

The microstructures of silicon nitride ceramics during hot-pressing transformations

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The microstructure of silicon nitride hot-pressed with a magnesium oxide additive has been studied by transmission electron microscopy. This includes material at various stages in a hot-pressing process: the initial ($\sim 90\%$) silicon nitride powder; specimens partially densified and partially transformed from α -silicon "nitride" ($\text{Si}_{11.5}\text{N}_{15}\text{O}_{0.5}$) to β -silicon nitride (Si_3N_4); and almost fully dense and fully transformed β - Si_3N_4 . The observations substantiate a solid/liquid/solid transformation mechanism, whereby Si and N are transported from α grains through a silicate liquid phase to nucleation sites for β at α /liquid interfaces or to β grains nucleated homogeneously in the liquid phase.

1. Introduction

Silicon nitride is now prominent as a ceramic material with potentially wide application via its good friction and wear resistance at ambient temperatures or good thermal shock and oxidation resistance required for elevated temperature use. The research described in this paper is concerned with silicon nitride prepared by mixing α -silicon nitride particles with a small amount of MgO additive and hot-pressing (at $\sim 1700^\circ\text{C}$) in a graphite die. The process, which has been described in detail by Lumby and Coe [1], results in a product of 100% density containing mainly β -silicon nitride crystals in the range 0.2 to 0.5 μm . The mechanism for the conversion of the α crystallographic form (S.G. P31c, $a = 7.75 \text{ \AA}$, $c = 5.62 \text{ \AA}$, $c/a = 0.725$) to the β crystallographic form (S.G. P6₃/m, $a = 7.61 \text{ \AA}$, $c = 2.91 \text{ \AA}$, $c/a = 0.383$) and the role of the additive are incompletely understood. The most complete description of the process to date has been given by Grieveson *et al* [2] following a crystal structure analysis of both α and β forms and an X-ray analysis of the progress of the hot-pressing reaction with varying temperature. They reported that the MgO additive reacts with free silica (associated with the α -silicon nitride particles) to form a forsterite (Mg_2SiO_4) crystalline phase in the temperature range 1000 to 1400°C . Above 1400°C , the forsterite reacts

with α -silicon nitride ($\text{Si}_{11.5}\text{N}_{15}\text{O}_{0.5}$) to give β -silicon nitride (Si_3N_4) and a vitreous phase of approximate composition MgSiO_3 . The presence of a liquid silicate phase of this composition is indicated by comparison of the liquidus temperature in the MgO-SiO₂ phase diagram and by the rapid densification which occurs in the presence of the liquid "flux" within the pores of the hot-pressed compact. They concluded that the liquid silicate cools without crystallization to the glassy state and provide additional support for this via the appearance of X-ray diffraction peaks from crystalline enstatite (MgSiO_3) in hot-pressed material (containing 10% MgO) which has been given a long annealing treatment.

The present study is an attempt (i) directly to confirm the presence of the glassy phase and to determine its microstructural distribution in relation to that of the β - Si_3N_4 grains and (ii) to determine the morphological features of the conversion of the α to β crystallographic forms of silicon nitride.

2. Experimental techniques

For complete characterization of the microstructure of fine-grained ($< 1 \mu\text{m}$) ceramic materials, the application of transmission electron microscopy and diffraction is essential. Because silicon nitride is chemically inert and insulating, conventional techniques for thin

section preparation, involving chemical or electrochemical dissolution, are not applicable.

Electron transparent specimens were prepared from the bulk hot-pressings (in the form of plates 3 cm × 3 cm × 0.5 cm) using the following technique. Thin slices, about 0.2 mm thick, were cut from the bulk material using an annular diamond saw and attached to a brass backing plate with wax. The slices were mechanically ground on silicon carbide papers until the appearance of perforations or a reduction in area indicating the presence of thin wedge-shaped sections. Fragments of these extremely thin slices were mounted in the rotating specimen holder of an ion-beam thinning apparatus such that part of the wedge section of vanishing thickness was near to the axis of specimen rotation and to the ion-beam axis. Both surfaces of the specimen were sputtered by 5 kV argon ions at 40° to the surfaces when rotating at 15 rpm. Specimens suitable for electron microscopy were produced after sputtering times of about 10 h. These were mounted in the goniometer specimen holder and examined in a JEM 200 kV electron microscope. The build up of static charges on the surfaces of some of the large fragments tended to distort the electron beam. This effect could be eliminated without serious loss of resolution by evaporation of a thin layer of carbon on to the specimen surfaces.

An alternative specimen preparation technique, involving the mechanical pre-thinning of the centre of a 3 mm × 0.5 mm disc shaped specimen has also been used. This results in easier specimen handling during the subsequent ion-beam thinning and electron microscopy but the much greater area of specimen surface enhanced the charging effect and made the carbon coating stage essential.

The silicon nitride particles were also examined in the electron microscope prior to hot-pressing. The particle samples were dispersed in a weak solution of collodion in amyl acetate using an ultrasonic probe. One drop of this solution was then placed on a carbon support film, backed by an electron microscope grid and allowed to dry. On examination, the particles were found to be embedded in the electron transparent collodion film with adequate dispersion.

The highest strength silicon nitride bodies are produced by hot-pressing a powder which contains mainly the α form. Such powders can be produced by nitriding silicon under controlled conditions of low oxygen partial pressure, to

reduce the production of other phases (β -Si₃N₄, SiO₂, Si₂ON₂). The α crystals are formed predominantly in the form of thin laths, as shown later. Magnesia additions of 1 to 7% are made to the α -silicon nitride and the mixture is thoroughly interdispersed using a wet-milling process. The charge is placed inside a graphite die which acts as a susceptor for r.f. inductive heating. The pressing sequence begins, gradually raising temperature and pressure with time. Typical pressing conditions to obtain a fully dense, mainly β , body are 1700° at 2 ton in.⁻² for 1 h. Different conditions have been used to obtain specimens at various stages in the process of transformation with extreme conditions of 1400°C at 0.6 ton in.⁻² for 5 min.

3. Microstructural analysis

3.1. Source materials

Fig. 1 is a low magnification electron micrograph of part of a powder sample dispersed in a collodion film. The portions marked A are polycrystalline regions of MgO additive. Examination at higher magnification has revealed three main types of particle morphology, shown in Fig. 2a to c. Fig. 2a is a micrograph and corresponding electron diffraction pattern which identifies this major particle as dislocation free α -silicon nitride in extremely thin lath-like or platelet morphology. The electron diffraction pattern used in identifying the α -phase is that obtained with a [2 $\bar{1}\bar{1}$ 0] electron beam direction. This pattern contains the (0001) and (01 $\bar{1}$ 1) diffraction spots corresponding to d -spacings of 5.62 Å and 4.32 Å. There are no similar spacings

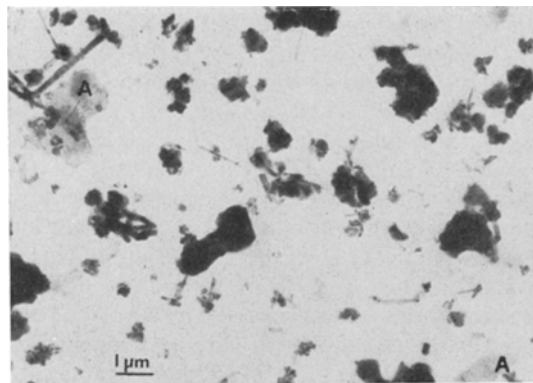


Figure 1 Low magnification electron micrograph of unpressed silicon nitride powder with magnesia additions of 7%. Areas marked A are polycrystalline regions of magnesia.

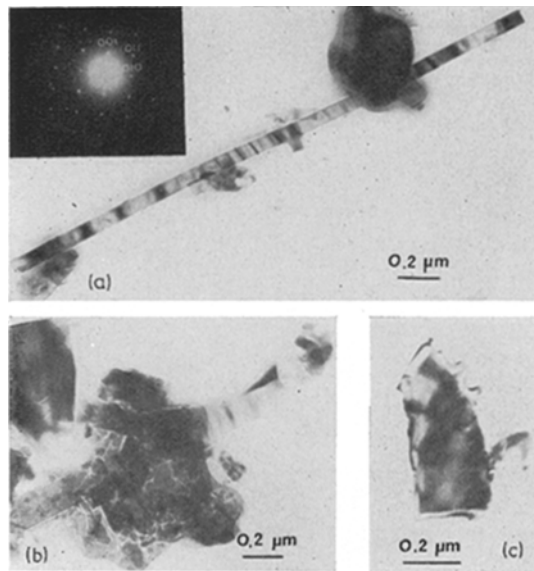


Figure 2 Electron micrographs of unpressed silicon nitride powder illustrating the three different types of particle. (a) A single crystal lath (indicated by sharp bend contours) of silicon nitride. The insert electron diffraction pattern has the characteristic α -silicon nitride $[2\bar{1}\bar{1}0]$ zone axis. (b) Partially sintered agglomerate of silicon nitride particles with lath crystalline shapes protruding. (c) Irregularly-shaped chip of α -silicon nitride, probably formed via solid-vapour reaction during nitriding of silicon.

in β - Si_3N_4 . The diffraction camera length of an electron microscope is very sensitive to specimen position but once calibrated for a particular specimen (using a known diffraction pattern), other patterns can be indexed and d -spacings obtained with 1% accuracy. The lath dimensions vary from 0.3 to 3 μm length by 500 \AA to 0.2 μm width. It is difficult to estimate the thickness, but the presence of sharp bend contours indicate that this dimension will be much smaller than the width of the laths. The inset diffraction pattern (Fig. 2a) demonstrates the consistently observed growth axis normal to $\{01\bar{1}\}$ planes. These lath-like particles have clearly been converted to α -silicon nitride by vapour phase reaction and deposition in the reaction crucible containing the silicon starting powders (which have irregular shapes and sizes).

The second particle type, shown in Fig. 2b, is of larger average size and consists of an agglomerate of elongated polycrystals. These are believed to be formed via a partial sintering of α -silicon nitride laths which are in mutual

contact in the reaction crucible. The small size of the individual grains inhibits identification of these particles but in many cases the characteristic lath shapes of α -silicon nitride can be observed as protrusions at the periphery of the agglomerate particles.

The third type of particle, which are infrequently observed, consist of microscopic chips of irregular shape (Fig. 2c) which give rise to single crystal diffraction patterns and which can be tentatively identified as α -silicon nitride. Hence they may be formed by a direct reaction of nitrogen with small silicon particles. The possibility that some of these may be crystalline silicate particles cannot be excluded in view of the observation of planar defects and the difficulty of distinguishing reciprocal lattice sections of silicates from certain sections of the silicon nitrides.

In summary, since an X-ray analysis of the starting powders usually gives an α -silicon nitride content of about 90% (the rest being mainly β - Si_3N_4), these particles are predominantly in the form of thin lath-like perfect crystals. These crystals may be elastically bent to very small radii of curvature, which must be beneficial in promoting particle-particle contact during pre-reaction densification. Analyses of these particles [3] show that they contain surface adsorbed oxygen (in addition to that included in the structure in stabilizing the α -crystallographic form). This is probably in the form of a glassy SiO_2 layer but is not detectable in electron microscope images.

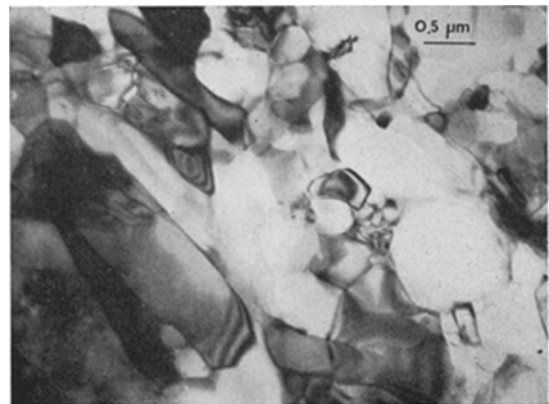


Figure 3 Electron micrograph illustrating general microstructural view of hot-pressed silicon nitride.

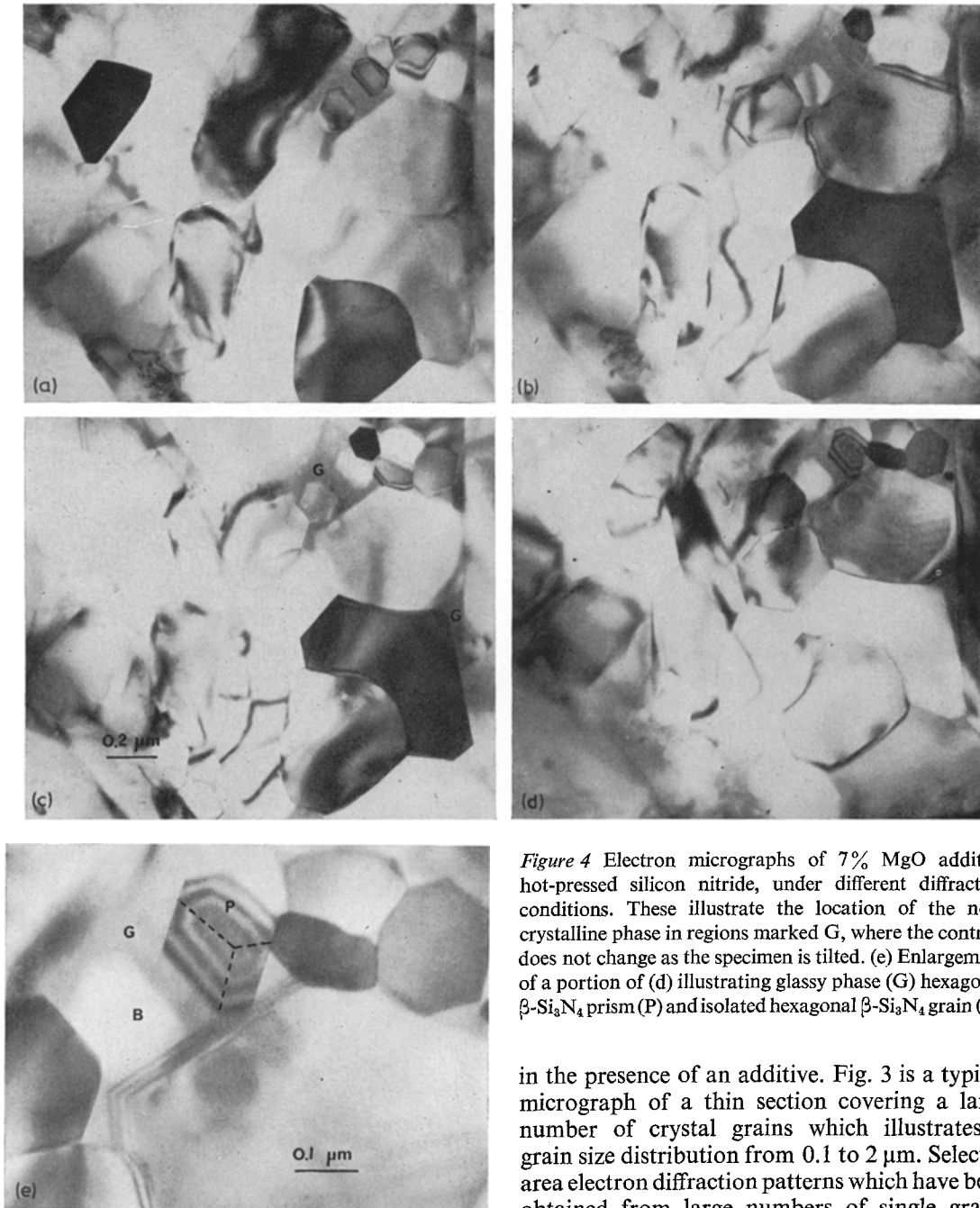


Figure 4 Electron micrographs of 7% MgO additive hot-pressed silicon nitride, under different diffracting conditions. These illustrate the location of the non-crystalline phase in regions marked G, where the contrast does not change as the specimen is tilted. (e) Enlargement of a portion of (d) illustrating glassy phase (G) hexagonal β - Si_3N_4 prism (P) and isolated hexagonal β - Si_3N_4 grain (B).

in the presence of an additive. Fig. 3 is a typical micrograph of a thin section covering a large number of crystal grains which illustrates a grain size distribution from 0.1 to 2 μm . Selected area electron diffraction patterns which have been obtained from large numbers of single grains show them to be the β crystallographic form in random orientations. α -grains have been identified in only a few cases although X-ray analysis indicates that there may be up to 10% α remaining in the material. It may be that the α exists as very small grains too small for selected area diffraction. Fig. 4 shows electron microscope images at higher magnification and under

3.2. Hot-pressed material

3.2.1. Fully transformed material

Thin sections from material which has been hot-pressed with 7% MgO have been most intensively studied with a view to determination of the mechanisms of densification and transformation

different diffracting conditions to emphasize the following microstructural features: (1) the strong preference for grain shapes which are hexagonal plates and hexagonal prisms. This is most clearly shown in Fig. 4 where the specimen has been tilted to bring different grains into a strongly diffracting condition (such that they appear in dark contrast). These grains always reveal the diffraction patterns of six-fold rotational symmetry of Fig. 5 showing systematic diffraction spots from planes having $[0001]$ as zone axis. They indicate that many of the grains have shapes which are determined by anisotropy in the β - Si_3N_4 surface energies such that the plane surfaces are parallel to $\{10\bar{1}0\}$ prism planes. The three-dimensional shape of some very small grains is occasionally revealed via wedge thickness extinction contours, e.g. grain P in Fig. 4e has a hexagonal prism shape bounded by the six prism planes and two basal (0001) surfaces. (2) All grain surfaces which show well-developed prism plane facets are adjacent to a small volume of non-crystalline phase. The lack of crystallinity in this phase may not be conclusively proven by selected area diffraction in view of its small volume. However, the absence of Bragg diffraction indicative of non-crystallinity may be demonstrated by specimen tilting and observations of variation in contrast in electron microscope images. Figs. 4a to d have been recorded from the same area of thin section under different diffracting conditions for the various β - Si_3N_4 grains and clearly show no marked contrast variation for the small non-crystalline volumes of material (labelled G in 4e which is a magnified portion of 4d) which fill space between the β - Si_3N_4 prism faces. The identification of a non-crystalline phase has been made easier by a correlation of the tilting experiments with the appearance of images after long exposure to 200 keV electron irradiation. The non-crystalline regions develop a spotty contrast under these conditions (Fig. 6) which is believed to originate from micro-cavities formed via electron irradiation damage of unknown mechanism. The Si_3N_4 grains reveal no visible damage following electron irradiation for long periods and neither phase appears to be damaged by the ion-beam sputtering process (although there is some evidence from Augèr spectroscopy for surface adsorption or implantation of argon ions).

The microstructure of silicon nitride which has been hot-pressed with a smaller MgO content

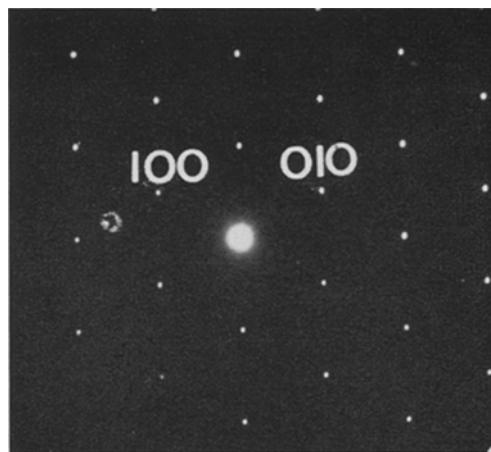


Figure 5 β -silicon nitride electron diffraction pattern with $[0001]$ zone axis.

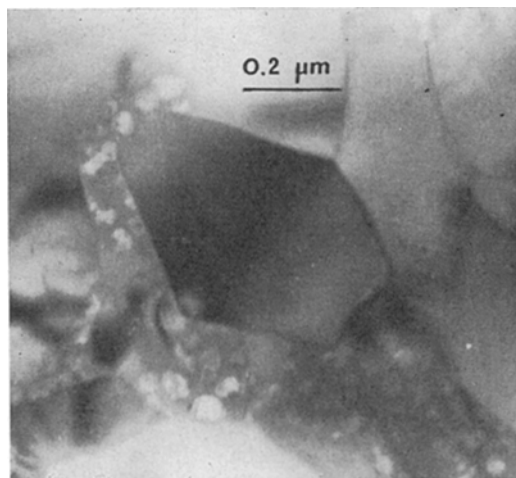


Figure 6 Formation of micro-cavities in the non-crystalline phase of hot-pressed silicon nitride after exposure to 200 keV electrons.

(1 to 2%) differs only in detail from that described above. The amount of non-crystalline phase is smaller than in the 7% additive material and observed mainly in the wedge-shaped morphology between smaller prism plane facets. Thus the number of irregularly shaped boundaries between β - Si_3N_4 grains is greater for the material with smaller MgO content. These boundaries have presumably formed by impingement of growing β - Si_3N_4 grains. Small volumes of non-crystalline material appear at the triple junctions of adjacent grains and appear to extend between grain boundaries and may become an unresolvable film.

An infrequent observation in all hot-pressed materials is that of abnormally large grains of β - Si_3N_4 , usually containing dislocations (Fig. 7). These grains may be up to 10 μm in their longest dimension.

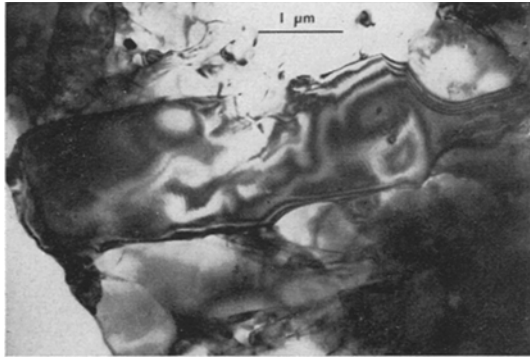


Figure 7 Abnormally large (5 μm) grain of β - Si_3N_4 in hot-pressed material.

3.2.2. Partially transformed material

To provide further information concerning the microstructural and crystallographic changes which occur during the hot-pressing process, several runs have been prematurely interrupted, thus obtaining partially transformed material.

A first specimen was pressed at 1500°C and 1 ton in.^{-2} pressure for 10 min; this was fairly dense and hard with an α/β ratio of 70/30. The microstructure consists of polyhedral grains with no evidence of the α laths. Diffraction phenomena indicate that there is considerably more glass present than in fully transformed material. It is clear that the disappearance of the lath-like α -silicon nitride crystals occurs very rapidly at the onset of densification. There is also evidence of hexagonal grains (which are presumably β - Si_3N_4) having grown in regions of glass phase (Fig. 8), where the irradiation damage is again present.

In a second specimen, pressed at 1400°C and 0.6 ton in.^{-2} for 5 min, there was little densification or transformation and it was impossible to cut specimens for ion-beaming. Instead, the material was gently ground to a powder and studied in the electron microscope, using the same technique used for the unpressed powder. The lath shapes were still present, but there was evidence for the initiation of dissolution of the laths by the loss of sharp bend contour contrast

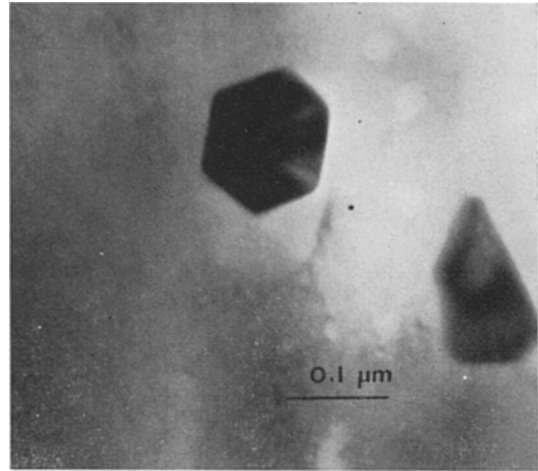


Figure 8 Isolated hexagonal crystal in partially transformed hot-pressed silicon nitride, containing 7% MgO additions and an α/β ratio of 70/30. The crystal is surrounded by the non-crystalline phase, which is indicated by electron irradiation damage.

in parts and by removal of the crystallographic facets at the lath periphery.

A third specimen was pressed at 1500°C at 1 ton in.^{-2} for 5 min. This material had an α/β ratio of 80/20 and it was just substantial enough to obtain ion-beamed specimens for electron microscopy. Even at this stage the lath morphology had been lost. Fig. 9 illustrates extremely fine-grained regions observed locally in this material, which corresponds to a high nucleation density for β - Si_3N_4 grains. The inhomogeneity of this observation is probably a consequence of uneven mixing of the MgO additive.

The origin of the various microstructural features will now be discussed. The suggested mechanisms are substantiated by the observations presented above.

4. A mechanism for microstructural development

4.1. The non-crystalline phase

The direct observation of a non-crystalline (glassy) minor phase in the hot-pressed material indicates that the main function of the MgO lies in the formation of a viscous magnesium silicate liquid at elevated temperatures. The silicate liquid is formed via the mechanism suggested by Grieveson *et al* [2] which has been outlined in Section 1. A compositional analysis of the glassy phase is not considered feasible in view of the inadequate spatial resolution nor-

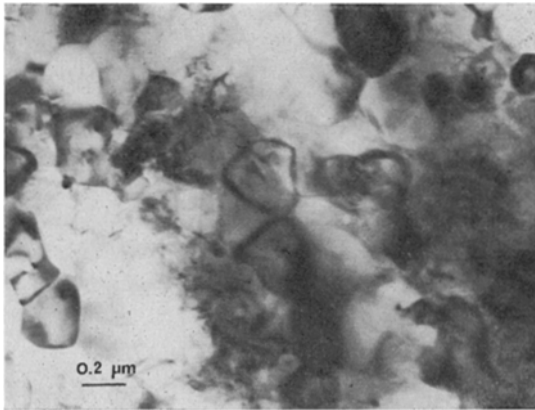


Figure 9 High nucleation density of β - Si_3N_4 grains in partially transformed 7% MgO material with an α/β ratio of 80/20.

mally available with electron probe techniques. An approximate analysis of this grain-boundary concentrated phase has been made in this laboratory using Augèr electron spectroscopy and will be briefly reported here. Hot-pressed bar-shaped specimens (from 7% MgO material) have been fractured at 1200°C and the fracture surfaces analysed by Augèr electron spectroscopy after removal of surface adsorbed atoms. A comparison of the elemental analysis from these fracture surfaces with analysis taken from a mechanically ground and ion-sputtered surface are markedly different. These observations, together with scanning electron micrographs of the surfaces, indicate that the high temperature fracture is mainly intergranular and that the fracture surface analysis should give an approximate idea of the glass composition. Thus Mg and Ca are present in the glass in similar concentration whereas they are barely detectable in the transgranular surface. The Ca must result from its presence in the impure silicon before nitriding to mainly α -silicon nitride. Other major impurities (mainly Al and Fe) are barely detectable in the glassy phase and must therefore be retained in the final β - Si_3N_4 structure. The implication is therefore that the high MgO silicate liquid initially present acts as a sink for excess oxygen, which forms an essential constituent of the α -silicon nitride structure (as suggested by Grievson *et al*), but also for large (probably interstitial) ions like Ca^{2+} . The smaller ions Al^{3+} ; Fe^{3+} are probably retained in

the final β - Si_3N_4 crystal in substitutional (Si) positions, as in the high alumina "sialon" materials (Jack *et al* [4]).

The presence of Ca in the silicate phase may reduce the equilibrium liquidus to that of the ternary eutectic temperatures, at about 1360°C for CaO-MgO-SiO₂ compositions near to CaO.MgO.2SiO₂*. It is significant that rapid densification during hot-pressing starts just above 1350°C [5].

4.2. β - Si_3N_4 grain formation

A detailed mechanism for the conversion of α to β silicon nitride has not been presented. The mechanism must be able to explain the gross morphological change from the predominantly thin lath and platelet α form to that of randomly orientated and frequently prismatic shaped β crystals. The frequently faceted and crystallographic external growth form of the β grains is indicative of a transformation which occurs via a liquid phase. In the 7% MgO high additive materials at least four of the six hexagonal prismatic faces are visible in a large number of the smaller grains and these faces frequently adjoin the clearly visible glassy phase. Some of the smallest grains occasionally appear to be completely surrounded by glass phase (e.g. grain B in Fig. 4e). This remarkable observation provides strong evidence for a liquid to solid precipitation reaction. This hypothesis is substantiated by observations recorded in Section 3.2.2 on partially transformed material, in particular the growth of a completely isolated hexagonal crystal in Fig. 8.

A probable mechanism for microstructural development based on the idea of a liquid \rightarrow solid transformation may be devised by the following reasoning. Firstly the possibility of the die contents at high temperatures being completely in the form of a viscous liquid, containing Si and N with only small amounts of O, Mg, Ca, Al, Fe, etc. is remote in view of the observed decomposition of silicon nitride at high temperatures at atmospheric pressure. Further, if the reaction was one of precipitation from a homogeneous liquid, the product would certainly not have such a fine grain size in the absence of very efficient nucleation catalysts (similar to glass ceramics). At the other extreme the transformation is unlikely to be that of a α solid \rightarrow β solid direct transformation in which the silicate

*An Augèr analysis of a 7% MgO material revealed a glass composition of (0.40 ± 0.03) CaO. (0.75 ± 0.1) MgO. 2SiO₂.

liquid acts firstly as a sink for excess oxygen and other impurity species (which are transported via solid-state diffusion) and secondly to fill the pores between new β grains. An adequate interpretation of the observed microstructure is that resulting from a transformation mechanism between the above extremes. It is believed that there is an appreciable solubility of silicon and nitrogen atoms in the silicate liquid at high temperatures and that these atoms are transported through the liquid phase after solution at the α /liquid interface and reprecipitated at the interface between the new β crystal and the liquid.

An idealized picture of the microstructural changes may be given as follows. The first stage concerns the formation of a silicate liquid of high MgO content following mechanical contact of the α particles and reaction between MgO and SiO₂. The temperature of the first liquid formation and its volume will depend on the relative amounts of MgO, surface SiO₂ (and therefore on α particle sizes) and of impurities which have diffused to the surface. Preferential solution of the α -lattice oxygen will occur together with Si, N and impurities (Al, Ca, Fe) which will reduce the liquidus temperature and increase the volume of liquid. The second stage involves the nucleation of new β -Si₃N₄ crystals at α /liquid interfaces, the α crystal being unstable on reduction in lattice oxygen. The nucleation density is very large due to the large total α -crystal surface area.

Growth of β crystals occurs into the liquid film by diffusion of Si and N atoms in the liquid phase following dissolution at the α -liquid interfaces adjacent to β nuclei. After a short period of growth the original morphological identity of α crystals is lost and the β crystals traverse the space previously occupied by the thin α laths, maintaining a liquid film adjacent to a number of hexagonal prismatic surfaces. Many of these planar β crystal surfaces will be rapidly eliminated by impingement with adjacent β crystals. For high MgO and high impurity content starting mixtures the amount of liquid remaining will be sufficient to maintain a large number of faceted β crystal surfaces.

In all materials the development of large β crystal facets will be a consequence of grain growth which results in an increase in the ratio of silicate liquid volume to grain surface area. A comparison of Figs. 4 and 9 indicates that grain growth may occur rapidly between 1500

and 1700°C.

The occurrence of isolated small β crystals, particularly in partially transformed specimens, may be explained either by a homogeneous nucleation process in regions of liquid with high Si and N concentrations or by a nucleation of β during cooling from the hot-pressing temperature. The latter process may occur if the Si and N solubilities are sufficiently temperature dependent to provide the supersaturation required for homogeneous nucleation of new crystals in addition to the growth of existing β grains.

5. Microstructure and mechanical properties

In conclusion, some of the implications of the microstructural analysis of hot-pressed silicon nitride in relation to its mechanical properties will be discussed.

It is believed that the preferred conditions for making a fine grained β -Si₃N₄ are the hot-pressing of thin lath-shaped and easily deformable α particles which have a large area of interface at which the transformation to β grains is nucleated. The occurrence of MgO or other metallic impurity ions is important in reducing the temperature at which a liquid silicate interfacial phase forms and enables the α to β conversion to occur via liquid phase transport. The optimum time and temperature for hot-pressing will be that for which the α to β transformation and accompanying densification are near to completion whilst still maintaining the small β crystal grain size required for high strength. The additional microstructural feature which results either from extended pressing time or from large additive and impurity content is that of a thick grain boundary silicate phase. This glassy, visco-elastic, phase will result in poor high temperature creep properties and, as indicated by a fracture surface analysis, predominantly intergranular fracture.

While the presence of a silicate liquid is known to be essential for a combined densification and α to β transformation, the effectiveness of the resulting glassy phase as a grain-boundary bond has not been established. Thus it is possible that the cohesion of this type of interface is greater than that of a pure large angle boundary between β -Si₃N₄ crystals in which the formation of a high strength, mainly covalent, bond requires that the nearest neighbour atomic spacings and interbond angles are maintained. The optimum microstructure may, therefore, be

that in which the silicate "phase" is only a few layers of atoms, sufficient to form bridging bonds between the atoms in adjacent grains which are frequently separated by distances much greater than their equilibrium crystal spacings. This condition might be approached by the formation of a silicate liquid of high Al_2O_3 content which would be partly removed by a solution of aluminium and oxygen in the $\beta\text{-Si}_3\text{N}_4$ structure with progress of the hot-pressing reaction. The residual grain boundary layer would be a high SiO_2 glassy phase.

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