JOURNAL OF MATERIALS SCIENCE 31 (1996) 6229–6240

Processing aspects of glass–nicalon fibre and interconnected porous aluminium nitride ceramic and glass composites

P. N. KUMTA
Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

Glass matrix-fibre and glass infiltrated ceramic composites with interconnected phases have been shown to have the potential for displaying optimum thermal conductivity and dielectric constant at 1 MHz making them useful as substrates for electronic packaging. Ceramic (Nicalon and silicon carbide grade (SCS)) fibre-borosilicate glass composites were fabricated using tape casting processes combined with pressure and pressureless sintering techniques. Experiments were also conducted to process AlN ceramics with interconnected porous channels which were then hot infiltrated with borosilicate glass. Results of optical characterization of the composites indicate that infiltration of Nicalon cloth with glass is achieved by hot pressing, while the tape casting and lamination approach followed by sintering is useful for fabricating composites of glass and Nicalon tows. The sintered aluminium nitride ceramics are comprised of $\approx 28\%$ (volume fraction) interconnected pores. Hot infiltration yielded ≈ 100 μm penetration of borosilicate glass into the pores of the nitride ceramic. The paper discusses the various scientific aspects involved in processing the glass-fibre and porous AlN composites containing 3-d interconnected pores. Results of the microstructural characterization of these composites are discussed particularly in regards to the desired microstructure essential for these composites to be useful as substrates in electronic packaging.

1. Introduction

Advancement in integrated circuit technology has lead to the miniaturization of devices. This has caused a rapid increase in the device density which has placed stringent requirements on substrate technology. The substrates therefore need to possess adequate thermal dissipation characteristics as well as be able to provide good signal transmission with minimum loss and delay. At present, in the ceramic packages used in microelectronic packaging, the main heat dissipation mechanism is by thermal conduction through the substrate, while signal propagation is based on the velocity (v) of the electric signal which is inversely related to the relative dielectric permittivity of the material (ε). Thus, the substrate materials need to possess excellent thermal conductivity and minimum dielectric constant. These criteria restrict the choice of the materials mainly to ceramics and polymers. The role of ceramic materials as substrates in several packages such as dual-in-line packages, chip carriers, pin grid arrays as well as the recently developed ball grid arrays and the low LTCC and high temperature co-fired ceramics HTCC is well known [1–8]. Ceramic packaging is therefore becoming one of the most actively pursued areas of research.

Ceramics have dielectric constants ranging from 4–10 000, thermal expansion coefficients matching silicon, and display a range of thermal conductivity behaviour making them one of the best insulators and heat conductors. Some of the materials even exhibit better heat conduction than aluminium metal at room temperature [1]. They are also highly refractory materials exhibiting excellent thermal and chemical stability at room temperatures making them good materials to be used in electronic applications requiring a good hermetic seal. The main drawback of ceramics possessing high thermal conductivity with respect to packaging is their moderate to high dielectric constant and the high processing temperatures. In view of the current focus of the electronics industry to fabricate high power and high speed packages, research in the development of materials for packaging application has been focused mainly at achieving objectives which include lower dielectric constant, lower processing temperatures, good thermal expansion match to silicon, improved thermal conductivity, improved materials design for power dissipation, multilayer processing, and high mechanical strength. The materials that have been identified and studied extensively for these purposes are AlN, BeO, SiC, and diamond, because of their high thermal conductivity [9–18]. Table I lists the crystalline ceramic materials of interest for electronic packaging. In a level one package containing devices mounted on a crystalline ceramic substrate,

0022-2461 © *1996 Chapman & Hall*

the heat dissipation is primarily from the bottom of the device through the substrate.

Glass-ceramics exhibit a low dielectric constant around 5 and an excellent thermal expansion match to silicon. They also co-sinter very well with copper or gold, which make them potentially one of the best candidate substrate materials for high-performance multilayer ceramic packages [19]. In addition, thin film metallization layers as well as dielectric materials could be easily deposited onto the surface of these substrates, therefore making them amenable for high performance application. Thus there has been considerable interest in studying glasses and glass-ceramics for electronic packaging [19]. The major disadvantage of glass-ceramics are their low thermal conductivity which make them poor materials for heat dissipation in packaging application where the chip is bonded to the substrate with the active end facing up. However, in the case of the application where the heat dissipation occurs from the back of the chip, such as in the flip-chip technology, this limitation is largely overcome by the use of external vias involving complex water cooling designs as in the thermal conduction module of IBM [20]. Table II lists some of the glass-ceramics, glass and ceramic materials that have been studied for packaging applications.

In the flip-chip technology, the active end of the device is bonded to the glass-ceramic while heat is extracted from the back of the chip. This configuration is very conducive for achieving high device densities although, requiring the implementation of expensive external cooling modes for heat dissipation as mentioned above. This is essential due to the poor thermal conductivity of the glass-ceramic substrate. As a result, there are basically two different types of packaging technologies to cope with the limitations of the substrate material. One geared towards high power devices employing crystalline ceramics possessing high thermal conductivity and the other directed towards high speed devices utilizing glass-ceramics exhibiting low dielectric constant. Considerable expenses are therefore incurred for fabricating the different packages and implementing the various package designs to maintain high quality performance. The need for these two technologies could be obviated by a composite with suitable thermal and dielectric properties. While the concept of composites has been researched extensively for high temperature structural applications, very little work has been concentrated in the area of electronic packaging [21]. This paper discusses the preliminary results on fabrication of two types of composites. One is a porous composite consisting of a thermally conducting ceramic as the primary matrix phase with interconnecting porous channels being the second phase. The porous channels are infiltrated with glass, the rationale for which will be discussed later. The second is a fibre and glass composite, the microstructural design of which will also be described later. The paper discusses the characterization of these composites which have been fabricated using existing processing techniques. The paper also provides a discussion pertaining to the rationale

TABLE I Properties of selected ceamic substrate materials

Substrate properties	AlN	SiC	BeO	Glass-ceramics	90% Alumina	Cubic BN	Diamond
Thermal conductivity* ($W m^{-1} K^{-1}$)	230	270	290	5	25	250	2000
Coefficient of thermal expansion 20–200 °C($\times 10^{-7}$ °C^{-1})	43	37	68	30–42	67	48	35
Dielectric constant at 1 MHz	8.9	42	6.8	5.0	9.4	7.1	5.6
Flexural strength (MPa)	350	420	250	210	280	–	–

*measured values at room temperature

TABLE II Properties of glasses, glass plus ceramics, and glass-ceramics

Materials	Dielectric constant	Coefficient of thermal expansion 10^{-7} °C^{-1}
Glasses		
B_2O_3–SiO_2–Al_2O_3–Na_2O	4.1	32
Glass + Ceramics		
$PbO + B_2O_3 + SiO_2 + (Al_2O_3)$	7.5	42
$MgO + Al_2O_3 + SiO_2 + B_2O_3 + Al_2O_3$	4.5	30
$B_2O_3 + SiO_2 + (Al_2O_3)$	5.6	45
$2MgO \cdot 2Al_2O_3 \cdot 5SiO_2 + (Al_2O_3)$	5.5	30
$CaO + Al_2O_3 + SiO_2 + B_2O_3 + (Al_2O_3)$	7.7	55
$Li_2O + SiO_2 + MgO + Al_2O_3 + SiO_2 + (Al_2O_3)$	7.3	59
$Li_2O + Al_2O_3 + SiO_2 + (Al_2O_3)$	7.8	30
Glass-Ceramics		
MgO–Al_2O_3–SiO_2–B_2O_3–P_2O_5	5.0	30
Li_2O–Al_2O_3–SiO_2–B_2O_3	6.5	25
B_2O_3–P_2O_5–SiO_2	3.9–4.4	–

behind fabrication of these composites and the type of microstructures necessary so that they can display the optimum dielectric and thermal properties.

2. Materials selection and methodology

As mentioned above, fabrication of the two types of composites and their effectiveness is dependent on the selection of the materials, the design of the composite and its microstructure. The formation of the fibre and glass composite is contingent upon selection of glass as the matrix and judiciously selecting the fibre for the second phase material. This identification and selection is very strongly dependent upon the dielectric constant and the thermal conductivity of the material since these are the two most important parameters relevant for electronic packaging. It is therefore desirable to select the two materials, one with the lowest dielectric constant and the other having a high thermal conductivity. In the low dielectric constant category, the materials that have received the most attention are cordierite and borosilicate glasses and glass-ceramics as shown in Table II. Other glasses have also been developed which show potentially lower dielectric constants such as borophosphosilicate glasses researched by Macdowell and Beall and the present authors [22–24]. However, since borosilicate glasses have been well studied and considerable information is available in the literature in regards to processing, electrical and thermal properties, its selection seemed appropriate for the current study. From the list provided in Table I, the choice of electrically insulating materials displaying high thermal conductivity are limited to AlN, SiC, BeO and diamond. Aluminium nitride (AlN) is a good choice over beryllia for high performance packages. Diamond on the other hand is an excellent material but the difficulty in synthesizing fine particles and sintering them to obtain a continuous phase limits its choice.

Silicon carbide as seen from Table I has a thermal conductivity of 270 $\mathrm{W m^{-1} K^{-1}}$. In the fibre form SiC based (Nicalon) fibre has been extensively studied for composite applications and is commercially available. The ceramic fibre grade however has oxygen impurities and is known to be an oxycarbide with a thermal conductivity of only 12 $\mathrm{W m^{-1} K^{-1}}$ along the fibre axis at room temperature, and a dielectric constant of 9 at 1 MHz, as reported by the manufacturers (Dow Chemicals). Nicalon was therefore selected as the second phase for these preliminary studies despite its rather poor thermal conductivity mainly to demonstrate the connectivity issue which will be discussed later in the section on microstructural design. The idea could then be used to fabricate composites employing fibres of high thermal conductivity such as AlN. There has been considerable amount of work reported in the literature as regards to processing and studying the mechanical properties of borosilicate glass and Nicalon composites [25, 26]. While there have been significant developments in regard to processing of glass and fibre composites for structural application, there has hardly been any work related to the application of these processing techniques to fabricate and design composites and test their applicability for electronic packaging.

As discussed above, the main goal of the study was to fabricate composites with a suitable microstructure so that the composite would display optimum thermal conductivity and dielectric values for applications as substrates in electronic packaging. The properties of such a composite can be predicted to some extent based on certain mathematical models. There are several models that exist, the one that is most well known is based on volume fraction additions [27–29]. According to the empirical rules set by the models, it can be seen that a certain volume fraction of two different phases could result in an optimum thermal conductivity and dielectric constant. However, what is important for thermal conductivity is the interconnectivity which the models do not take into account. Thermal conductivity and dielectric constant in a particular direction are influenced more by connected rather than dispersed phases. Thus, using ceramic fibres having high thermal conductivity and adjusting the orientation and geometry could serve to be quite effective in achieving the desired optimal thermal and electrical properties. In such cases, the effective dielectric and thermal conductivity are more realistically predicted by the percolation theory and the effective medium theory [30]. Currently, commercially available Nicalon fibres do not possess the high thermal conductivity as displayed by the bulk material. However, the availability of high purity SiC or AlN fibres in the future would make the concept very viable.

Percolation theory [30] was initially originated to study the effect of cluster size of randomly connected solids and was particularly important for predicting the properties of materials resulting from polyfunctional polymerization and condensation of hydrolyzed metal alkoxy groups occurring in sol–gel reactions. The principal basis for this theory is the non-applicability of a simple linear-mixing law to predict the effective general physical properties for composite media. Thus, the effect of particle size, shape and distribution; and wetting properties of the component phase are extremely important in addition to the volume fraction. The theory takes into account the volume fraction of the different phases and is based on a threshold value. At this transition value the phases would become interconnected, and the thermal properties for example, are dictated by the phase that has the higher value. Thus, in the present case if the fibre-glass composite is fabricated such that the fibres are interconnected and stacked to represent a 0–90 orientation, the thermal properties would be very well dictated by the fibres since they possess a higher thermal conductivity.

Button *et al.* [30] have indicated that for systems which have extreme variations in the values of properties such as thermal conductivity and dielectric constant, the effective-medium-theory (MET) provides a more accurate representation of the percolation theory. This has been verified by calculations and simulations in the literature [31, 32]. In fact Webman *et al.* [31] have shown that it can successfully predict morphological dependence. The EMT approach in summary consists of replacing a continuous composite by a homogeneous, effective medium that has identical macroscopic and physical properties as the original composite. The effect of variations in the form and shape as well as in the volume fractions are then evaluated by replacing a small portion of the effective medium by one of the starting materials of the composite. A set of self consistent equations can then be derived by setting the volume fractions of the two phases, which effectively represent the weighted changes in the fields to zero. These equations are known as the EMT equations which relate the effective values of the physical properties to the volume fractions, and the individual values of the two component phases. In the case of a composite containing a fibre such as the present case, the principal symmetry directions are along the *c*-axis (the longitudinal (*l*) direction) and the direction normal to the *c*-axis which is the transverse direction (*t*) or the *a*-axis direction. The physical properties can therefore be evaluated along these two directions as reported by Button *et al.* [30]. The corresponding EMT equation for a certain physical property $X_j (j = l \text{ or } t)$ (such as dielectric constant, k and thermal conductivity, K) in the two directions is

$$[1 - F_j(e)]X_j^2 + \{X_1[F_j(e) - f_1] + X_2[F_j(e) - f_2]\}X_j - X_1X_2F_j(e) = 0$$

where f_1 and f_2 are the volume fractions and X_1 and X_2 the isotropic physical properties of the two starting materials, respectively. The function $F_j(e)$ is a function that is related to the geometry of the individual components and depends on the eccentricity, e which in turn depends on the aspect ratio c/a where c is the major axis and a is the minor axis of a spheroid. In the case of the fibre along the longitudinal direction which is important for the present case, $F_l = 0$ and $F_t = 0.5$ since $F_t = (1 - F_l)/2$. Using this relation one can obtain a variation of the effective thermal conductivity (K) and dielectric constant (k) with the volume fraction of the fibre or filler material. Thus a 60% volume fraction of Nicalon as the filler material would yield an effective thermal conductivity of 10 $\text{Wm}^{-1}\text{K}^{-1}$ along the fibre-axis. The effective thermal conductivity of the composite is therefore largely dependent on the thermal conductivity of the fibre material. However, the concept can be clearly exploited for the fabrication of substrates in electronic packaging.

In regards towards connectivity, one can also envisage the use of thermally conducting aluminium nitride as a composite material if it is possible to intentionally introduce continuous pores. This would essentially involve fabricating a two phase material having interconnected pores as one phase and thermally conducting aluminium nitride as the second phase. Initial experiments on sintering of aluminium nitride by Prochazka and Bobik [33] have indicated that during heat treatment of the green bodies there is essentially coarsening in absence of densification. This suggests that the geometry of the interconnected structure remains unchanged while the grain size increases with temperature. They also performed surface area measurements which indicate an effective surface to surface transport process operating at relatively low temperature. Aside from the these preliminary studies by Prochazka and Bobik, very little work has been reported on the processing and use of porous AlN for electronic packaging [21].

The effective thermal conductivity of such a composite could be easily predicted using the Maxwell–Eucken (M–E) relationship [27]. If we assume that the composite has a ceramic phase whose volume fraction and thermal conductivity are denoted as K_c and V_c respectively, then the effective thermal conductivity of such a composite could be given as

$$K_e \approx K_c[(1 - V_d)/(1 + V_d)]$$

where V_d is the volume fraction of the pores and K_m is the effective thermal conductivity of the composite. For the present example comprising of AlN as the matrix phase, if we assume that 70% of the fabricated composite in AlN and 30% of the volume fraction is comprised of pores that are interconnected then one can expect the effective thermal conductivity of the composite from the M–E equation to be ≈ 100 $\text{Wm}^{-1}\text{K}^{-1}$. It should be mentioned that the above prediction from the M–E relations does not take into account the nature of the porous channels (thickness, length and the tortuosity). These are of course variables that will determine the effective thermal conductivity. The effective value of K determined by the M–E equation is solely governed by the continuous nature of the major ceramic phase. Nevertheless the M–E relationship still provides a conservative estimate of the effective thermal conductivity. The porous nature of such a composite would make it very vulnerable to humidity and moisture which would limit its applicability as a substrate material. However, infiltration of a glass into the pores to a small depth would ensure a good hermetic seal making it viable as a substrate for packaging.

The present paper discusses the results of preliminary experiments conducted on two aspects. One based on the fabrication of glass matrix–Nicalon fibre composites using concepts reported by Button *et al.* [30]. They had fabricated laminate composites of polymer resins reinforced by AlN fibres and had demonstrated the possibility of controlling the geometry to achieve the desired connectivity. Using similar concepts, if a glass-fibre and porous ceramic composite exhibiting the desired microstructure can be fabricated it could potentially exhibit good optimal dielectric constant and thermal conductivity as predicted above, and could be used for both low (room temperature) and high temperature ($\approx 700\,^{\circ}\text{C}$) devices. This paper discusses only the processing aspects of fabricating the two composites. The fibre-glass composites were fabricated using hot pressing, and infiltration of the glass slurry into the fibre tows followed by lamination of the tape-cast glass. Porous aluminium nitride compacts were fabricated using standard sintering procedures. Borosilicate glass was then infiltrated into the pores of the compacts to fabricate a porous glass and ceramic composite. The paper also discusses the results of the microstructural characterization conducted to evaluate the nature of the composites. This included evaluating the chemical stability, fibre glass interface structure and the interconnectivity of the fibres in the case of the fibre-glass composites while analysing the porous AlN compacts for presence of continuous pores. The paper does not focus on the electrical and thermal measurements which is currently ongoing and will form a part of a subsequent publication.

3. Experimental procedure

The experimental section will be divided into two parts one related to the fabrication of glass-fibre and the other related to the processing of porous aluminium nitride composites.

3.1. Processing of glass-fibre composites

Since the thermally conducting phase is the fibre as discussed above, good interconnectivity in three dimensions could be envisioned by using a 3-d interwoven cloth. However, considering the preliminary nature of the work, in order to test the feasibility of the concept, it was decided to use a plain weave Nicalon 2-d woven cloth (Nippon Carbon Co. Ltd., Japan). The matrix material chosen was a 7760 grade borosilicate glass commercially obtained from Corning. The properties of both these materials relevant for the present work, supplied by manufacturers are shown in Table III.

Experiments were designed in order to identify the most economical and viable process. Accordingly, two different approaches were followed mainly based on (I) sintering laminates of tape-cast glass and fibre and (II) hot pressing the glass and fibre compacts.

3.1.1. Tape casting and sintering (I)

In this case, the borosilicate glass powder was initially dispersed into solution using Fish oil as the dispersant. The dispersed glass was then mixed with a binder (Butvar B-76) and a plasticizer (Santicizer S-160) to blend the glass with the binder. The resultant colloidal dispersion was then cast into a 8 mil tape [34]. The tapes were then stripped from the tape casting bench and then laminated with the Nicalon cloth. Four different routes based on the tape casting and sintering approach were followed in order to ascertain the best process to fabricate these composites. Fig. 1 shows a schematic of the different routes which are discussed below.

TABLE III Characteristics of materials selected for the glass-fibre composite.

I. **Glass System**
  Borosilicate glass (Corning grade 7760)
    Composition:
    silica 70–80%
    boron oxide 10–20%
    sodium oxide 1–10%
    alumina 1–10%
    arsenic oxide <1%
    potassium oxide 1–10%
  Properties
  Dielectric constant: 4.5 @ 1 MHz, 20 °C
II. **Fibre**
  Nicalon (2-d) cloth (Plain weave 1 sq.m., Nippon Carbon Co. Ltd., Japan)
  Properties
  Dielectric constant: 6.2 @ 1 MHz
  Thermal conductivity: 12 W m^{-1} K^{-1}

3.1.1.1. Method 1 In this route, the tapes were laminated directly with the Nicalon cloth at a temperature of 15 °C for 15–30 min. The laminated tapes were then sintered using a controlled heat treatment cycle. The first cycle consisted of heating the tapes to a temperature of 500 °C at the rate of 2 °C min^{-1} in flowing oxygen at a pressure of 3.4×10^4 N m^{-2}, and holding the samples at the temperature for 1 h. After the 1 h hold, the samples were then heated in vacuum to 880 °C ($\approx$50 °C above the softening point) at 5 °C min^{-1} and held for 1 h and 20 min to initiate and complete the sintering processes involved in fabricating the composite. The atmosphere was then switched to argon and the samples were cooled to room temperature using a cooling rate of 2 °C min^{-1}. At the end of this step, the composites were sectioned and the cross-sections observed using optical microscopy.

3.1.1.2. Method 2 In this route, the slurry used for tape casting was vacuum infiltrated into the Nicalon cloth whose sizing was earlier removed by soaking the cloths at 600 °C in air for 5–15 min. The vacuum infiltrated specimens were then laminated between six 8 mils thick tape cast tapes at a temperature of 15 °C for 30 min. The laminated tapes were then heated at 2 °C min^{-1} to 500 °C in flowing oxygen to remove the organics. A graphite slab weighing 120 g was arbitrarily selected as a dead weight in order to facilitate the glass to flow into the tows of the cloth. After a hold of 80 min, the samples were then heated in vacuum to 1000 °C at 10 °C min^{-1} and held for 80 min. The composite specimens were held at 1000 °C for 80 min after

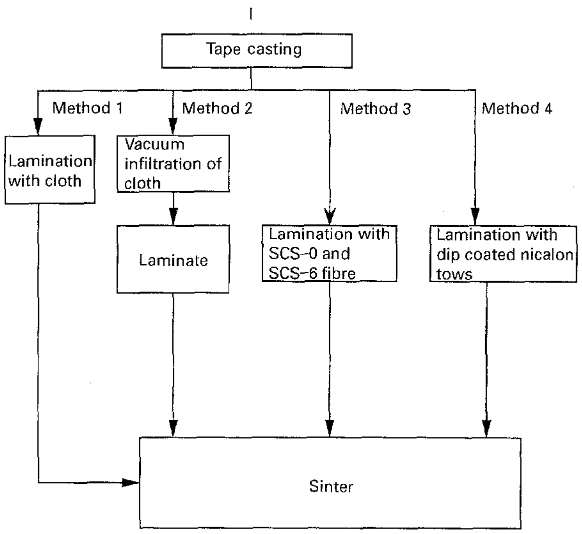

Figure 1 Flow sheet showing the different paths followed in the tape casting and sintering approach.

which the samples were cooled very slowly at 2 °C min^{-1} under an atmosphere of argon to 500 °C, and were held at this temperature for 3–5 h before they were cooled down to room temperature at 2 °C min^{-1}. In another sample, a load of 100 g was placed on the laminated specimens, while placing two layers of the Nicalon cloth between tapes for lamination. The samples were then analysed using optical microscopy.

3.1.1.3. Method 3 In this route instead of the 2-d woven Nicalon cloth experimental trials were conducted using SCS–0 and SCS–6 fibre as the second phase. The fibres were initially rolled onto aluminium foils at an interfibre distance of 8 mils to form a pre-preg. The pre-pregs were then laminated using 3.2 mm tape cast tape at 93 °C initially for 5 min and then applying a very slight load for 10 min. Four pre-pregs were laminated each between two layers of tape in 0–90 orientation so that a configuration similar to the 2-d woven cloth could be attained. A final lamination was performed at 121 °C for 15 min initially and then applying a slight load for an additional 15 min. The laminates were then subjected to a similar heat treatment as described above in methods 1 and 2. Identical procedures were also followed using the SCS–6 fibres.

3.1.1.4. Method 4 In this procedure commercially obtained Nicalon tows whose sizing was removed were used as the second phase. The procedure consisted of initially removing the sizing from the fibre tows by heating them in air at a temperature of 600 °C for 15 min. The tows were then dip coated with the slurry containing the borosilicate glass powders used for tape casting. The dip coated tows were then dried in air and then laminated between four layers of tape using similar procedures as described in methods 1 and 2. The tapes containing the dip coated tows were then subjected to an initial burn out at 500 °C and then sintered in vacuum at 900 °C according to methods 1 and 2. A similar procedure was also followed using dip coated Nicalon tows placed in 0–90 orientation except that the sintering was conducted at a temperature of 1000 °C.

3.1.2. Hot pressing (II)

This procedure was followed only using the 2-d woven Nicalon cloth along with the borosilicate glass powder (7760 grade from Corning). The detailed experimental procedure consisted of the following steps. The 2-d woven cloth was initially treated for removal of sizing at 600 °C for ≈8–12 h. The cloths were then vacuum infiltrated with the slurry used for tape casting. Immediately following vacuum infiltration, the wet cloth was placed between two 8 mils or 16 mils thick tapes and then dried in air. The dried tapes were then laminated once again between two 8 mils or 16 mils thick tapes at 15 °C for 10 min initially and then with a load at 15 °C for an additional 10 min. The laminated samples were then placed in an ashing furnace (Fisher Scientific) for removal of organics and binder. The samples were heated at the rate of 2 °C min^{-1} to 500 °C and kept for 80 min after which the temperature was brought down at 2 °C min^{-1} to room temperature. After this treatment, these samples were then loaded into a die and packed with the glass powder after placing graphoil foils at the bottom and top of the die cavity. Fig. 2 shows the sequence followed in processing these samples. A stacking sequence consisting of placing alternate layers of glass powder and Nicalon cloth was used. Initial experiments consisted of using just the laminated cloth without packing any additional glass powder. The experiments were then modified with two layers of cloth alternating with glass powder. Finally, five layers of laminated cloths were stacked in the die with alternating layers of glass powder in order to minimize the

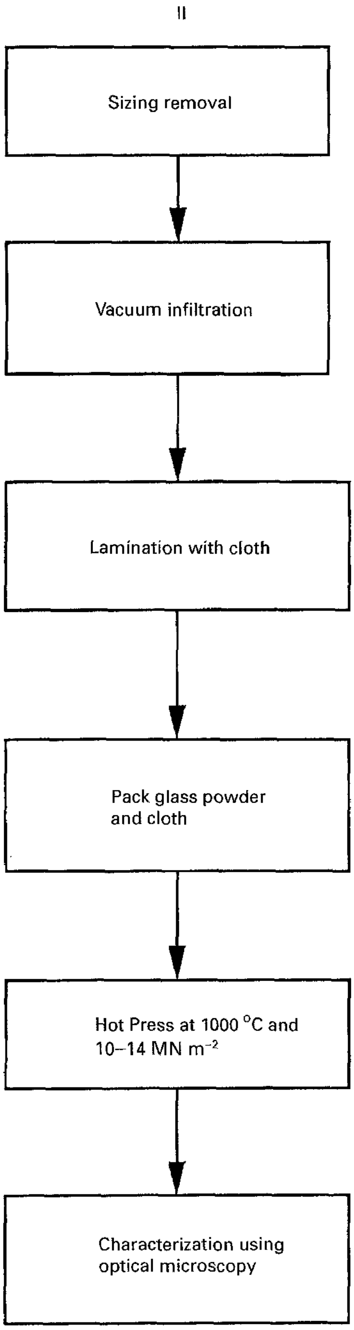

Figure 2 Flow sheet showing the steps followed during hot pressing to form the glass-fibre composite.

distance between the cloth layers and to enhance the connectivity.

After the samples were stacked into the die, the die was loaded into the hot press (GCS Corporation, Vacuum Industries, Somerville, MA). The system was then pumped down to 4.665×10^3 Nm^{-2}. The die was then heated to 1000 °C in vacuum and then a pressure of 10–14 MN m^{-2} was then applied to the samples. The load was kept constant for $\approx$30 min after which the samples were cooled down to room temperature. The samples were then recovered from the die and observed for penetration of glass into the fibre using optical microscopy.

3.2. Processing of porous aluminium nitride

The experimental procedure consisted of using commercially obtained aluminium nitride from Starck chemicals in Germany. The as-received powders were mixed with acetone and cold pressed into pellets (6 mm thick) and 13 mm in diameter by application of pressure $\approx$1000 psi. The cold pressed pellets were dried overnight and then cold isostatically pressed at $\approx$240 MN m^{-2} to a final dimension of 5.6 mm thickness and 11 mm diameter. The pellets were then placed in a closed graphite crucible covered with loose aluminium nitride powder. The hot press chamber was evacuated and back filled with nitrogen. The pellets were then sintered in this static nitrogen atmosphere of 1.013×10^5 MN m^{-2}. Initial experiments were conducted by hot pressing the cold isostatically pressed powders at 1800–1880 °C for 1 h. Another set of experiments were conducted on powders that were ball milled in ethanol for 24 h and then cold pressed followed by a cold isostatic press to form green compacts. This procedure was followed to see the effect of particle size on the nature of the porous composite. These compacts were then sintered under identical conditions except at a temperature of 1900–1920 °C for 1 h. After the sintering experiments, the samples were polished and observed under an optical microscope. Meanwhile, glass infiltration experiments were conducted on both the pellets using the borosilicate glass. The infiltration was conducted by placing the pellets in a graphite die covered with the 7760 grade glass commercially obtained from Corning that was used in Section 3.1. The loaded die was then heated to 1000 °C and a pressure of 10–14 MN m^{-2} was then applied for 30 min. The samples was then recovered and the cross-sections observed under an optical microscope to observe the infiltration of glass into the porous ceramic.

4. Results and discussion

The results of the experimental work will be presented in three sections. Section 4.1 will discuss the results of the experiments conducted primarily on tape casting, lamination and sintering of plain Nicalon tows, Nicalon 2-d cloth, the SCS–0 and SCS–6 fibres. Section 4.2 will discuss the results of the work conducted on hot pressing of the Nicalon cloth infiltrated with the glass slurry and borosilicate glass powder. Section 4.3 will then discuss the results of processing the porous aluminium nitride compacts and also describe the results of the preliminary trials conducted on infiltration of borosilicate glass into the porous aluminium nitride ceramic.

4.1. Tape casting and sintering

4.1.1. Method 1: Tape casting and lamination of 2-d Nicalon cloth followed by sintering

In order to fabricate the composite, initial trials were conducted to observe the feasibility of direct lamination of the Nicalon cloth placed between two 8 mil cast tapes of borosilicate glass. The tapes with the cloth were laminated and then sintered following the schedule described above in the experimental section. The resulting composite on removal from the furnace was extremely fragile and would peel off at several places. This provides indication that the glass was not properly adhering to the fibre surface due to inadequate wetting. There were noticeable surface cracks probably due to thermal stresses generated within the glass matrix during cooling. The cracks could not have arisen due to variations in thermal expansion since the thermal expansion coefficients of the Nicalon fibre (4×10^{-6} °C^{-1}) and 7760 grade borosilicate glass (3.7×10^{-6} °C^{-1}) are similar. The samples were cut and mounted on epoxy and then polished following standard ceramic polishing procedures. The optical micrograph obtained on the cross-section of the sample is shown in Fig. 3. The micrograph clearly shows that only the surface of the fibre tows have been wet by the glass without resulting in any penetration at all. This could be because of several reasons. First, the temperature of 880 °C is not adequate to cause the glass to be sufficiently fluid ($\eta \approx 10^7$ poise) enough to penetrate the fibres [35]. Second, the fibre spacing $\approx$10 μm is too small requiring extremely high capillary pressures to cause penetration of the glass through the fibre spacing. For example, assuming that the glass possesses a surface energy of 3 J m^{-2} the capillary pressure amounts to 6 MN m^{-2} [36]. This

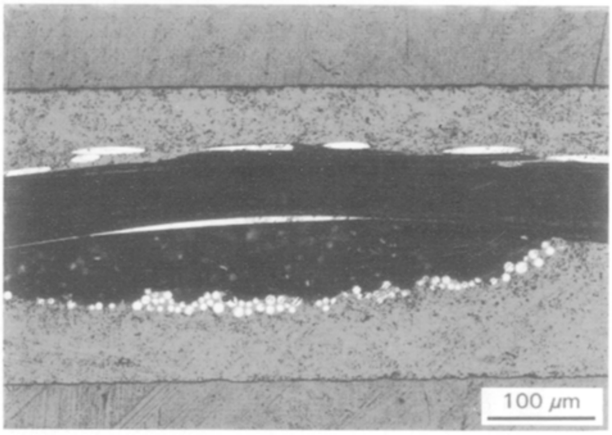

Figure 3 Optical micrograph showing the polished cross-section of glass-fibre (2-d cloth) composite obtained using the tape casting and sintering approach.

itself suggests the need for significant amount of external pressure to be provided on top of the composite during sintering to obtain any reasonable penetration of the glass into the fibre spacing. Hence, a series of experiments were performed to ascertain the effects of increased temperature and pressure.

4.1.2. Method 2: Effect of increased temperature, vacuum infiltration and pressure

Based on the above results, it was decided to penetrate the glass into the Nicalon fibre spacing by vacuum infiltration. This would help to promote wetting of the fibre by the glass. Hence, the Nicalon cloth was initially pretreated to remove the sizing and then vacuum infiltrated with the borosilicate slurry. After infiltration, the cloth was placed between two tapes and then laminated. The laminated tape was then heated to a higher sintering temperature of 1000 °C and after the initial hold of 80 min was then subjected to a slow cool (2 °C min^{-1}) to 500 °C. The composite was held at this temperature for at least 3 h before cooling down to room temperature. This thermal schedule was followed in order to minimize the surface cracks that were seen on the glass in the earlier experiments discussed above. In order to induce penetration, an arbitrary dead weight of ≈ 120 g was placed on top of the composite. Modification of the initial conditions appeared to cause visible changes in the composite. Fig. 4 shows the cross-section of the composite observed under an optical microscope after routine grinding and polishing of the composite samples. The micrographs clearly show an improvement over the earlier case in terms of penetration of the glass into the fibre spacing. However, the glass had still not completely penetrated into the fibre tows. Since the two layers of the cloth were laminated after infiltration, the micrographs also show the longitudinal cross-section of the fibres. Although, some improvements can be seen in terms of penetration of glass into the fibre spacing, there still appears to be regions of porosity in the glass matrix due to possible loss of adsorbed water from the glass. Pretreatment of the fibres and the glass frit and the use of anhydrous solvents during the synthesis of the slurry could help in minimizing the porosity. Repeating the procedure using a dead weight of 100 g however once again showed considerable porosity in the glass although, there were regions wherein the glass had penetrated into the fibre spacing.

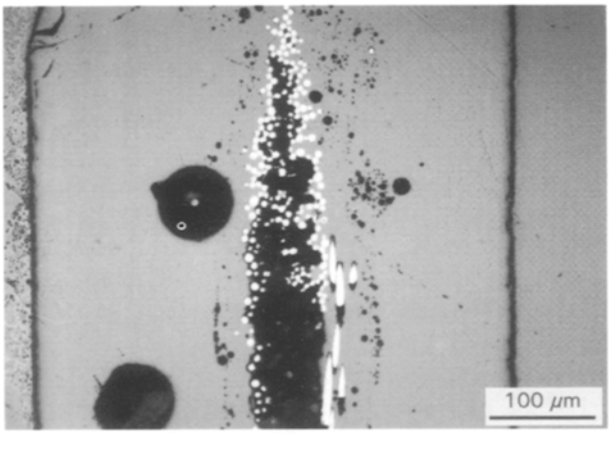

Figure 4 Optical micrograph showing the polished cross-section of glass-fibre (2-d cloth) composite processed using vacuum infiltration and sintered at a higher temperature using a dead weight of 120 g. The micrograph shows improved penetration of the glass into the fibre tows.

These experiments therefore suggest that vacuum infiltration combined with a higher temperature and use of a dead weight helped to improve the penetration of the glass melt into the fibre spacing. However, the concept of tape casting and sintering seems to be quite inadequate on its own to result in a good composite with complete wetting of the glass and the fibre cloth. As mentioned, one of the main reasons is the high viscosity of the glass melt and the tremendous capillary pressures that consequently need to be overcome to cause penetration into the fine fibre spacing. On the other hand, it should be mentioned that the glass powder is quite coarse with an average particle size of $\approx 10\,\mu\text{m}$. Thus, vacuum infiltration of the coarse glass particulate slurry does not result in adequate penetration into the fibre spacing. However, the use of a sol–gel derived sol of a glass powder consisting of much finer particle sizes could result in improved wettability enhancing the quality of the composite.

4.1.3. Method 3: Tape casting and lamination of SCS-0 and SCS-6 fibre followed by sintering

These experiments were conducted since the tape casting and sintering approach failed to provide an adequate quality composite on which the electrical and thermal properties could be measured. Initial experiments were conducted using the SCS-0 grade fibre which is essentially non stoichiometric SiC with excess carbon and some oxygen. The fibres were initially rolled onto a pre-preg as described in the experimental section and then laminated onto the borosilicate tapes. Similar sintering procedures were followed as with the 2-d Nicalon cloth. Four layers of the fibres were placed in 0–90 orientation and laminated following identical procedures as in the case of the 2-d Nicalon cloth. The composites were heated to 1000 °C for sintering and cooled down at 2 °C min^{-1} to 500 °C at which temperature it was kept for almost 4 h before cooling down to room temperature. The composite however, was not at all transparent and appeared dark and unclear indicating the presence of possible unburnt binder trapped inside the composite. The cross-section of the composite also revealed the presence of considerable porosity visible to the naked eye suggesting fibre degradation. This could possibly be because of a chemical reaction occurring at the glass-fibre interface. A possible reaction could be the formation of sodium silicate due to the migration of Na^+ ions from the glass to the fibre as has been observed using the SCS-0 fibres with sodium containing glass [37]. A detailed microchemical analysis of the fibre-glass interface would be necessary to verify this hypothesis.

In the case of the SCS–6 fibres, once again similar sintering procedure reported for the Nicalon cloth was followed. Four layers of the fibres were laminated in 0–90 orientations and then subjected to sintering at 1000 °C after burning out the binder at 500 °C. Fig. 5 shows the cross-section of the composite observed under an optical microscope. The micrographs clearly indicate fibre swimming that has occurred during the sintering process. At the same time considerable porosity is seen particularly close to the fibres. The SCS–6 fibres are chemically made up of a central carbon core, an inner coating covering the core, four SiC layers deposited on the inner coating, and an outermost coating whose composition has long been a controversy [37–40]. However, recently Ning *et al.* [38] have reported the results of microchemical analysis of the SCS–6 fibre. Their studies indicate that the outermost layers are made up of four different layers of SiC, the Si to C ratio not being exactly stoichiometric. The porosity could arise from the reaction of the outer core with the glass. A possible reaction being that of carbon with sodium oxide to form CO which escapes from the glass resulting in the porosity as seen in Fig. 6. Another possibility is the loss of adsorbed water from the fibre and the glass through the viscous melt leading to the formation of pores.

4.1.4. *Method 4: Tape casting and lamination of Nicalon fibre tows followed by sintering*

All the above processes with the cloth as well as with pre-pregs of SCS–0 and SCS–6 seemed to indicate problems of inadequate penetration. In the case of the fibres, there was also degradation due to reaction with the glass. It was therefore decided to study and apply the tape casting and sintering approach to commercially obtained Nicalon tows. The sizing was stripped off from the tows by heating in air at 600 °C. They were then dipped into the borosilicate glass slurry. The dip coated tows were laminated and sintered following identical processes as those discussed earlier in method 1. Two sets of experiments were conducted using the dip coated tows, one in which the composites were heated to 900 °C and the other in which the composites were heated to 1000 °C with the tows arranged in 0–90 orientation. Fig. 7 shows the cross-section of the composites observed under an optical microscope. The micrographs clearly indicate very good wetting of the fibre with the glass in contrast to the composites fabricated employing the Nicalon cloth, although some random porosity is evident. In the case of the tows arranged in the 0–90 orientation also, it can be seen that there is good wetting obtained. Thus this appears to be a viable process for processing glass-fibre composites for electronic packaging.

4.2. Hot pressing of the glass and the Nicalon cloth

From the discussion above it can be seen that the tape casting and sintering approach shows some promise in

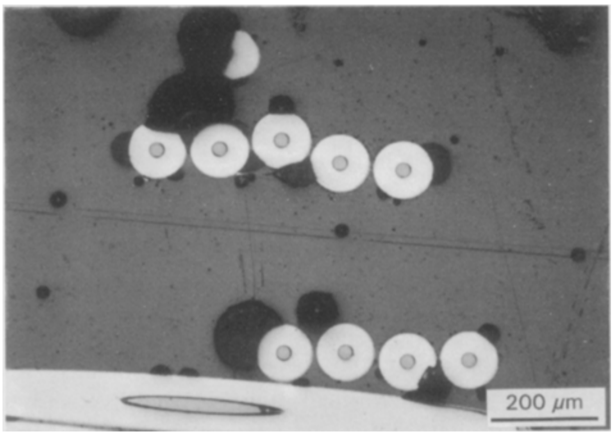

Figure 6 Optical micrograph showing the polished cross-section of glass-SCS–6-fibre composite. The micrographs show fibre swimming as well as porosity near the fibre possibly due to degradation of the outer fibre coating.

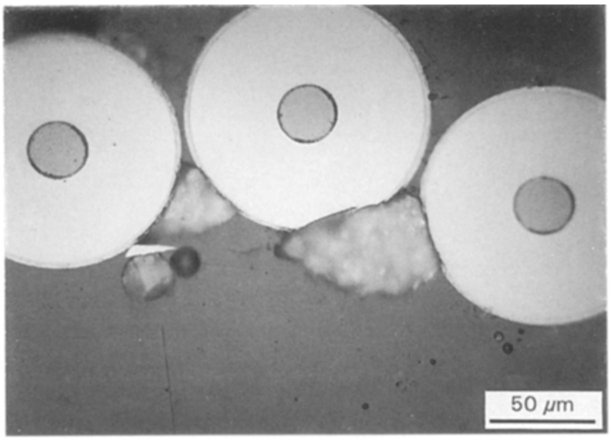

Figure 5 Optical micrograph showing the polished cross-section of glass-SCS–6-fibre composite. The micrographs show fibre swimming and possible degradation of the outer carbide coating.

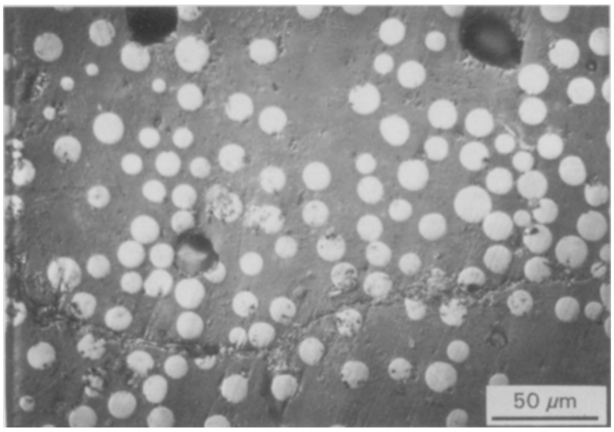

Figure 7 Optical micrograph showing the polished cross-section of glass and Nicalon fibre tows dip coated in glass slurry. The micrograph shows good penetration of glass into the fibre spacing.

the case of fabrication of composites using vacuum infiltrated Nicalon tows. On the other hand, it is extremely difficult to achieve good penetration of the glass into the fibre tows using the Nicalon 2-d cloth. The close spacing of the weave prevents the glass from entering the fibre tows both at the vacuum infiltration and sintering stages. It was clear that in order to achieve adequate penetration there is need for application of pressure in addition to increasing the sintering temperature. Hot pressing was therefore seen as a solution to the problem. Several sets of samples were hot pressed in order to obtain the right combination of processing parameters of temperature (1000 °C) and pressure ($\approx$ 10–14 MN m^{-2}). The samples were hot pressed for 30 min and then cut, mounted and polished to be observed under the optical microscope. Fig. 8 shows the cross-section of a representative composite. The micrograph clearly shows regions where the glass has completely penetrated the fibre tows in a uniform fashion. There are very few regions where the glass has not penetrated into the fibre spacing. Another noticeable effect is the densification of the glass with very minimum porosity. Thus, it was possible to fabricate uniformly penetrated glass-fibre composites using the hot pressing technique at a temperature of 1000 °C and pressure of 7 MN m^{-2}. Future experiments will be directed at processing composites using this approach and evaluating them for their dielectric constant and thermal conductivity.

4.3. Processing of porous aluminium nitride

The as-received aluminium nitride powders were cold pressed and then isostatically pressed to form a green pellet. The resulting pellets were then sintered in nitrogen at 1900 °C for 1 h. The samples were polished and observed under an optical microscope. Fig. 9 shows the optical micrograph of the polished specimen. The micrographs clearly indicate the presence of connected pores continuous to the surface. The densities of the sintered porous samples were also measured using a pycnometer which indicated the densities to be 3.257 g cm^{-1} very close to the theoretical density (3.26 g cm^{-1}). At the same time the apparent density of the samples was calculated to be 2.32 g cm^{-1}. A comparison of the two therefore indicates presence of $\approx$28% porosity in the samples. The porous nature of the samples coupled with the pycnometric studies yielding theoretical density suggests the interconnected nature of the pores. These results are extremely promising particularly for the application of these composites as substrates in electronic packaging since the interconnected nature of the pores could provide for optimum dielectric constant and thermal conductivity as discussed earlier in Section 2. These measurements are currently in progress.

Following these encouraging results, it was decided to infiltrate the nitride ceramic with borosilicate glass. The hot infiltration was conducted at 1000 °C using a pressure of 10 MN m^{-2}. The resulting composite was mounted, sectioned, polished and observed under the optical microscope. Fig. 10 shows the cross-section of the polished samples. The micrograph indicates that the glass has penetrated only to a distance of 75–100 μm. These results therefore suggest

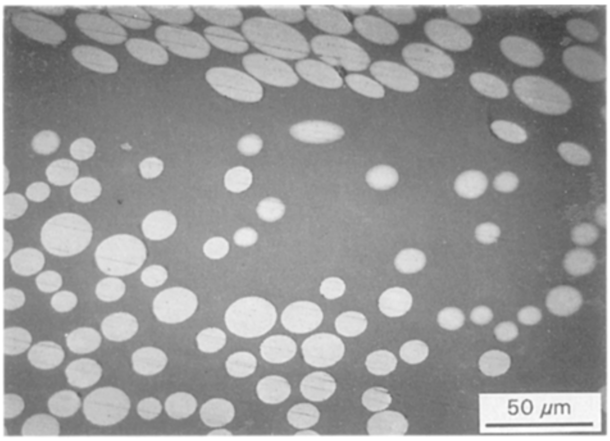

Figure 8 Optical micrograph showing the polished cross-section of hot pressed glass-fibre (2-d cloth) composite processed at 1000 °C and 10 MN m^{-2} pressure. The micrograph shows good penetration of the glass into the fibre spacing. The glass is also visibly dense with no porosity.

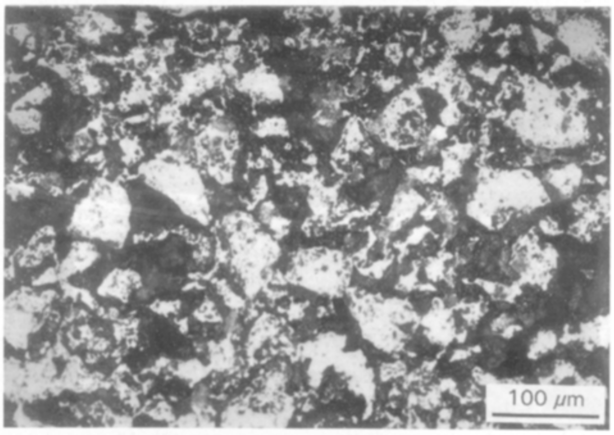

Figure 9 Optical micrograph showing the polished cross-section of the sintered aluminum nitride pellet. The micrograph shows the presence of well connected porosity.

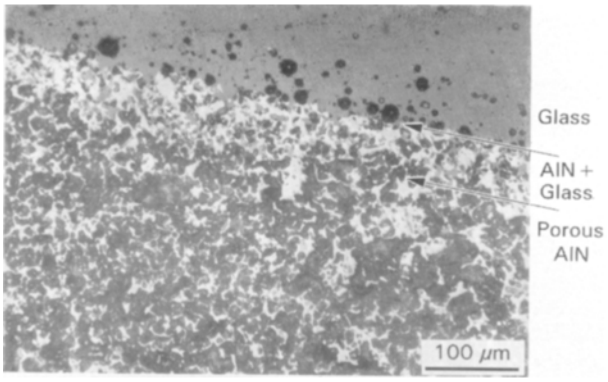

Figure 10 Optical micrograph showing the polished cross-section of sintered aluminum nitride hot infiltrated with borosilicate glass. The glass has penetrated to a distance of $\approx$100 μm into the pores in the nitride ceramic.

the potential of these experiments for obtaining porous AlN ceramics that would satisfy both the electrical and thermal requirements. The low penetration distances of the glass into the ceramic in fact could provide a good hermetic seal which is important for the ceramic to be useful as a substrate material. Future work will be directed towards measuring the thermal and electrical characteristics of these composites.

5. Conclusions

The results of the preliminary studies conducted on processing of glass-fibre composites indicate the extreme difficulty encountered in employing the tape casting and sintering approach particularly, in the case of the 2-d woven fibre cloth. Nevertheless, the results of the work suggest the potential of this approach for processing composites using slurry coated Nicalon tows where successful penetration of the tows with the glass was achieved. Hot pressing of borosilicate and Nicalon cloth at 1000 °C and $10\,\mathrm{MN\,m^{-2}}$ also resulted in the formation of good composites with successful penetration of the fibre tows with glass. Substantial fibre degradation was however observed in the case of the SCS–0 fibre due to a possible chemical reaction of glass with the fibre. At the same time preliminary sintering studies conducted on commercially obtained AlN powders resulted in a ceramic with $\approx 28\%$ connected porosity. Hot infiltration of the ceramic provided ≈ 75–$100\,\mu\mathrm{m}$ penetration of the glass into the connected pores. These results particularly, those with the AlN are therefore quite encouraging in terms of demonstration of its potential as a composite material for electronic packaging.

Acknowledgements

The author would like to acknowledge the support of Drs Ron Kerans, Alan Katz and Paul Jero for providing the opportunity to participate in the Air Force summer faculty program. The author would also like to thank Drs Rollie Dutton and Edmund Moore for useful technical assistance. The help of Kristi Keller, Cathy Gustafson, Charlie Cook, Marlin Cooke, Mark Dodd, George Cornish and Dennis Petri of UES and all the support staff in the ceramics group at Wright Patterson Laboratories is also acknowledged. Ms Kim Andrews and Ms Cindy Emerick are also thanked for their help in the polishing and preparation of samples for characterization. The author would also like to acknowledge the support of the National Science Foundation (DMR Grant 9301014) and the NSF Research Initiation Award, RIA (Grant 9309073).

References

1. 'Microelectronic Packaging Handbook', Edited by R. R. Tummala and E. J. Rymaszewski, (Van Nostrand Reinhold, New York 1989).
2. G. GEIGER, *Bull Amer Ceram Soc* **69** (1990) 1131.
3. E. M. RABINOVICH, *J. Electronic Packaging* **111** (1989) 183.
4. R. R. TUMMALA and R. B. SHAW, High Tech Ceramics, edited by P. Vincenzini, (Elsevier Science Publishers B.V. Amsterdam, 1987) p. 75.
5. J. L. SPRAGUE, *IEEE Transactions on Components, Hybrids, and Manufacturing Technology* **13** (1990) 390.
6. K. R. KINSMAN, *J. Metals* **6** (1988) 7.
7. J. U. KNICKERBOCKER and M. S. COLE, *Advanced Packaging* **January/February** (1995) 20.
8. R. L. BROWN, A. A. SHAPIRO and P. W. POLINSKI, *The Intnl. J. Microelectronics and Elec. Packaging* **16** (1993) 328.
9. N. KURAMOTO, H. TANIGUCHI and I. ASO, *Cerm Bull* **68** (1989) 883.
10. N. KURAMOTO and H. TANIGUCHI, *J. Mater. Sci. Lett.* **3** (1984) 471.
11. T. B. TROCZYNSKI and P. S. NICKOLSON, *J. Amer. Ceram. Soc.* **72** (1989) 1488.
12. N. S. VAN DAMME, S. M. RICHARD and S. R. WIZER, *ibid* **72** (1989) 1409.
13. ATSUHIKO HIAI, TAKAISHI: KAZUO WAKIMURA, SENNAN: MASAO TANAKA, SAKAI: TAKAO TANAKA SHIMONOSEKI, Mitsui Toatsu Chemicals Inc, Tokyo, Japan, U.S. Patent No. 4869925 (1989).
14. U. KLABUNDE, W. CHESTER, E. J. NEWITT, C. FORD, F. N. TEBBE, H. DEL, U.S. Patent No. 4865830, (1989).
15. S. L. DOLE, R. H. ARENDT, W. D. PASCO, U.S. Pat. No. 4843042, (1989).
16. S. KURATANI, K. UNO, S. MIZUNO, H. SAKURAMOTO and S. NISHIYAMA, U.S. Pat. No. 4843038, (1989).
17. S. MIZUNO, S. KURATANI, K. UNO, H. SAKURAMOTO and S. NISHIYAMA, U.S. Pat No. 4833108, (1989).
18. A. IKEGAMI, K. OTSUKA and T. YASUDA, in: "High Thermal Conductive SiC Substrate and Its Applications", Proceedings of the 5th European Hybrid Microelectronics Conference, Stresa, Italy (International Society for Hybrid Microelectronics, Stresa, 1985) 465.
19. R. R. TUMMALA, *J. Amer. Ceram. Soc.* **74** (1991) 895.
20. A. J. BLODGETT, Jr., *Scientific American* **249** (1983) 2.
21. T. J. MROZ and E. A. GROAT, paper E-65-94, presented at the 94th. Annual meeting of the American Ceramic Society held in Indianapolis, IN, April 24–28, 1994.
22. J. F. MACDOWELL, G. H. BEALL, in Proceedings of the 1st International Science and Technology conference, "Materials and Processes for Microelectronic Systems", Ceramic Transactions, edited by K. M. Nair, R. Pohanka and R. C. Buchanan, Vol. 15 (1989) 259.
23. *Idem.* Materials Research Society Symposium Proceedings, "Advanced Electronic Packaging Materials", edited by A. T. Barfknecht, J. P. Partridge, C. J. Chen and Che-Yu Li, Vol. 167 (1989).
24. R. S. HSU, P. N. KUMTA and T. P. FEIST, *J. Mater. Sci.*, **30** (1995) 3123.
25. V. RAMAKRISHNAN and N. JAYARAMAN, *Ibid* **27** (1992) 2423.
26. M. BARSOUM and A. ELKIND, *Ibid* **30** (1995) 69.
27. W. D. KINGERY, H. K. BOWEN and D. R. UHLMANN, "Introduction to Ceramics" 2nd Edn (John Wiley & Sons, NY, 1976) p. 635.
28. A. J. MOULSON and J. M. HERBERT, "Electroceramics, Materials, Properties and Applications", (Chapman and Hall London 1990) p. 79.
29. L. E. CROSS and T. R. GURURAJA, Materials Research Society Symposium Proceedings, "Electronic Packaging Materials Science II", edited by K. A. Jackson, R. C. Pohanka, D. R. Uhlmann and D. R. Ulrich, Vol. 72 (1986).
30. D. P. BUTTON, B. A. YOST, R. H. FRENCH, W. Y. HSU, J. D. BOLT, M. A. SUBRAMANIAN, H. M. ZHANG, R. E. GIEDD, A. J. WHITAKER and D. G. ONN, Advances in Ceramics, Vol. 26, "Ceramics Substrates and Packages for Electronic Applications", edited by M. F. Yan, K. Niwa, H. M. O'Bryan, Jr., and W. S. Young, (American Ceramic Society 1989) pp. 87–105.
31. I. WEBMAN, J. JORTNER and M. H. COHEN, *Phys. Rev. B* **11** (1975) 2885.
32. W. Y. HSU, T. D. GIERKE, and C. J. MOLNAR, *Macromolecules* **16** (1983) 1945.

33. S. PROCHAZKA and C. F. BOBIK, Materials Science Research, Vol. 13, "Sintering Processes", edited by G. C. Kuczynski, Proceedings. 5th International Conference on Sintering and Related Phenomena, University of Notre Dame, Indiana, June 18–20 (1979) 321.
34. C. M. GUSTAFSON, R. E. DUTTON and R. J. KERANS, *J. Amer. Ceram. Soc.* **78** (1995) 1423.
35. N. P. BANSAL and R. H. DOREMUS, "Handbook of Glass Properties", (Academic Press, London 1986).
36. R. H. DOREMUS, "Glass Science", (John Wiley & Sons, New York, 1973) 284.
37. T. MAH, Private Conversation, (1993).
38. X. J. NING, P. PIROUZ and S. C. FARMER, *J. Amer. Ceram. Soc.* **76** (1993) 2033.
39. J. A. DICARLO, *J. Mater. Sci.* **21** (1986) 217.
40. J. I. ELDRIDGE and F. S. HONECY, *J. Vac. Sci. Technol.* **A8** (1990) 2101.

Received 10 August 1995
and accepted 21 December 1995