

Chemical Reactions in the System $\text{Si}_3\text{N}_4\text{-SiO}_2\text{-B}_2\text{O}_3$

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Abstract

Chemical interactions in the system of silicon nitride with borosilicate glass have been studied as part of an evaluation of glass encapsulated HIP. Theoretical calculations have been performed to predict the thermodynamically stable phases under conditions reflecting different stages in a HIP-cycle. Experimental studies were made on heat treated mixtures of the silicon nitride and the silicate glass. These samples were evaluated with X-ray diffraction. At temperatures commonly used for densification, the system reacted to BN and $\text{Si}_2\text{N}_2\text{O}$ in agreement with the theoretical calculations. At typical temperatures for pressure application no chemical reactions could be detected but the theoretical calculations showed that BN and, for larger amount of silicon nitride, also silicon oxynitride were stable. Minor amounts of the phases may have formed or non-equilibrium conditions could be explanations for the absence of the expected phases.
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Introduction

One method to produce advanced ceramics, such as silicon nitride, is glass encapsulated hot isostatic pressing, (HIP). This technique promotes high densities, close tolerances and can be used for complicated shapes.¹ Since one of the main drawbacks of structural ceramics is the high cost of machining densified material, a great advantage of HIP is the potential for net or near net shape production. This means that the quality of the produced surface is of great importance; it is essential to obtain high quality surfaces without machining or with as little machining as possible. It is therefore of interest to know the chemical reactions taking place at the ceramic surface.

In glass encapsulation HIP, a glass is applied to the ceramic surface. The glass acts as a gas-tight

pressure transmitting medium during HIP consolidation. The temperature is first increased until the viscosity of the glass allows the pressure to be applied. After pressure application the heating is continued until the desired temperature is reached. When the densification cycle is finished the glass has to be carefully removed, without damaging the surface of the ceramic. Because of the intimate contact between the encapsulating glass and the ceramic surface during densification, one point of interest is the interface between the materials. This study focuses on possible chemical reactions taking place at this interface during HIP. Of special interest is what happens at the temperature of pressure application, i.e. when the encapsulating glass and the surface of the ceramic green body develop close contact. One question that arises is whether or not a reaction product such as BN is formed at an early stage of the HIP cycle since this phase could prevent glass penetration into the still porous ceramic body.

Here, a model system of silicon nitride with an encapsulating glass of borosilicate has been studied. Silicon nitride is an important advanced ceramic and is also used in composites as a matrix material. Borosilicate containing glass is known to be used as an encapsulating glass for HIPing of ceramics.^{1,2} Experimental studies as well as theoretical calculations were performed on the model system in order to evaluate what chemical reactions could take place during a HIP cycle, especially at the temperature for pressure application.

Glasses with high SiO_2 content have very high viscosity even at relatively high temperature which can cause them to react very slowly and thus deviate from equilibrium condition for long times. Nonetheless, knowledge of equilibrium conditions is of interest because it gives an indication of the reaction tendency. Even if non-equilibrium is at hand on a larger scale, equilibrium may occur on a sub-micron scale. This may be of importance where

the diffusion distances are short, e.g. in the pore openings and fine pore channels of the green body when it gets in contact with the glass.

Thermodynamic calculations for part of the model system have been published by Hillert *et al.*³ They present data for the systems of Si–O–N but without any boron present. Colenz and Lewis⁴ worked with B₂O₃ and Si₃N₄ in order to make BN-toughened composites by an in-situ reaction. According to the theoretical calculations for their conditions BN should form. However, in the experiments no BN could be detected after vacuum hot pressing at 1620°C, 350 bar and 1 h hold time. They mention the constraining effects of the rather large volume increase occurring with the reaction as a possible factor influencing the result. The volume change does, however, seem to be over-estimated which makes this suggestion less probable. Turan and Knowles⁵ found BN in samples of SiC/Si₃N₄ composites after HIPing in tantalum cans in the presence of B₂O₃. The cans were sealed in vacuum and HIPed at a temperature of 2100°C. According to their calculations BN should be a stable phase under these conditions.

Experimental Work

The pressure in the HIP-cycle is normally applied at a temperature where the glass is soft but still has quite a high viscosity; here 1200°C was chosen as representative temperature. A typical densification temperature for HIPed silicon nitride is 1750°C. Thus, these two temperatures were selected as a basis for the temperature profile used in this study.

The experimental studies were made with silicon nitride powder from Permascand AB, (Siconide P95). Yttria (3 wt%) was added to the nitride powder as a sintering aid. The glass was produced by heat treating a mixture of 30 w/o B₂O₃ and 70 w/o SiO₂ at 900°C for 24 h. The resulting glass was crushed, sieved and ground to obtain a fine powder. The grinding procedure used results in a d₅₀ of approximately 30 microns. This glass powder was mixed with the silicon nitride powder at a ratio of 50/50 (w/o) and cold isostatically pressed to specimens at a pressure of 300 MPa. In this way the surface area available for reactions was maximised thereby increasing the detectability of possible reaction products. The heat treated samples were examined with X-ray diffraction (XRD) at room temperature and the phases were identified according to the files listed in the Appendix.

If only a limited amount of BN is formed in the system, the detectability of small amounts of BN is of importance. In Fig. 1 diffractograms of pure powders are shown. The strongest BN peak (002), $d=3.35$, is overlapped both by the low quartz (101) peak, and the α -Si₃N₄ (200) peak. To evaluate the detection limit for BN, mixtures of silicon nitride/glass (50/50) and different amounts of BN were studied. Peaks at $d=2.88$, 3.35 and 4.27 were used for the calculations. From the $d=2.88$ peak the silicon nitride content in the other peaks can be calculated. Then the silica content in the $d=3.35$ peak can be estimated from the residual of peak $d=4.27$. Remaining counts at $d=3.35$ are presumed to originate from BN. Figure 2 shows a comparison between a heat treated silicon nitride glass mixture (1200°C, 9 h) and a reference mixture

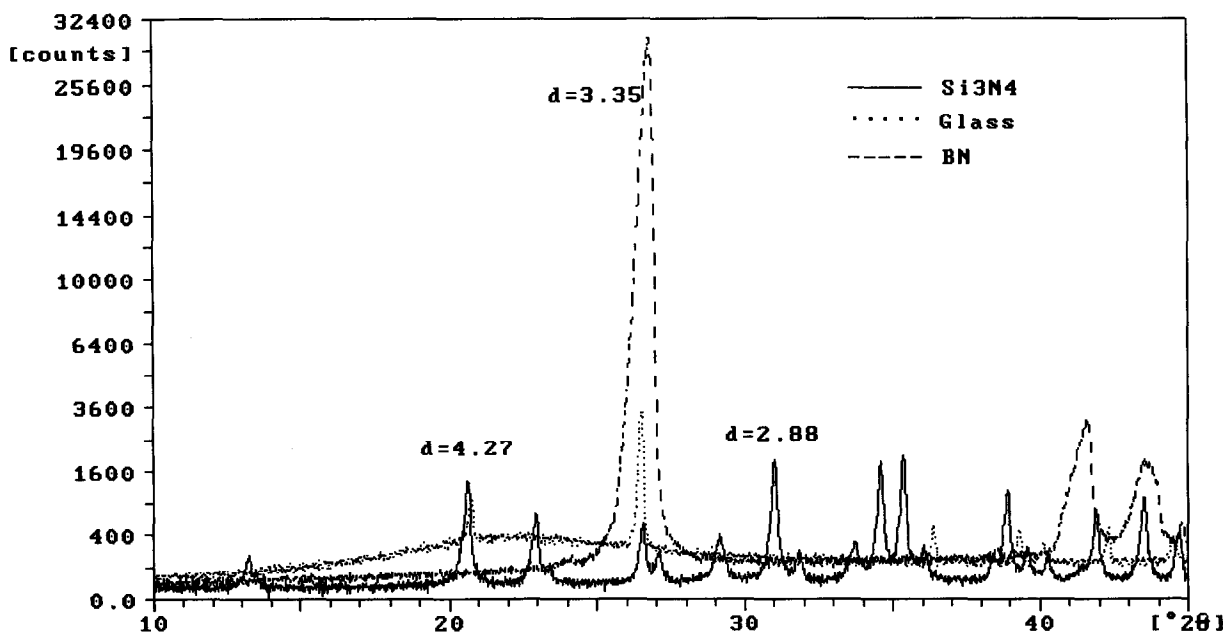


Fig. 1. XRD curves of silicon nitride, glass and boron nitride before heat treatment. (The glass has some remaining low quartz.)

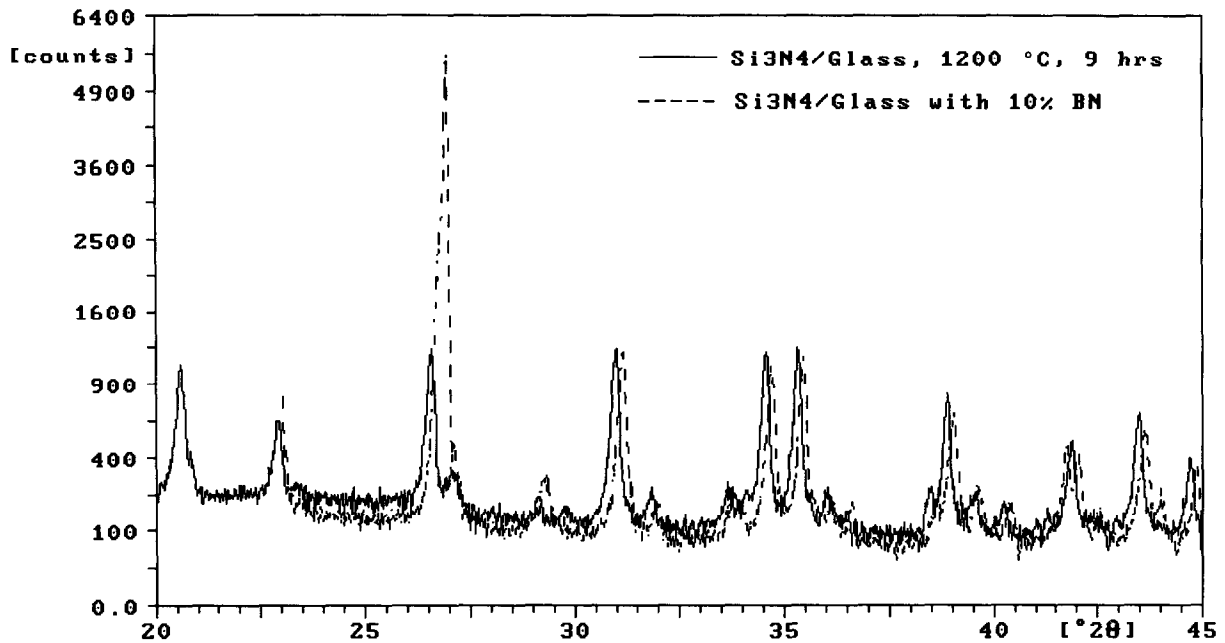


Fig. 2. XRD curves of silicon nitride/glass mixture after heat treatment at 1200°C for 9 h and of the silicon nitride/glass mixture with 10% boron nitride added.

with 10 v/o BN added. The largest BN peak is easily detected in the 10% BN reference mixture, but not in the heat treated sample. Similar tests with 5% BN did not show satisfactory detectability. Also $\text{Si}_2\text{N}_2\text{O}$ has an overlapping peak at the large BN (002) peak. With $\text{Si}_2\text{N}_2\text{O}$ present the contribution at the BN peak can be calculated from the (110) and (020) peaks of $\text{Si}_2\text{N}_2\text{O}$, $d=4.67$ and $d=4.44$.

Since the atmosphere may influence the equilibrium situation, oxygen partial pressure in the furnace was measured using a galvanic cell with zirconia as a solid electrolyte and iron/iron oxide as the reference system. The method is described by Paulsson *et al.*⁶ and the equation for the reference system is given by Fredriksson *et al.*⁷ Oxygen partial pressure was measured between 1000–1200°C which is around the temperature for pressure application. Measurements were done both with the probe placed in an empty graphite crucible as well as with the probe placed in a powder mixture of silicon nitride and glass in the same type of crucible.

The thermodynamic calculations on the system were made with the program ChemSage, developed by Eriksson *et al.*⁸ In these calculations thermodynamic data were taken from SGTE (Scientific Group Thermodata Europe) and for silicon oxynitride from Hillert *et al.*³ Thermodynamic properties of quartz, cristobalite and amorphous SiO_2 are taken from Richet *et al.*⁹ The liquid in the system $\text{SiO}_2\text{-B}_2\text{O}_3$ is treated as a regular solution. The enthalpy of mixing in this system has been measured by Hervig and Navrotsky,¹⁰ and is described by the equation

$$\Delta H_{\text{mix}} = 12950 \times x_{\text{SiO}_2} \times x_{\text{B}_2\text{O}_3} \text{ (J/mole)} \quad (1)$$

Using this equation (with the assumption of zero excess entropy) and data for the different polymorphs of silica, the calculated silica liquidus and metastable liquid–liquid miscibility gap are in good agreement with the experimental results of Rockett *et al.*¹¹ and of Charles,¹² respectively. The calculated phase diagram is depicted in Hervig and Navrotsky.¹⁰ Yttria and the phases in the B–Si system have not been included in the calculations.

The equilibrium phase compositions of the B–Si–N–O systems with a given B/Si mole ratio were calculated as a function of oxygen and nitrogen partial pressure at 1200 and 1750°C, respectively. At 1200°C the total pressure was 1 bar and at 1750°C the pressure was 1600 bar. Only the pressure influence on the gaseous species was considered in the calculations since the mole volume changes for the condensed phases are thermodynamically insignificant. Calculations have been performed for B/Si ratios in the range 10^{-2} – 10^0 . The experimental mixture of 50 w/o glass and 50 w/o silicon nitride corresponds to a B/Si ratio of 0.26.

Equilibrium phase compositions were also calculated for different relative amounts of glass and silicon nitride. The calculations also gave oxygen and nitrogen partial pressures as a function of mole ratio glass/silicon nitride. This was done in order to evaluate what happens within a sealed glass–silicon nitride system since the furnace atmosphere in a HIP is sealed off from the ceramic parts whenever the encapsulation glass is gas tight.

Results and Discussion

The example with the four component system B–Si–N–O for a B/Si ratio of 0.26 (50 w/o glass/50 w/o silicon nitride) is given in Tables 1 and 2. Table 1 shows the stable phases for the system at 1200°C as a function of nitrogen and oxygen partial pressures. BN can only be formed if the oxygen partial pressure is below a critical value. This value is dependent on the corresponding nitrogen partial pressure. At very low oxygen and nitrogen partial pressures the system will form B–Si phases like B₆Si.¹³ Table 2 shows the situation at 1750°C and a total pressure of 1600 bar. Here BN is stable up to a higher oxygen partial pressure. If silicon nitride is to be stable, the oxygen partial pressure must be below 10⁻¹⁴ bar and the nitrogen partial pressure must be quite high (1 bar). The same results were found for the whole B/Si ratio range examined except that for higher ratios no SiO₂ was in equilibrium with the liquid phase. The results found for silica, silicon oxynitride, silicon nitride and silicon are in good agreement with the calculations of Hillert *et al.*³

The result of the oxygen partial pressure measurements are shown in Fig. 3. At a temperature of 1200°C the oxygen partial pressure is 10^{-12.2} bar. The measurement with the empty crucible gave the same result. This implies that in these tests the oxygen partial pressure is not governed by the reactions going on in the mixture but by the C–CO–CO₂ reactions taking place within the furnace. With 50% glass and 50% silicon nitride, as in the experimental study, and an oxygen partial pressure governed by the furnace atmosphere,

10⁻¹² bar, only SiO₂ and the borosilicate melt are stable (Table 1).

The results from the calculations with different relative amounts of glass and silicon nitride are shown in Figs 4–6. Figure 4 gives the resulting oxygen and nitrogen partial pressures for a range of glass/silicon nitride ratios. The equilibrium oxygen partial pressure differs, at the temperature of 1200°C from 10⁻²⁸ bar for the lowest ratio calculated (0.1) up to 10⁻¹² bar for simple glass. The corresponding values for 1750°C and 1600 bar HIP pressure are 10⁻¹⁷ bar and 10⁻⁷ bar. The nitrogen partial pressure shows a more limited variation with glass silicon nitride ratio, 10⁻⁵–10⁻⁶ bar at the lower temperature and 10⁻¹–10⁻² bar at the higher temperature for the ratios examined.

In Figs 5 and 6 are shown the condensed phases present at equilibrium at 1200 and 1750°C for different glass/silicon nitride ratios, as well as the relative distribution of Si and B in the different condensed phases. It can be seen that BN is stable at both temperatures even with only a very limited amount of Si₃N₄ added. With Si₃N₄ present the B₂O₃ in the melt reacts to BN. When all B₂O₃ in the melt is consumed Si₂N₂O is formed. [At 1750°C there is a small amount B₂O₃ in the melt (0.1% of the melt) in equilibrium with Si₂N₂O.] It can be noticed that with a very low glass/Si₃N₄ ratio Si is also stable, but this is only a small fraction of the total molar content. (With a glass/Si₃N₄ ratio of 0.1 the molar amount of Si is 0.002% at 1200°C and 0.007% at 1750°C.) Since Figs 5 and 6 give the relative distributions of Si and B, the volume percentages of the different phases can be calculated if the molar weights and the densities are known;

Table 1. Phases at equilibrium, T = 1200°C, P = 1 bar, Ar, 'bsl' stands for borosilicate liquid, mole ratio B/Si = 0.26 which corresponds to a system of 50 w/o glass and 50 w/o silicon nitride

Log p _{N₂} , bar							
-1	BN Si ₂ ON ₂	BN Si ₂ ON ₂	BN Si ₂ ON ₂	BN SiO ₂	bsl SiO ₂	bsl SiO ₂	bsl SiO ₂
-2	BN Si ₂ ON ₂	BN Si ₂ ON ₂	BN SiO ₂	BN SiO ₂	bsl SiO ₂	bsl SiO ₂	bsl SiO ₂
-3	BN Si ₂ ON ₂	BN Si ₂ ON ₂	BN SiO ₂	bsl SiO ₂	bsl SiO ₂	bsl SiO ₂	bsl SiO ₂
-4	BN Si ₂ ON ₂	BN Si ₂ ON ₂	BN SiO ₂	bsl SiO ₂	bsl SiO ₂	bsl SiO ₂	bsl SiO ₂
-5	BN Si ₂ ON ₂	BN SiO ₂	BN SiO ₂	bsl SiO ₂	bsl SiO ₂	bsl SiO ₂	bsl SiO ₂
-6	BN Si	BN SiO ₂	bsl SiO ₂	bsl SiO ₂	bsl SiO ₂	bsl SiO ₂	bsl SiO ₂
	-24	-22	-20	-18	-16	-14	-12
							Log p _{O₂} , bar

Table 2. Phases at equilibrium, T = 1750°C, P = 1600 bar, Ar, 'bsl' stands for borosilicate liquid, mole ratio B/Si = 0.26 which corresponds to a system of 50 w/o glass and 50 w/o silicon nitride

Log p _{N₂} , bar							
0	BN Si ₃ N ₄	BN Si ₃ N ₄	BN Si ₃ N ₄	BN Si ₂ ON ₂	BN bsl	bsl	bsl
-1	BN Si	BN Si	BN Si	BN Si ₂ ON ₂	bsl	bsl	bsl
-2	BN Si	BN Si	BN Si	BN bsl	bsl	bsl	bsl
-3	BN Si	BN Si	BN Si	BN bsl	bsl	bsl	bsl
	-20	-18	-16	-14	-12	-10	-8
							Log p _{O₂} , bar

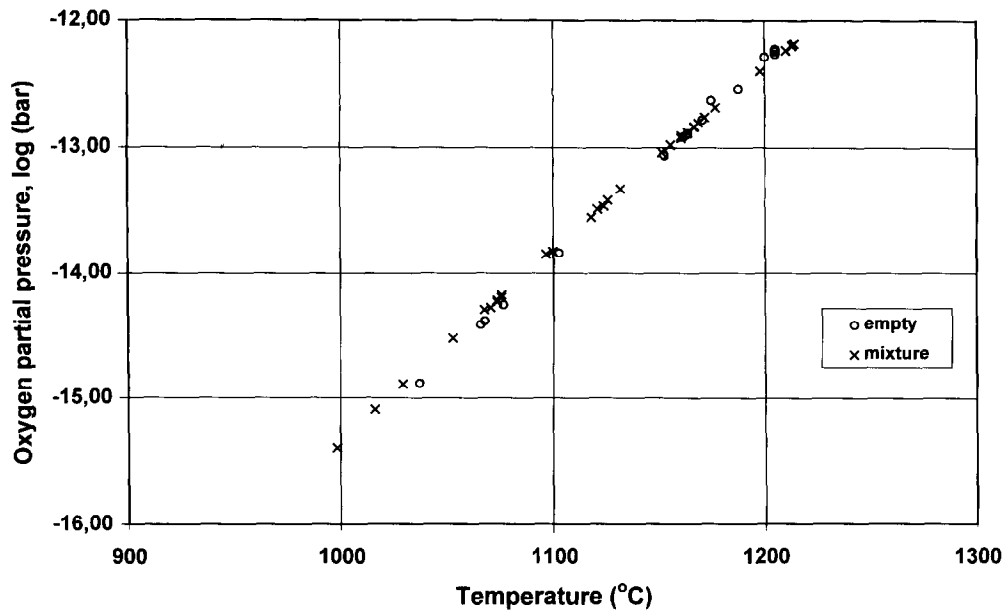


Fig. 3. Oxygen partial pressure as a function of temperature in a mixture of Si_3N_4 and glass melt, as well as in an empty crucible, in a graphite furnace.

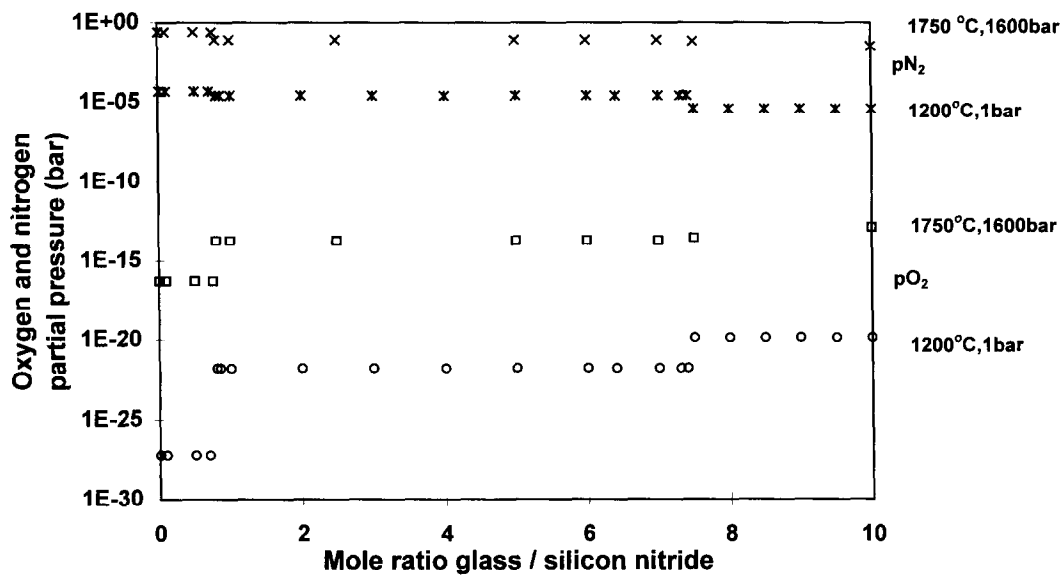
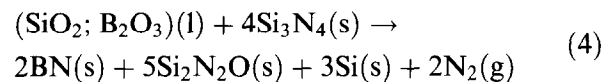
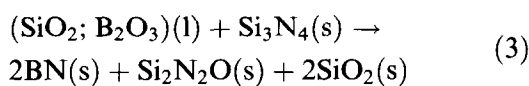
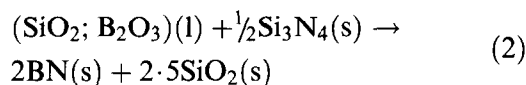


Fig. 4. Oxygen and nitrogen partial pressure as a function of mole ratio glass/silicon nitride and temperature.

e.g. for the experimental mixture of 50 w/o glass and 50 w/o silicon nitride (molar ratio 2:2) at 1200°C the equilibrium phase content can be calculated to 12 v/o BN, 44 v/o SiO_2 and 44 v/o $\text{Si}_2\text{N}_2\text{O}$.

For different amounts of silicon nitride compared to the amount of glass, reactions at 1200°C can according to the thermodynamic calculations be written



The XRD evaluation of the phases present after heat treatment of the powder mixture at 1200°C for 2 h can be seen in Fig. 7. The crystalline phases detected were α - and β -silicon nitride, low quartz and yttria. No BN was detected. The same phases were found in the reference sample before heat treatment. (Some remaining quartz is present in the glass.) If the atmosphere was governed by the furnace, i.e. an oxygen partial pressure of 10^{-12} bar, the phases at equilibrium can be obtained from Table 1. No BN or any other species should be formed under these conditions, instead Si_3N_4

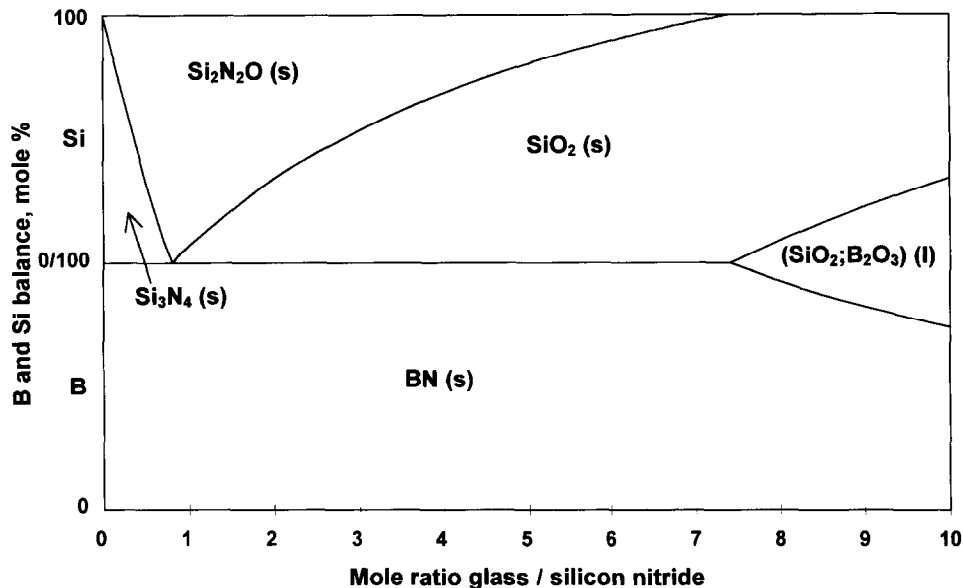


Fig. 5. Calculated phases at equilibrium with the relative amount of glass and silicon nitride as a variable, 1200°C, 1 bar. The y-axis indicates how the B and Si are distributed respectively in the different phases, in relation to the total B and Si content.

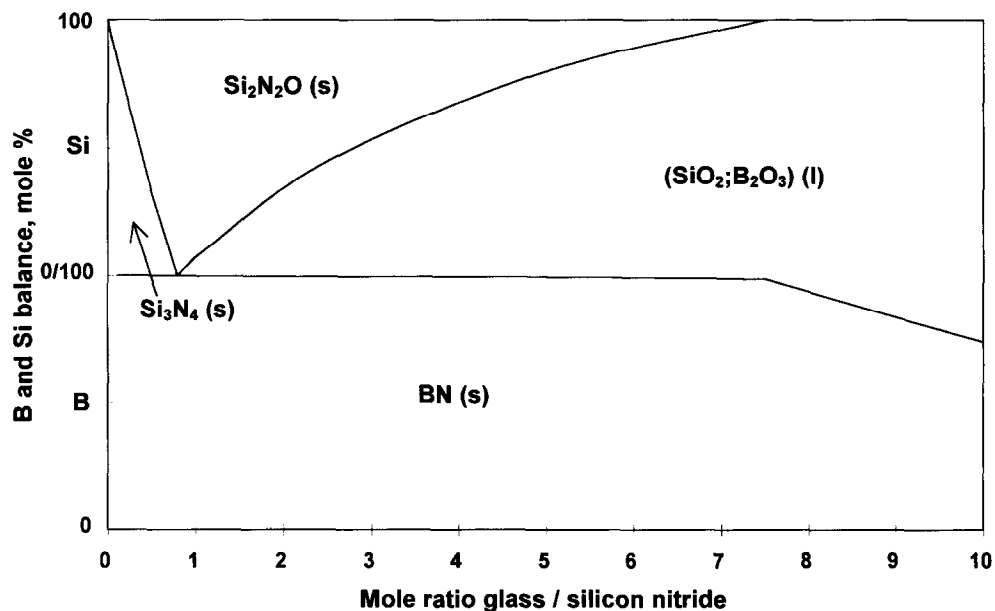


Fig. 6. Calculated phases at equilibrium with the relative amount of glass and silicon nitride as a variable, 1750°C, 1600 bar. The y-axis indicates how the B and Si are distributed respectively in the different phases, in relation to the total B and Si content.

should be oxidised and increase the SiO_2 -amount of the glass melt, causing some of it to crystallise. In the heat treated sample silicon nitride is still present, which could mean that 2 h at 1200°C is not enough to reach equilibrium in the sample. A complementary heat treatment was done with the powder mixture encapsulated in the glass, in order to facilitate creation of a 'local' atmosphere not determined by the furnace. Still no reactions could be detected in the diffractograms. Reasons for this discrepancy from the equilibrium compositions (BN , SiO_2 and $\text{Si}_2\text{N}_2\text{O}$ according to Fig. 5), could also be of a kinetic nature. The high viscosity of the glass and the relatively low temperature could

make the reactions too slow. If the reaction is slow only limited amounts of product phases are formed. If, for example, a layer of BN with a thickness of 1 nm is formed on the sub-micron particles of silicon nitride, the amount can be estimated as less than one percentage, too low to detect as well as too thin to diffract X-rays.

The phases of a powder mixture after a HIP-densification cycle, 1750°C, 4 h and 1600 bar, analysed at room temperature, are presented in Fig. 8. Here the reaction speed should be much higher compared to the situation at lower temperatures. None of the original phases were detected in the XRD but the sample had reacted forming the crystalline phases

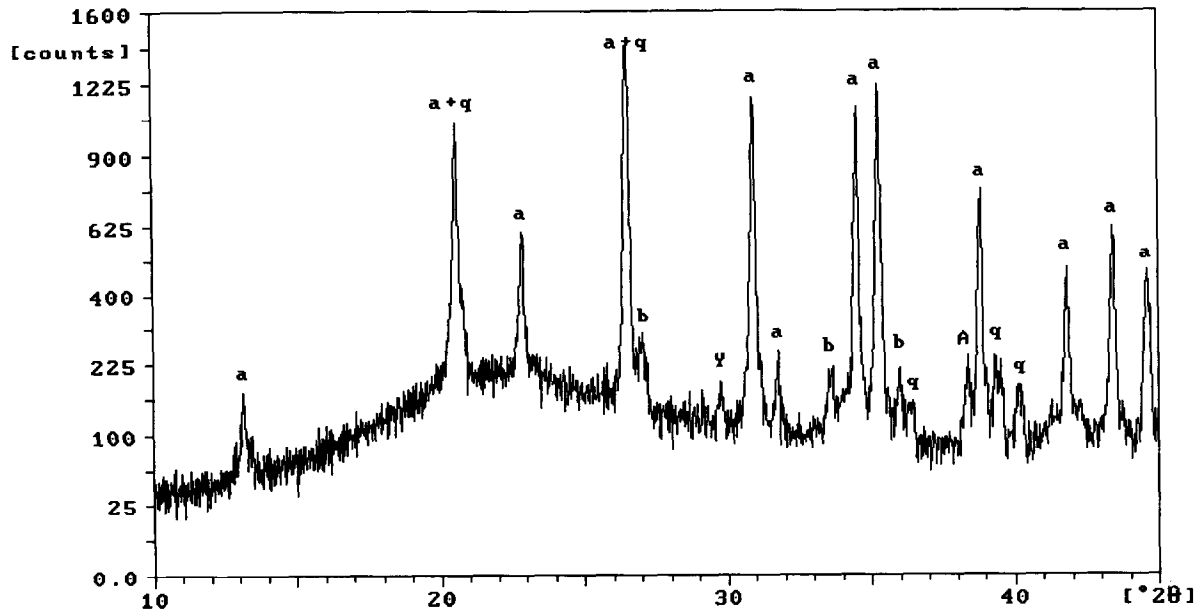


Fig. 7. XRD curve of a mixture of silicon nitride and glass, heat treated at 1180°C for 2 h; a stands for $\alpha\text{-Si}_3\text{N}_4$, q stands for low quartz, b stands for $\beta\text{-Si}_3\text{N}_4$, Y stands for Y_2O_3 and A stands for Al (from the sample holder).

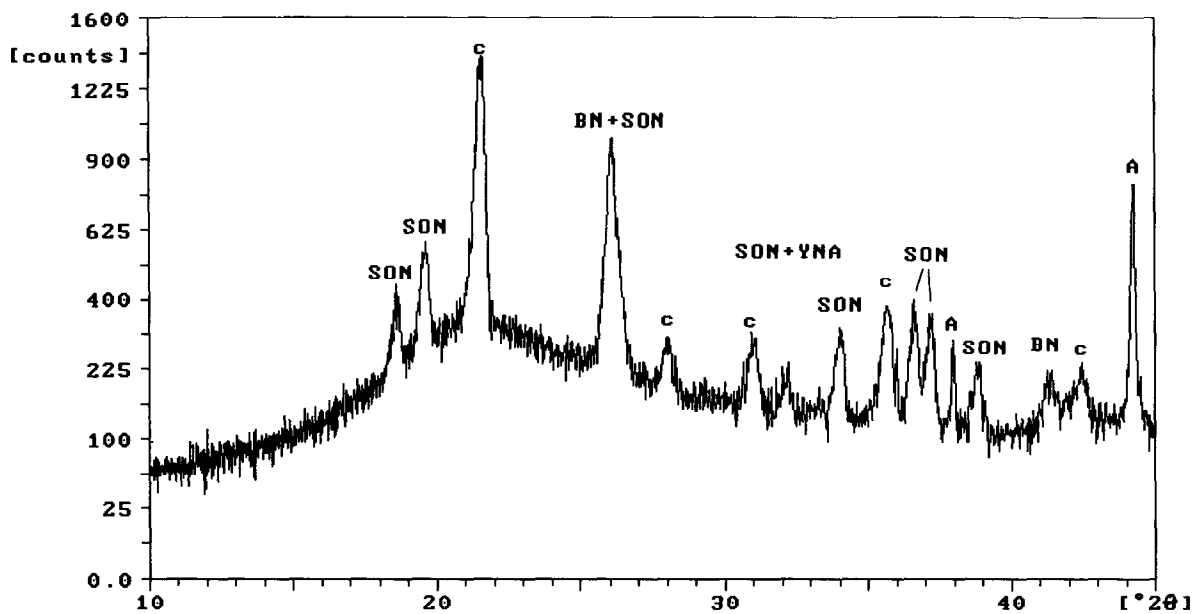


Fig. 8. XRD curve of a mixture of silicon nitride and glass, HIPed at 1750°C, 1600 bar, 4 h; SON stands for $\text{Si}_2\text{N}_2\text{O}$, c stands for low cristobalite, YNA stands for Y,N-apatite and A stands for Al (from specimen holder).

silicon oxynitride, BN, low-cristobalite, and possibly yttrium–nitrogen apatite. A glass phase is also seen in the XRD-chart. When this is compared with the theoretical calculations (Fig. 6, mole ratio 2:2) the only discrepancy is the presence of cristobalite. This phase was probably formed during cooling since a comparably low cooling rate was used, 140°C h^{-1} , which can give time for crystallisation from the borosilicate melt (with the composition much drawn towards the SiO_2 -rich side).

The yttria has not been included in the theoretical calculations. Tests with yttria added to the system and with yttria thermodynamic data from

SGTE, gave no changes in the results for the lower temperature range. However, thermodynamic data for the activity of yttria in the liquid are not known. At the early stage of heat treatment, for example when pressure is applied, the activity of the yttria in the liquid can be regarded as relatively low due to its high melting temperature.

Summary and Conclusions

Theoretical calculations predict that with the studied system of sealed encapsulation glass and

ceramic material, BN should be formed at the temperature of pressure application in the HIP-cycle. No BN peak was detected after heat treatment but the XRD peaks are overlapped by peaks of other phases present in the studied system which limits the detectability. The high viscosity of the liquid phase for the chosen glass system as well as the relatively low temperature could also retard the reactions and give a non-equilibrium situation. Nonetheless, BN is thermodynamically stable in the studied system even at the low temperature for pressure application. Even a very limited formation of BN, just some atom layers, may influence on, for example, the wetting properties. This knowledge leads to the need of further studies on a sub-micron level, to learn if chemical reactions are playing a role at the interface between the encapsulation glass and the silicon nitride.

At the temperature of HIP densification the glass-Si₃N₄ system reacts to form BN and oxygen containing phases like Si₂N₂O and SiO₂-B₂O₃ melt. No phases present in the original powder mixture remained after the completed HIP-cycle. This result was supported by the theoretical equilibrium calculations. At this higher temperature the speed of the reactions is much increased and the viscosity of the glass is lower. When a silicon nitride specimen is encapsulated in a borosilicate glass and HIPed, Si₂N₂O is detected at the surface of the dense specimen.¹⁴ This also implies BN formation.

The chemical reactions and thereby the phases formed are very much dependent on the temperature and time, the atmosphere and the relative amount of the glass and the silicon nitride. A gradient in the composition across the interface between encapsulation glass and the Si₃N₄-ceramic in a HIP charge, means that local equilibrium situations are formed. The temperature-time schedule of the HIP cycle is of great importance. Factors such as when the furnace atmosphere is sealed off, the progress of densification such as closing of the open pores in the ceramic and also the total reaction time will be of importance regarding the relative amounts of phases present at the interface and thus the final quality of the as-HIPed surface.

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APPENDIX

Phases are detected according to the following files: α -Si₃N₄, ASTM 9-250; β -Si₃N₄, ASTM 33-1166; low quartz, ASTM 33-1161; low cristobalite, ASTM 11-695; Si₂N₂O, ASTM 18-1171; Y₂O₃, ASTM 25-1200; Y,N-apatite (Y₁₀Si₆O₂₄N₂), ASTM 30-1462; BN, ASTM 34-421.