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The effect of impurities on the densification of reaction-bonded silicon nitride (RBSN)

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The sintering behaviour of commercial and high purity RBSN with and without MgO and Y_2O_3 additions has been studied by high temperature dilatometry with nitrogen overpressure. Activation energies for densification are in the region 500 to 600 kJ mol^{-1}. Commercial RBSN shows some shrinkage and α–β Si_3N_4 conversion without addition. High purity RBSN retains 74% αSi_3N_4 after 1 h at 1750° C and shows only 0.2% linear shrinkage. The effect of calcium, aluminium and iron impurities was examined. The densification curves obtained with MgO as additive show a transient expansion in the early stages of sintering which is associated with the gas overpressure. In the absence of a powder bed, decomposition was impracticably high. Both a powder bed and nitrogen overpressure were needed to suppress decomposition.

1. Introduction

The production of high density silicon nitride components of complex shape and good dimensional tolerances can be achieved by densifying reaction-bonded silicon nitride (RBSN) [1–3]. Sintering aids, usually MgO or Y_2O_3, are added to the RBSN by incorporating them in the silicon powder prior to nitridation [1, 3], by filling the pore structure of RBSN with a soluble salt [2], or by allowing MgO to migrate into the RBSN from a powder surround during sintering [1].

It is thought that the additive reacts with silica normally present on the nitride surface [4] to give a silicate which is liquid at the sintering temperature [5]. This liquid wets RBSN surfaces and penetrates grain boundaries [6] allowing liquid phase sintering mechanisms [7–13] to proceed. Three main processes influence the final density, namely, decomposition of the silicon nitride, either by direct sublimation or by reaction with components of the furnace atmosphere such as O_2, H_2O, CO, loss or gain of sintering aid to and from the surroundings, and loss of porosity by densification mechanisms. Loss of sintering aid and decomposition can be prevented by packing the component in a silicon nitride powder with the same proportion of sintering aid; sintering of the powder can be prevented by an addition of BN powder [1]. High nitrogen pressures have been used to prevent direct decomposition [14, 15].

In the present study a high pressure, high temperature dilatometer has been used to compare the sintering behaviour of high purity RBSN without additives with that of a commercially obtained RBSN. Selected additives typical of the impurities in commercial silicon [16] were then individually introduced into high purity RBSN prior to nitriding to study their effect on densification. Also, the effects on the densification behaviour of addition of MgO and MgO/Y_2O_3 to high purity RBSN and of MgO to commercial RBSN have been studied.

2. Experimental details

Semiconductor grade silicon* was ground in a cast iron "shatterbox"† and air-classified‡, the 5 to 10 μm fraction being selected. The powder was washed in 5 M HCl at 80° C for 170 h with continuous stirring. The iron content, assayed by HF

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*ex Monsanto Ltd., Belgium.
†Glen Creston, UK.
‡Alpine zig-zag classifier.

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dissolution followed by atomic absorption spectrophotometry, was <100 ppm. Additions of Fe_2O_3, CaO, Al_2O_3, MgO, Y_2O_3 were mixed in an agate mortar with the silicon powder to give the required wt % after nitridation. The powders were isostatically pressed at 210 MPa into 8 mm diameter compacts 10 mm long. These were nitrided in flowing $N_2/5\% H_2$ (flow rate 100 ml min^{-1}) in a molybdenum-wound alumina tube furnace. For the MgO and Y_2O_3 additions the samples were covered during nitridation with Si_3N_4 powder mixed with the same proportion of additive to that required in the final product. The ratio of powder weight to sample weight was $\geqslant 1.5$. The heating schedule was 1100 to 1400° C over 120 h with temperature increments at 9 and 15 h intervals alternately. Silica was added to the pure RBSN by controlled oxidation at 1000° C in air. MgO was added to commercial RBSN* by 5 successive infilatrations of saturated aqueous magnesium nitrate after evacuation. Each infiltration was followed by a slow calcination to 500° C. The weight gain suggested a 4% MgO addition had been made and magnesium assay by atomic absorption spectrophotometry following KOH fusion indicated 4.5 wt % MgO. The α/β proportions were determined by XRD using Cu$K\alpha$ radiation and the method of interpretation described by Gazzara and Messier [17].

The densification kinetics were obtained using a high temperature–high pressure dilatometer described elsewhere [18]. The furnace comprised r.f. heated graphite inside a water-cooled pressure vessel capable of 2.1 MPa N_2 pressure. The dilatometer was a closed-ended BN tube and push-rod connected to a displacment transducer. Before use the vessel was pumped down to 1 Pa and backfilled with N_2, pressurizing finally to 1.4 MPa. The sintering temperatures were achieved within 5 min from cold. At temperature above 1750° C shrinkage began up to 1 min before the desired temperature was reached.

3. Results and discussion

An initial study showed that commercial RBSN undergoes a modest shrinkage without additives. Samples were cut without coolant to avoid contamination and packed into an RBSN tube with silicon nitride powder† prepared from semiconductor grade silicon. The shrinkage and weight loss after heating at 1750° C for 120 min with a 1 MPa N_2 overpressure are shown in Table I. Fig. 1 shows shrinkage curves obtained from the dilatometer for similar samples at different temperatures. The initial rates were plotted in Arrhenius form in Fig. 8 so that an estimate of activation enthalpy could be made (500 kJ mol^{-1}). This slight sintering is also accompanied by α–β Si_3N_4 conversion (Fig. 3).

TABLE I Densification and weight loss for commercial RBSN with and without 4.5% MgO. 1750° C, 120 min, 1 MPa N_2. ρ_0: initial density; ρ_f: final density

Condition	Linear shrinkage (%)	Weight loss (%)	ρ_0 (kg m^{-3})	ρ_f (kg m^{-3})
No additives	1.9	3.8	2480	2490
	1.1	1.5	2480	2510
	1.8	2.8	2480	2530
4.5% MgO	8.7	3.9	2570	3130
	7.8	2.2	2570	3100

The sintering behaviour of high purity silicon nitride prepared from semiconductor grade silicon without additives was then examined. Fig. 2 shows that the linear shrinkage is extremely small (0.2%) at 1750° C after 1 h. Fig. 3 shows that 75% α–Si_3N_4 was retained after this heat treatment. This is in agreement with earlier studies of the α–β Si_3N_4 conversion [19] which emphasise the importance of the presence of liquid for the transformation.

It is likely that impurities present in the commercial materials (typically calcium, aluminium, iron) provide, in conjunction with surface silica, a small amount of the necessary liquid. The relative importance of these impurities was therefore examined by making individual additions of their oxides in substantial amounts to high purity RBSN. Fig. 4 shows shrinkage curves for additions of 10% oxide heated at 1750° C. The addition of SiO_2 alone, made by oxidation, has no effect on sintering. The Fe_2O_3 often present above 0.5 wt % and sometimes added to silicon as a nitriding aid [1] has only a very slight effect. On the other hand calcium and aluminium oxide do enhance sintering but the effect is not very dramatic taking into account the large amount added. The significance of the distribution of additive in the compact was evident; in the case of the CaO addition the shrinkage curves varied within a 50% band depending

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* ex A.E.D. Ltd, UK.
† In house.

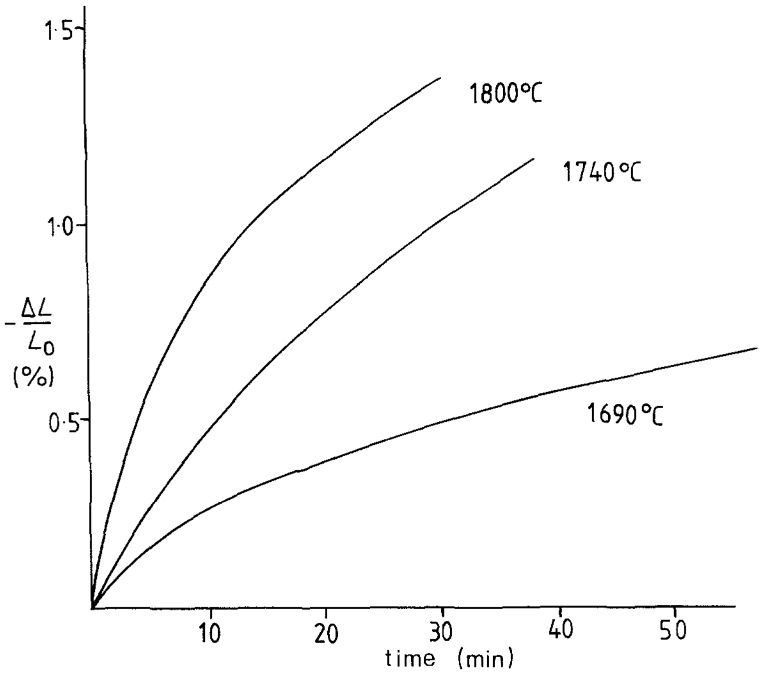

Figure 1 Shrinkage of commercial RBSN without additives (smooth average curves). $\rho_0 = 2500\ \mathrm{kg\,m^{-3}}$.

upon mixing time. It is possible therefore that the strong effect of Al_2O_3 is related to good dispersion because of the fine particle size (0.3 μm)*. If this interpretation is correct the effect of the impurities in the commercial material may be attributable not so much to their concentrations as to their thorough distribution brought about during silicon processing and nitridation.

Magnesia was then added to commercial RBSN by the method of infiltration giving 4.5 wt % MgO and the samples packed into an RBSN tube with silicon nitride powder containing 5 wt % MgO. Table I shows that high densities can be obtained in quite short times under such conditions. The shrinkage curves for these samples were also measured with nitrogen overpressure, but without

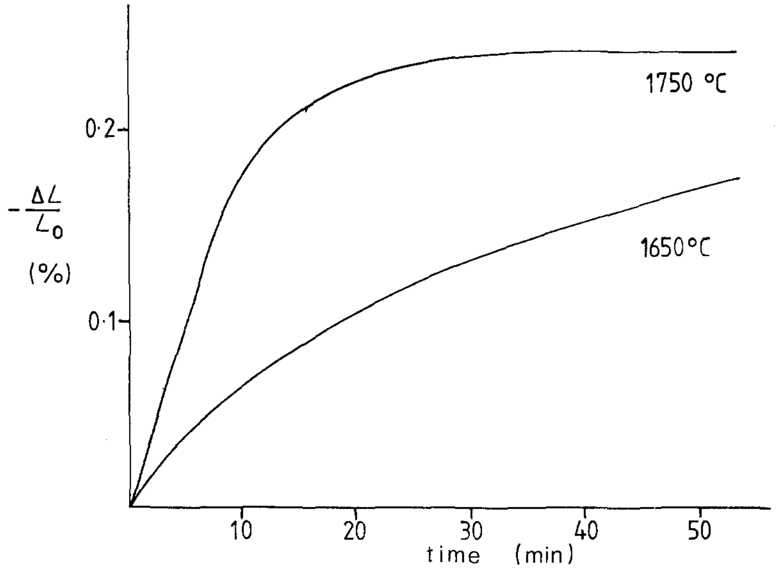

Figure 2 Shrinkage of high purity RBSN without additives. $\rho_0 = 2200\ \mathrm{kg\,m^{-3}}$.

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*Linde A.

a powder bed, over a range of temperatures using the dilatometer. The curves (Fig. 5) exhibit a plateau in the early stages which tends to be displaced to longer times at lower temperatures. The initial rates plotted in Arrhenius form in Fig. 8 yielded an activation enthalpy of 570 kJ mol^{-1}. Table II clearly demonstrates that a nitrogen overpressure alone was insufficient to suppress decomposition at higher temperatures. One cause of the weight loss was traced to water vapour desorbed from the inner surface of the walls of the pressure vessel during a run. The walls quickly became coated with a fine deposit of "SiO" which served as a large surface substrate for water adsorption when the vessel was opened between runs.

High purity silicon with 8 wt % MgO addition was reaction-bonded by nitridation under a powder bed of Si_3N_4–5 wt % MgO and magnesium assay showed that the product contained 4 wt % MgO [20]. The experiments with the high purity material were performed with a powder bed consisting of 60 wt % Si_3N_4, 35 wt % BN, 5 wt % MgO surrounding the sample in the dilatometer and with a 1.4 MPa N_2 overpressure. The weight losses at the higher temperatures (Table III) were significantly less than those for samples treated without a powder bed (Table II). The experiments suggest that both a powder bed and N_2 overpressure are desirable in order to suppress weight losses. This material had a lower density (2250 kg m^{-3})* than the commercial RBSN because of the narrow silicon powder size fraction and the method of comminution. The shrinkage curves (Fig. 6) showed a more pronounced transient expansion in the early stages and the initial densification rates were so high that they were not accurately measured by the dilatometer.

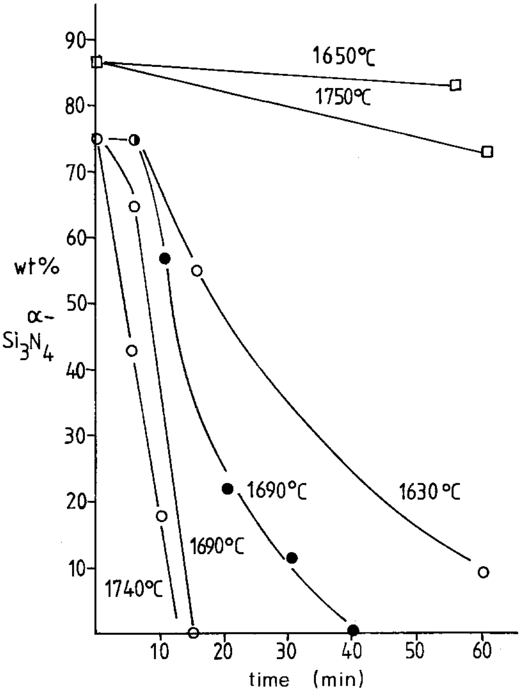

Figure 3 Extent of α–β conversion during sintering for: □ high purity RBSN without additives; ● commercial RBSN without additives: ○ commercial RBSN–4.5 wt % MgO.

When small additions of aluminium, calcium and iron impurities were added as oxide powder to high purity RBSN–4% MgO, the shrinkage curves did not differ significantly from those in Fig. 6. In contrast Greskovich [21] found that iron and calcium added as aqueous nitrate increased the densification of Si_3N_4 powder, again suggesting that the impurity distribution is important. In addition to their effect on densification, calcium may affect the high temperature strength [22],

TABLE II Weight losses for commercial RBSN + 4.5 wt % MgO sintered in nitrogen, 1 MPa at various temperatures without powder bed

Sintering temperature (° C)	Average weight loss per hour (%)	Standard deviation, SD	Number of measurements, *N*
1620	1.2	0.7	2
1640	1.9	0.5	5
1665	1.6	–	1
1690	4.7	3.3	10
1720	3.2	1.5	2
1740	5.8	2.5	6
1800	16.5	–	2

TABLE III Weight losses for high purity RBSN + 4% MgO sintered in nitrogen, 1.4 MPa at various temperatures

Sintering temperature (° C)	Average weight loss per hour (%)	Standard deviation, SD	Number of measurements, *N*
1600	1.3	1.3	3
1650	0.9	1.6	5
1700	1.4	0.9	3
1750	1.4	0.4	2
1800	2.9	1.5	3
1900	3.1	2.0	5

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*By mercury displacement.

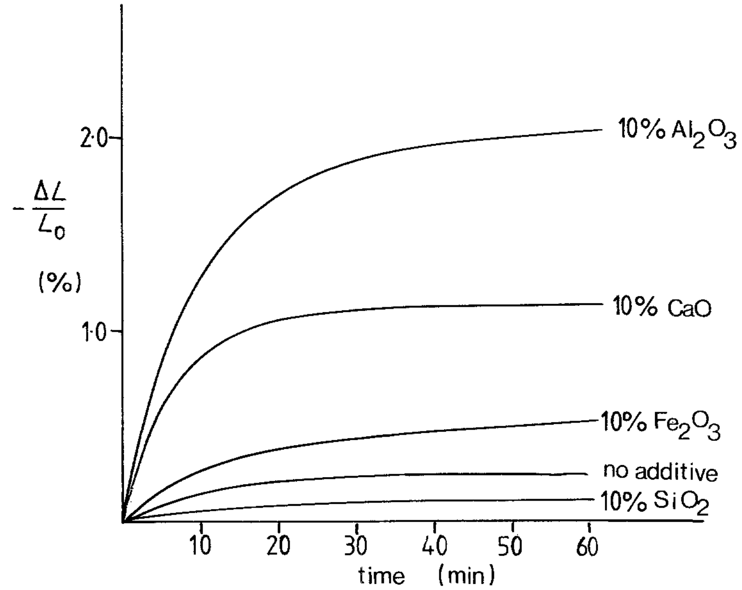

Figure 4 The effect of individual impurity oxides at the 10 wt % level on the shrinkage of high purity silicon nitride at 1750° C.

and stability of the grain boundary glass may be affected by iron [23].

The densification of high purity RBSN with 8 wt % Y_2O_3–1 wt % MgO over a range of temperatures is shown in Fig. 7. The activation enthalpy derived from initial rates is similar to that observed for commercial RBSN–MgO but the pre-exponential constants are very different, reflecting the different melting and viscosity characteristics of the grain boundary phases. The activation enthalpies for densification of RBSN are in the same range as those reviewed by Raj and Morgan [24] for densification, creep and grain boundary sliding in HPSN and approach the sublimation enthalpy for Si_3N_4; they are thought to represent the enthapy of solution in the grain boundary liquid.

Logarithmic plots of the densification kinetics yield values of the time exponent ranging from 1/2 to 1/5 as sintering proceeded. It is therefore not possible at present to deduce information about sintering processes from such an approach because of complicating factors such as the effects of decomposition [25], additive distribution,

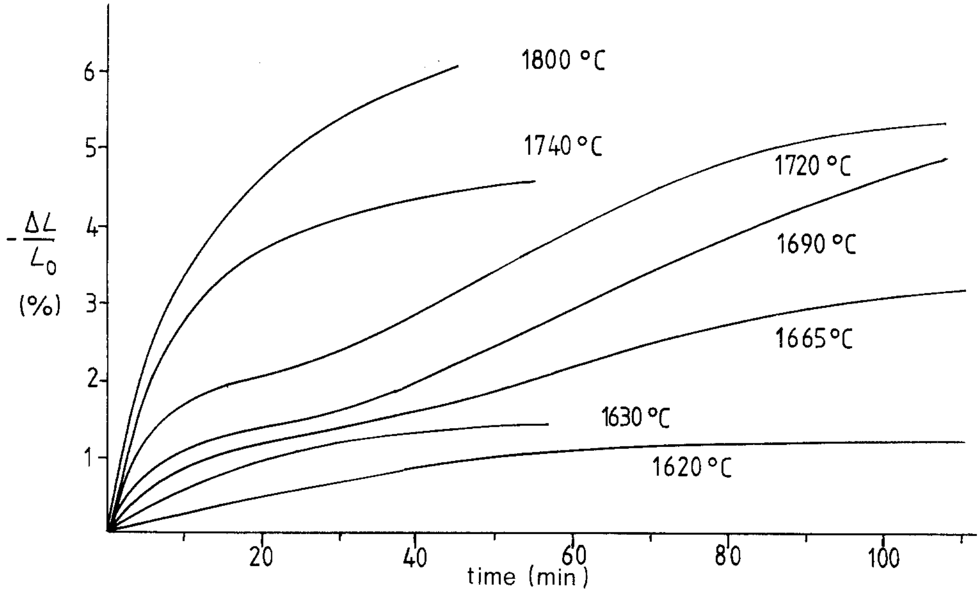

Figure 5 The shrinkage of commercial RBSN–4.5 wt % MgO (smoothed average curves). $\rho_0 = 2570\,\text{kg m}^{-3}$.

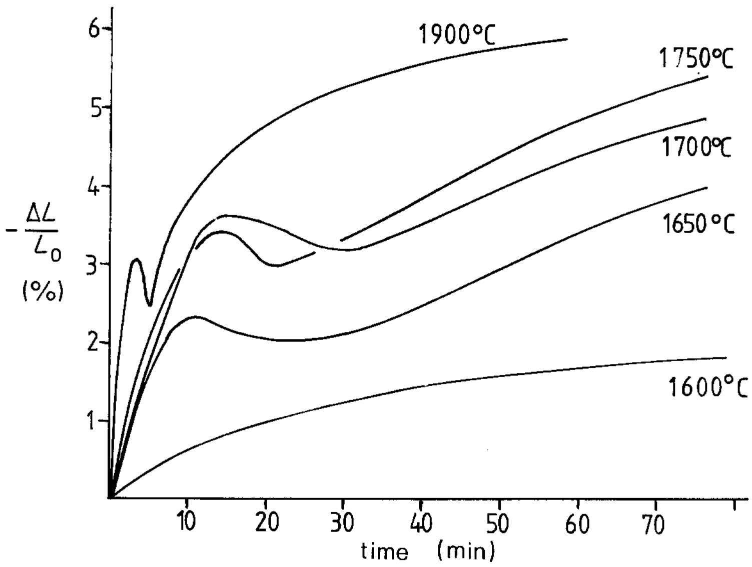

Figure 6 The shrinkage of high purity RBSN–4 wt % MgO (smoothed average curves). $\rho_0 = 2250\,\mathrm{kg\,m^{-3}}$.

transient expansion and heating rate. The latter variable is important for isothermal densification studies where high initial heating rates are needed. However it has been found [20, 26] that high densities are favoured by slow heating rates.

Optical microscopy confirmed the importance of achieving good MgO distribution in the preparation of RBSN for subsequent densification. The MgO powder used* in the preparation of the high purity RBSN–MgO had a tendency to agglomerate during processing. These agglomerates led to the formation, during sintering, of large pores surrounded by regions of nearly full density. This observation evidenced the remarkable mobility of MgO under the sintering conditions [1, 27] and emphasized the importance of thorough mixing of additives [28].

The cause of the transient expansion has not been identified; although it could be detected when low nitrogen overpressure (35 kPa) was used, it was enhanced by nitrogen pressure, as shown in Fig. 9. These samples of commercial RBSN were first oxidized to give 2% SiO_2 and then 2% MgO was added by infiltration of aqueous magnesium nitrate. With this composition the expansion overrides shrinkage in the initial stage.

4. Conclusions

Commercial RBSN without sintering additives undergoes some shrinkage and some α–β Si_3N_4

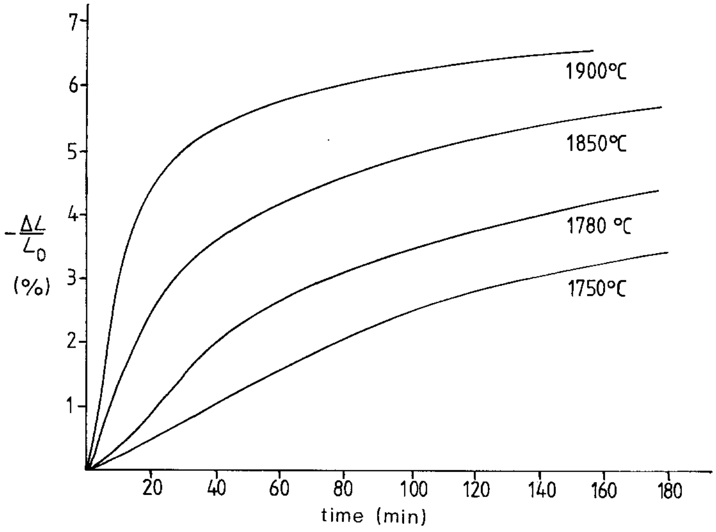

Figure 7 The shrinkage of high purity RBSN–8 wt % Y_2O_3 1 wt % MgO (smoothed average curves).

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*BDH Chemicals.

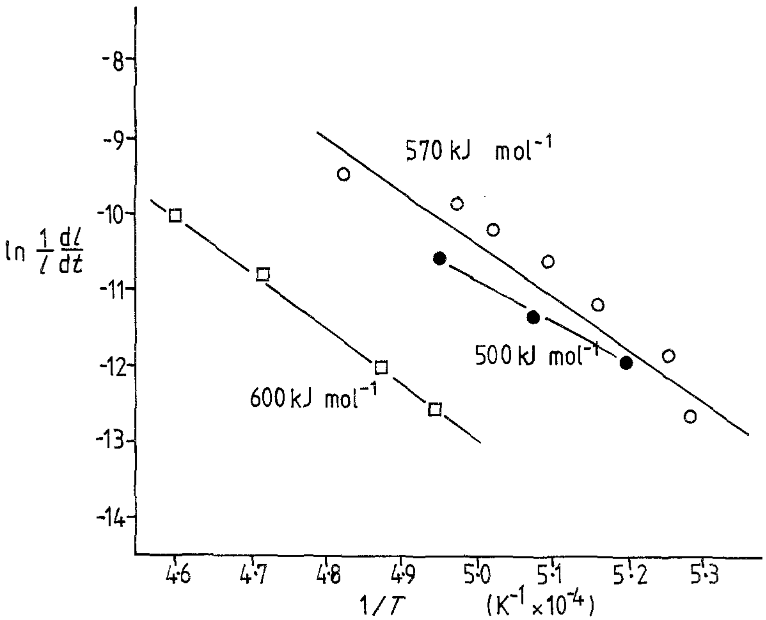

Figure 8 Arrhenius plots from initial shrinkage rates for: ○ commercial RBSN–4.5 wt% MgO; ● commercial RBSN no additives; ▫ high purity RBSN–8 wt% Y_2O_3 1 wt% MgO.

conversion in the region 1750 to 1800° C. High purity RBSN shows negligible shrinkage at similar temperatures and very little α–β Si_3N_4 transforma-occurs.

SiO_2 and Fe_2O_3 added as individual impurities do not significantly affect the sintering of high purity RBSN, but CaO and Al_2O_3 enhance sintering. It is likely that the distribution of such additives is as important as their content. Thus the effect of impurities in commercial RBSN may be largely the result of their thorough distribution. Focusing attention on volatility as a dispersing mechanism for sintering aids may thus be rewarding.

Also good distribution of MgO and Y_2O_3 powders in the silicon is important as additive agglomerates may lead to the formation of large pores in the sintered RBSN.

With the sintering aids MgO and Y_2O_3/MgO, the activation enthalpy for densification was in the range 570 to 600 kJ mol^{-1} which is similar to activation energies for densification of HPSN.

Weight loss was inhibited by both sintering in a powder bed and using a N_2 overpressure. The presence of water in the furnace atmosphere was a major cause of decomposition.

In the early stages of densification a temporary dilation of the RBSN–MgO was observed, its magnitude being related to the N_2 overpressure.

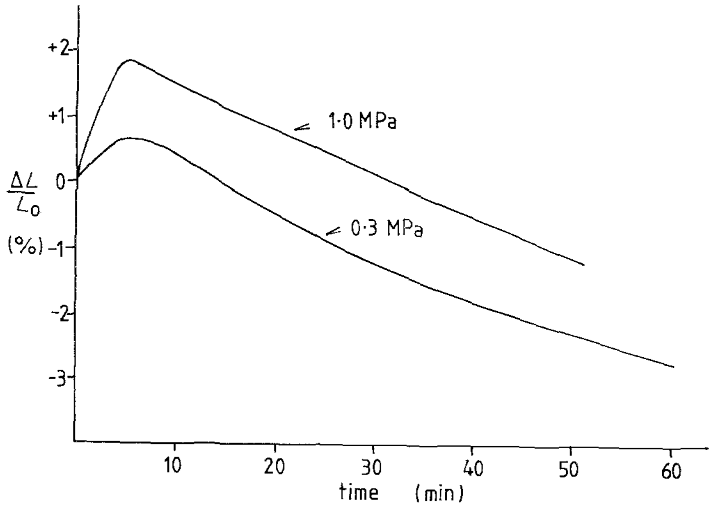

Figure 9 Expansion and shrinkage of commercial RBSN ≈ 2 wt% SiO_2 2 wt% MgO, heated at 1700° C under various N_2 pressures.

The conditions needed to obtain good isothermal densification kinetics, particularly high rates of heating to the temperature under consideration, are incompatible with the conditions for optimum densification, namely low heating rates.

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