Ceramics International 22 (1996) 107–112

0272-8842/96/$15.00
0272-8842(95)00064-X

Thermal Shock Resistance of SiC Whisker Reinforced Si_3N_4 Ceramic Composites

D. C. Jia, Y. Zhou & T. C. Lei

School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, People's Republic of China

(Received 21 November 1994; accepted 27 February 1995)

Abstract: Thermal shock resistance of hot-pressed SiCw/Si_3N_4 (w = whisker) composites was investigated by thermal shock resistance parameters and water quenching test. The results showed that the thermal shock resistance to fracture initiation and crack-stable repropagation deteriorated with increasing SiCw content in spite of the improvement of fracture toughness, K_{IC}. This could be attributed to the great decrease of strength, σ, and the considerable increase of Young's modulus, E, and thermal expansion coefficient, α, resulting from the addition of SiC whiskers. The curves of the residual strength, σ_r, after water quenching versus thermal shock temperature difference, ΔT, e.g. σ_r–ΔT, showed good relationships with the calculated thermal stress fracture resistance parameter, R, and thermal stress crack stability parameter, R_{st}. The crack propagation of SiC whisker reinforced Si_3N_4 occurred primarily in a quasi-static manner, and it could be mainly attributable to SiC whiskers' pulling-out and bridging toughening effects.

1 INTRODUCTION

Silicon nitride ceramics as one of the most promising high-temperature structural materials have been under active development for demanding elevated temperature applications.[1–4] Unfortunately, like most other kinds of ceramics they also have a tendency toward catastrophic failure especially upon severe thermal shocking, which remains a major obstacle to their more widespread utilization.

To evaluate the thermal stress crack initiation and propagation behaviour of ceramics, three thermal shock resistance parameters are usually used. The first one is the thermal stress fracture resistance parameter, R, expressed by:[5–7]

$$R = \sigma(1-\nu)/(\alpha E) \qquad (1)$$

where σ is the tensile strength of the material, ν is Poisson's ratio, α is the thermal expansion coefficient, and E is the Young's modulus. R represents the critical temperature difference, ΔT_c, for thermal stress crack initiation.

The second parameter is the thermal stress damage resistance parameter, R^{IV}, represented by:[5–7]

$$R^{IV} = E\gamma_f/[\sigma^2(1-\nu)] \approx (K_{IC}/\sigma)^2/(1-\nu) \qquad (2)$$

where γ_f is the fracture surface energy and K_{IC} is the fracture toughness. R^{IV} decides the resistance to catastrophic crack propagation of ceramics under a critical temperature difference, ΔT_c.

The third is the thermal stress crack stability parameter, R_{st}, which indicates the resistance to crack repropagation after a critical temperature difference, ΔT_c. R_{st} is represented by:[7]

$$R_{st} = [\gamma_f/(\alpha^2 E)]^{1/2} \qquad (3)$$

From the above three equations, it can be clearly seen that the thermal shock resistance of ceramics is decided by many factors, such as strength, σ, Young's modulus, E, fracture surface energy, γ_f, fracture toughness, K_{IC}, and thermal expansion coefficient, α. Therefore, in developing high thermal shock resistance composites, all the above factors should be taken into consideration synthetically.

In order to avoid or mitigate catastrophic failure of monolithic silicon nitride, it is believed that additional improvements in strength and fracture toughness are needed,[4] and this can be achieved by making composites through introduction of fibres, particulates and whiskers. Previous studies[8,9] on SiCw/Si_3N_4 showed that room and elevated temperature strength and fracture toughness of the composites really could be raised simultaneously. However, not enough attention was paid to other parameters, such as Young's modulus, E, and thermal expansion coefficient, α, which are at least as important as strength, σ, and fracture toughness, K_{IC}, especially for applications under severe thermal shocking.

Hence, in the present work, the influence of SiC whiskers on microstructure, flexural strength, σ, Young's modulus, E, fracture toughness, K_{IC}, and thermal expansion coefficient, α, of SiCw/Si_3N_4 composites was studied; thereafter the influence of SiC whiskers on thermal shock resistance parameters including R, R^{IV} and R_{st} was investigated. The relationships between the thermal shock resistance parameters and the curves of residual strength versus thermal shock temperature difference are discussed.

2 SPECIMEN PREPARATION AND EXPERIMENTAL PROCEDURE

SiCw/Si_3N_4 composites with different volume percentages of SiCw including 0, 10, 20 and 30% were prepared by hot-pressing. High-purity sintering aids: 2 wt% Al_2O_3 + 3 wt% Y_2O_3 were added. The characteristics of the starting Si_3N_4 powder are α-Si_3N_4, fraction: 94·5%, average grain size: 0·5–0·6 μm. SiC whiskers supplied from Tokai Company of Japan are 1·0–1·4 μm in diameter and 20–30 μm in length, with β-SiC phase structure. After the matrix powder, sintering aids, and SiCw were blended, the mixture was milled using ZrO_2 balls in plastic bottle filled with alcohol for 24 h and then dried in air. Green bodies were prepared by pressing under 200 MPa pressure in air, then hot-pressed at 1800°C in N_2 atmosphere under 25 MPa for 1 h. The sintered bodies were cut into 3 mm × 4 mm × 40 mm flexural bars. The surfaces especially the tensile ones were finely ground along the longitudinal direction, and the edges were bevelled. The tensile surface in three-point bending test was normal to the hot-pressing direction.

Densities of specimens were measured by Archimedes' method and their relative densities were calculated. The phase analysis of the composites was conducted using an X-ray diffractometer with CuK_α ray, and the ratio of the residual α-Si_3N_4 content to the overall Si_3N_4 was calculated based on the relationship between composition and X-ray diffraction intensity ratio $(I_{\alpha(102)} + I_{\alpha(210)})/(I_{\alpha(102)}+I_{\alpha(210)}+I_{\beta(101)}+I_{\beta(210)})$.[10] The bending strength at room temperature was determined in a three-point bending test with a span length of 30 mm, and a crosshead speed of 0·5 mm/min. Load–strain curves were recorded by attaching strain gauges to the tensile surfaces of specimens, so that Young's modulus could be calculated. The toughness was measured by SENB test with a span length of 16 mm and a crosshead speed of 0·05 mm/min using specimens with notches of 2 mm in depth, 0·25 mm in width in the middle of them. Four to six bars for each sample were tested to calculate strength, Young's modulus and toughness. Thermal expansion coefficient only along the direction vertical to the hot-pressing direction was measured.

To evaluate the thermal shock resistance of the composites, three thermal shock resistance parameters, R, R^{IV} and R_{st}, were calculated and a water quenching test was conducted. Sets of five or six specimens were held at a predetermined temperature for 10 min in an Al_2O_3 tube which was then tilted to drop the specimens into a container of room-temperature water. The furnace temperature was controlled to H±2°C. The residual strengths of the shocked specimens were measured under the same conditions as those of the unshocked ones. Microstructure of the composites and fracture morphology after thermal shock were observed on an S-570 type SEM.

3 RESULTS AND DISCUSSION

3.1 Microstructure

The relative density and residual α-Si_3N_4 content of the composites are shown in Fig. 1, which illustrates that the relative density decreases gradually with increasing SiCw content, and the residual α-Si_3N_4 content increases markedly with increasing SiCw content. That is to say, not only the densification

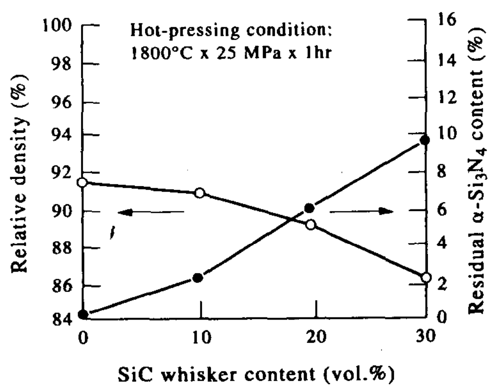

Fig. 1. Relative density and residual α-Si_3N_4 content of SiCw/Si_3N_4 composites as a function of SiC whisker content.

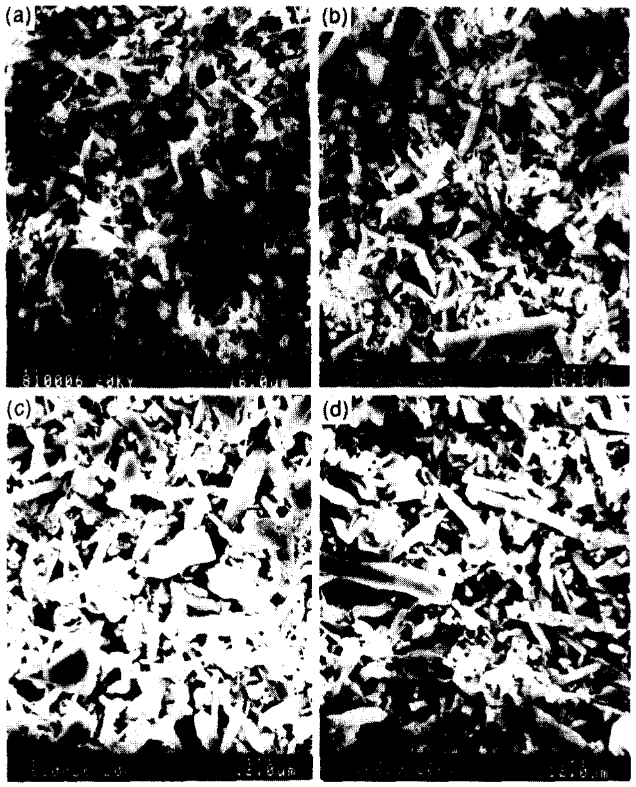

Fig. 2. Microstructures of $SiCw/Si_3N_4$ composites: (a) 0 vol% SiCw, (b) 10 vol% SiCw, (c) 20 vol% SiCw, (d) 30 vol% SiCw. (Polished surfaces were etched in molten NaOH at 350°C, (a),(b) for 80 s and (c),(d) for 50 s.)

of the composites but also the $\alpha \rightarrow \beta$ transformation of Si_3N_4 is retarded by the addition of SiCw.

Figure 2 shows the microstructures observed by SEM. The elongated β-Si_3N_4 grains of the composites can be clearly seen; additionally, with increasing SiCw content, the equiaxial residual α-Si_3N_4 grains are more easily discerned, and the porosity of the composites is increasing. All of these are consistent with the density and α-Si_3N_4 content testing results. Comparing Figs 2(a) and 2(b), it can also be seen that the worse developed β-Si_3N_4 grains in SiCw/ Si_3N_4 are smaller than that of the monolithic Si_3N_4.

3.2 Mechanical properties

The bending strength, Young's modulus and fracture toughness of the composites are demonstrated in Fig. 3. As shown, the bending strength of the composites decreases drastically with increasing SiCw content. This might be mainly attributed to two points. One is that the reinforcement by SiCw of the matrix is offset by the decreasing density. The other is that the self-reinforcement of elongated β-Si_3N_4 grains is impaired not only by their decreasing content but also by their worse developed smaller β-Si_3N_4 bars with increasing SiCw content.

By contrast, the Young's modulus of the composites increases from 210 GPa for those without SiCw to 250 GPa for that with 20 vol% SiCw, and then decreases substantially at higher SiCw contents. It can be concluded that when the density decrement of the composite is small, the considerably high Young's modulus (400–700 GPa) of SiCw compared with that (200–310 GPa) of Si_3N_4 can compensate for the decrease of Young's modulus resulting from the decreasing density. However, when the density decreases beyond a critical point, its influence will have precedance over that of the reinforcement by SiC whiskers.

The change of fracture toughness of the composites with SiCw content is roughly similar to that of Young's modulus. When SiCw content attains 10 vol%, it has the best toughening effects.

3.3 Thermal expansion coefficient

SiCw has a higher thermal conductivity than Si_3N_4; from the point of view of lowering the temperature gradient of the composite, it will be beneficial to the thermal shock resistance to introduce SiCw to monolithic Si_3N_4. However, SiCw has a larger thermal expansion coefficient, so it will inevitably raise the thermal expansion coefficient of the composite, which is much more

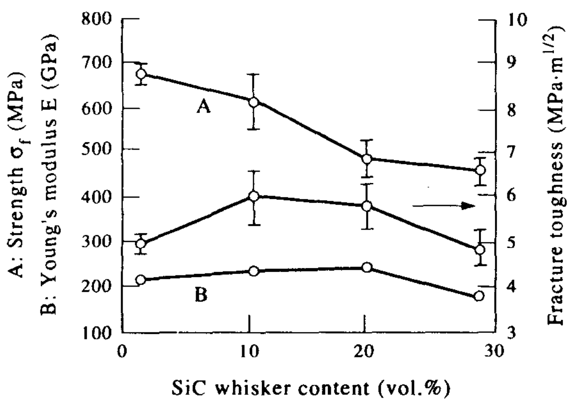

Fig. 3. Mechanical properties of $SiCw/Si_3N_4$ composites as a function of SiC whisker content.

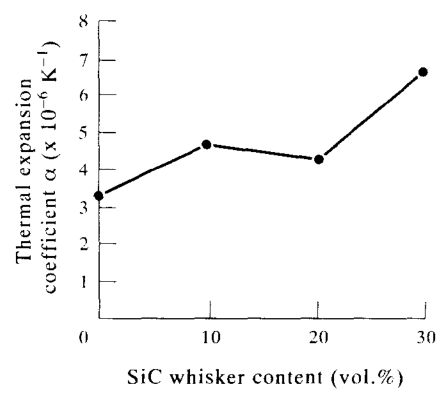

Fig. 4. Thermal expansion coefficient of $SiCw/Si_3N_4$ composites as a function of SiC whisker content.

important than thermal conductivity's influence especially for the composites to be used under a severe thermal shock environment. Thermal expansion coefficient testing results are illustrated in Fig. 4. The thermal expansion coefficient of the composites shows a strongly increasing tendency with increasing SiCw content, and this is unfortunately harmful to their thermal shock resistance.

3.4 Thermal shock resistance

The calculated thermal shock resistance parameters are presented in Table 1 showing that with increasing SiCw content, the thermal stress damage resistance parameter, R^{IV}, greatly increases. In contrast, the thermal stress fracture resistance parameter, R, and the thermal stress crack stability parameter, R_{st}, diminish substantially. The results above indicate that the thermal shock resistance to catastrophic crack propagation might be improved with increasing SiCw content, but the resistance to crack repropagation especially to fracture initiation deteriorated dramatically.

The curves of the residual strength, σ_r, versus water-quenching temperature difference, ΔT, are given in Fig. 5. As shown, for the monolithic Si_3N_4, σ_r remains constant up to ΔT = 1200°C. By contrast, for SiCw/Si_3N_4 composites, σ_r drops when ΔT reaches 1000°C or less. So the first point which could be drawn from the figure is that the critical temperature difference, ΔT_c, for strength degradation decreases with increasing SiCw content, which is consistent with the change of parameter R shown in Table 1. However, ΔT_c values shown in the curves were much higher than the calculated R values shown in Table 1. This can be explained as follows. Firstly, the thermal expansion coefficients used in the calculation of R are the values normal to the hot-pressing direction, and they might be much larger than their actual effective values because of the anisotropic thermal expansion coefficient of the hot-pressed composites. Secondly, the water-quenching speed may play a role. Insufficiently rapid quenching and the limit of water cooling rate could make the actual temperature difference the specimens experienced lower than the recorded temperature difference. Nevertheless, neither of the two factors influenced the changing tendency of ΔT_c with increasing SiCw content.

The second point that could be drawn from Fig. 5 is that the decrement of strength increases with increasing SiCw content for $\Delta T > \Delta T_c$, and such a tendency could be more clearly seen from residual strength rate values (for ΔT=1200°C)

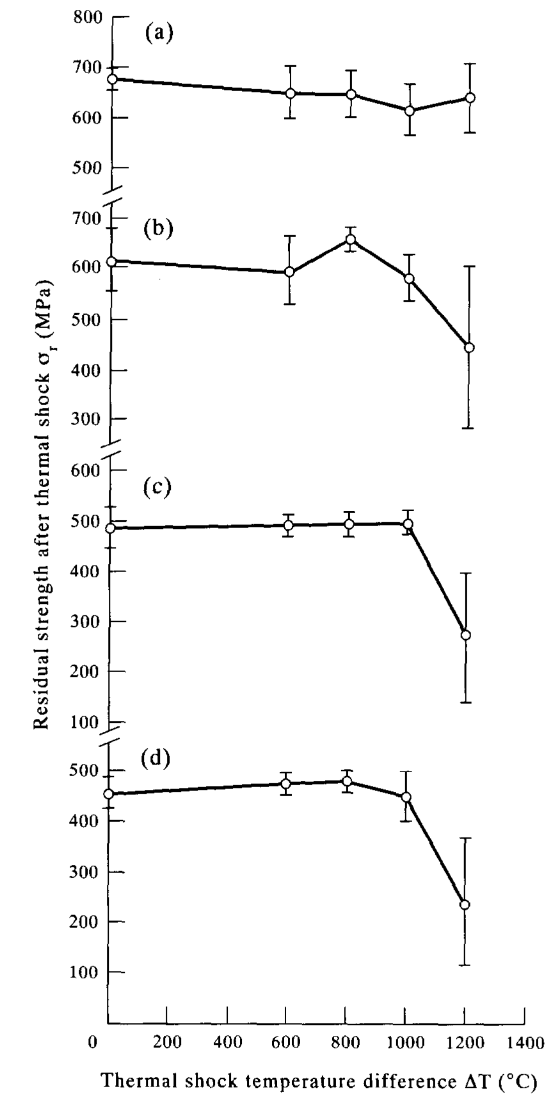

Fig. 5. Thermal shock behaviour of SiCw/Si_3N_4 composites: (a) 0 vol% SiCw, (b) 10 vol% SiCw, (c) 20 vol% SiCw, (d) 30 vol% SiCw.

Table 1. Thermal shock resistance parameters of SiCw/Si_3N_4 ceramic composites and the residual strength rate when ΔT=1200°C

SiCw content (vol%)	$R=\sigma_f(1-\nu)/(\alpha E)$ (°C)	$R^{IV}=(K_{IC}/\sigma_f)^2/(1-\nu)$ (μm)	$R_{st}=(\gamma_w/\alpha^2 E)^{1/2}$ ($\mu m^{1/2}$. °C)	Residual strength rate (ΔT= 1200°C) σ_r/σ_o
0	942 (1 − ν)	88.4/(1 − ν)	6261	95·4%
10	555 (1 − ν)	118·6/(1 − ν)	6046	73·1%
20	452 (1 − ν)	119·6/(1 − ν)	4949	57·2%
30	405 (1 − ν)	151·0/(1 − ν)	4982	53·7%

Flexural but not tensile strengths were used to calculate the parameters R and R^{IV}. In the calculation of R_{st}, γ_w was converted according to the Irwin equation: $K_{IC}^2=2\gamma E$.

shown in Table 1. This is roughly consistent with the change of parameter R_{st} shown in Table 1.

From the above two points, it can be seen that the σ_r–ΔT curves of the composites had relatively good relationships with the calculated parameters R and R_{st}. According to the results, R^{IV} might lose its significance though it increases with increasing SiCw content, which theoretically means the improvement of resistance to instantaneous crack propagation at critical temperature difference, ΔT_c. This may be the result of the fact that the critical cracks in the composites might be larger than their respective R^{IV} values due to their low densities.

Crack propagation in the SiCw/Si_3N_4 composites shown by the curves in Fig. 5 occurs primarily in a quasi-static manner. This could be attributed to two points. One may be connected with the relatively low density of the composites, which made the critical cracks in them large enough to become the original large cracks predicted by the unified theory of fracture initiation and crack propagation.[11] While other studies[12,13] on Si_3N_4, showed that density has little influence on crack propagation, it is said that unstable crack propagation had occurred for all grades of dense and reaction-bonded Si_3N_4, even for very low-strength materials. In contrast, some other kinds of ceramics such as porous SiC[14] clearly show crack-stable propagation. So, the difference between them needs further research. The other and maybe the more important point is the toughening effects of SiCw. The fracture SEM photographs in Fig. 6 show SiC whiskers' pulling-out and bridging traces, which proves that the existence of SiCw is beneficial to mitigating instantaneous crack propagation. From this point of view, it is beneficial to introduce SiCw into monolithic Si_3N_4, but this will be unfortunately at the expense of the decrease of critical temperature difference, ΔT_c.

The above results have some practical implications in designing SiCw/Si_3N_4 composites for thermal shock applications. When relatively mild thermal shock is involved, i.e. fracture initiation should be avoided, it is harmful to introduce SiCw to monolithic Si_3N_4, which will diminish the critical temperature difference, ΔT_c. In an application involving severe thermal shock, in which fracture cannot be avoided even in monolithic Si_3N_4, i.e. when the extent of catastrophic crack propagation should be minimized, it may be beneficial to introduce SiCw in appropriate amount to monolithic Si_3N_4, at the same time lowering the density of the composites.

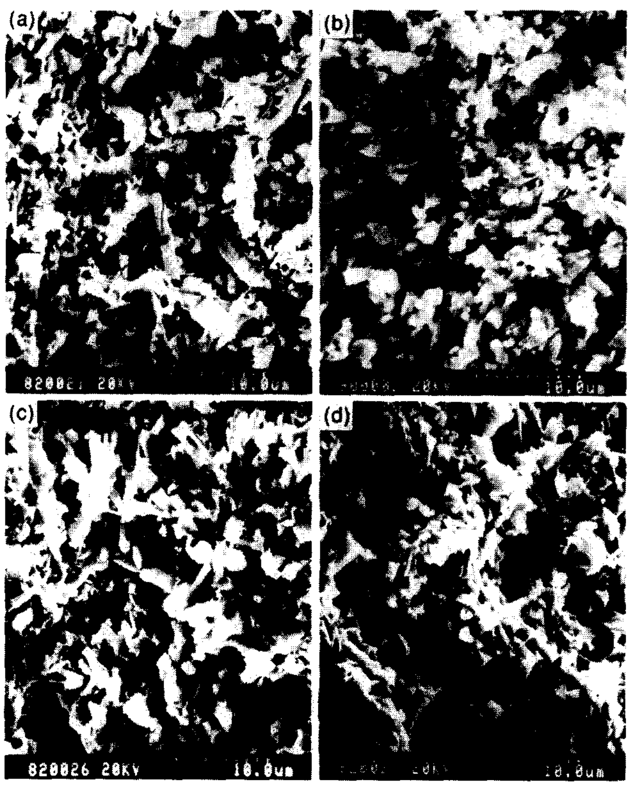

Fig. 6. Fracture surfaces of thermally shocked SiCw/Si_3N_4 composites (ΔT=1200°C); (a) 0 vol% SiCw, (b) 10 vol% SiCw, (c) 20 vol% SiCw, (d) 30 vol% SiCw.

4 CONCLUSIONS

(1) The thermal shock resistance to fracture initiation and stable crack propagation of SiCw/Si_3N_4 composites deteriorated with increasing SiCw content.
(2) The curves of the residual strength, σ_r, after water quenching versus thermal shock temperature difference, ΔT, e.g. σ_r–ΔT, showed good relationships with the calculated thermal stress fracture resistance parameter, R, and thermal stress crack stability parameter, R_{st}.
(3) The crack propagation of SiCw-reinforced Si_3N_4 composites occurred primarily in a quasi-static manner as a result of pulling-out and bridging toughening effects of SiC whiskers and the relatively low density of the composites.

REFERENCES

1. UENO, K., *et al.*, Influence of sintering conditions on the mechanical properties of SiC whisker/Si_3N_4 ceramic composite. *J. Ceram. Soc. Jap.*, (Internat. edn), **100** (1991) 526–9.
2. FUNAHASHI, T., ISOMURA, K., *et al.*, Mechanical properties and microstructure of Si_3N_4–BN composite ceramics. *Ceram. Mater. & Components for Engines*, (1988) 968–76.
3. ZIEGLER, G., HEINRICH, J., *et al.*, Relationships between processing, microstructure and properties of dense and reaction-bonded silicon nitride. *J. Mater. Sci.*, **22** (1987) 3041–86.
4. BULJAN, S. T. & SARIN, V. K., Silicon nitride-based composites. *Composites*, **18**(2) (1987) 99–106.

5. HASSELMAN, D. P. H., *Bull. Am. Ceram. Soc.*, **49** (1970) 1033.
6. NAKAYAMA, J., In *Fracture Mechanics of ceramics*, Vol. 2, ed. R. C. Bradit, D. P. H. Hasselman & F. F. Lange. Plenum Press, New York, 1974, pp. 759–78.
7. ZHANG, Q. C., *Mechanical Properties of Ceramic Materials*. Chinese Science Press, Beijing, 1987, pp. 279–304.
8. SARIN, V. K. & RUBLEE, A., Microstructural studies of ceramic-matrix composites. *Composites*, **18**(18) (1987) 129–34.
9. BULJAN, S. T., *et al.*, Si_3N_4–SiC composites. *Am. Ceram. Soc. Bull.*, **66**(2) (1987) 330–3.
10. SUZUKI, K. & SUGANO, Y., *Yogyo Kyokaishi*, **92** (1984) 55–6.
11. HASSELMAN, D. P. H., Unified theory of thermal shock fracture initiation and crack propagation in brittle ceramics. *J. Am. Ceram. Soc.*, **52**(11) (1969) 600–4.
12. ZIEGLER, G., *et al.*, *Werkstofftech.*, **16** (1985) 12.
13. ZIEGLER, G. & HASSELMAN, D. P. H., *Ceramurg. Int.*, **5** (1979) 126.
14. KOUMOTO, K., *et al.*, Thermal shock resistance of porous SiC ceramics. *J. Ceram. Soc., Jap.* (Internat. edn), **90**(1) (1991) 32–3.