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The Effect of Process Atmosphere on the Intergranular Phase in Silicon Nitride Ceramics

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Abstract

The influence of the process atmosphere in the gas pressure sintering of silicon nitride has been investigated, particularly with regard to formation of the intergranular phase. The intergranular phases identified after different gas pressure sintering cycles were compared with that present in a material fabricated by the hot isostatic pressing of an identical powder composition, allowing comparison of the two processing methods. The results suggested infiltration of the nitrogen processing gas into the sintering body, which adversely affected the intergranular phase formation in a composition that had been tailored for optimal mechanical behaviour. The duration of exposure to the processing gas and the post-sintering cooling cycle were identified as being critical factors in the intergranular phase crystallisation. Copyright © 1996 Elsevier Science Ltd

Introduction

The potential for improving the mechanical properties of silicon nitride ceramics arises from greater microstructural control, mainly achieved by finely tailoring the initial powder composition and optimising the fabrication conditions. As is well known, limitations to the possible high-temperature applications of these ceramics are mainly imposed by the properties of the residual intergranular phase formed after the reaction of sintering additives with the silicon nitride grains. The chemical composition of this phase is critically important to the overall oxidation resistance while the viscosity of the liquid phase, formed above the eutectic temperature, influences the microstructural development during sintering and also determines the interfacial characteristics that affect creep behaviour. A considerable amount of research has been carried out specifically related to the composition of the intergranular phase, with sintering additives being selected for the optimum combination of their ease of sintering and the compatibility of the residual phase with Si_3N_4 and its oxidation product, SiO_2. A well-known intergranular phase associated with improvements in high-temperature mechanical properties is $Y_2Si_2O_7$, which has been formed in hot isostatically pressed (HIPed) Si_3N_4 ceramics using a correctly balanced mixture of Y_2O_3 and SiO_2 sintering additives.[1]

The powder composition used for this investigation is one that has been well researched in HIPed ceramics and is associated with an absence of creep cavitation.[1] In the research presented here, the ceramics have been fabricated using gas pressure sintering (GPS), a less expensive form of fabrication, to enable the particular influence of the GPS processing method to be evaluated.

The GPS process allows unusually high temperatures to be reached during sintering while suppressing the thermal decomposition of Si_3N_4 via the application of external N_2 pressure. The high sintering temperatures encourage the β-Si_3N_4 grains to grow abnormally and this leads to enhanced fracture toughness from mechanisms of crack bridging and pull-out and to improved reliability of the final ceramic. The ceramic powders are not generally encapsulated during the processing, in contrast to the HIPing procedure where encapsulation typically results in some surface oxidation to Si_2N_2O due to the interaction of the ceramic powders with the glass encapsulant. This means that the ceramic phase formation is much more susceptible to the atmospheric effects of the processing environment. For example, Neidhardt *et al.*[2] found an oxygen/nitrogen gradient to exist in GPS-fabricated ceramics as a result of the reduction potential of the graphite sintering crucible in the nitrogen atmosphere.

Possible atmospheric effects of the nitrogen processing atmosphere on the intergranular ceramic phases were of particular interest in this investigation.

Experimental Procedures

The Si_3N_4 powder used was UBE SN-E10, with the initial oxygen content found to be 1·6 wt%. The composition prepared was 7·5 wt% Y_2O_3, 2·5 wt% SiO_2 and 90 wt% Si_3N_4. These powders were ball-milled together for 72 hours in propanol, then dried and cold isostatically pressed into billets at 90 MPa. Two-stage GPS was carried out at T & N, Rugby, at 1800–1900°C and 10–100 bar. Additionally, some fully densified material of the same composition, already fabricated by HIPing at 1775°C and 150 MPa, was processed further by GPS for comparison of the resulting intergranular phases and microstructure. After sintering, the phases present in the ceramics were evaluated using Cu K_α X-ray diffraction and the densities were determined according to Archimedes' principle. Annealing was carried out in argon, at 1200°C for 24 hours, to promote crystallisation of the glassy phases. For more detailed investigation by transmission electron microscopy (TEM), slices of the resultant ceramics were diamond-ground to a thickness of 30 μm, polished to a finish of $^1/_4$ μm and finally thinned to electron transparency by argon ion beam bombardment.

Ceramic Characterisation

The major phase identified in all the GPS-fabricated ceramics was β-Si_3N_4, indicating a complete phase transformation of the initial α-Si_3N_4 powder. However, it should be noted that the occurrence of this phase transformation during GPS is not necessarily accompanied by full ceramic densification.[3]

(i) Intergranular phase

The HIPed material contained α-$Y_2Si_2O_7$ as the intergranular phase prior to the additional GPS processing and was assumed to be fully dense. At the high sintering temperatures during GPS, the α-$Y_2Si_2O_7$ phase reverted to the liquid state and after GPS was recrystallised during post-GPS annealing at 1200°C, forming a mixture of β-$Y_2Si_2O_7$, α-$Y_2Si_2O_7$ and the 'y-yttrium silicate' phase,[4] with no evidence of the higher temperature γ-$Y_2Si_2O_7$ and δ-$Y_2Si_2O_7$ polymorphs. Figure 1 shows a comparison between the XRD spectra for the initial HIPed material and that from the same material after the additional GPS processing and annealing in air for 70 hours at 1200°C. After similar annealing treatments, the same intergranular phases were identified in the ceramics fabricated by GPS.

As was also found in the previous research on the HIPed Si_3N_4, carried out at Warwick and reviewed in Ref. 5, the post-sintering crystallisation of the residual intergranular phase was extremely sensitive to the cooling rate, with mainly glassy phase formation occurring at 'natural' cooling rates of 20–30°C/min. Therefore, the ceramics were annealed to promote crystallisation of the glassy phases. The results of this earlier research had shown that the β-$Y_2Si_2O_7$ polymorph tends to crystallise in the range 1500–1400°C at the slowest cooling rates inside the HIP furnace (4°C/min), with subsequent nucleation of the α-$Y_2Si_2O_7$ polymorph at temperatures below this. As the crystallisation proceeds, the likelihood of 'y-phase' formation is believed to increase as the liquid volume is reduced, which enhances the effect of impurities in stabilising this phase.[4] Liddell and Thompson[4] have discussed the various explanations for the 'y-phase' occurrence, attributing its formation either to localised, high concentrations of impurity ions in the intergranular glass, which give rise to crystallisation of a phase with formula $RY_5Si_6O_{21}$ where R represents the impurity cation or to the oxidation of the Y-Si-O-N intergranular glass.

It is well known that the simultaneous presence of both the α- and β-$Y_2Si_2O_7$ polymorphs is detrimental to the mechanical properties since tensile stresses are introduced by the different atomic volumes of the polymorphs causing isolated β-$Y_2Si_2O_7$ regions to be held in compression. From the earlier research,[5] the crystallisation of β-$Y_2Si_2O_7$ seemed to occur readily during the annealing (1200°C) of residual glassy phases, except in those cases where the α-$Y_2Si_2O_7$ phase had already crystallised and then remained stable. Once formed, the β-$Y_2Si_2O_7$ polymorph showed no tendency to transform into the α-$Y_2Si_2O_7$ phase and a mixture of β-$Y_2Si_2O_7$ and the 'y-yttrium silicate' has even been observed to remain after 500 hours at 1400°C. Hence, to tailor the intergranular phase for the optimal mechanical properties, it is apparent that formation of the most desirable α-$Y_2Si_2O_7$ polymorph and avoidance of β-$Y_2Si_2O_7$ are critically controlled by the post-sintering cooling cycle.

Further GPS runs were carried out to examine the frequency of the yttrium disilicate intergranular phase formation with some variations in the GPS thermal cycle. Some typical results following annealing from the different GPS runs are given in Table 1. The intergranular phases identified after the shorter sintering cycles were comparable with those formed after HIPing this composition and the GPS environment appears to have had little

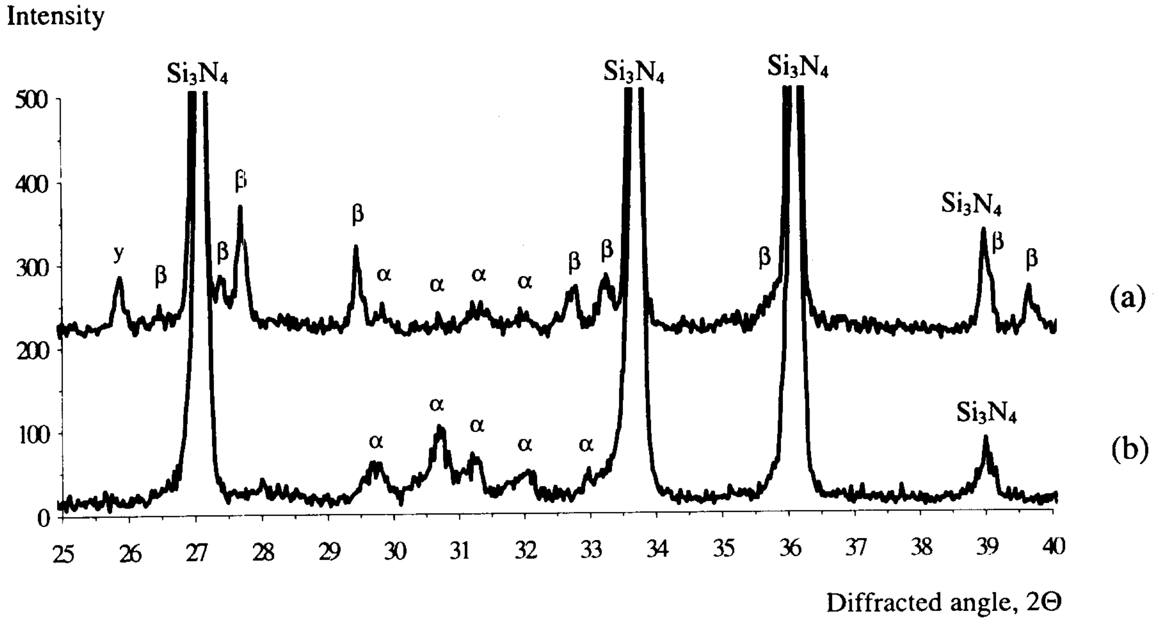

Fig. 1. XRD comparison of intergranular phases present in (a) HIPed material after additional GPS processing and annealing and (b) after HIPing only. Peaks marked 'α', 'β' and 'y' refer to α-$Y_2Si_2O_7$, β-$Y_2Si_2O_7$ and 'y'-$Y_2Si_2O_7$, respectively.

Table 1. Intergranular phase variation with different GPS cycles

	Temperature (stage 1) (°C)	*Pressure (stage 1) (bar)*	*Dwell time (stage 1) (h)*	*Temperature (stage 2) (°C)*	*Pressure (stage 2) (bar)*	*Dwell time (stage 2) (h)*	*Post-annealing intergranular phases*
1	1800	10	1	1900	70	1	α and β-$Y_2Si_2O_7$ and y-phase (trace)
2	1800	10	1	1900	100	1	α and β-$Y_2Si_2O_7$
3	1800	10	2	1900	70	1·5	β-$Y_2Si_2O_7$, y-phase, and apatite (trace)
4	1725	2	2	1900	100	2·5	Apatite and melilite
5	—	—	—	1900	65	6	Apatite and melilite
6	1880	10–20	4	1950	100	4	Melilite only

effect on the intergranular phase formation in these instances. However, from Table 1, it is apparent that the nitrogen content of the sintering liquid increased during longer exposures to the N_2 processing atmosphere, resulting in the formation of apatite ($Y_5N[SiO_4]_3$) and the more nitrogen-rich melilite ($Y_2Si_3N_4O_3$) phase, both of which are known to cause severe degradation in Si_3N_4 ceramics during oxidation. The nitrogen dissolution into the sintering liquid is believed to arise from gaseous infiltration of the processing gas, aided by the relatively high liquid phase content, and hence good interconnectivity between the Si_3N_4 grains and also from the partial decomposition of Si_3N_4 at internal pore surfaces. Kang and Greil[6] have investigated the influence of the gas pressure on densification during liquid phase sintering, finding that the difference between the internal pore pressure and exterior surface decreased with increasing applied gas pressure. Hence, the contribution of the internal Si_3N_4 decomposition to the nitrogen dissolution would be expected to become less significant with higher gas processing pressure and unlikely to occur during HIPing. Although one advantage of the GPS process over HIPing is that no encapsulation is required, an encapsulant might provide a protective barrier to prevent the formation of more nitrogen-rich phases in this composition during the longer 'stage 2' dwell times required to promote high temperature grain growth.

(ii) Constitutional variations

After prolonged GPS processing the HIPed material developed a mottled appearance, associated with a marked increase in porosity. Figure 2 is taken from a polished cross-section of the HIPed material after the additional GPS (there was no further heat treatment). This shows some evidence of gaseous evolution and as silicon and oxygen were the only elements identified by EDX analysis in this region, the oxygen being detected from the residual intergranular phase, it is believed that some thermal decomposition of the Si_3N_4 had taken place. This may result from a reducing atmosphere existing inside the graphite sintering crucible,[2] or may indicate that the applied nitrogen pressure was insufficient to suppress decomposition within the pores.[6]

In all the GPS-fabricated ceramics, some difference between the surface region and the bulk was visible as optically diffuse bands extending 50–100 μm from the outer surfaces. Figure 3, taken from a specimen fabricated in run 6 (see Table 1), illustrates the difference between the corresponding XRD spectra from the surface and the bulk regions and in which there is an apparent absence of any secondary phase in the bulk material. The reduction of any detectable crystalline intergranular phase in the bulk material was linked to a decrease in density from the surface to the bulk region, since the smaller quantities of the intergranular phase present in the central, porous regions were less easy to detect by XRD. An additional factor which may have inhibited the densification is the dissolution of nitrogen into the sintering liquid, which is believed to increase the liquid phase viscosity.[7]

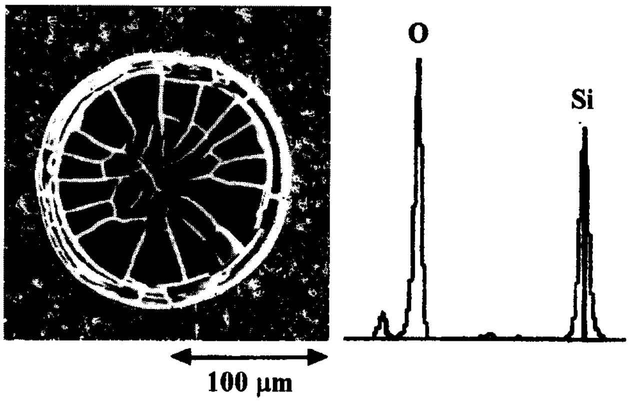

Fig. 2. Secondary electron microscope image showing evidence for a burst gas bubble, with EDX analysis from the central region.

The microstructure formed in this composition after GPS is shown in Fig. 4, taken from the same specimen as for Fig 3. The intergranular network is the phase of darker contrast surrounding the Si_3N_4 grains. The grain size variation seen in Fig. 4 is typical of GPS-fabricated Si_3N_4 and, unlike the more uniform, fine-grained microstructure observed in HIPed ceramics, contains some anisotropic grains of several μm in diameter, which may contribute towards an enhanced fracture toughness. Although the intergranular phase could not be detected by XRD from the central regions, TEM revealed pockets of the intergranular network, together with extensive porosity (not shown here). The intergranular phase in these regions was identified by electron diffraction as being the same nitrogen-rich phase as that present in the surface regions, suggesting that the nitrogen/oxygen ratio remained constant from the surface to the bulk. As the relatively high sintering liquid content in this composition provides a continuous network between the Si_3N_4 grains, this has enabled the uniform dissolution of the processing gas into this network.

Conclusions

The intergranular phases formed in the Si_3N_4 ceramics fabricated with this high-additive composition were found to vary according to the length of exposure to the N_2 processing gas, which evenly

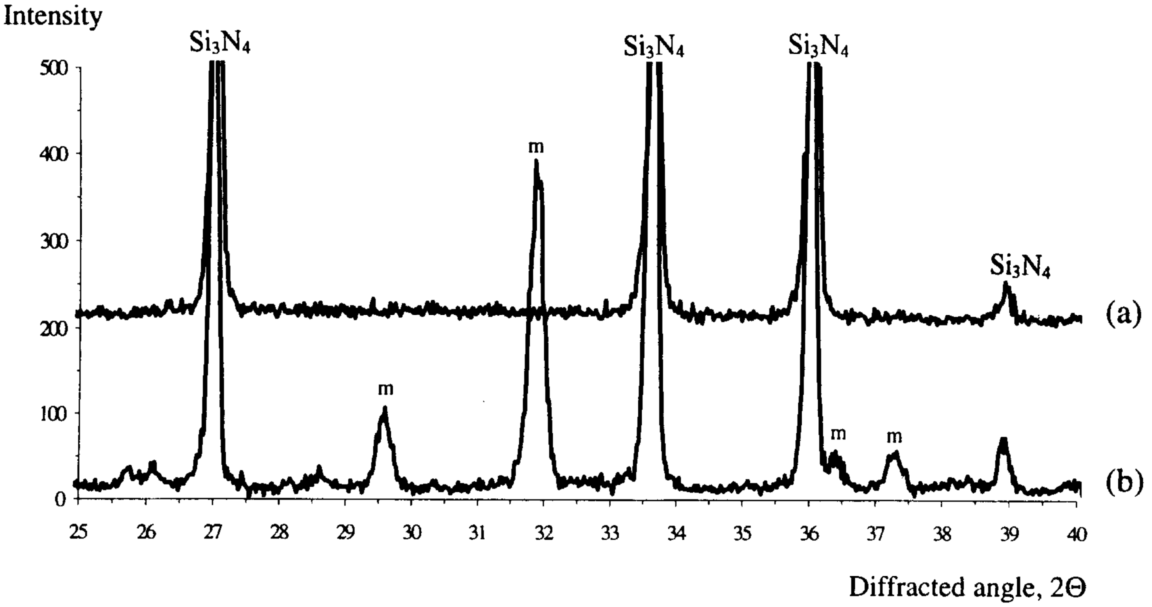

Fig. 3. Comparison of the XRD spectra from two different regions of a ceramic fabricated from GPS run no. 6: (a) a few hundred μm into the bulk and (b) the outer surface. The peaks marked 'm' identify the melilite phase present in this ceramic.

Fig. 4. TEM microstructure of a GPS-fabricated ceramic from run no. 6 (see Table 1), with electron diffraction pattern identifying the melilite intergranular phase.

infiltrated the sintering liquid. A substantial variation in the oxygen/nitrogen ratio was detected in the intergranular phase found in ceramics fabricated according to different GPS cycles, although no phase variation was identified within individual ceramic specimens. It was found that the formation of nitrogen-rich phases could be avoided only for the shorter GPS cycles, which were of insufficient duration to promote more pronounced grain growth than is typically observed in GPS-processed Si_3N_4.

The GPS process allows more rapid cooling than HIPing and the control of the post-sintering cooling cycle was found to have a significant influence on the intergranular phase formation. This was particularly important since the annealing treatments to promote crystallisation from a rapidly-cooled glass often resulted in an undesirable combination of the $Y_2Si_2O_7$ polymorphs.

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