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The Effect of Heat-Treatment on the Performance of Sub-Micron SiC$_p$-Reinforced α-β Sialon Composites: I. Preparation of Agglomerate-Free Starting Powders

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Abstract

In order to prepare good-quality, dense, SiC$_p$-reinforced α-β sialon composites by hot-pressing, a technique was developed to prevent agglomeration of the SiC grains during powder processing. For this purpose, the surfaces of the SiC particles were selectively covered with long organic molecular chains by soaking in a solution of polyethylene glycol in isopropanol; the resulting powder not only resisted re-agglomeration, but was also readily dispersible within the sialon matrix. Infra-red absorption was used to demonstrate that the PEG-modified SiC grains had been successfully coated with OH groups. The dispersion role of PEG is mainly influenced by the molecular weight of the surfactant, the surfactant concentration, the pH value of the suspension and the soaking time of the SiC powder in the solution. © 1997 Elsevier Science Limited. All rights reserved.

1 Introduction

Recently, an increasing amount of attention has been devoted to the development of ceramic composites because of the potential they offer for achieving specific properties. It is now generally accepted from research carried out during the last twenty years that compositional design, processing route, microstructure and mechanical properties of composites are closely interrelated, i.e. the properties of composites are critically affected by the starting composition and processing history, since these control the amount, grain size and grain shape of the different phases, thereby determining the microstructure and hence the mechanical properties. Current research on structural ceramic composites has therefore focused on strengthening, toughening and hardening mechanisms, and also on the relationship between microstructure and properties. Recent studies of Si$_3$N$_4$/SiC$_p$ composites[1-6] have shown that an Si$_3$N$_4$ matrix can be significantly reinforced by a dispersion of SiC particles[7,8] because (i) small second-phase particles are not deleterious to bulk strength in the same way as large particles in Si$_3$N$_4$/SiC$_p$ composites, because additional strengthening mechanisms become operative, (ii) the sintering temperature of SiC-reinforced composites is lower than that of monophasic SiC and therefore the SiC particles can essentially maintain their original size during sintering and remain dispersed in the matrix, (iii) beneficial local stresses remain in the matrix after cooling from the sintering temperature due to the thermal expansion mismatch between Si$_3$N$_4$ and SiC, and (iv) a coherent non-bonded interface exists between SiC and Si$_3$N$_4$ grains in densified composites because no chemical reaction occurs between these phases at sintering temperatures.

From a preparative point of view, if sialon rather than silicon nitride is chosen for the matrix, it is much easier to control the microstructure and properties of composites because of the increased flexibility in selection of the starting composition. However, it is rather difficult to obtain a homogeneous dispersion of small SiC particles in a sialon matrix by traditional mixing methods because of the large specific surface area and agglomeration of the SiC powder. For these reasons, the present paper focuses on the preparation of agglomerate-free SiC$_p$ containing mixed α-β sialon starting powders. To achieve good dispersion of SiC particles in the matrix, an organic surfactant (PEG)

was used to separate individual SiC powder grains and produce the spatial inhibition necessary to avoid particle agglomeration during mixing of the starting powders. As part of the study, it was necessary to explore the effects of parameters such as the molecular weight and concentration of PEG, and the pH and the soaking time of the SiC particles in the solution.

2 Experimental Procedure

In the published literature on the crystallography and phase relationships of metal sialon systems, it is well established that rare earth elements from Nd upwards can be incorporated into the α-sialon structure.[9-11] Therefore, starting compositions were selected to give a pure α-sialon phase of composition $Ln_{0.33}Si_{9.3}Al_{2.7}O_{1.7}N_{14.3}$ (i.e. $m=1$ and $n=1.7$ in the general α-sialon formula $Ln_{m/3}Si_{12-(m+n)}Al_{m+n}O_nN_{16-n}$), with Ln = Nd and Yb. Additions of 0, 10 and 20 wt% of submicron SiC particles were included in the starting mix. Si_3N_4 (Grade LC10, HC Starck, Berlin), Al_2O_3 (Grade A17, Alcoa Chemie GmbH), AlN (Grade B, HC Starck, Berlin), Nd_2O_3 (99.9%, Rare Earth Products) and Yb_2O_3 (99.9%, Aldrich Chemical Co.) powders were used along with 280 μm size SiC (Ibiden Company, Japan). The surfactant PEG (polyethylene glycol) was used to prevent agglomeration, and three grades of PEG were tried with molecular weights 400, 1000 and 1540. Sialon starting powders (i.e. Si_3N_4, Al_2O_3, AlN and Ln_2O_3) were ball milled using Si_3N_4 balls in isopropanol (IPA) for one day. The SiC powder was soaked in IPA/PEG surfactant solution for one day and given one hour of magnetic stirring to prepare a well-mixed suspension. Aqueous ammonia was added to change the pH of this solution.

For the preparation of Nd-sialon/SiC$_p$ composites, the sialon- and SiC-containing suspensions were separately dried and then mixed together in an agate pestle and mortar. Finally, the mixed powder was fired to burn out the surfactant at 330°C. In this case, extensive agglomeration of SiC particles was found in the final composite. For the preparation of Yb-sialon/SiC$_p$ composites, the two suspensions were mixed by magnetic stirring, dried and then sieved. Finally the powder was fired to burn out the surfactant at 330°C. In this case, SiC particles were well dispersed within the matrix.

Cylindrical green pellets of the mixed powders were compacted by applying uniaxial pressure in 25-mm diameter steel dies, and the pellets were cold isostatically pressed at 175 MPa. The discs
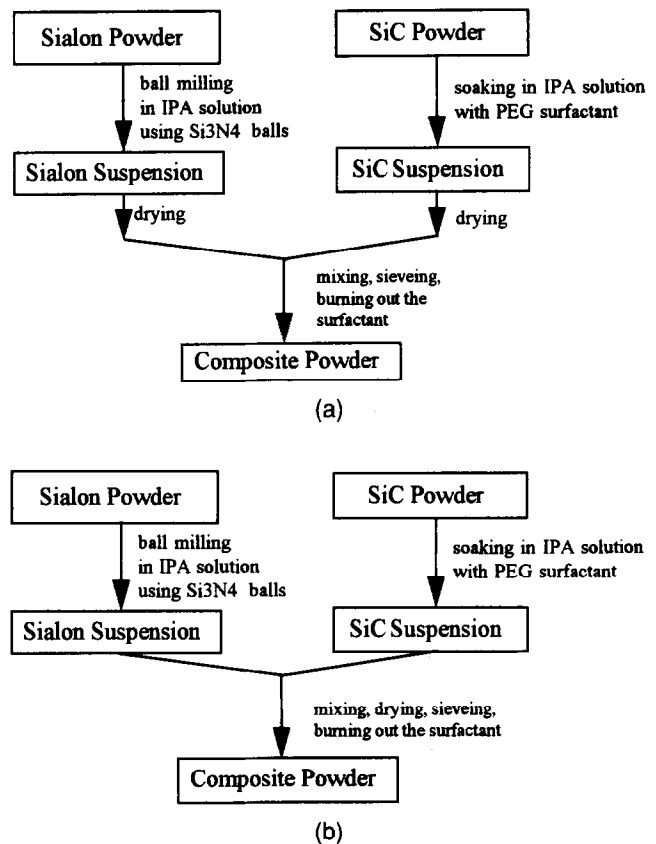

Fig. 1. Flow charts showing the preparation of Ln-sialon/SiC$_p$ mixed powders in (a) the Nd- and (b) the Yb-sialon systems.

were hot-pressed at 1800°C for 45 min at a pressure of 25 MPa. Relative densities of the composites were measured using a mercury displacement balance.

Characterisation of the powders before and after treatment was carried out by IR, DTA and TG methods; the sintered microstructures were examined by TEM and SEM using JEOL-200CX and Camscan S4-80DV instruments respectively. The IR spectra were recorded using a Nicolet-7000 Fourier Transform Infrared Spectrometer. The IR spectra of SiC and PEG-modified SiC, mixed with KBr powder, displayed very strong absorption due to skeletal vibrations. The thermal stability of the powder was examined by Thermal Gravimetry (TG) and Differential Thermal Analysis (DTA) to determine the burn-out temperature for removing the PEG surfactant from the mixed powders.
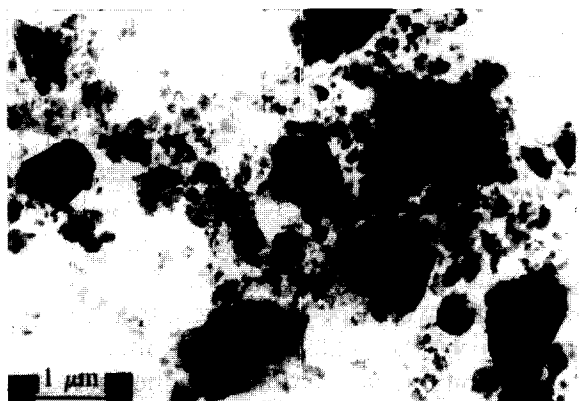
3 Results and Discussion

3.1 Effect of PEG surfactant on the dispersion of SiC particles
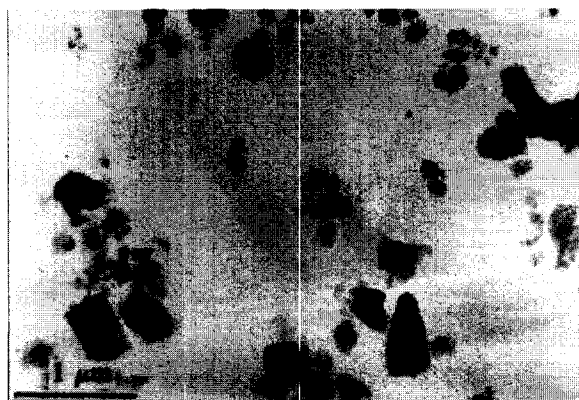
For optimum properties of the final composites, it is important to obtain a homogeneous dispersion of SiC particles in the matrix, and in the present

study, PEG was used as a surfactant to achieve this objective. PEG (HO(CH$_2$CH$_2$O)$_n$H) is a non-ionic surfactant in which the hydrophilic and hydrophobic parts have zero charge, but the C–O, C–H and O–H bonds are all highly polar, with OH in particular capable of forming linkages via hydrogen bonding. For a solid/liquid system, the surface state of the powder critically affects its wettability by the liquid and this in turn determines its dispersibility within the liquid. In the present case, the most important role of the surfactant was to reduce the interfacial energy at the solid/liquid interface, thereby changing the strength of inter-particle interactions in the suspension. In this way, the surfactant served to inhibit re-agglomeration of dispersed particles. For closely grouped SiC particles, the surfactant also assisted the dispersion process by improving wettability, thereby enabling the liquid to access narrow channels between grains and accelerating break-up of weak agglomerates. Another helpful function was the weakening of links between solid particles by adsorption at surface defects.[12,13]

Figure 2 shows the dispersion of SiC before and after treatment in PEG-containing IPA. Clearly the PEG treatment is modifying SiC particle sur-

faces, and this is believed to be because at pH values of 7–8, the SiC particle surfaces have been capped by a layer of PEG on hanging bonds or surface defects on the SiC particles. Thus, on soaking in PEG/IPA solution of controlled pH, the surfaces of SiC particles adsorb OH$^-$ groups, and these in turn bond on to PEG molecules, which in turn can adsorb further OH$^-$ and PEG molecules by hydrogen bonding, so that PEG-shelled SiC particles are formed, i.e.:

$$H(OCH_2CH_2)_nOH - HO - \overset{\displaystyle OH...}{\underset{\displaystyle OH...}{(SiC)_p}} - OH - HO(CH_2CH_2O)_nH$$
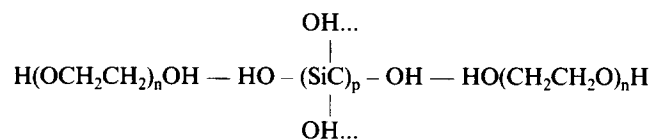
Figure 3 shows IR absorption spectra of SiC powder and PEG-modified SiC powder. For the pure SiC powder, the strongest absorption band corresponds to the Si-C skeletal vibration at 880 cm^{-1}. The sharp bands at 1090 and 1190 cm^{-1} are associated with surface Si–O–Si stretching or to a deformation mode of H-bonded Si-OH groups. Weaker absorption bands of Si-C between 1620 and 1310 cm^{-1} correspond to overtones and combinations of the fundamental optical and acoustic modes of SiC, which appear to be insensitive to surface phenomena. In addition, the broad peak corresponding to O-H (free or bound) at 3400 cm^{-1} illustrates that the nominally pure SiC still contains a small amount of water or OH$^-$ which can either be adsorbed on the SiC surface or coordinated with SiC.[14-17] It is well known that many alcohol-related compounds exhibit two absorption bands, one from O-H stretching frequencies at 3400–3200 cm^{-1} in the high-frequency region of the spectrum and one from the O-H deformation and/or C-O stretching near 1100 cm^{-1} in the low-frequency region. The frequency of the bonded

(a)

(b)

Fig. 2. Dispersion of SiC powder (a) before, and (b) after treatment in PEG-containing IPA.
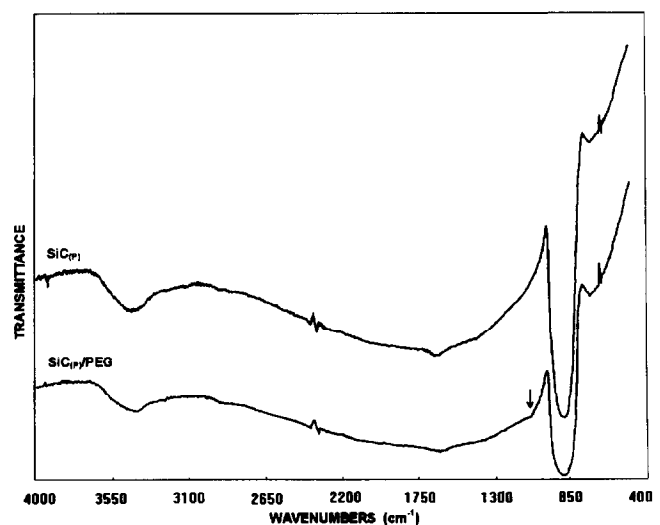

Fig. 3. Infrared absorption spectra in the range 4000–400 cm^{-1} for (a) pure SiC powder, and (b) PEG-modified SiC powder.

O-H absorption band is always lower than that of the unbonded O-H band. If strong intermolecular hydrogen bonds exist, the OH frequency shifts considerably towards lower values,[18] as observed here for polyethylene glycol. Some of the spectra recorded for SiC particles modified by PEG surface treatments give different peaks which can be interpreted in terms of surface vibration modes (see, for example Spectrum (b) in Fig. 3). The change in spectra at 1100 cm⁻¹ (as indicated by an arrow) arises because of weakened Si-O-Si stretching or enhanced H-bonded Si-OH groups and C-O stretching; the Si-O-Si stretching peak results mainly from SiO_2 on the surface of the SiC powder. After soaking in PEG/IPA solution at pH values in the range 7–8, the surfaces of the SiC powder grains were modified and their surface vibration modes were characterised by the H-O and C-O absorption bands in PEG. The slight change in spectra at 1100 cm⁻¹ could be related to a conjugate structure involving PEG and Si atoms or alternatively to the formation of a thin layer of amorphous silica at the surface of the SiC powder.

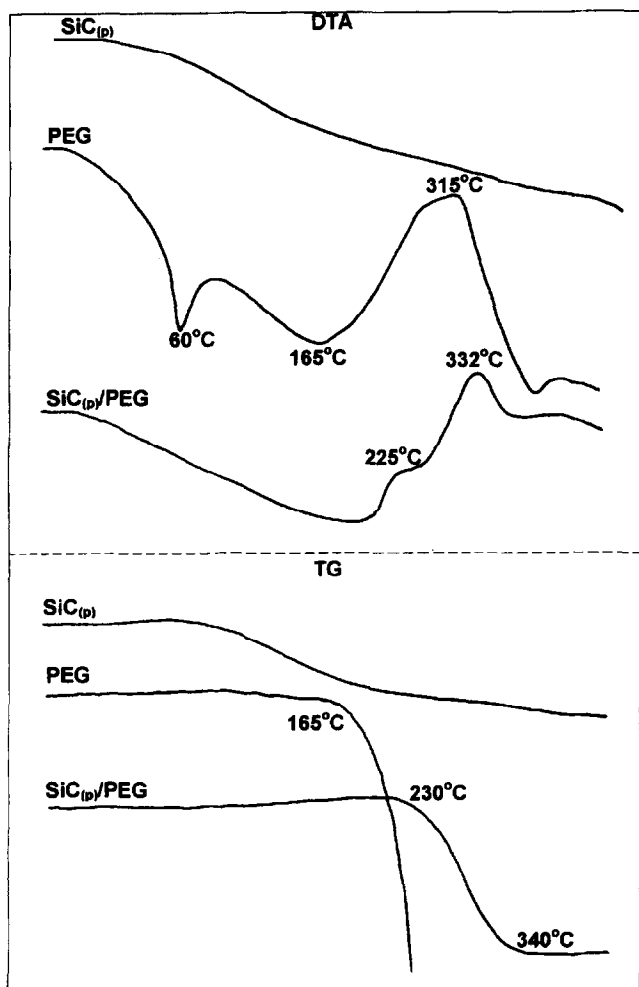These results show that the PEG surfactant selectively modifies the surfaces of the SiC particles by anchoring organic chains on the surface, and the resulting capped grains are strongly resistant to re-agglomeration. Further experiments were carried out using different concentrations of the surfactant and different molecular weights of the starting PEG. It was found that the optimum conditions for the dispersion of SiC_p were a PEG molecular weight of 1540, a minimum content of surfactant of ≈ 30 mg of PEG per 1 g of SiC, a pH value of 7–8 and a one-day soaking time in the PEG/IPA solution.

After dispersing the SiC particles in the sialon powder, residual organic material was burnt out. Figure 4 shows the DTA and TGA results. It was found that PEG-capped SiC powder showed excellent burn-out properties, with the residual PEG decomposing at quite low temperatures (≈ 230°C).

3.2 Location of SiC particles in sintered composites

The above discussion of IR spectra has shown that the PEG-capped SiC particles were dispersed as individual grains within the starting powders. When the sialon- and SiC-containing suspensions were mixed together, dried and the green pellets hot-pressed at 1800°C, SiC particles still remained as separate grains within the sialon matrix, and in general were sited at grain boundaries. Figure 5 shows the distribution of SiC particles in Yb-sialon/SiC_p composites prepared in this way. However, when the sialon and SiC suspensions were dried separately and then mixed together, the 1800°C hot-pressed pellets demonstrated serious agglomeration, as shown for the Nd–sialon/SiC_p sample in Fig. 6. From a consideration of the experimental results given above, it is suggested that after the two suspensions are mixed together, the grains in the sialon powder mix enhance spatial inhibition, which therefore helps to keep the capped SiC particles from getting too close
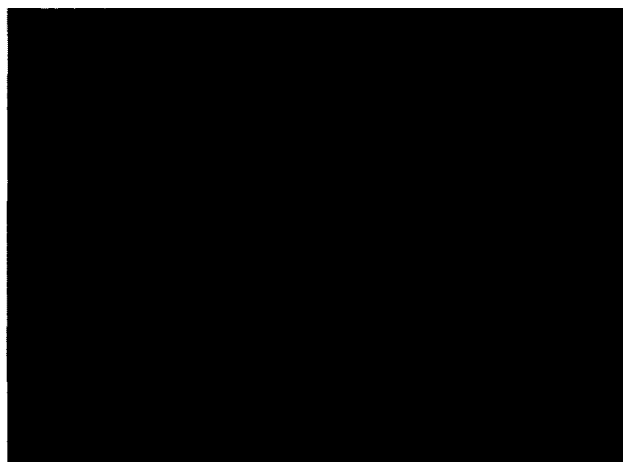

Fig. 4. DTA and TG traces of SiC_p, PEG-modified SiC_p and PEG powders.

Fig. 5. Dispersion of SiC particles in Yb-sialon/SiC_p composites containing 10 wt% SiC; general microstructure showing well-dispersed SiC grains.

Fig. 6. Dispersion of SiC particles in Nd–sialon/SiC$_p$ composites containing 10 wt% SiC, showing seriously agglomerated SiC particles.

Table 1. Densities (g cm^{-3}) of Ln-sialon/SiC$_p$ composites

Sample	0% SiC$_p$	10% SiC$_p$	20% SiC$_p$
Yb–sialon	3·42	3·39	3·37
Nd–sialon	3·35	3·33	3·30

to each other; in this way, the small SiC particles remain in a stabilized condition in the matrix. Densities of the sintered composites were measured and are listed in Table 1. Further details of the microstructure, heat-treatment and properties of these materials are given in subsequent papers.[19,20]

4 Conclusions

Good dispersion of SiC particles within sialon ceramic matrices has been achieved by using PEG as a surfactant. This selectively modifies the surfaces of the SiC grains by anchoring organic chains, so that the resulting SiC particles are resistant to re-agglomeration and show a good dispersability. The dispersion capability of PEG was found to be determined by the molecular weight of the surfactant, the surfactant content, the pH value of the suspension and the soaking time of SiC powder in the liquid (IPA). From these experiments, the optimum conditions for dispersion were a PEG molecular weight of 1540, a minimum surfactant content of 30 mg of PEG per 1g SiC, a pH value of 7–8, and a one-day soak time. Using powder prepared in this way, dense, agglomerate-free, SiC$_p$-reinforced α-β sialon ceramics were fabricated, containing well-distributed dispersions of sub-micron SiC particles.

References

1. Akimune, Y., Ogarawara, T. & Hirosaki, N., Influence of starting powder characteristic on mechanical properties of SiC-particles/Si$_3$N$_4$ composites. *J. Ceram. Soc. Jpn*, **100** (1992) 463–467.
2. Akimune, Y., Hirosake, N., Ogasawara, T. *et al.*, Mechanical properties of SiC-particle/sialon composites. *J. Mater. Sci. Lett.*, **10** (1991) 223–226.
3. Niihara, K., New design concept of structural ceramics — ceramic nanocomposites. *J. Ceram. Soc. Jpn*, **99** (1991) 974–982.
4. Akimune, Y., High-temperature strength of SiC whisker sialon composites. *J. Mater. Sci. Lett.*, **9** (1990) 816–817.
5. Niihara, K., Nanostructure design and mechanical properties of ceramic composites. *J. Jpn Soc. Powder and Powder Metall.*, **37** (1990) 348–351.
6. Buljam, S. T., Pasto, A. E. & Kim, H. J., Ceramic whisker- and particulate-composites: properties, reliability, and applications. *Am. Ceram. Soc. Bull.*, **68** (1989) 387–394.
7. Greskovich, C. & Palm, J. A., Observations on the fracture toughness of β-Si$_3$N$_4$–β-SiC composites. *J. Am. Ceram. Soc.*, **63** (1980) 597–599.
8. Lange, F. F., Effect of microstructure on the strength of Si$_3$N$_4$–SiC composite system. *J. Am. Ceram. Soc.*, **56** (1973) 445–450.
9. Mandal, H., Thompson, D. P. & Ekstrom, T., Reversible α=β sialon transformation in heat-treated sialon ceramics. *J. Eur. Ceram. Soc.*, **12** (1993) 421–429.
10. Mandal, H., Thompson, D. P. & Ekstrom, T., Heat treatment of sialon ceramics densified with higher atomic number rare earth and mixed yttrium/rare earth oxides. *Proc. Special Ceramics 9*. The Institute of Ceramics, Stoke-on-Trent, UK, 1992, pp. 97–104.
11. Mandal, H., Thompson, D. P. & Ekstrom, T., Heat treatment of Ln-Si-Al-O-N glasses, *Proc. 7th Irish Mater. Forum Conf. IMF7*, ed. M. Buggy & S. Hampshire. Trans Tech. Publications, Switzerland, 1992, pp. 187–203.
12. Tadros, Th. F., *Surfactants*. Academic Press, London, 1985, pp. 197–220.
13. Myers, D., *Surfactant Science and Technology*. VCH Publishers, Inc., New York, 1988, pp. 273–325.
14. Beri, J. B., Infrared study of OH and NH$_2$ groups on the surface of dry silica aerogel. *J. Phys. Chem.*, **70** (1966) 2937–2940.
15. Patrick, L. & Choyke, W. J., Lattice absorption bands in SiC. *Phys Rev.*, **123** (1961) 813–815.
16. Ramis, G., Busca, G., Lorenzelli, V. *et al.*, Surface chemistry and structure of ultrafine silicon carbide: an FT-IR study. *J. Am. Ceram. Soc.*, **72** (1989) 1692–1697.
17. Ramis, G., Busca, G., Lorenzelli, V. *et al.* In *Surface and Interface of Ceramic Materials*, ed. L. C. Dufour *et al.* Kluwer Academic Publishers, 1989, pp. 173–184.
18. Bellamy, L. J., *The Infra-red Spectra of Complex Molecules*. Methuen & Co. London, 1958, pp. 95–111.
19. Liu, Q., Gao, L., Yan, D. S., Mandal, H. & Thompson, D. P., The effect of heat-treatment on the performance of sub-micron SiC$_p$-reinforced α-β sialon composites: II. Heat-treatment studies (this volume).
20. Ibid, III. Mechanical properties (this volume).