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The effect of rheological behavior of tape casting on the green sheet and sintered silicon carbide

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Abstract

The primary purpose of this study is to develop the technology of fabricating silicon carbide thin substrate by means of tape casting in these experiments; silicon carbide ceramic by addition of Al_2O_3 and Y_2O_3 sintering aids can exhibit both high strength and toughness, simultaneously. The variables of these explorations include (1) silicon carbide raw powders: particle size and crystalline phase; (2) slurry formula: relative content of solvent and dispersant binder. To investigate the correlation /ships among the aforementioned variables are discussed by the green density, uniformity, Sintered density as well as microstructures. Based on prior experimental results, the best parameters of organic additives and tape casting processing for manufacturing silicon carbide thin tape are suggested. Furthermore, the green tapes with superior properties are densities by pressureless sintering to 97.5%.

Keywords: A. Tape casting; D. SiC; Rheological behavior; Slurry

1. Introduction

Owing to its intrinsically excellent high hardness, good resistance of corrosion and oxidation, high thermal conductivity, superior thermo/mechanical as well as thermophysical properties, Silicon carbide (SiC) ceramic has been widespread used in mechanical seal, valve, heat exchanger, silicon wafer boat and high density electronical ceramic package [1–3]. In the aforementioned applications, the excellent mechanical properties and good stability were required and was a subject of constant interest for many ceramic researchers. The first work was pioneered by Prochazka [4] who developed a dense SiC ceramic with the addition of B and C as sintering aids by means of a solid-state sintering mechanism. In spite of sufficient flexural strength, SiC ceramics with B and C sintering aids exhibited little enhancement in fracture toughness. Omori and Takei [5] who used alumina and yttrium as sintering aids by liquid-phase sintering mechanism, acquired a dense SiC with an improved fracture strength of greater than 650 MPa. The other investigators, Lee and Kim [6], obtained a dense SiC ceramic with a fracture toughness as high as $\sim$8.3 MPam$^{0.5}$, by allow elongated growth of SiC grains at 2000 °C to form a microstructure containing considerable amounts of plate-like α-SiC grains. However, the fracture strength of their SiC ceramics decreased to $\sim$450 MPa. A lot of investigations [6–8] showed the importance of sintering aids, which play a crucial role in changing the mechanical and high temperature properties. More recently, the present author Fu et al. have demonstrated that dense SiC ceramics with a four-point flexural strength above 600 MPa and a fracture toughness as good as $\sim$6.0 MPam$^{0.5}$, simultaneously, are achieved through the control of microstructure evolution in monolithic SiC ceramic, via starting with a mixture of α-SiC and β-SiC powders and a two-step pressureless sintering procedure [8]. Furthermore, this high performance SiC ceramics should be fabricated and machined to several complicated ceramic components before they can be used practically. Thus, it is essential to pay much attention to investigate the shaping engineering and behavior of this SiC ceramic.

Tape casting process is the best method for manufacturing large, thin and flat ceramic single layer or

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being laminated into multilayered components. This technology is widely used in ceramic multilayered capacitors, inductors, varistors, electronically packaged, ceramic fuel cells, lithium ion battery as well as electrical static chucks[9,10]. During the last few years, tape casting has been usually based upon a nonaqueous solvent as the liquid medium because the drying process of nonaqueous solvent was easer evaporated than that of water-based system. However, at the present time, the environmental and health concerns with the use of organic solvents have been emphasized. An added benefit is the cost reduction involved with the use of water. More recently, the thickness of tape has been successfully miniaturized to around 5 μm [11] and extensively enhanced the electronic functions of ceramic material. This potential technology of ceramic tape casting is approached by using very fine powders and improved dispersants. Owing to the thinner green tape, the drying process becomes easier to greatly enhance the mass-produced possibility of aqueous systems. Although a few investigations of tape casting were conducted by oxide ceramics in water [12], the relevant reports on the SiC–Al_2O_3–Y_2O_3 systems have not been found in literature, particularly in high performance SiC ceramics which have been reported to exhibit prominent fracture toughness. The primary purpose of this study is to develop the thin SiC substrate fabricated by tape casting in water system. The rheological behaviors of SiC–Al_2O_3–Y_2O_3 slurry using different SiC particle size, dispersant and solid content were discussed. The correlations among rheological behaviors, green density as well as microstructures were investigated.

2. Experimental procedures

2.1. Raw material

The alpha SiC powders used in this investigation were Showa Denko (Japan, grade A-1, denoted A) and Nun Hsing (Japan, grade GC-8000, denoted G). The beta SiC powder employed in this study was Mitsui (Japan, grade MSC-20, denoted M). The mean particle size, measured by laser diffraction techniques, were 0.48, 2.0 and 0.21 μm, respectively. The purity was all higher than 99%. The average particle size of Al_2O_3 and Y_2O_3, which was acted as sintering aids, were 0.5 and 1.0 μm, separately. The purity of both powders was greater 99%. The organic additives of polyvinyl alcohol (PVA, Taiwan Chang Chun Co., grade BP-05) and polyethylene glycol (PEG, Taiwan USI Co., grade PEGT-200) were used as binder and plasticizer, respectively. The dispersant was applied by a commercial product (denoted D) which was the best dispersing effect among 10 commercial dispersants.

2.2. Manufacturing procedures

The ceramic slurry containing 90 wt.% SiC, 6.2 wt.% Al_2O_3 and 3.8 wt.% Y_2O_3, deionized water and properly organic agents were prepared by ball milling in a high purity Al_2O_3 jar for 24 h. The homogeneous slurry was formed by tape casting to a flat sheet with 0.3 mm in thickness and then dried under the ambient temperature for several days. The green sheets were placed in air furnace and raised the temperature to 500 °C for 2 h to remove organic agents. Further then, the green tapes were pressureless sintered to 2000 °C for 2 h in Ar atmosphere.

2.3. Characterizations

The rheological characteristics of homogeneous slurry were determined by a concentric cylinder viscometer (RV-20, Haake Mess-Technik GmbHu. Co., Germany).

The green density of ceramic tape was measured by a mercury proximate (Autopore 9220, Micrometeritics Instrument Corp., GA). The density of the sintered SiC bodies was evaluated by using Archimedes' principle. Microstructure of green tape and sintered SiC body were examined by using scanning electron microscopy (SEM, Cambridge Instruments, S-360).

3. Results and discussion

3.1. Rheological behaviors of SiC slurry

While the content of dispersant was 3 wt.%, the rheological behavior of six SiC slurries all exhibited a typically shear thinning or pseudoplastic behavior (as shown in Fig. 1) which was the desired character to acquire a homogeneous and flat green sheet in the tape casting techniques [13]. Initially, as the shear rate of slurry increasing, the apparent viscosity extensively decreased. This phenomenon was raised from the higher shear forces to separate as well as slide SiC particles one another and lead to the lower slurry viscosity. Furthermore, while the shear rate was higher than 50 s^{-1}, the shear rate of these slurry showed little dependence on the viscosity and became nearly Newtonian behavior. In this moment, there is weak or even no interacted force among particles in the suspension. The viscosity of SiC slurry is greater when the particle size is finer as well as the solid content is higher. But, the trend between viscosity and shear rate is similar.

As the solid content of slurry was 55%, the correlations between viscosity and dispersant content were illustrated in Fig. 2. Initially, the variation of viscosity was remarkably decreased with increasing dispersant content and reached a minimum value. Then, the viscosity was gradually increased with higher dispersant content. The former is caused from the monolayer coverage of the SiC particle by the dispersant molecule to separate particles well and reduce the viscosity. The amount of monolayer coverage upon particle initially increased with dispersant content and greatly declined the viscosity of slurry. The minimum viscosity implies that a monolayer adsorption onto particle may be achieved to a saturated equilibrium state [14]. The latter case indicated that the excess of dispersant beyond the saturated equilibrium value is left in the supernatant and causes a slightly flocculated or ridged effect between particles through the polymeric chain. This reason arises due to an increase in slurry viscosity and/or degree of flocculation, corresponding to an increased resistance to flow, at higher dispersant content. Generally, the monolayer coverage of the particle by the dispersant molecule is roughly estimated by using the specific surface area of the particle. The finer particle with a greater specific area needs a higher dispersant content to cover the monolayer onto particle. In this case, the specific surface area of G–SiC, A–SiC and M–SiC are 4.2, 15.0 and 35 cm^2/g, respectively. Therefore, the value of saturated dispersant content for A–SiC slurry is at 3.0wt% and higher than that of G–SiC slurry at 2.0 wt%. Owing to the addition of finer particle with 30 wt.% M to A and G–SiC slurry, not only the saturated dispersant content increases to 4 and 3 wt.%, respectively, but also the viscosity of two SiC slurry becomes greater. In most cases, the binder content of slurry in tape casting is higher than that in slip casting and seriously hinders dispersant from reaching the surface of particle. Therefore, the saturated dispersant content for A and G–SiC slurry is 3.0 and 2.0 wt.%, respectively, in tape casting and decreased to 0.75 and 0.15 wt.%, respectively, in slip casting [14].

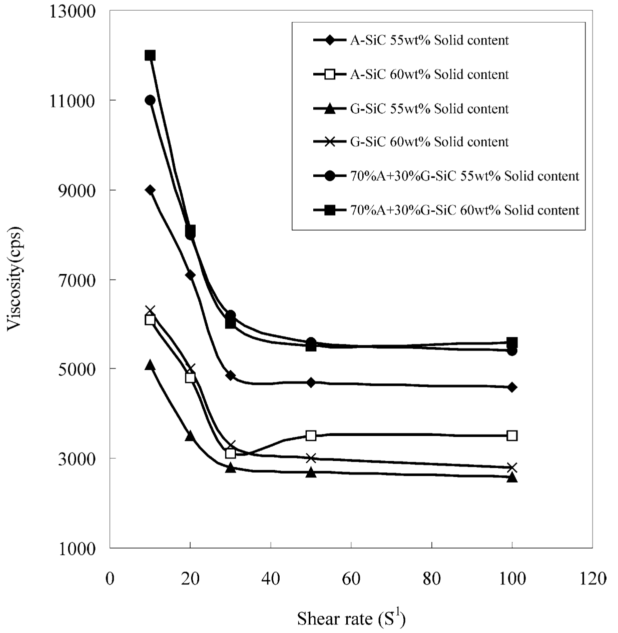


Fig. 1. The dependence of shear rate solid on the viscosity of six SiC slurries with 55–60 wt.% solid content.

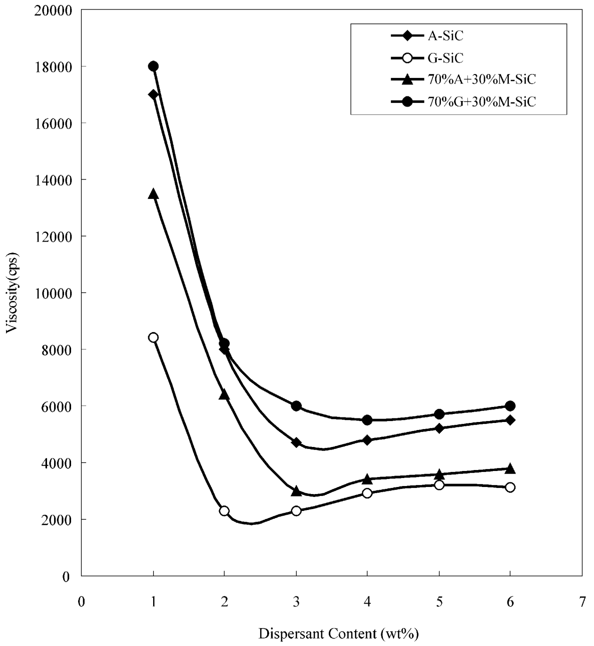


Fig. 2. The correlation between viscosity and dispersant content in four SiC slurry with 55 wt.% solid content.

3.2. Properties of green sheet and sintered SiC bodies

The green density of SiC green sheets exhibit a strong association with the type powder used and dispersant

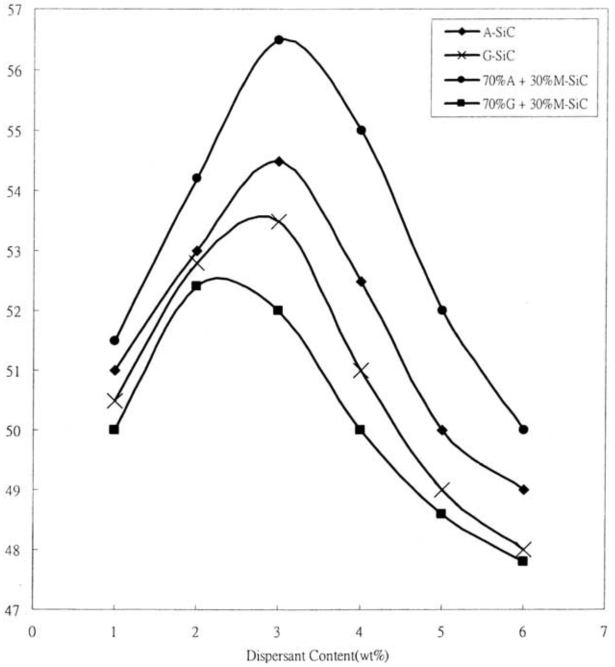


Fig. 3. The dependence of dispersant content in 55 wt.% solid loading SiC slurries on the green density of green sheets after tape casting processing.

content, as indicated in Fig. 3. The green densities achieved with A–SiC powder are higher than those achieved with the G-SiC powder, and both, after reaching a maximum green density of ~55 and ~53% for A– and G–SiC, respectively, then show a decreased green density as the concentration of dispersant increases. Based on the available data from both manufacturers, it is demonstrated that the G–SiC powder has a wider particle size distribution (0.6–6 μm) than that of the A–SiC powder (0.2–2 μm).This is illustrated by slurries containing narrow sized distribution and finer powders can be consolidated to green sheets with higher density which is consistent with the experimental results reported by Roosen and Bowers in the alumina–aqueous system [15]. The green density for both powders extensively decreased with further increasing dispersant content. It is proposed that a poorly dispersed or even a flocculated slurry due to possible bridging effect by the dispersant. Due to the addition of finer M–SiC (β phase) to A and G–SiC (α phase), the maximum green density rises to 56.7 and 53.8%, respectively. Based on the principles of particle packing behavior [16], the packing density for the blending of discrete sizes can be greater than that of one size particle. Therefore, the green density of A and G–SiC green sheets is raised by incorporating finer M–SiC particles.

It is worthy to note that the highest green density for four types of SiC powders occurs when the slurries exhibit at the lowest viscosity. This result illustrates that the SiC particles slide more easily over one another and better rearrangement at the lowest viscosity to achieve the greater packing structure as well as higher green density.

The typical microstructures of the surface on the green sheet for A–SiC powder at the dispersant of 1 and 3 wt.% are observed in Fig. 4(a) and (b), respectively. Both green compacts contain small voids which are approximately 0.5–2 μm in size. There are some evidently irregular pores exhibiting the poorly dispersed compacts [Fig. 4(a)] containing 1 wt.% dispersant. However, the nearly spherical SiC particles with a smooth surface, as shown in Fig. 4(b), are revealed on the well packing green sheet, which further substantiates the previous discussions on acquiring higher packing density (Fig. 3).

Fig. 5 shows the dependence of sintered density of both types of α-phase SiC ceramic on the dispersant contents .In addition to the greater green density, the mean particle size of A–SiC ($D = 0.5$ μm) green sheets is finer than that of G–SiC ($D = 2.0$ μm) to achieve a faster densification rate. So, the A–SiC ceramic is given to a

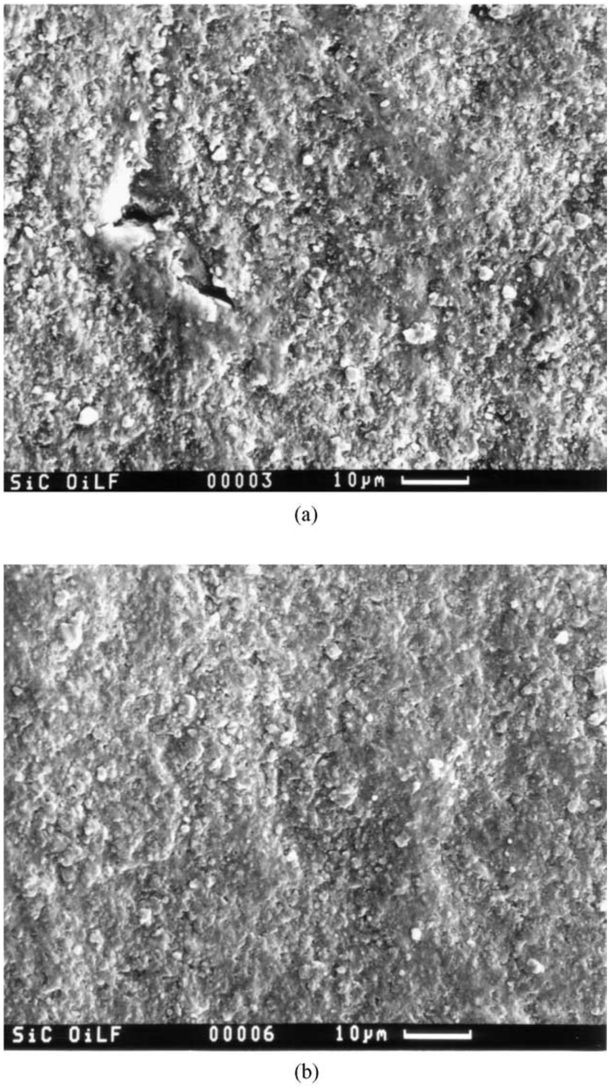


Fig. 4. Scanning electron micrograph of fractured surface of ceramic green sheets prepared at (a) 1.0 wt.% and (b) 3.0 wt.% dispersant.

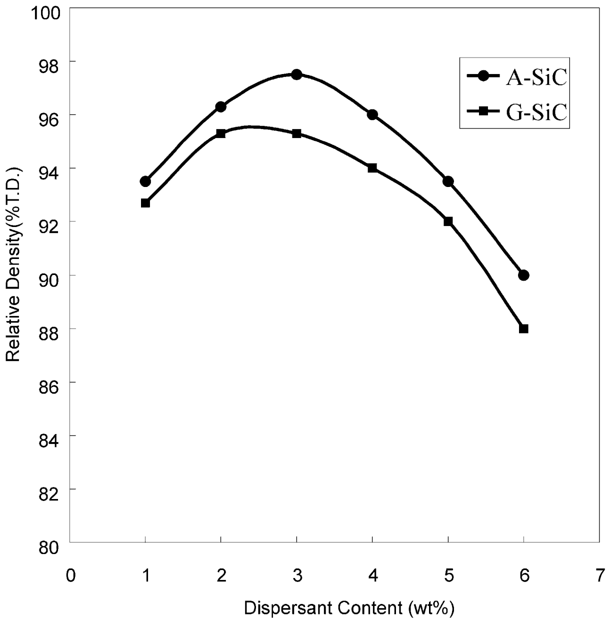
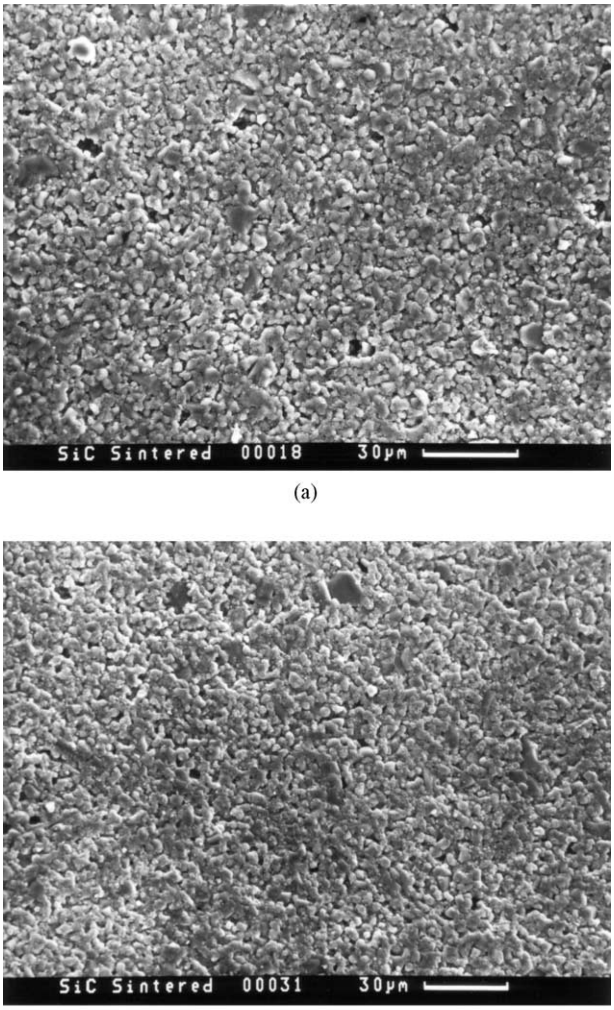


Fig. 5. Sintered density of G–SiC and A–SiC ceramics, prepared at various dispersant contents.

higher density than that of G–SiC ceramic. The variations of sintered density for both A–SiC and G–SiC ceramics correlate well with the trend related to the dispersant content as seen in green density (Fig. 3). The maximum sintered density is 97.5 and 95.3% T.D. (3.21 g/cm^3 for SiC ceramic) for A–SiC and G–SiC ceramics, respectively. An examination of surface for A–SiC sintered body at 1.0 and 3.0% dispersant is shown in Fig. 6(a) and (b), respectively. It can be easily observable that the sintered A–SiC ceramic fabricated from the slurry with 3 wt.% dispersant exhibits a more uniform microstructure, particular in pore size and its distribution than those for 1 wt.% dispersant. Owing to the shrinking rate for larger pore being lower, there are some evident flaws, as shown in Fig. 6(a), which originally exist in the green compacts and are difficult to eliminate during the sintering process. Although containing more organic binder content, the sintered densities presented in this study were greater than those prepared by Omori and Takai [5] with various ratios of Al_2O_3/Y_2O_3 as sintered aids, followed by pressureless sintering at 2100 °C.



(a)

(b)

Fig. 6. Scanning electron micrograph of the as-sintered surface prepared at (a) 1 wt.% and (b) 3 wt.% dispersant.

4. Conclusions

Both rheological behavior and green density of the slurries for three types of commercial SiC powders were explored by tape casting processes. To obtain the lowest viscosity slurry with 55 wt.% solid content, a suitable amount of dispersant N, i.e. ~0.2 and ~0.3 wt.% for the G–SiC and A–SiC powders, respectively, was required. Further increase of the dispersant concentration raised the viscosity of slurry. The maximum green density reached ~53 and ~55% for G–SiC and A–SiC powders, respectively. For the same type powder, the lowest viscosity which was indicated to easily slide and rearrange, was required to achieve the maximum density of green compact. Based on this experimental result, a narrow-sized as well as fine- particle-containing slurry with optimal viscosity is essential to obtain a uniform and high density microstructure. Due to the addition of 30 wt.% finer M–SiC powder (b phase) to G–SiC and A–SiC powders, the green density was enhanced to 53.8 and 56.7%, respectively. The possible reason was resulted from which the packing density with two discrete size powders was greater than that with one size powder. The maximum density of pressureless sintered body was attained to 95.3 and 97.5% T.D. for G–SiC and A–SiC powders, respectively. The greater green density together with finer powder could lead to a higher sintered density.

Acknowledgements

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References

[1] S.J. Dapkunas, Ceramic heat exchanger, Am. Ceram. Soc. Bull. 65 (1988) 388–391.
[2] Y.S. Takeda, Development of high-thermal-conductive SiC ceramics, Am. Ceram. Soc. Bull. 67 (12) (1988) 1961–1963.
[3] Y. Takeda, K. Nakamura, Y. Matsusnita, The influence of manufacturing conditions on the characteristics of SiC ceramics with addition of BeO, J. Am. Ceram. Soc. Japan, International edn. 99 (1991) 62–63.
[4] S. Prochazka, Sintering of silicon carbide, in: J.J. Burke, A.E. Gorum, R.M. Katz (Eds.), Proceedings of the Conference on Ceramics for High Performance Applications (Hyannes, MA, 1973), Brook Hill Publication Co., Chestnut Hill, MA, 1975, pp. 7–13.
[5] M. Omori, H. Takei, Preparation of pressureless sintering SiC–Al_2O_3–Y_2O_3, J. Mater. Sci. 23 (1988) 3744–3749.
[6] S.K. Lee, C.H. Kim, Effect of A-SiC versus B-SiC starting powders on microstructure and fracture toughness of SiC sintered

with Al_2O_3 additives, J. Am. Ceram. Soc. 77 (6) (1994) 1655–1658.

[7] Y. Ikuhara, H. Kurishita, H. Yoshinaga, Grain boundary and high temperature strength of sintered SiC, Yogyo-Kyokai-Shi 96 (6) (1987) 638–645.

[8] B.W. Lin, C.T. Fu, D.M. Liu. Method for making high performance self-reinforced SiC using a pressureless sintering process. US Patent number 5,656,218, 12 August, 1997.

[9] W. Toshiya, K. Tetsuo, Effect of additives on the electrostatic force of alumina electrostatic chucks, J. Ceram. Soc. 100 (1) (1992) 1–6.

[10] D.H. Larry, Electrostatic wafer holding, Solid State Technol. Jan (1993) 87–90.

[11] DreiTek, Inc., Ceramic Thin Tape Casting 5 Microns, Am. Ceram. Soc. Bull. 76 (9) (1997) 164.

[12] E.M. Richard, Tape casting: past, present, potential, Am. Ceram. Soc. Bull. Oct (1998) 82–86.

[13] J.S. Reed (Ed.), Principles of Ceramics Processing, A Wiley-Interscience Publication, New York, 1995, pp. 525–541.

[14] D.M. Liu, C.T. Fu, Effect of rheological behavior on properties of cast and sintered SiC, Ceram. Int. 22 (1996) 101–106.

[15] A. Roosen, H.K. Bowen, Influence of various consolidation techniques on the green microstructure and sintering behavior of alumina powders, J. Am. Ceram. Soc. 71 (11) (1988) 70–77.

[16] J.S. Reed (Ed.), Principles of Ceramics Processing, A Wiley-Interscience Publication, New York, 1955, pp. 215–243.