ where $\Delta\varphi$ is the step size (5° in our case), then the actual volume fraction of whiskers within this range is given by

$$\Phi = \frac{\langle I \rangle \sin(\varphi + \Delta\varphi/2)}{\sum \langle I \rangle \sin(\varphi + \Delta\varphi/2)} \quad (1)$$

The related geometry is schematically shown in Fig. 5.

5. Results and discussions

Figs. 6–9 show the (1 1 1) SiC pole figures constructed for the composites by neutron diffraction techniques where the center of all pole figures coincides with the HPA. As expected,

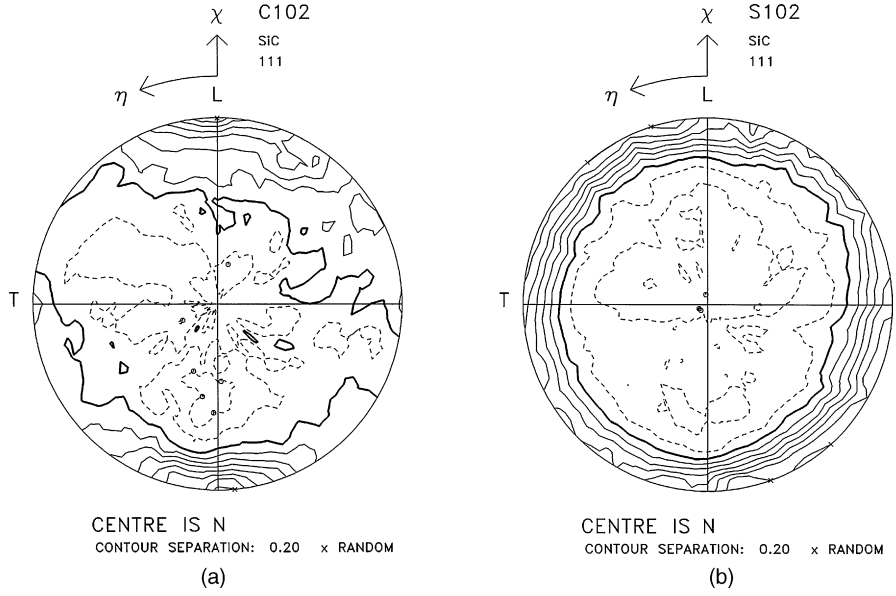

Fig. 6. Pole figures of $(1\,1\,1)_{SiC}$ from (a) C102 and (b) S102.

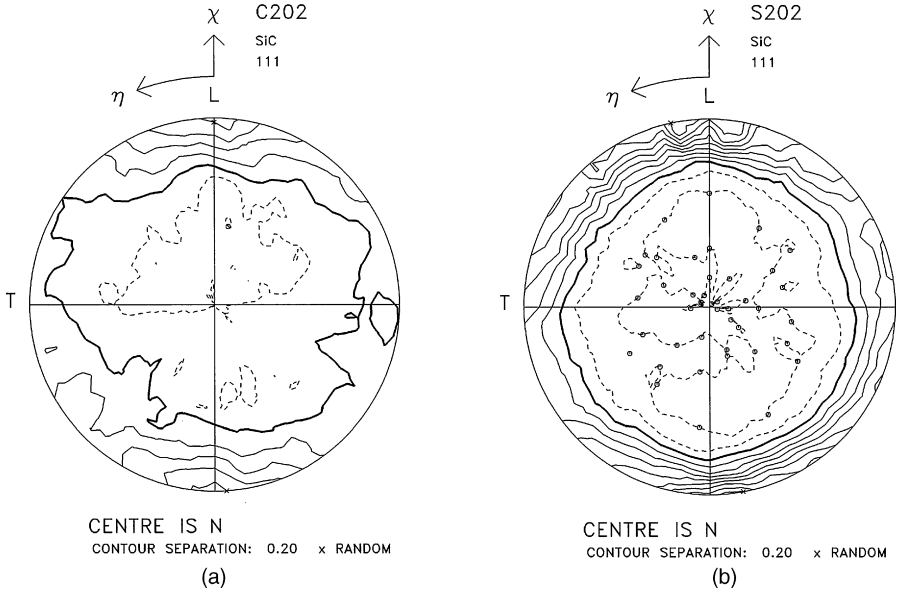

Fig. 7. Pole figures of $(1\,1\,1)_{SiC}$ from (a) C202 and (b) S202.

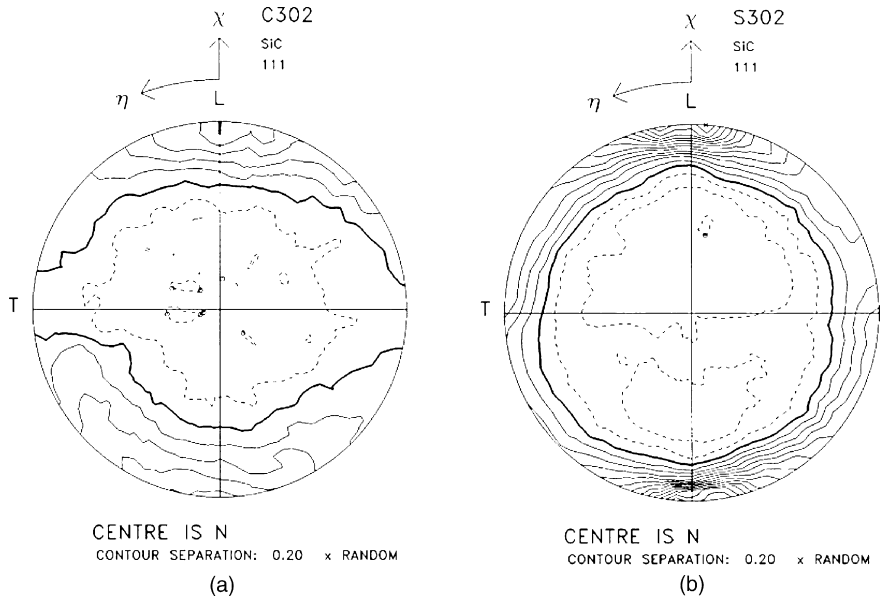

Fig. 8. Pole figures of $(1\,1\,1)_{SiC}$ from (a) C302 and (b) S302.

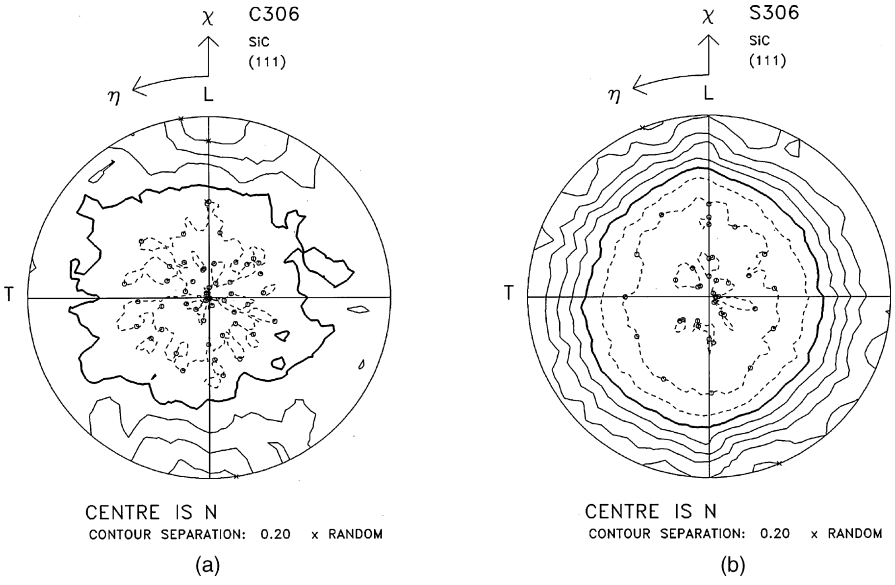

Fig. 9. Pole figures of $(1\,1\,1)_{SiC}$ from (a) C306 and (b) S306.

whisker alignment is already developed within green samples and enhanced alignment is seen after hot pressing. The common feature in all pole figures is the concentration of multiple of random density (MRD) contours around the periphery of the pole figures, which suggests that whiskers tend to align with their axes lying close to the plane normal to the HPA. Furthermore, in most pole figures the higher density of contours around the **L** direction indicates a preferred whisker orientation along the long dimension of the sample and this effect is more pronounced in the hot pressed samples with higher whisker content and pH 2.

Fig. 10 presents the calculated volume fraction of whiskers with their axes lying within a given angular range with respect to the HPA before and after firing. Because of similarity, the results are presented for only two composite samples with the same whisker content (30 vol.%) but made under different slurry pH (2 and 6). As shown, the effect of pH upon the angular distribution of whiskers is not significant. The effect of whisker content was also found to be little.[11] Now, the average angle between HPA and whisker axes can be found as

$$\bar{\varphi} = \frac{\int_0^{\pi/2} \varphi\psi(\varphi)d\varphi}{\int_0^{\pi/2} \psi(\varphi)d\varphi} \simeq \frac{\sum_{i=1}^{n} \varphi_i \psi(\varphi_i)\Delta\varphi}{\sum_{i=1}^{n} \psi(\varphi_i)\Delta\varphi} \quad (2)$$

where $\psi(\varphi)$[g] is the whisker orientation function with respect to the HPA and n is the number of angles covered during tex-

[g] For a given angular range (α,β) the whisker volume fraction is given as $\int_\alpha^\beta \psi(\varphi)d\varphi$.

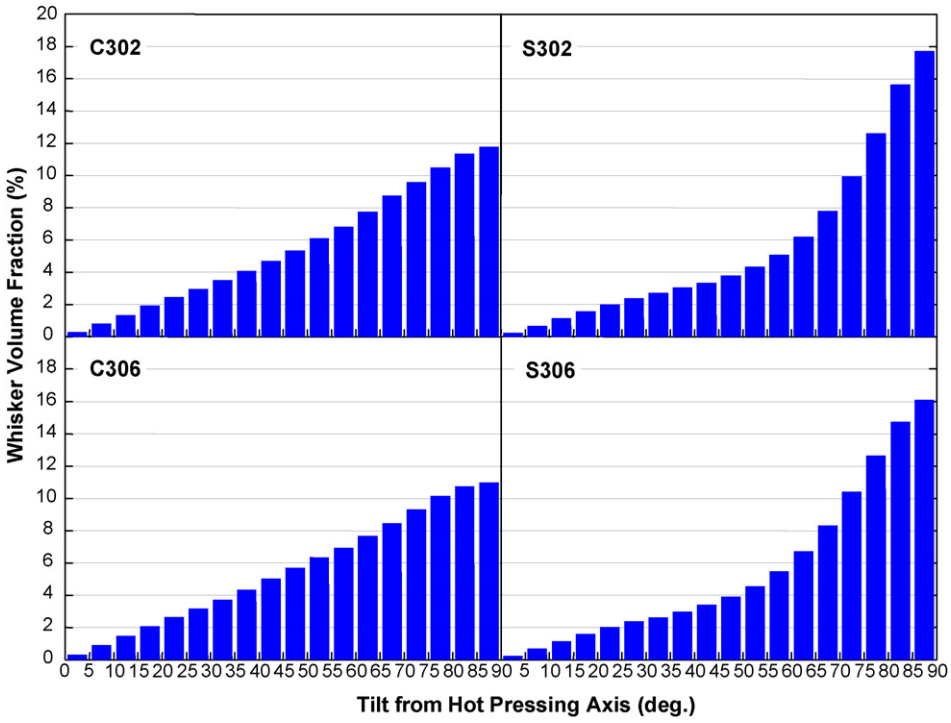

Fig. 10. Angular distribution of whiskers with respect to HPA. The results are shown for the composites before and after firing (from left to right). They contain the same amount of SiC whiskers (30 vol.%) but involved different pH (2 and 6).

ture measurement. Table 2 shows the calculated $\bar{\varphi}$ for composite materials before and after hot pressing and the corresponding rotation angle $\Delta\bar{\varphi}$. As shown significant whisker alignment has been developed within green samples and the subsequent uniaxial hot pressing further aligned the whiskers, however, not by a substantial margin. For example, with 30 vol.% of whiskers in the alumina matrix the average out-of-plane angle $(90 - \bar{\varphi})$ was about 26° which was reduced to about 21° after firing. Although the rotation angle $\Delta\bar{\varphi}$ showed a slight increase with increasing whisker volume fraction, the overall effect was found to be minimal in both green and final products.

In the initial course of this work, the effect of slurry pH on the whisker texture was of a particular interest with the desire of varying the extent of whisker alignment to a sufficient degree. However, the hypothesis was not supported by the experimental results. Nevertheless, it is important to note that the spatial distribution of whiskers was found to be dependent on slurry pH. This is evidenced by the striking difference in the microstructures shown in Figs. 11 and 12. As shown in Figs. 8 and 9 the (1 1 1) pole figure of C306 showed little difference as compared with C302, but the corresponding pole figures from the hot pressed samples showed a remarkable difference in that S302 exhibited a preferred orientation along the long dimension of the sample while S306 did not. This implies different whisker network configuration especially the nature of whisker contact points within the green bodies prepared at different slurry pH. As discussed above, presumably, at pH 6 alumina particles are strongly flocculated, leading to the formation of whisker clusters throughout the microstructure. Since the whiskers are well interconnected within the clusters, during green processing and subsequent hot pressing, their motions would be highly restricted. However, at pH 2, whiskers are well dispersed, resulting in uniformly dis-

Table 2
The calculated average angle between whisker axes and the HPA, and the corresponding change in the angle due to hot pressing

	C302	S302	C202	S202	C102	S102
$\bar{\varphi}$	64.1	69.3	63.0	67.2	63.7	67.5
$\Delta\bar{\varphi}$	5.2		4.2		3.8	

The unit is in degrees and the associated uncertainty is ±0.6°.

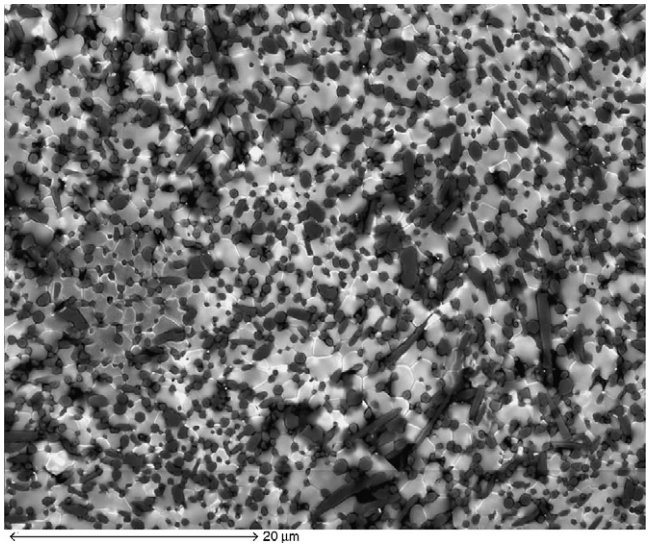

Fig. 11. A SEM micrograph of S302 with the sample surface parallel to the HPA. The scale bar equals 20 μm.

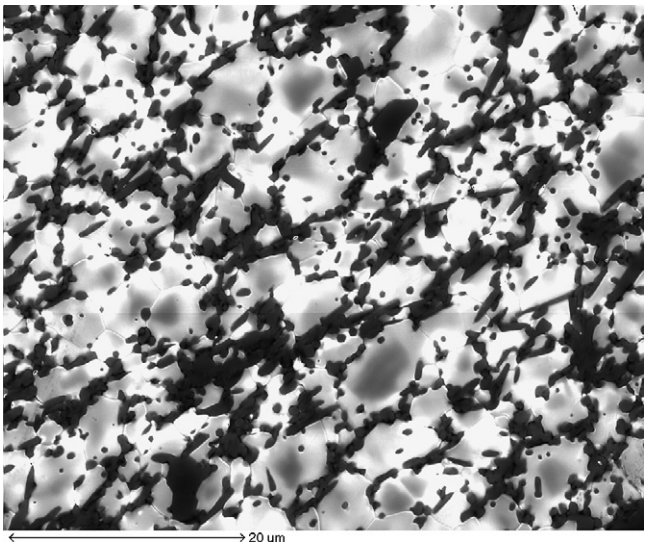

Fig. 12. A SEM micrograph of S306 with the sample surface parallel to the HPA. The scale bar equals 20 μm.

tributed whiskers with perhaps loose interparticle contacts in the green body. Consequently, during subsequent hot pressing whiskers would have more freedom to align themselves; thus, the preferred orientation along the long dimension of the sample is further enhanced.

These results seem to suggest that pH does not lend itself to a good control over the overall whisker texture level; nonetheless, it is a critical factor that contributes to the interparticle potentials in the suspension that determine the nature of the particle network.[19] For instance, it has been shown that green bodies of pure alumina powder prepared by pressure filtration from well-dispersed slurries often released the stored strain energy through body flow (dissipation through plastic deformation) upon load removal while those prepared from the flocculated slurries exhibited an elastic response. This was ascribed to the difference in particle network configuration.[20] It can be envisaged in binary colloidal systems where the inclusions form a network that if the elastic property of this network is sensitive to the pH, different mechanical response of consolidated bodies is expected. Therefore, the importance of pH cannot be emphasized more. As observed in this work, different pH led to a much different spatial distribution of whiskers in the matrix. It might be interesting to study the result of this difference in terms of mechanical response. Although tape casting could be employed to achieve further alignment of whiskers, it requires use of additives and binders that will likely remain in the microstructure after firing. The resultant 'unclean' grain boundaries and interfaces will make the comparison with slip cast samples difficult.[12,13] Therefore, no tape casting was attempted.

6. Concluding remarks

We have analysed the effect of whisker loading and colloidal processing parameters on the distribution of SiC whiskers within alumina matrices before and after hot pressing. Neutron diffraction techniques were used to characterize the development of whisker texture at various conditions. The spatial distribution of whiskers was found to be dependent on the slurry pH. It is speculated that at low pH (2–4) the positively charged fine alumina particles were drawn to the negatively charged surface of SiC whiskers. This prevented forming large whisker clumps in the suspension, and led to, after sintering, a uniform distribution of whiskers within the fine-grained alumina matrix. At high pH ($\geq$6) it is likely that strong flocculation of alumina particles left the SiC whiskers rejected and clustered, leading to the formation of whisker agglomerates and larger matrix grains in the final products. The neutron diffraction results indicate that significant whisker alignment was present even in the green state. Although the subsequent uniaxial hot pressing further increased the alignment, the increment was not substantial. It was also found that the overall whisker alignment with respect to the hot pressing axis could not altered dramatically by adjusting slurry pH, whisker loading and solids loading.

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