SELF-STRENGTHENING AND HIGH TEMPERATURE SINTERING IN BINDER-FREE SILICON NITRIDE
A thermoanalytical study

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A thermal strengthening process, which occurs during low-temperature heating of binder-free silicon nitride, has been investigated using simultaneous thermal analysis, dilatometry and FTIR and shown to occur in separate stages over clearly identifiable temperatures. Reactions which give the strengthening are the loss of physically and chemically combined water and the decomposition of ammonium carbonate and various hydrosilicates. Compacts have bend strengths of 8–10 MPa after strengthening at 500°C and 30–34 MPa after strengthening at 900°C.

High-temperature dilatometry shows several stages of sintering. The maximum rate occurs at 1800°C with shrinkage commencing at 1450°C. Densities of 98.3% theoretical are obtained on heating to 1900°C.

Keywords: self-strengthening, simultaneous thermal analysis, temperature sintering

Introduction

Engineering ceramics based on silicon nitride are employed in many high-technology applications because they have high strength, good thermal shock and oxidation resistance. The production of high-quality parts is a complicated process with several expensive stages being required to obtain the necessary properties in the products. Accordingly, there is a major challenge to devise simple and effective processing techniques that allow the fabrication of silicon nitride ceramics into dense parts of high reliability. A promising method which al-

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lows the production of near-net-shape parts by uniaxial pressing without binder addition has been reported elsewhere [1]. The uniaxial pressing of binder-free mixes of β–Si_3N_4 (containing 10% α–Si_3N_4), with additions of fine Al_2O_3, MgO and Y_2O_3, gives 70–80% theoretical density when ultra-fine alumina (20–200 nm particle size) is used together with a bi-modal size distribution of silicon nitride particles [1]. This paper presents data on both the thermal strengthening and high-temperature densification of these pressed powders. Medium- and high-temperature dilatometry, simultaneous thermal analysis (TG/DTA), and fast Fourier-transform infrared spectroscopy (FTIR) have been used as the main experimental methods.

Experimental procedure

Materials

The following powders were used in this investigation: silicon nitride (95% β-phase) made by self-propagating high-temperature synthesis (SHS), which has been attritor milled to give a surface area of 7 m^2/g; silicon nitride (98% α-phase) manufactured by plasma-chemical synthesis (PCS) of silicon powder using direct nitriding to give a surface area of 25 m^2/g; and PCS-produced alumina, magnesia and yttria powders, all with surface areas of 25 m^2/g. In addition, small amounts (<1%) of ultra-fine oxides obtained by precipitation of hydroxides and controlled low-temperature decomposition were also added to the powder mixes.

In accordance with the results of preliminary experimentation [1], the ratio of PCS to SHS silicon nitride was selected as 1:9, (i.e. close to 10% for the $\alpha/\alpha + \beta$ ratio), in order to achieve maximum green density. The reference designations of the samples (used henceforth in this paper) include an initial letter of an oxide following a number which represents its wt% concentration in the powder mix. For example, designation 10A4Y3 means SHS silicon nitride (major) with 10 wt% PCS silicon nitride, 4 wt% alumina and 3 wt% yttria.

Thermal analysis

Simultaneous TG/DTA was carried out on 25 mg 'press ready' powder samples at a heating rate of 10 deg/min up to 600°C using Seiko STA 320/200 equipment. A flow rate of air of 25 ml/min was used for all experiments.

Two mixes of powder, selected on the basis of previous optimization to contain a total oxide addition of 7 wt% but of differing Al_2O_3:MgO ratio, were studied dilatometrically at rates of 1°–5 deg·min^{-1} in static air at temperatures up to 1000°C. The green specimens for these studies were 5×5×3 mm and were pressed uniaxially at 0.2 GPa. Mass change data were determined by weighing

samples after heating to various critical temperatures indicated by the dilatometric data.

Studies of the sintering of a 10A2 mix in nitrogen were performed using a 402E/7 high-temperature dilatometer at Netzsch Gerätebau GmbH (Selb, Germany). The sintering was carried out at a heating rate of 10 deg·min^{-1} using boron nitride as an embedding powder.

Material characterization

FTIR was used to study surface chemical changes that occurred on heating powder specimens [2]. The infrared spectrum was determined using a Nicolet 5DX spectrometer with fast Fourier transform of the resulting interferogram. The powders were mixed with pure KBr (1.64 wt%) and then pressed in a steel die at 750 MPa to give thin discs. The resultant transmittance curves were smoothed by digital interpolation with a spectra resolution of 4 cm^{-1}. Three-point bend tests were used to determine the strength of pressed powder specimens after heat treatment at 200°, 500° and 900°C.
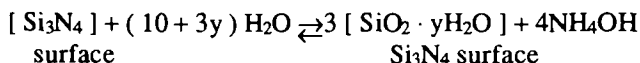
Results and discussion

Thermal analysis

Thermal strengthening treatment

Figure 1 shows STA data up to 600°C for the mix 10A3Y2M2, which is representative of all mixes investigated. There are two main stages of decomposition at 50°–120°C and 220°–400°C respectively. The reaction at 50°–120°C is a sharp endothermic process, whilst that commencing at 220°C is represented by a broad exotherm which is possibly a doublet of overlapping peaks. The DTA data are substantiated by the TG data which show a mass loss of 3 wt% associated with the low-temperature reaction and a further 3.5–4 wt% loss (in two overlapping stages) with the higher temperature process.

Equivalent dilatometric data are shown in Fig. 1, where two stages of shrinkage can be seen to be associated with the events at 50°–120°C and 220°–400°C. The first shrinkage is only 0.04% whereas the second is more significant at 0.3%. Figure 2 shows further dilatometric data, at a lower sensitivity but up to 1000°C. It is clear that a second significant contraction occurs over the temperature range 800°–900°C. Between the two regions of significant shrinkage (220° –400°C and 800° –900°C) there is a steady expansion on heating.

The first slight contraction, which is accompanied by the sharp endothermic event and mass loss of the order of 3 wt%, is associated with the loss of physically adsorbed water. However, during the powder processing prior to pressing there

are many opportunities for the chemical association of water also to occur by a range of hydrolysis reactions with the very fine powders used in this work. In particular, the production of hydrated silica complexes on the surface of silicon nitride is of importance. Such reactions may be represented by

$$[Si_3N_4] + (10 + 3y) H_2O \rightleftarrows 3 [SiO_2 \cdot yH_2O] + 4NH_4OH$$
$$surface \qquad\qquad\qquad\qquad Si_3N_4 \text{ surface}$$

As a result, ammonium hydroxide and complex silica hydrates, with different 2D and 3D networks are produced [3]. These complexes may incorporate the other oxides as a result of the hydration process. Such knowledge of the surface chemistry of 'raw' and 'processed' powders is of vital importance in the successful utilization of fine powders and has been the subject of a number of recent studies [4–5]. Decomposition of these complex hydrates occurs over the temperature range 220°–400°C to give the mass loss of approximately 3.5 wt% and the first significant shrinkage of the pellets. The products of decomposition are very reactive, SiO_2-rich surface films. The low-temperature results are in agreement with Kawamoto et al. [6] who identified progressive loss of H_2O from silicon nitride by temperature-programmed desorption analysis (TPD).
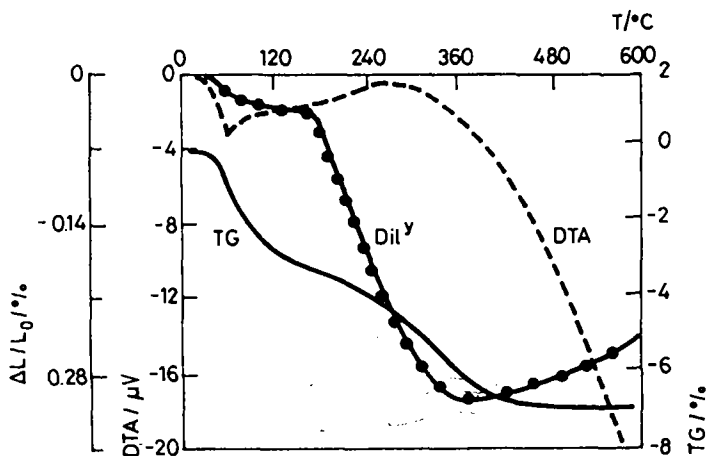

Fig. 1 STA of 10A3Y2M2 (10 deg · min^{-1}, air flow 25 cm^3 · min^{-1}) and dilatometry (5 deg · min^{-1}, static air)

The second major shrinkage, shown in Fig. 2, over the temperature range 800°– 900°C, occurs whilst a mass gain results. The intermittent mass-change measurements revealed that the maximum mass loss of 6–7 wt% had occurred by 500°–600°C. On subsequent heating from 600° to 900°C a mass gain of 2–3 wt% was observed, resulting from oxidation of the compacts. Microstructural examination of compacts revealed that the fine Al_2O_3 particles located on the sur-

faces of the much larger Si_3N_4 particles disappeared on heating over the range 800°–900°C. It is postulated that these fine particles reacted with the active decomposition products of the hydrated silica complexes and the freshly oxidised Si_3N_4 surfaces to produce glassy alumino-silicates as surface layers. The disappearance of the Al_2O_3 particles is clearly associated with the shrinkage over the range 800°–900°C and with the development of increased strengths in the compacts. It seems, therefore, that the reaction product acts as an inorganic binder phase for the compacts. Fracture surfaces of compacts heated to temperatures of 850°C and above contained smooth grain surfaces which appeared to be coated with a glassy phase.
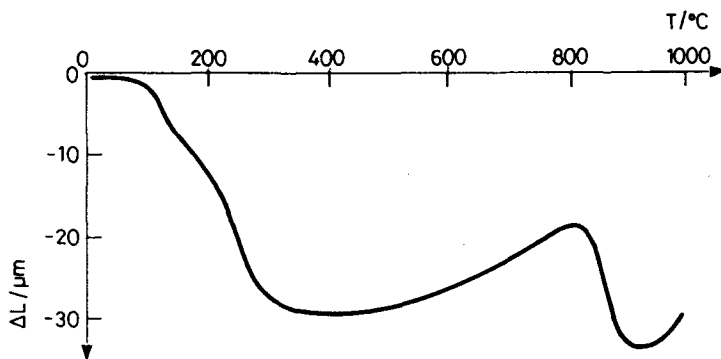

Fig. 2 Dilatometry of 10A4Y2M1 (1 deg · min^{-1}, static air)

High-temperature sintering

Data obtained in preliminary studies of the high-temperature sintering of a powder mix 10A2 (containing alumina only) are presented in Fig. 3. As indicated earlier this sintering was carried out in boron nitride embedding powder. It is evident that there are at least three different stages of densification, each of which has a different shrinkage rate. Although sintering first begins at 1450°C it is not until approximately 1750°C before a marked increase in sintering rate occurs. This is followed by a plateau which extends from 1800°C up to approximately 1840°C, after which the maximum rate of sintering occurs. Sintering is completed by 1900°C giving a final density of 98.3% theoretical. The maximum shrinkage is equivalent to approximately 38.6% by volume. During these final stages of densification a mass loss of approximately 5–6 wt% is observed due to loss of nitrogen. The rapid rate of sintering at 1800°C is associated with the formation of a liquid phase, whereas the lower temperature densification is more likely associated with solid-state processes.

Bend strength as a function of low-temperature heat treatment

Figure 2 shows that critical temperatures during low-temperature thermal strengthening are 200°, 500° and 900°C. The results of three-point bend tests performed on specimens heated at these temperatures for 1 hour and cooled to room temperature are presented in Table 1. Ten samples were prepared at each temperature.

Table 1 Bend strength (MPa) of the specimens after TST

Temperature of TST	Mix	Mix
°C	10A3Y2M2	10A4Y2M1
200	5.4±0.3	4.6±0.3
500	8.9±0.5	8.9±0.3
900	34.5±3.6	30.9±3.2

It is evident that a large increase in bend strength occurs on heating to 900°C when the glassy surface phases are produced. However, useful increases in strength result from heat treatment at 500°C.

FTIR spectroscopy

The relationships between wave number, % transmittance and heat treatment temperature are shown in Fig. 4 for the 10A3Y2M2 powder mix. For the powder in the 'green' state and after heat treatment at 200°C the FTIR spectra are very similar. Both spectra show deep transmittance valleys at approximately 1385°C and 1640 cm^{-1} with full absorption in the range 800–1100 cm^{-1}. After heat treat-
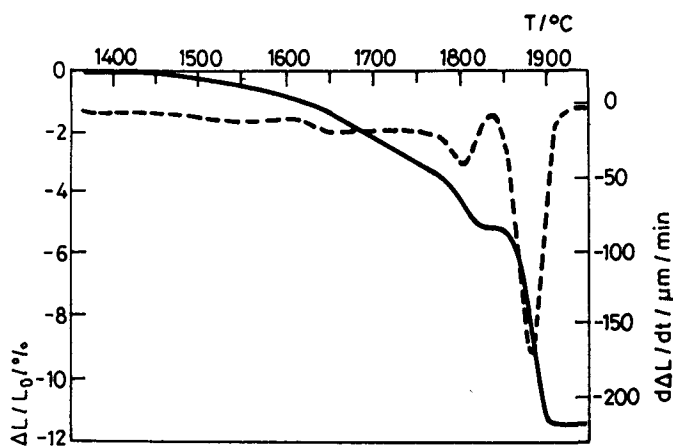
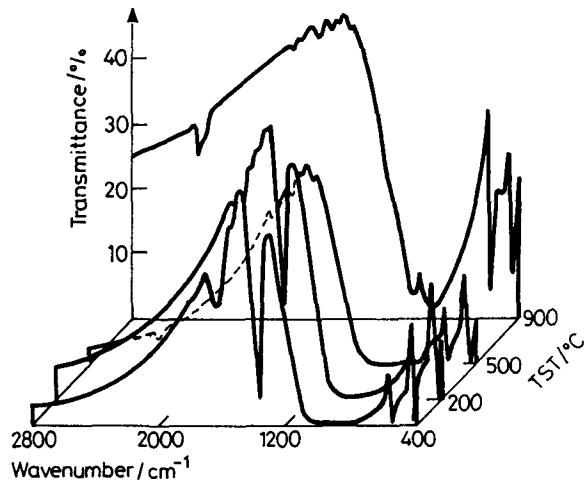**Fig. 3** High-temperature dilatometry of 10A2 (10 deg · min^{-1}, nitrogen)

Fig. 4 FTIR transmittance of 10A3Y2M2 as function of wave number and TST temperature

ment at 500° and 900°C, the valleys at 1385 and 1640 cm^{-1} disappear and two new ones occur at 450 and 600 cm^{-1} for all samples studied. It is interesting to note that these two valleys are both associated with the presence of SiO_3^{2-} (495, 600 cm^{-1}) and indicate that all surfaces are oxidised in the powder mixes. (The valleys are characteristic of both SHS and PCS silicon nitride which have also been studied as pure individual powders.) Powder mixes heated to both 500° and 900°C show a small sharp decrease in the transmittance spectra at approximately 2400 cm^{-1}, with that at 900°C being more pronounced than that at 500°C. These characterise the formation of HCO_3^- (2370 cm^{-1}) and indicate possible reaction with atmospheric CO_2 on heating. The valleys at 1385 and 1640 cm^{-1} have not yet been identified conclusively, but appear to be associated with the hydrated complexes discussed in the previous section.

Conclusions

1) It is evident that the chemical changes occurring to the powder surfaces on heating up to 900°C, which cause the shrinkages, mass losses and increases in strength, are complicated. These changes involve the loss of physically and chemically combined water, the oxidation of surfaces and formation of carbonates, and the reaction of an active silica-containing surface with very fine active Al_2O_3 to produce an inorganic, glassy binder phase.

2) The roles of Y_2O_3 and MgO in low-temperature thermal strengthening are considered to be very limited because the phenomenon has been observed without these additions provided that Al_2O_3 is present.

3) These studies show that it is possible to achieve usable green densities and strengths without the additions of binders. The strengths achieved at 500° and 900°C are sufficient to permit mechanical handling and machining.

4) The high-temperature densification of silicon nitride containing alumina additions occurs at a maximum rate at 1850°C with the formation of a liquid phase. Significant sintering occurs over the temperature range 1750°–1800°C, prior to a region of stability which extends from 1800°C to approximately 1840°C.

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Zusammenfassung — Mittels simultaner Thermoanalyse, Dilatometrie und FTIR wurde der bei schwachem Erhitzen von bindemittelfreiem Siliziumnitrid ablaufende thermische Verhärtungsprozeß untersucht, der nachweisbar in verschiedenen Schritten bei eindeutig definierbaren Temperaturen abläuft. Zu den zur Verhärtung führenden Reaktionen gehören der Verlust von physikalisch und chemisch gebundenem Wasser sowie die Zersetzung von Ammoniumcarbonat und verschiedenen Hydrosilikaten. Preßlinge besitzen nach dem Verhärten bei 500°C eine Biegefestigkeit zwischen 8 und 10 MPa und nach dem Verhärten bei 900C eine Biegefestigkeit von 30-34 MPa.
Dilatometrie bei höheren Temperaturen zeigt verschiedene Sinterschritte. Die Höchstgeschwindigkeit tritt mit einem Schrumpfbeginn bei 1450°C bei einer Temperatur von 1800°C auf. Bei Erhitzen auf 1900°C werden Dichten von 98,3 % des theoretischen Wertes erreicht.