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Sintering anisotropy in slip-cast SiC-whisker/Si_3N_4-powder compacts

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Sintering anisotropy in slip-cast SiC-whisker/Si_3N_4-powder compacts was studied at 1750 °C in 0.1 MPa N_2 or at 1825 °C in 1.0 MPa N_2. It was shown that whiskers oriented parallel to the mould surface and nearly 1.5-dimensionally along the slip flow direction when the whisker content was 10 wt%. Linear shrinkage was largest perpendicular to the mould surface and smallest perpendicular to the whisker alignment. It was shown that the retardation of densification by whiskers is due to the formation of a rigid network along the whisker alignment, which is in accordance with percolation theory. The addition of up to 20 wt% whisker did not affect sintering kinetics but lowered sinterability by 2-dimensional alignment of the whiskers. The anisotropy in fracture toughness is related to the orientation of the whiskers.

1. Introduction

Reinforcement of silicon nitride ceramics by SiC whiskers has been studied extensively [1–6]. It has been shown that the densification of whisker-reinforced ceramics is fairly difficult, even in Al_2O_3 matrix composites when whisker content exceeds 10 wt% [7]. Therefore, hot-pressing [1–4] or hot-isostatic-pressing [5, 6] has been employed to fabricate high density Si_3N_4 composites. Pressureless sintering of the composites has also been tried, to lower the fabrication cost [8–11]. Pressureless sintered composites have good thermal shock resistance and have been applied as ceramic parts for aluminium die casting [9].

Compacts with 2-dimensional alignment of the whiskers have been formed by slip casting [8, 9]. High density composites with < 10 wt % SiC whisker have been fabricated from slip-cast compacts by pressureless sintering. It was calculated in the system with 2-dimensional and randomly oriented whiskers that the percolation threshold decreases dramatically with an increase in the aspect ratio of the whisker, i.e. the sinterability decreases with the aspect ratio of the whisker [12, 13]. It was also calculated that the percolation threshold is lower in the system with 3-dimensional and random orientation of the whiskers than that with a 2-dimensional one [13]. These results suggest that the anisotropic orientation of the whisker may increase sinterability of whisker-reinforced ceramics. Although there are some reports on anisotropy in sintering and mechanical properties in materials with 2-dimensional alignment of the whisker [8–11, 14], there seems to have been no effort made to increase the sinterability of SiC whisker-reinforced silicon nitride ceramics by increasing the 1-dimensional orientation of the whiskers.

The present work intends to prepare compacts with 1-dimensional alignment of the whiskers by slip casting and to examine the relation between whisker alignment and sintering behaviour. The anisotropy in fracture toughness will also be shown.

2. Experimental procedure

The Si_3N_4 powder (8S grade, Japan Metals & Chemicals Co., Japan), SiC whisker (TWS100 grade, Tokai Carbon Co., Japan), sintering additives and a deflocculant were mixed in deionized water with an alumina ball mill for 46 h. The average diameter and aspect ratio of as-received SiC whisker was determined by transmission electron microscopy (TEM) as 0.35 μm and 28, respectively. The average aspect ratio of the whisker decreases to 22 after ball milling. The amount of SiC whisker was 0, 10 or 20 wt %. 8 wt % Y_2O_3 (99.99% pure, Shin-etsu Chemical Co., Japan), 5 wt % Al_2O_3 (AKP-20 grade, Sumitomo Chemical Co., Japan) and 2 wt % cordierite ($Mg_2Al_4Si_5O_{18}$, SS600 grade, Marusu Yuyaku Co., Japan) were used as the additives. A polycarbonate based deflocculant (Sannopco Co., Japan) was used in the present work. After adjusting the viscosity to about 40 ± 10 mPa s with a solid content of about 70 wt %, the slip was flowed on to a vertical mould made of plaster of Paris. After drying, the specimens (about 10 × 10 mm cross-section and 8 mm thick) were cut from the upper part of the casted compacts.

The sintering was performed at 1750 °C in 0.1 MPa N_2 or 1825 °C in 1.0 MPa N_2. A dilatometer was set in the furnace to investigate sintering behaviour during heating at a rate of 25 °C min^{-1} and keeping at a fixed temperature. The compact was covered with Si_3N_4 powder. The sintering behaviour was determined in three directions of a compact. The bulk density of green or sintered material was determined from the size and the weight. The accuracy of measurement is lower (± 0.5 %) for green compacts and higher (± 0.1 %) for sintered materials. The accuracy for linear shrinkage is therefore about ± 0.5 %. The alignment of whiskers was observed on fractured surfaces by scanning electron microscopy and on polished surfaces by optical microscopy.

The fracture toughness was measured by the micro-indentation method [15] under 10 kg load. The value was analysed in relation to the whisker alignment.

3. Results

The density of the green compact increases by addition of 10 wt % SiC whisker. The density decreases slightly with 20 wt % whisker, but the value is still higher than that of monolithic compact, as shown in Table I. The fractured surface of a green compact with 10 wt % whisker is shown in Fig. 1. It was fractured nearly parallel to the mould surface. It is revealed that whiskers align nearly parallel to the slip flow direction and with a 1-dimensional orientation.

The microstructures of materials with 10 wt % whisker obtained by heating at 1750 °C for 1 h is observed on polished surfaces. The relation between slip flow and microstructure is shown in Fig. 2. The figure shows that most whiskers align parallel to mould surface and flow direction. The difference between the *y* and *z* surfaces is not apparent in the optical micrograph.

The linear shrinkage in a compact with 10 wt % whisker is observed during heating at 25 °C min^{-1} and keeping at 1750 °C for 1 h. The results are shown in Fig. 3. The shrinkage is largest perpendicular to the plaster surface (*z* axis). It is smallest along the slip flow (*x* axis), and in between along the *y* axis. This fact suggests that whisker alignment is not 1-directional but in between 1- and 2-directional. Although

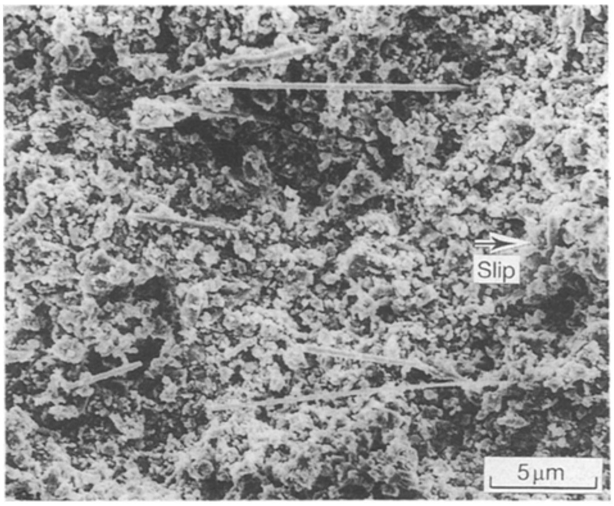

Figure 1 Fractured surface of a compact with 10 wt % whisker.

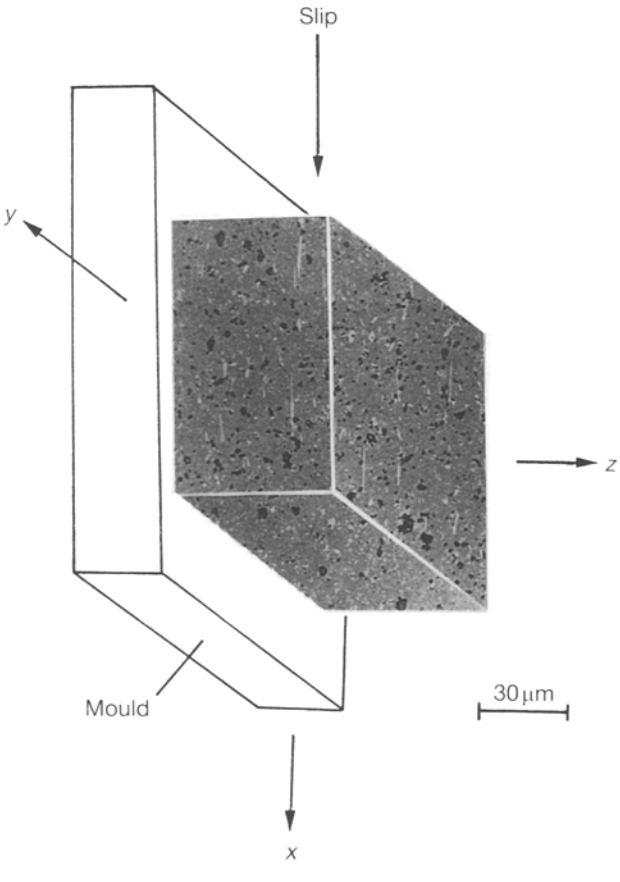

Figure 2 The optical micrograph of materials with 10 wt % whisker sintered at 1750 °C for 1 h and shown in relation to slip flow.

TABLE I Green and sintered densities, and linear shrinkage in slip-cast composites

Sintering Temp. (°C)	Time (h)	N_2 pressure (MPa)	Whisker (wt %)	Relative density (%) Green	Sintered	Linear shrinkage (%) *x*	*y*	*z*
1750	1	0.1	0	64.1	97.4	14.0	13.5	14.3
1750	1	0.1	10	67.1	94.3	5.9	10.3	14.2
1750	3	0.1	10	67.2	98.0	7.5	12.0	16.3
1750	1	0.1	20	66.2	86.9	4.9	7.3	14.5
1825	1	1.0	20	66.7	92.7	6.1	8.8	16.1
1825	3	1.0	20	66.4	96.4	7.3	10.4	18.1

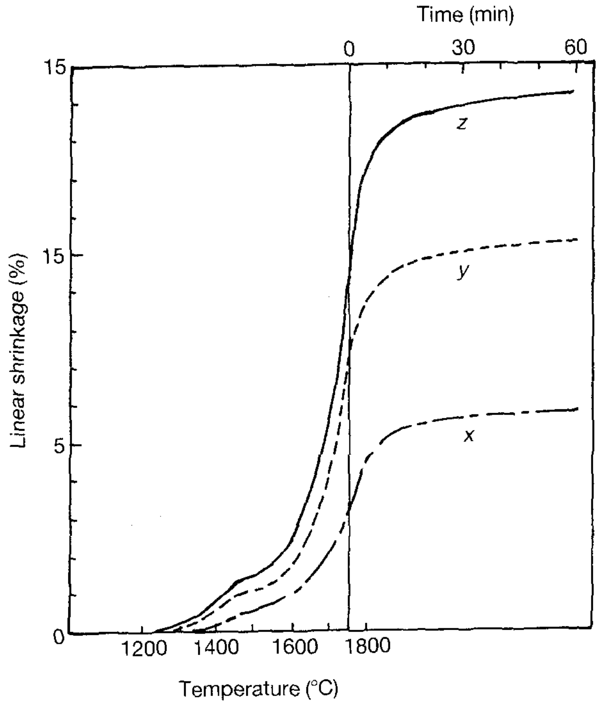

Figure 3 Linear shrinkage of a compact with 10 wt % whisker along different directions, observed during heating at 25 °C min^{-1} and keeping at 1750 °C.

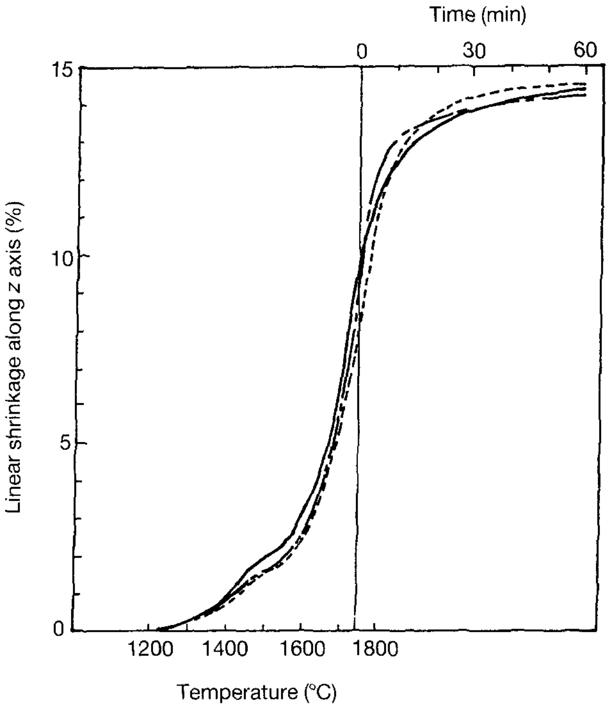

Figure 4 The effect of whisker content on linear shrinkage along the z axis during heating at 25 °C min^{-1} and keeping at 1750 °C. (———) 0 % whisker; (—·—) 10 % whisker; (- - - - - -) 20 % whisker.

absolute shrinkage depends on the direction, the relation between relative shrinkage and sintering temperature or time is nearly the same in all directions. This suggests that the presence of whisker does not change the sintering mechanism but affects the direction of material diffusion during liquid phase sintering.

The linear shrinkage along the *z* axis is not largely dependent on the amount of whisker, as shown in Fig. 4. The rearrangement of Si_3N_4 particles and SiC whiskers observed at 1400–1500 °C [16] was retarded by whisker addition. Considering the higher green density of composite compacts than that of the monolithic compacts, the densification along the *z* axis should be higher in the composites. The linear shrinkage in the other direction of the composite is also compared with that in the monolithic compact in Table I. The monolithic compact shrinks nearly the same in all directions. The shrinkage anisotropy increases in the composites with 10 wt % whisker. The difference in shrinkage between the *x* and *y* directions becomes small in the compact with 20 wt % whisker. The relative densities of sintered composites are also listed in Table I. High density composite with 10 wt % whisker has been obtained at 1750 °C. It is difficult to densify the composite with 20 wt % whisker to high density at 1750 °C. High density composites with 20 wt % whisker are obtained by heating at 1825 °C for 3 h.

The dependence of fracture toughness on the surface and crack direction is shown in Table II. The value on the *x* plane with 10 % whisker is isotropic and about the same as that without whisker. A slight anisotropy developed with 10 % whisker addition in other planes. A toughness increase in the *z* direction and a decrease in the *x* direction on the *y* plane are shown. The increase in the *z* plane is only observed in the *y* direction. The same phenomena was detected in materials with 20 wt % whisker. It is shown in the present work that the toughening by SiC whisker works only when cracks propagate perpendicular to the whiskers.

TABLE II The anisotropy in fracture toughness as measured by the microindentation method

Sintering Temp. (°)	Time (h)	Whisker (wt %)	Indentation Plane	Direction	Fracture toughness (MPa m$^{1/2}$)
1750	1	0			4.5
1750	1	10	*x*	*y*	4.4
				z	4.5
			y	*x*	3.4
				z	5.0
			z	*x*	4.6
				y	6.0
1825	3	20	*x*	*y*	3.8
				z	4.8
			y	*x*	4.3
				z	5.6
			z	*x*	4.8
				y	5.7

4. Discussion

A sintering anisotropy in slip-cast SiC reinforced Si_3N_4 ceramics has been reported [8–10]. These works concern only materials with 2-dimensional alignment of whiskers, i.e. random orientation of whiskers on a plane. Hoffman and co-workers [8, 9] determined densification behaviour perpendicular and parallel to the whisker alignment. They reported that the shrinkage was higher for perpendicular and lower for parallel surface-to-whisker orientation than that for without whisker, respectively.

The present work shows that the shrinkage is different in three directions. The presence of whisker did not affect densification along the z axis. The shrinkage stresses caused by the presence of non-sinterable cores in sinterable matrices were supposed to be one of the reasons for the retardation of densification by whiskers [17, 18]. However, it is the most likely that the stresses were released during liquid phase sintering, because densification along the y and z directions in the x plane was not retarded, as shown in Fig. 4. The main reason for the retardation of densification by whisker might be due to the formation of a rigid network of whiskers. The lowest shrinkage along the x axis is thus related to preferential orientation of whiskers along the slip flow [8]. This phenomena is explained by a percolation theory [12, 13]. The theory predicts the percolation threshold, over which the densification should be retarded, in relation to the aspect ratio and the volume fraction of whiskers. The result for materials with 2-dimensional alignment of whiskers shows that the threshold is about 15 vol % when the aspect ratio is 22. The sinterability of composite compacts cannot be simply discussed by the attained densities, because there are many parameters which affect sinterability of the compact, i.e. powder characteristics of Si_3N_4 [19], the amount and the composition of additives [20, 21], and the diameter and the aspect ratio of the whisker [10, 22]. But the most data on attained densities revealed that the density decreases at 15 wt % whisker addition or more, which agrees well with the percolation theory, although the decreases were not as drastic as predicted. The theory also predicts that the percolation threshold should be very low with 3-dimensional alignment of whiskers [13]. The results suggest that the sinterability should be improved by increasing the fraction of 1-dimensionally aligned whiskers.

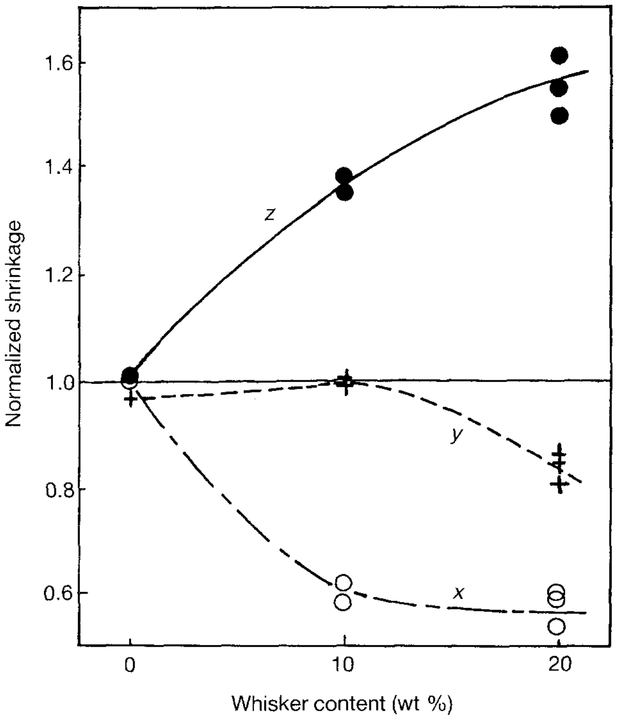

Figure 5 Shrinkage anisotropy revealed by normalized shrinkage.

Hoffman and co-workers [8] discussed the sintering anisotropy by plotting normalized shrinkage with whisker content. The normalized shrinkage (Sn) is defined by

$$Sn = \frac{1 - (L_s/L_0)}{1 - (V_s/V_0)^{1/3}} \tag{1}$$

where, L and V denote the length and volume of the green (0) and sintered (s) compacts, respectively. The Sn value is 1.0 for isotropic shrinkage. Shrinkage is higher than average when the Sn value is > 1.0, and lower when Sn is < 1.0.

The calculated Sn values for the present work are shown in Fig. 5. The shrinkage increases along the z axis and decreases along the x axis with the increase of whisker content. The normalized shrinkage along the y axis should be equal to that along the z axis in a compact with 1-dimensional alignment of the whiskers, and equal to that along the x axis in a compact with 2-dimensional alignment. The present results show that the alignment is about 1.5-dimensional in compacts with 10 wt % whisker and approaches 2-dimensional in compacts with 20 wt % whisker.

It is not easy to characterize whisker alignment in compacts [23]. The present work shows that sintering anisotropy is a good measure for the characterization of whisker alignment. High density composites with 20 wt % whisker should be easily fabricated by preferential orientation of whiskers along the slip flow.

There was no toughness increase on the x plane, as shown in Table II. The polished surface in Fig. 2 reveals that SiC whiskers appear mostly as SiC particles in the plane. It has already been reported that the presence of sub-micron SiC powder in Si_3N_4 ceramics did not increase fracture toughness of composites [24, 25]. The present results agree with those of previous works. Toughening on the y plane was only detected along the z direction, reflecting the alignment of the whiskers parallel to the slip flow and the mould. The same phenomena was also reported in hot-pressed composites which have 2-dimensional alignment [4]. The toughness increase in the z plane was mainly observed along the y direction, in accordance with preferential alignment of whiskers along the slip flow. A slight increase in toughness was detected along the x direction when the whisker content was 20 wt %, at which the degree of 2-dimensional alignment increases. The results reveal that the toughening mechanism works in only one direction, perpendicular to whisker alignment.

The fracture toughness is shown by

$$K_{1C} = K_0 + dK_w \tag{2}$$

in which K_0 and dK_w are the fracture toughness of the matrix and the toughness increase by whisker addition, respectively. The toughness increase (dK_w) might increase with whisker addition. The observed toughness increase in Si_3N_4 composites was fairly small, as

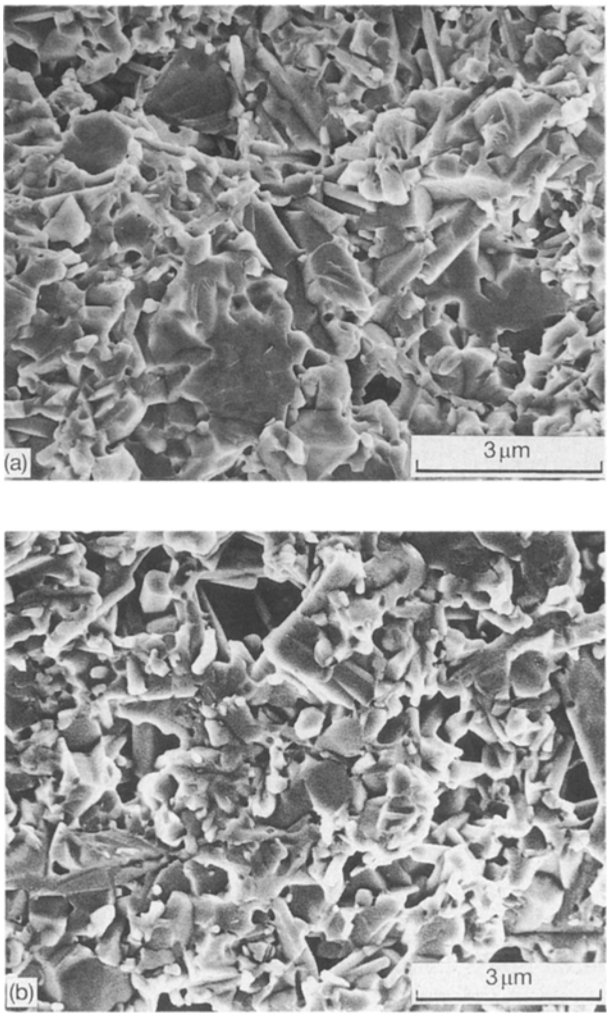

Figure 6 Fractured surface of materials sintered at 1750 °C for 1 h, (a) with 10 wt % whisker, and (b) with 20 wt % whisker.

reported on sintered composites [8–11]. There are some abnormally grown large grains in sintered Si_3N_4 ceramics, which contribute to the toughening by crack bridging (26, 27). The addition of whiskers inhibits not only the densification but also the grain growth, as shown in Fig. 6. It suggests that the toughness of the matrix (K_0) is not constant and decreases with the amount of whisker. This might be a reason why the toughening of Si_3N_4 ceramics is more difficult than that of Al_2O_3 ceramics [28].

The toughness decreases when cracks propagate along whiskers [4]. The decrease was also shown along the x direction in the y plane in the present work (Table II). Although there have been some reports on microstructures of SiC whisker-reinforced Si_3N_4 ceramics [29, 30], the reason for this weakening has not been clarified. The anisotropic distribution of residual pores, which is suggested from the anisotropic shrinkage in Fig. 3, is supposed to be the main reason. Further work is necessary to correlate the toughness anisotropy with microstructures.

5. Conclusions

The sintering behaviour of a slip cast SiC-whisker/Si_3N_4-powder compact was studied in three directions. It was shown that linear shrinkage perpendicular to the mould surface was larger and that along the slip flow was smaller than that in a monolithic compact. The sintering anisotropy was related to preferential orientation of whiskers in parallel to the mould surface and along the slip flow. The alignment of whisker was about 1.5-dimensional in materials with 10 wt % whisker and approaches 2-dimensional in materials with 20 wt % whisker. The retardation of densification by whiskers is explained by percolation theory. The toughening by whisker was observed only when cracks propagated perpendicular to the whiskers.

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