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Interaction of Encapsulation Glass and Silicon Nitride Ceramic During HIPing

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Abstract

Interaction between ceramic compacts and the encapsulation glass during the HIP process has been studied in a model system of silicon nitride and borosilicate glass. Attention has been focused on what happens when the pressure is first applied in the HIP-cycle, i.e. between about 1200 and 1500°C. At this stage the pore system of the ceramic green body is still rather unaffected by sintering. The model system was characterised to evaluate a possible viscous flow of glass into the green body. Two glass compositions, one with high and one with low viscosity, were used, measurements being made of their viscosity and their contact angle on the nitride. Applying Darcy's law it was predicted that the encapsulation glass with the lowest viscosity should penetrate about 1200 microns into the still open pore structure at 1450°C, but this was not observed experimentally. In the calculations no chemical reactions were assumed to take place. However, increases in hardness of heat-treated mixture of glass and silicon nitride powder indicates that nitrogen dissolves in the glass. It is known that nitrogen increases the viscosity of the glass and this would result in a more limited glass intrusion. After HIP the surface region of the dense ceramic exhibited a phase composition gradient of silicon oxynitride, down to approximately 100–200 microns into the bulk. © 1999 Elsevier Science Ltd. All rights reserved

Keywords: encapsulation, hot isostatic pressing, glass, Si_3N_4, interaction.

1 Introduction

In most applications of ceramic materials the surfaces are of great importance. The surface of a component is usually exposed to the largest stresses, the highest temperatures and the most severe abrasion. Since machining of dense ceramic materials is time-consuming and costly it is essential that the need for machining is minimised. Hence the quality of the as-processed surfaces is critical. During glass encapsulated, hot isostatic pressing (HIPing), which can be used for complicated shapes with good reproducibility of final density,[1] the encapsulation glass and the porous ceramic green body are brought into intimate contact and possible glass/ceramic interaction might be crucial for the surface quality of the densified component. In the present work—to obtain a better understanding of possible interactions between glass and ceramic—a model system of borosilicate encapsulation glass and silicon nitride with yttria as a sintering aid has been studied.

In an earlier investigation of the same model system, attention was focused on possible chemical reactions taking place between the glass and the ceramic.[2] Powdered mixtures of silicon nitride and borosilicate glass were heat treated and the samples were evaluated with X-ray diffraction (XRD). After heat treatment at temperatures typical of those at which pressure is first applied during the HIP cycle, no chemical reactions could be detected although the theoretical calculations predicted boron nitride formation. Limited amounts of boron nitride, below the limits of detectability of the XRD technique, may have formed but it is also expected that the reaction rates are low at these temperatures. At 1750°C, a temperature typical for the densification stage of the HIP cycle, the system reacted to silicon oxynitride and boron nitride in accordance with the theoretical calculations. In another study of this glass/ceramic combination, gradients in mechanical properties close to the glass/ceramic interface of a HIPed compact were investigated.[3] A reduction in Young's modulus was observed within 150 microns of the interface.

In this present study the possible viscous flow of the encapsulation glass into the porous green body

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of silicon nitride was investigated. The conditions of interest are those of the early part of the HIP cycle, when the pressure is first applied and the temperature is in the range 1200–1450°C, i.e. when the glass is soft and gas-tight but the pore system of the ceramic body is still open and has not to any significant extent been affected by sintering.

2 Methods

A model system of silicon nitride and borosilicate glass was chosen. The silicon nitride (Siconide P95 from Permascand AB, BET $8{\cdot}9\,m^2\,g^{-1}$) was prepared with 3 w/o yttrium oxide as a sintering aid. In order to create different characteristics of the green body ceramic surfaces, two different forming methods were selected, firstly, injection moulding and secondly, cold isostatic pressing (CIP), 300 MPa, followed by machining. The ceramic compacts were in the form of cubes with dimensions $10\times10\times10\,mm^3$. To vary the glass characteristics without introducing any new species, two different compositions (i.e. different SiO_2/B_2O_3 ratios) of borosilicate glass were prepared (see Table 1). They were produced by mixing the oxides, heat-treating at 900°C in argon for 24 h and finally crushing. Since boron oxide and the boron containing glasses are hygroscopic, pre-heating to eliminate water was sometimes necessary.

The glass encapsulation was applied by a proprietory technique. The HIP-cycle, employing an argon pressure medium, involved a temperature increase to 1180–1200°C and a hold time at this temperature of 1 h during which the pressure was increased to 130 MPa. After this the temperature was raised at $600°C\,h^{-1}$ to a maximum of 1750 °C while the pressure was raised to 160 MPa. The hold time at maximum temperature was one hour. Some cycles were interrupted at 1180–1200 °C.

Table 1. Glass compositions

Glass I	70 w/o SiO_2 and 30 w/o B_2O_3
Glass III	40 w/o SiO_2 and 60 w/o B_2O_3

In order to be able to compare the experimental observations with theoretical estimates of possible viscous flow, it was necessary to have information on the relevant properties of the glass as well as some characteristics of the pore system of the silicon nitride. The glass viscosity was determined by heating the glass until a substantially bubble free melt was obtained and then measuring the viscosity by a rotating cylinder viscometer as a function of decreasing temperature. The wetting angles of the glasses on silicon nitride were determined in an argon atmosphere at 1075–1080°C using green compacts of silicon nitride as substrates.

The pore size distributions of the silicon nitride green bodies were determined for pore sizes from 14 μm down to 0·011 μm using mercury porosimetry. The surface tension of mercury was set to $0.484\,N\,m^{-1}$ and the wetting angle to 140°. This technique also gave an estimate of the porosity level of the green body. Another way to characterise a pore system is to measure the permeability. Since no standard method suitable for the ceramic specimens in this study was available, a permeability test was devised and performed in the following way. Glycerol, a fluid with known viscosity, was pushed into the porous body for a certain time. The sample was broken and the distance of the intrusion was measured. This was repeated with different hold times and it was found that the intrusion length was proportional to the square root of time, see Fig. 1) consistent with Darcy's law [eqn (1)].[4]

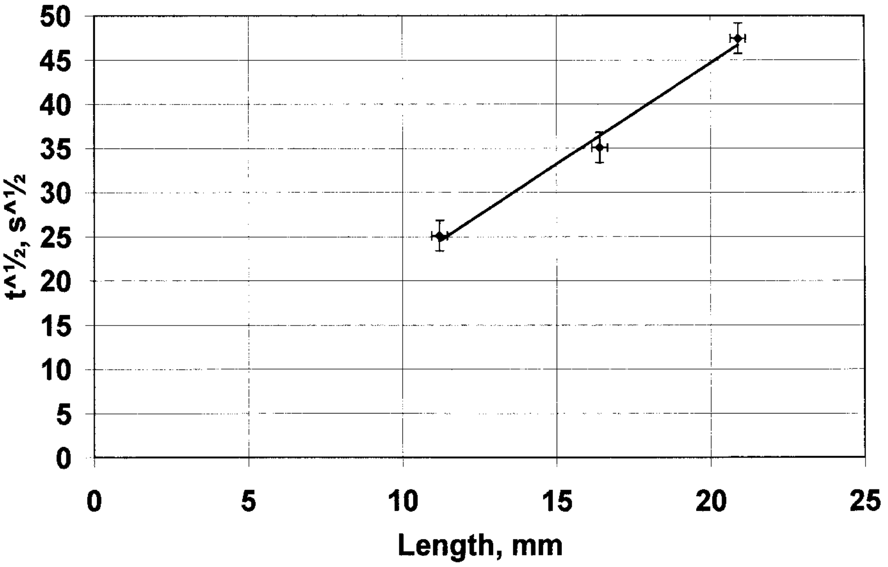

Fig. 1. Glycerol intrusion into a silicon nitride green body.

The permeability could then be calculated from Darcy's law:

$$\Delta L = (B\Delta Pt/\eta)^{1/2} \tag{1}$$

where ΔL is the distance of flow, B is the permeability, ΔP is the pressure difference, t is the time, and η is the dynamic viscosity.

Scanning electron microscopy (SEM) was used to study the microstructure of the interface region between the glass and the ceramic. Samples from completed HIP cycles as well as from interrupted cycles were examined.

Compositional gradients from the interface were examined using secondary ion mass spectrometry (SIMS) with primary ions of oxygen on polished cross-sections. The probe diameter was 100 microns and the steps 10 microns.

Gradients of phase composition were investigated using X-ray diffraction (XRD). After HIP the surfaces of the samples were normally glass bead blasted in order to remove carefully excess encapsulation glass. The samples were ground in steps of up to 30 microns from this surface on 800 or 1200 mesh SiC paper. Estimates of the proportions of detected phases were made in accordance with a method described by Mencik and Short.[5]

To investigate possible dissolution of nitrogen into the encapsulation glass during HIP, hardness tests were carried out on powder mixtures of glass and silicon nitride powder subjected to HIP conditions. Powder mixtures of glass with up to 25% of silicon nitride were CIPed and heated in molybdenum crucibles with argon as a protective atmosphere. The heating cycles were interrupted at 1200 to 1500°C, sometimes with a hold time at maximum temperature. The furnace was then switched off, giving a cooling rate of approximately $1000°C\,h^{-1}$ down to 950°C and $600°C\,h^{-1}$ for the interval 950–500°C. Sample sectioning for hardness evaluation was carried out with water-free cooling and lubrication due to the solubility of boron oxide in water. The hardness was measured using Vickers indentation with a load of 0·98 N and a hold time of 15 s.

2.1 Calculation of viscous flow

Viscous flow of a Newtonian liquid in a porous body can generally be described by Darcy's law[4] which implies that the intrusion depth is proportional to the square root of time. This general expression based on studies of flow through a bed of approximately equal sized balls is given in eqn (1). The intrusion tests with glycerol carried out in this work is consistent with this linear behaviour (see Fig. 1) and therefore yield an estimate of the permeability of the green compacts. Thus, if the borosilicate glass can be regarded as a Newtonian fluid, i.e. has constant viscosity for different shear deformation rates, Darcy's law can be used to estimate the glass intrusion.

Summarising earlier studies on glass viscosities from many investigators, the general finding is that the viscosity of glass melts is not a function of applied force or velocity of flow, implying that glasses are Newtonian liquids.[6] One work concerning soda–lime–silicate glass at 655°C reports a deviation from Newtonian behaviour for low shear stresses namely below 0·05 MPa, maybe indicating some elastic deformation in the viscous glass before it starts to flow.[7] The maximum shear stresses when a liquid is pushed into a capillar occur at the pore walls according to eqn (2),

$$\tau = -1/2 \times r \times \Delta P/\Delta l \tag{2}$$

where τ is shear stress, r channel radius and $\Delta P/\Delta l$ the pressure drop over intrusion length. In this present study, if only 1 nm is assumed to penetrate, a pressure of 0·004 MPa give rise to shear stresses higher than the threshold value given above. If this Bingham behaviour exists it has a very limited influence and is neglected in this study.

In later works another type of non-Newtonian behaviour of glasses is reported for high deformation rates or high stress levels. A pseudoplastic or shear thinning response is found, meaning lower viscosity at higher deformation rates. Most of the studies has been in the high viscosity range around 10^{11}–10^{15} P (e.g. Refs 8 and 9). The onset of the non linear behaviour occurs at higher strain rates for higher temperatures and lower viscosities. Simmons *et al.*[10] have studied glass flow at low viscosities. They found the same pseudoplastic behaviour for a soda–lime–silica glass as at low Newtonian viscosity as 10^6 P. Very high shear strain rates had to be applied for this to happen. (Critical deformation rate was $7\,s^{-1}$ for a viscosity of 10^6 P) In the present work the viscosities were even lower. Furthermore, the pressure increase rate was very limited, 130 MPa/30 min, which gives deformation rates on a much lower scale. Thus, Newtonian behaviour can be assumed.

To estimate the intrusion using the Darcy law, the permeability has to be determined experimentally. There are alternative models that describe viscous flow in a porous bed having a similar form to the Darcy model (i.e. with intrusion length proportional to square root of time) but which attempt to take into account the morphology of the pore system. Two of these were applied in this study as a comparison with Darcy's law. The first is that proposed by Poiseuille,[11] who studied laminar flow in a circular tube:

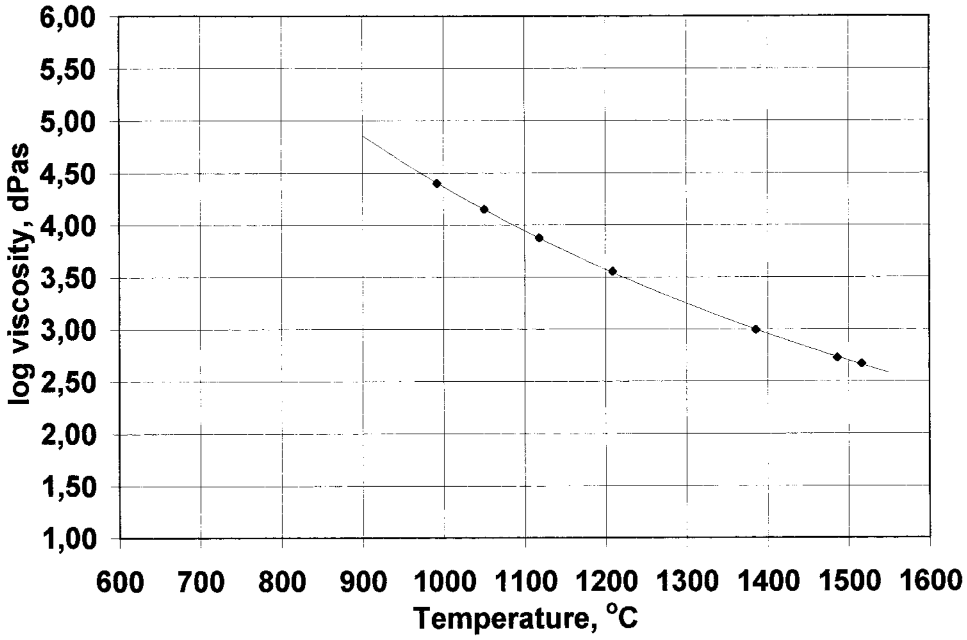

Fig. 2. Viscosity of Glass III as a function of temperature.

$$\Delta L = \left(d^2 \Delta P t/(32\eta)\right)^{1/2} \qquad (3)$$

where d is the diameter of the tube.

Kozeny[12] and Carman[13] described the laminar flow through a packed bed as flow through a system of capillaries, the diameter of the capillaries being described by the expression

$$d_H = 4\varepsilon/((1-\varepsilon)S_v) \qquad (4)$$

where d_H is the hydraulic diameter, ε is the porosity and S_v is the specific area of the powder particles. This leads to the equation:

$$\Delta L = (\varepsilon^3 \Delta P t/(f\rho^2(1-\varepsilon)^2 \eta S_v^2))^{1/2} \qquad (5)$$

where f is around 5 (dependent on the particle geometry and the shape of the capillary cross-section).

3 Results and Discussion

Due to the very high viscosity for Glass I it was impossible to get a bubble free melt, even after a long hold time at 1450°C. After 6 h an approximate viscosity at this temperature was determined to $\eta = 10^{4 \cdot 5}$ dPas. The viscosity of Glass III was measured from maximum temperature of 1515°C and also here it was difficult to obtain a completely bubble free melt. The viscosity–temperature relation for Glass III is shown in Fig. 2 and can be described by the equation

$$T = B/(\log \eta + A) + T_o \qquad (6)$$

with the constants $B = 8547{\cdot}0$, $A = 1{\cdot}872$ and $T_o = -369{\cdot}6$. At 1200°C the viscosity of Glass III was $10^{3 \cdot 6}$ dPas. Values found in the literature[14] for glasses of similar compositions to Glasses I and III at 1200°C are $10^{4 \cdot 3}$ and $10^{3 \cdot 2}$ dPas, respectively.

The wetting angle of the glasses are shown in Table 2. No significant differences could be seen between the glasses. The wetting angle based on these measurements can be set to 140°. Thus the glasses were non-wetting against the ceramic material.

A typical pore size distribution for the powder bodies can be seen in Fig. 3. The injection moulded samples had only slightly finer pore openings than the CIPed samples. The d_{50}-values were 0·056 μm for the CIPed and 0·053 μm for the injection-moulded green bodies.

SEM studies of densified samples did not show any differences in microstructure between the samples formed by the different methods. Some samples encapsulated with Glass III showed a tendency to crack six to seven microns from the edge and the sample encapsulated in Glass I exhibited some porosity. Figure 4 shows samples encapsulated in Glass III. The dense samples revealed a lighter zone some two to three microns wide at the edge [Fig. 4(a)]. In Fig. 4(b) are shown micrographs of samples from an interrupted HIP cycle. No clear evidence of glass intrusion could be found. However, due to the small differences in average atomic numbers of the ceramic and glass and also because of the fine pore structure, the possibility of glass infiltration cannot be excluded.

Table 2. Wetting angle at 1075–1080°C

Glass I	144° ± 16°
Glass III	136° ± 13°
Mean (eight samples)	140° ± 14°

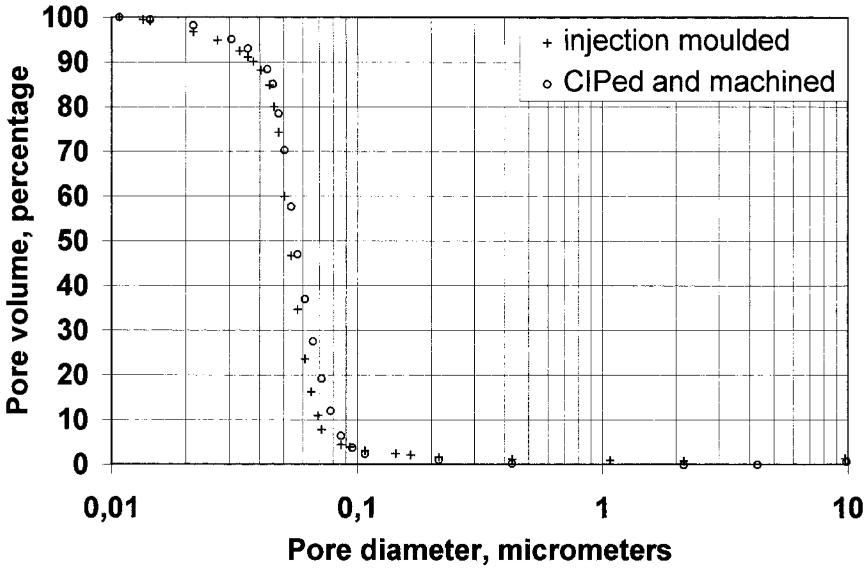

Fig. 3. Pore size distribution in green bodies of injection moulded and CIPed samples.

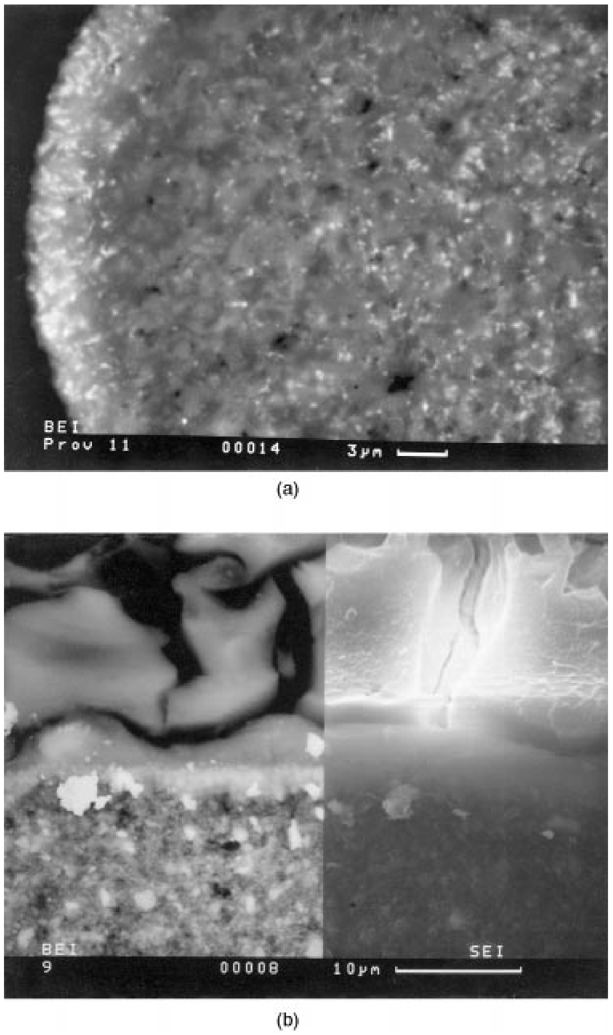

Fig. 4. HIPed silicon nitride; the sample was formed by injection moulding; the encapsulation was Glass III: (a) completed HIP cycle (BEI), (b) HIP-cycle interrupted at 1180°C, 130 MPa (backscattered electron image to the left and secondary electron image to the right).

The XRD measurements made in conjunction with stepwise grinding revealed a silicon oxynitride gradient in the sample encapsulated in Glass III (see Fig. 5). The oxynitride content falls to values corresponding to the bulk content at a depth of 100–200 microns.

SIMS analysis results are illustrated in Figs 6 and 7. Figure 6 refers to a sample (CIPed, Glass I) heat treated at 1180°C for 1 h. The boron gradient reached to around 200 μm into the ceramic. The yttrium gradient penetrated to around 40 μm into the glass and minor amounts of other elements, such as aluminium, were enriched at the interface. The results for a sample exposed to a prolonged hold time of 12 h at 1200°C, are shown in Fig. 7. Boron reached a depth of around 550 μm in the ceramic and yttrium penetrated to around 275 μm in the glass. The boron content did not fall to zero which might indicate boron transport through the sample. However, analysis of a dense sample as well as an untreated CIPed sample showed the same boron content indicating that the bulk boron did not originate from the encapsulation glass.

The boron gradient in this sample permitted the estimation of a diffusion coefficient, D, for boron into the ceramic body. The parameter was calculated according to the thin-film solution to Fick's second law, assuming constant D:

$$c = \alpha \times \exp(-x^2/4Dt)/\left(2(\pi Dt)^{1/2}\right) \qquad (7)$$

where c is concentration, α is quantity of solute, t is time and x is the distance from initial solute film. When ln c is plotted against x^2, the slope $(-4Dt)^{-1}$ gives D. On this basis the diffusion coefficient for boron into the porous silicon nitride body at 1200°C, 130 MPa was calculated as $2\times10^{-12}\,\mathrm{m^2\,s^{-1}}$.

3.1 Viscous flow

Tests at room temperature with glycerol and CIPed silicon nitride showed a linear relation between

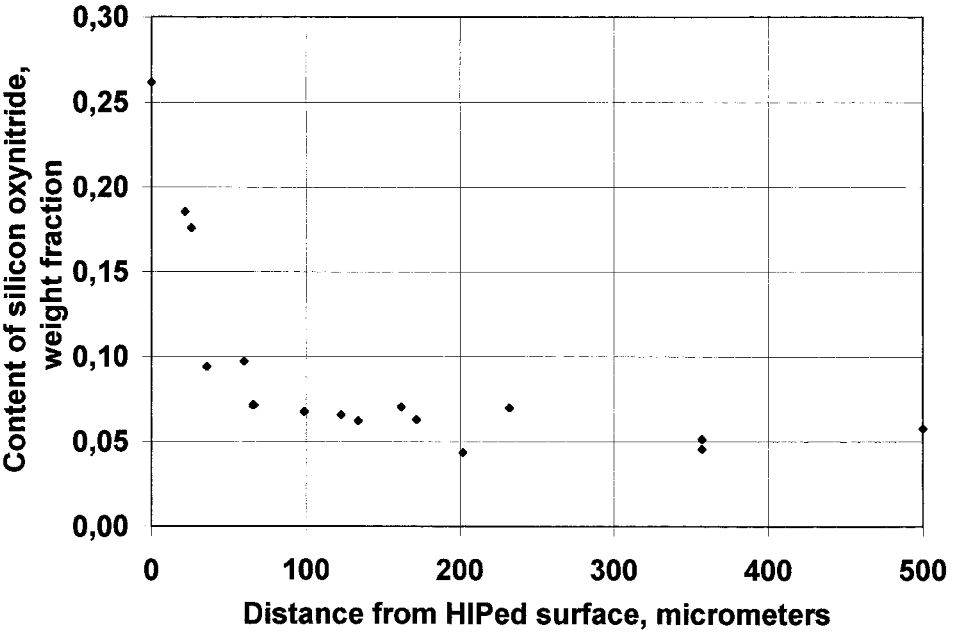

Fig. 5. Silicon oxynitride content as a function of distance from the surface (encapsulation Glass III).

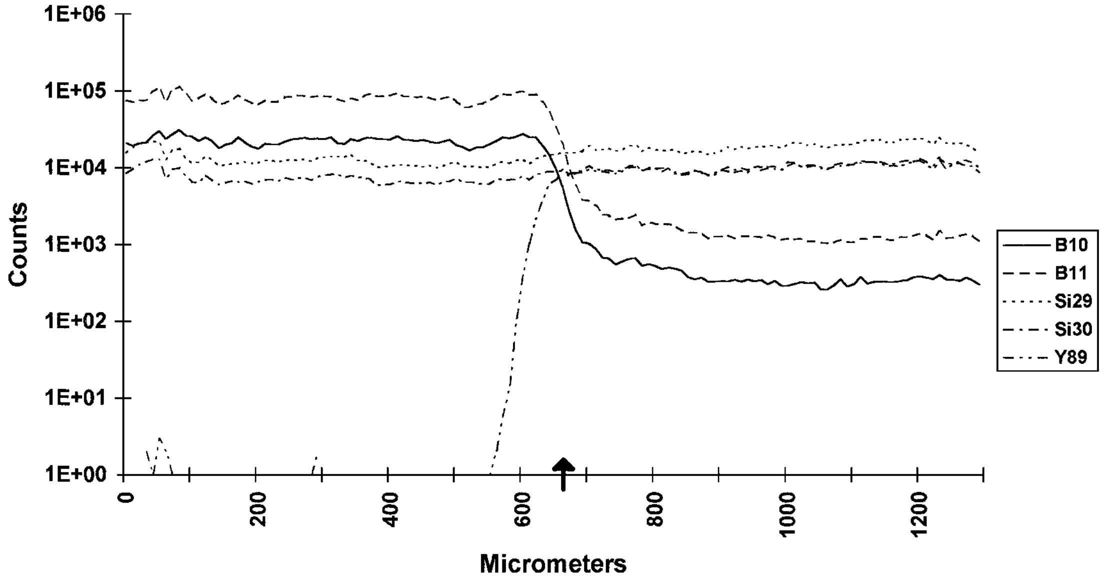

Fig. 6. SIMS profile across the glass/ceramic interface, (0.5 h hold time at 1180 °C, 130 MPa, encapsulation Glass I). The glass is to the left; the arrow indicates the interface.

intrusion length, l, and square root of time, t, permitting an estimate of permeability according to eqn (1). The glasses were considered to be Newtonian fluids. The eqns (1), (3) and (5) were used to calculate intrusion length with the following values of the parameters: permeability = 1·2 ± 0·3 E-16 m^2, pore radius = 0·027 microns, porosity = 0·48, specific surface area = 8·9 $m^2 g^{-1}$, density = 3·2 $g cm^{-2}$ and f set to 5. Table 3 gives the intrusion lengths for Glass III at 1200°C, 130 MPa and with 30 min hold time before pressure application. The different equations are in relatively good agreement. Darcy's law was chosen for the further calculations since it utilises permeability obtained experimentally, while the other two equations use indirect permeability estimates.

The lowest eutectic temperature for silicon nitride with the sintering aids used in the model system can be set to approximately 1440°C.[15] Before that temperature is reached the green body can be assumed to be little affected by the sintering process. Above that temperature the glassy phase in the green body affects the pore system and the densification accelerates. This makes intrusion or penetration by the encapsulation glass much slower. Table 4 shows intrusion depths calculated for different stages in the HIP-cycle, from 1200°C and pressure application up to 1450°C. The viscosity of Glass I was not determined for this temperature interval, but was higher than that of Glass III. Calculated intrusion depths for glasses having viscosities 10 and 100 times larger than that of Glass III are included in Table 4 for comparison.

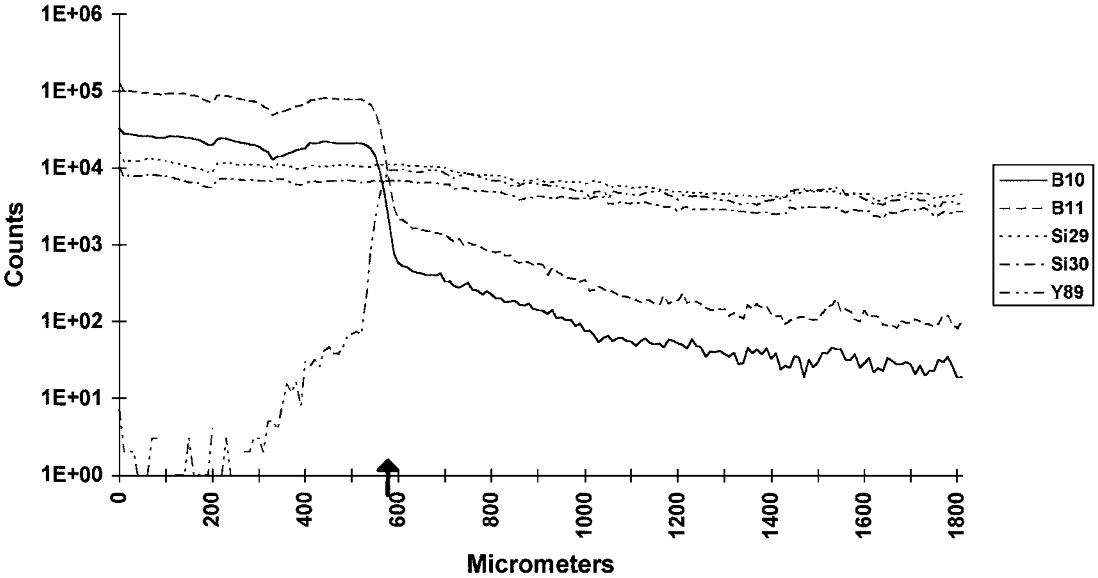

Fig. 7. SIMS profile across the glass/ceramic interface, (12·5 h hold time at 1200°C, 130 MPa, encapsulation Glass I). The glass is to the left; the arrow indicates the interface.

The calculated intrusion depth at 1450 °C of approximately 1200 microns for Glass III would become even deeper during the later part of the HIP-cycle, even if a decreasing permeability and a probably stronger interaction with the pore walls would limit the intrusion. However, property gradients found in dense HIPed silicon nitride indicate a much smaller penetration, e.g. mechanical properties, 150 microns[3] or phase composition, e.g. silicon oxynitride, 100–200 microns (see Fig. 5). If Darcy's law [eqn (1)] is valid, the permeability is correctly determined and the applied pressure is known, then a reduced intrusion velocity must be explained by an increased viscosity. Many studies (e.g. Refs 16 and 17) of the glassy phase in silicon nitride (e.g. yttrium silicate glasses) indicate dissolution of nitrogen from the silicon nitride into the glass. Nitrogen in the glass leads to an increased cross-linking which produces a more rigid glass. The presence of nitrogen leads to increased viscosity, lower eutectic temperature and larger melting range. It seems reasonable to assume that nitrogen could dissolve into the encapsulation glass and thereby increase its viscosity during temperature rise. In system studied here an increased viscosity of approximately $10^{1\cdot 5}$ dPas would be sufficient to explain a reduction of intrusion to the range found in the dense material.

Table 3. Intrusion length for Glass III at 1200 °C, 0·5 h hold time with 1 MPa, 0·5 h pressure increase to final pressure 130 MPa. Estimated errors are ± 10% for the first two and ± 12% for the third one

Darcy's law	400 μm
Poiseuille's law	350 μm
Kozeny–Carman's law	330 μm

Table 4. Intrusion depth calculated with Darcy's law for different viscosity values. Estimated errors in the figures are ± 10%

At different stage in the HIP-cycle	$\eta_{Glass\ III}$ (μm)	$10\times\eta_{Glass\ III}$ (μm)	$100\times\eta_{Glass\ III}$ (μm)
1200°C, 1 MPa	24	8	2
1200°C, 130 MPa	400	130	40
1300°C, 135 MPa	630	200	63
1400°C, 141 MPa	960	300	96
1450°C, 144 MPa	1200	390	120

It has been shown that dissolved nitrogen in glass leads to an increased hardness.[17] The results of hardness measurements on the glass/silicon nitride mixtures studied here, heat treated at 1500°C, can be seen in Table 5.

The glass material prepared with silicon nitride additions had higher hardness than samples of encapsulation glass without nitride. The samples with silicon nitride were not homogenous; some residual grains could be seen. The measurements were performed at areas which were homogeneous to the eye. Some glass/silicon nitride mixtures were also heat treated at lower temperatures, 1200–1400°C. These samples were too inhomogeneous and porous to be evaluated with hardness tests. Hampshire *et al.*[17] found that Y–Si–Al–O–N glass hardness increased by approximately 10% for a

Table 5. Hardness, mixture of glass and silicon nitride, after heat treatment, 1500°C, 1 h, 150 MPa

Material	$HV_{0\cdot 98N}$ *(GPa)*
Glass III	2·6 ± 0·1
Glass III + 5 w/o Si_3N_4	3·0 ± 0·2
'Undissolved' grain (only two indentations)	9·2 ± 0·6

nitrogen content of 5 e/o (equivalent concentration anions/cations). The corresponding viscosity increase was about sixfold. The hardness increase is comparable with our results for a glass with 5 w/o silicon nitride (5·2 e/o nitrogen), even though not all of the silicon nitride was dissolved. If a similar viscosity increase occurred in the present study, then a nitrogen content of approximately 11 e/o would be sufficient to limit the viscous flow of Glass III to a depth in the range of 200 micrometers.

4 Conclusions

Estimates have been made of glass penetration into silicon nitride green bodies assuming no chemical reaction between nitride and glass and no change in pore morphology. For the borosilicate glass with the higher boron content (60 w/o B_2O_3), calculations predicted penetrations to a depth of around 1200 microns into the ceramic body. Glass with lower boron content was predicted to penetrate to a much lower extent. Significant glass intrusion could not be verified by SEM, but XRD measurements on serial sections showed a 100–200 μm deep silicon oxynitride gradient and SIMS analysis revealed a boron gradient into the silicon nitride of around 200 μm. Hardness tests on heat treated glass/silicon nitride mixtures indicate that nitrogen is dissolved in the glass. Dissolved nitrogen is expected to raise the viscosity of the glass which could explain why the observed penetration depths are less than the calculated prediction. The wetting angle of borosilicate glass on silicon nitride was found to be approximately 140°. The diffusion coefficient of boron in the porous silicon nitride body was determined as $2\times10^{-12}\,m^2\,s^{-1}$ at 1200°C.

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