New heat treatment methods for glass removal from silicon nitride and sialon ceramics

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Sialon ceramics were discovered simultaneously (but independently) in late 1971 at Newcastle University and also at the Toyota Research Laboratories in Japan. During the 30 years since their original discovery, the Newcastle laboratory has made a significant contribution to current understanding of the science and technology of these materials. Sialons are of interest as engineering materials for high temperature ($>1000°$C) applications because they can be pressureless-sintered to high density and be designed to retain good mechanical properties even up to $\approx1350°$C, whereas competing metallic materials are weaker and prone to corrosion. A characteristic disadvantage of all nitrogen ceramics is that an oxide additive is always included in the starting mix to promote densification, and this remains in the final product as a glassy phase distributed throughout the grain boundaries of the final microstructure. Since the glass melts at $\approx1000°$C, the high temperature properties of the final ceramic are in fact determined by the properties of the grain-boundary glass. The most common method of improving high-temperature performance is to heat-treat the material at temperatures of 1100–1350°C in order to devitrify the glass into a mixture of crystalline phases. More specifically it is desirable to convert the glass into a sialon phase plus only one other crystalline phase, the latter having a high melting point and also displaying a high eutectic temperature (max $\approx1400°$C) in contact with the matrix sialon phase. Previous studies have shown that there are a limited number of possible metal-silicon-aluminium-oxygen-nitrogen compounds which satisfy these requirements. The present paper gives an overall review of this subject area and then summarises recent work at Newcastle aimed at total removal of residual grain boundary glass. This has been achieved by: (1) a post-preparative vacuum heat treatment process to remove the grain boundary glass from silicon nitride based ceramics in gaseous form, (2) above-eutectic heat-treatment (AET) of sialon-based ceramics to crystallize grain-boundary liquid into five-component crystalline sialon phases.
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1. Introduction

Si_3N_4 based ceramics densified by liquid phase sintering contain a residual nitrogen-containing metal silicon oxynitride intergranular phase inherited from the sintering medium. This phase can be glassy (amorphous) or crystalline depending on factors such as overall composition and the applied cooling conditions.

Wötting *et al*. showed that the mechanical properties of silicon nitride based ceramics remain constant between room temperature and the softening temperature of the amorphous grain boundary phase and are mainly controlled by a combination of the effects of residual porosity, aspect ratio, amount of glassy phase (especially at room temperature), and only to a lesser degree by the growth of the silicon nitride grains [1]. Therefore optimization of mechanical properties at temperatures up to about 1000°C can be achieved by controlling the microstructure to consist of a high proportion of small grains with high aspect ratios.

However at higher temperatures, mechanical properties are strongly dependent on the nature of the grain boundary phase(s). Lange showed that the softening of the intergranular glassy phase at 900–1000°C was such that even small stresses are sufficient to cause extensive grain boundary sliding creep, subcritical crack growth and ultimate failure of the material after very

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short life times [2]. Raj and Ashby have reported that failure occurs at high stress levels by the nucleation of cavities in two or three grain junctions [3]. Cavity growth occurs by viscous flow or solution reprecipitation, and subsequent coalescence of facet-sized cavities into discrete cracks with subsequent crack extension to critical dimensions. Iskoe *et al.* also demonstrated that impurities such as calcium, which concentrate easily in the glassy phase, significantly impair the strength and creep performance of Si_3N_4 based materials [4].

Therefore the intergranular phase (especially if glassy) is critically important in determining the mechanical and chemical properties of silicon nitride based ceramics particularly at high temperature. It has been observed during the last 15 years by many researchers that the onset of creep deformation and degradation of strength in such materials can be significantly reduced or even eliminated by decreasing the amount of intergranular glassy phase or by modifying it to produce more refractory crystalline phases.

There have been several approaches used to decrease the amount of glassy intergranular phase in dense nitrogen ceramics or lessen its effect on high temperature properties, namely;

(a) use of densification aids which form liquids which display high solidus temperatures and have high viscosities [5–8],

(b) reduction in the amount of sintering additive and also in the level of impurities in the starting powders coupled with the use of more intensive sintering processes, such as HIP or GPS [9–12],

(c) selecting starting compositions in which the sintering aids can substantially dissolve in the Si_3N_4 lattice to form a single or low concentration second phase product [13],

(d) using controlled additions of other additives beside the main sintering additive [14, 15],

(e) by post fabrication sintering [16],

(f) devitrification of residual glassy phase by post-sintering heat treatments [17–20].

The most common and well understood method of modifying the grain boundary microstructure is that of devitrifying the intergranular glassy phase into a mixture of crystalline phases. The principle of heat treating nitrogen ceramics to remove (minimize) grain boundary glass and therefore improve the high temperature properties is well understood. However, a combination of thermodynamic instability, low eutectic temperatures, phase transformations and limited refractoriness cause a disappointing shortage of suitable refractory crystalline phases for Si_3N_4 and sialon ceramics. Therefore, many of the 5-component crystalline oxynitrides are only stable at low temperatures ($<1400°C$). Clearly there is scope for exploring systems in which alternative M-Si-Al-O-N compounds occur, and also for devising new methods of improving the refractoriness of dense sialon ceramics.

Ever since the initial production of dense silicon nitride by hot-pressing using oxide additives, researchers interested in getting the best high-temperature mechanical properties from this material have investigated methods of totally removing the residual grain-boundary glassy phase [21].

Initially, it was thought that the presence of some glass was inevitable because the surface silica on the starting silicon nitride grains could not be incorporated into the silicon nitride lattice; ways of producing a more refractory glass were therefore explored and the substitution of MgO by Y_2O_3 as the densifying additive allowed the softening temperature of the grain boundary glass to be increased by $≈150°C$, thereby achieving some improvements in refractoriness [22]. A further improvement was obtained by giving the grain-boundary glass a post-sintering heat-treatment to convert it into a mixture of refractory crystalline phases. This raised the temperature at which the mechanical properties of the final ceramic started to deteriorate by a further 100–200°C, the limit now being determined by the eutectic temperature in the appropriate M-Si-O-N system. The same procedure was applied to sialon ceramics, and whereas $≈850°C$ and $≈1000°C$ are typically the maximum operating temperatures for glassy MgO- and Y_2O_3-densified Si_3N_4 ceramics, crystallization allows this temperature to be raised to $≈1350°C$ in the case of ß-sialon-YAG ceramics. In these materials, Jasper and Lewis have shown that clean glass-free grain boundaries can be achieved by careful heat-treatment procedures [23]. However, the temperature of 1350°C, ever though a distinct improvement on previous glass-containing materials, is still far short of 1873°C, the decomposition temperature of silicon nitride, and also much less than 1650°C, the maximum use temperature of silicon carbide ceramics, the main competitors to silicon nitride for high-temperature engineering applications. More recently, HIPing and gas pressure sintering procedures have enabled nitrogen ceramics to be densified with much smaller amounts of oxide additive, and these materials show slight improvements in refractoriness compared with the materials described above [24].

Measurements of high temperature properties generally show a correlation between creep resistance and oxidation resistance. In both cases the glassy phase contributes to enhanced creep degradation and oxidation, with accelerated effects as the glassy phase softens and becomes a viscous liquid. Diffusion of the densifying cation to the surface of the sample during oxidation, leads to the formation of a low-melting, low viscosity liquid phase on the surface which allows much faster oxygen diffusion into the grain boundaries, with consequent rapid corrosion. Clearly, any technique which entirely removes the grain boundary glass prevents these degradative processes taking place, and if silica is the only oxidation product on the surface, the viscosity of this remains high enough up to temperatures in excess of 1600°C to perform a passivating role, so that good mechanical properties are retained up to these temperatures. Such materials can be regarded as stronger, tougher versions of silicon carbide and represent the ultimate limit in refractoriness and mechanical performance of silicon nitride.

This paper describes new heat treatment techniques aimed at improving the refractoriness and optimizing mechanical properties.

2. Vacuum heat treatment of nitrogen ceramics

Recent work at Newcastle has shown that residual grain boundary glassy phase in Si_3N_4 ceramics can be totally removed from samples densified using a relatively volatile metal oxide by a post-preparative heat-treatment in vacuum at temperatures some 200–300°C below the original sintering temperature [25–27]. In this case, the grain boundary M-Si-O-N phase, which is liquid at the vacuum heat-treatment temperature, boils off as a mixture of metal vapour, silicon monoxide and nitrogen, and this is accompanied by a slight shrinkage, as a result of which densities in excess of 99% of the theoretical density of silicon nitride can be retained. This is the first time that pure, dense, bulk samples of ß-Si_3N_4 have been prepared. The highest final densities are obtained using the least amount of sintering additive consistent with the achievement of a fully- dense initial sintered microstructure. Fig. 1a shows the centre of a sample of silicon nitride hot-pressed with 2% MgO after vacuum heat treatment. This is identical in appearance to the surface of the same sample etched in hydrofluoric acid to selectively remove grain-boundary glass (Fig. 1b) confirming that the glassy phase has been removed from the vacuum heat treated sample. The surface contrast is not porosity, but pullout of grains during sample preparation. Fig. 1c shows a micrograph of a sample of silicon nitride hot-pressed with only 0.5% of MgO, which exhibited less weight loss on vacuum heat treatment and gave a higher final density and a much smoother microstructure. Similar results can be obtained for sialon ceramics, but total removal of the grain-boundary glassy phase is more difficult, because removal of aluminium-rich species from grain-boundary liquid phases in the form of Al_2O requires higher temperatures than can be used, bearing in mind thermal decomposition of the sialon phase itself in vacuum.

During the course of this work, some experiments were carried out to study the effectiveness of hydrogen in the place of vacuum as an agent for the removal of grain boundary material. It was found that hydrogen (in a carbon environment) could satisfactorily remove volatile metals (e.g. Mg, Li), but the residual silica and nitrogen in the glass remained as the crystalline phase Si_2N_2O. This phase has comparable refractoriness to silicon nitride, and is therefore perfectly acceptable as an additional constituent of the microstructure, with the added advantage that it has a 10% lower density (2.82 compared with 3.20 g/cm^3), as a result of which it fills up a considerable amount of the grain boundary volume originally occupied by glass, and therefore less shrinkage is needed during the heat-treatment step to retain a good final density. Materials prepared in this way would be expected to show excellent creep and oxidation resistance up to temperatures in excess of 1450°C.

Fig. 1d shows a sample of silicon nitride hot pressed with 1% of MgO after post-preparative hydrogen heat treatment. The microstructure is much smoother than for vacuum heat treated samples, consistent with a lower weight loss and slightly lower final porosity. Fig. 1e is an EDX spectrum of this sample after sintering and Fig. 1f is the corresponding EDX spectrum after vacuum heat-treatment showing disappearance of the magnesium peak. All hydrogen treatments described in this work were carried out in a 90% N_2, 10% H_2 gas mixture.

Fig. 2 shows the Vickers microhardness (HV10) of silicon nitride hot-pressed with 1 and 2% MgO, compared with the same samples after VHT (i.e. zero %MgO) indicating that the heat-treated materials are harder than the as-sintered ceramic. This diagram clearly shows that previous statements of the hardness of α and ß-Si_3N_4/sialon ceramics should be modified to take into account the not inconsiderable changes in hardness due to different amounts of glassy phase in the microstructure.

Fig. 3 shows a low magnification optical micrograph of a sample of silicon nitride, hot pressed with 2% MgO and VHTed for 3 hours at 1575°C, after oxidation for 24 hours at 1650°C. The sample showed a weight increase of less than 1% and came out with only a slight glaze on the surface. Oxidation experiments at lower temperatures again showed negligible levels of oxidation. As expected, in the absence of a glassy phase, the oxidation of pure silicon nitride is slow, and a passivating layer of silica forms on the surface up to temperatures of ≈1600°C. In fact, the present work has shown that pure, dense silicon nitride oxidizes in a similar manner to high-purity, dense, silicon carbide.

Clearly the final vacuum heat-treated material is suitable for high-temperature applications, and it is anticipated that even though the room temperature strength will show some reduction compared with the as-sintered material, this strength will be retained up temperatures of at least 1500°C, and the formation of a pure silica layer on the surface in oxidizing atmospheres will give improved protection at these temperatures. More importantly, the absence of grain boundary phases prevents mechanisms of grain boundary diffusion of metallic species into the bulk of the sample, and therefore corrosion resistance with respect to gaseous environments is expected to be considerably improved compared with conventional materials. Thus, as regards molten metal attack (for example by aluminium, copper, steel), reduced corrosion is expected, because the main agent of attack is the oxide slag on the molten metal which reacts with glassy/liquid grain boundary phase in the silicon nitride ceramic. This mechanism can now no longer occur, and even though attack of the silicon nitride via silicide formation may possibly still take place, the rate of material degradation will be considerably reduced compared with conventional materials. In this context, it should be mentioned that vacuum heat-treated material is essentially a dense form of reaction-bonded silicon nitride (RBSN), which is already used widely as a container material for molten aluminium. It is unlikely that vacuum-heat
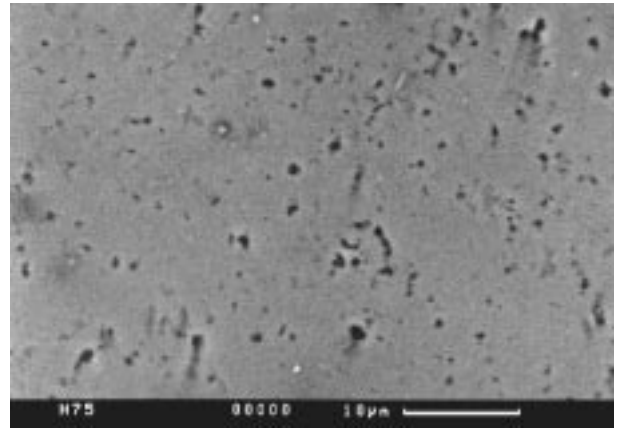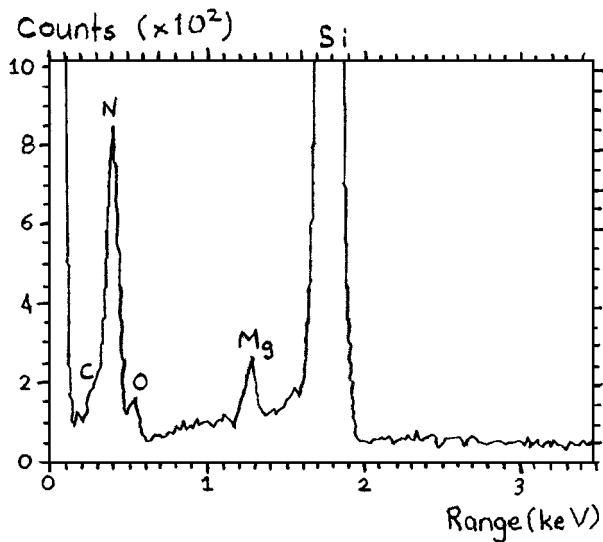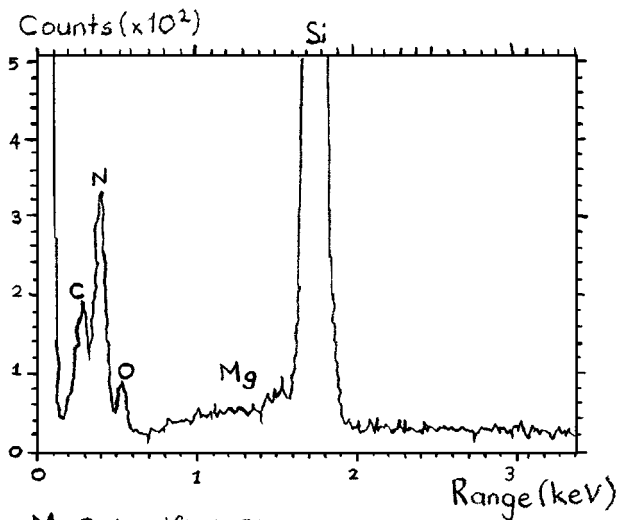
(a)

(b)

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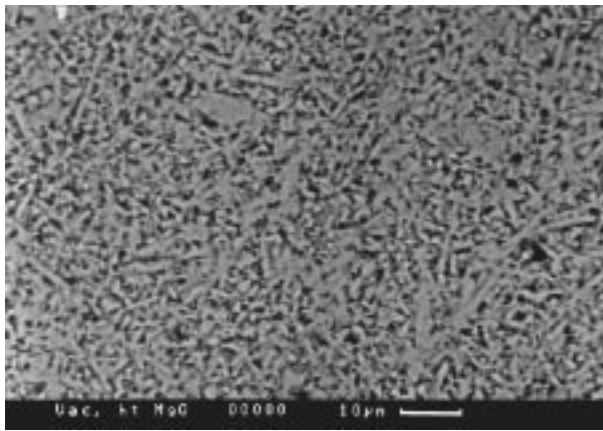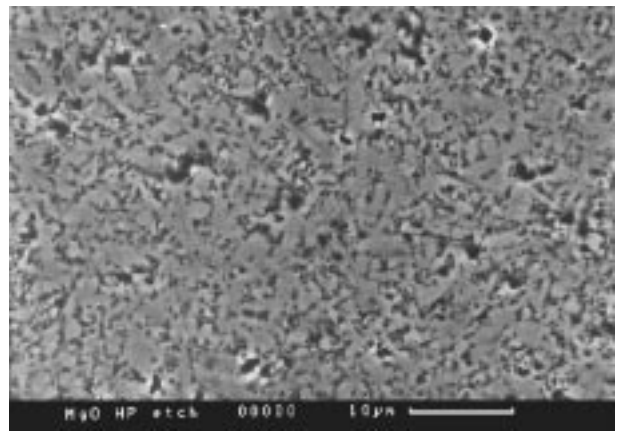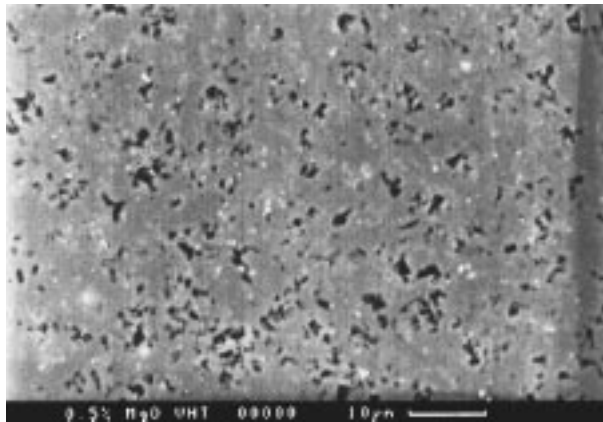
(f)

Figure 1 SEM micrographs of Si_3N_4 (a) hot-pressed with 2 w/o MgO and vacuum heat treatment at 1575°C for 3 hours, (b) hot-pressed with 2 w/o MgO and etched in 40% HF for 10 seconds, (c) hot-pressed with 0.5 w/o MgO and vacuum heat-treatment at 1575°C for 3 hours, (d) hot-pressed with 2 w/o and heat treated in 90%N_2/10%H_2 at 1650°C for 4 hours and EDX spectra for (e) Si_3N_4 hot-pressed 2 w/o MgO, and (f) the sample shown in (a).

treated material will out perform RBSN for the latter application, and in any case the cost of VHTed material is significantly higher. However, for liquid copper and liquid steel, the improved strength of the VHTed material and the absence of pores in RBSN are significant advantages that are expected to lead to improved performance.

3. Above-eutectic heat treatment of sialon ceramics

An important strand of nitrogen ceramic research has been the development of materials which can be sintered to full density by pressureless sintering and which at the same time retain good mechanical properties up to high temperatures. These aims are to some extent
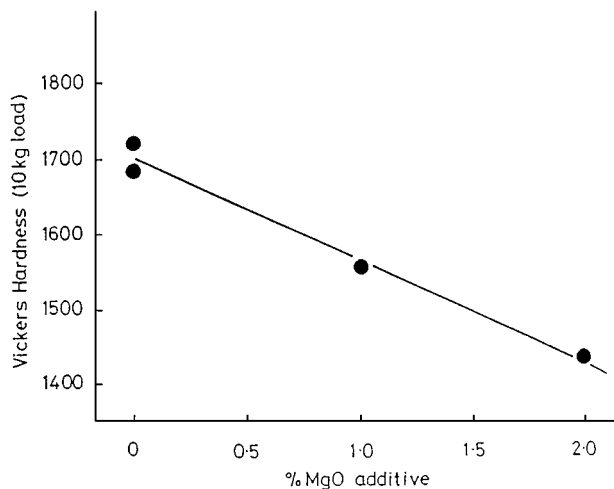
Figure 2 Hardness (HV10) data for hot-pressed and VHTed Si_3N_4 ceramics densified with MgO.
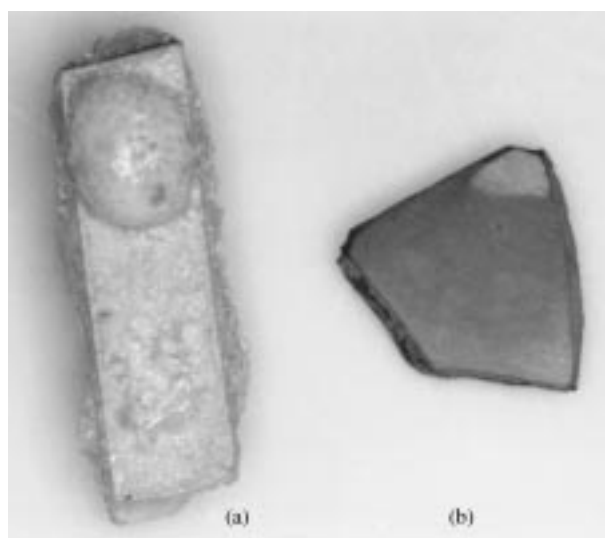

Figure 3 2% MgO hot-pressed Si_3N_4 oxidized for 24 h at 1650°C (a) as sintered, (b) after a post sintering heat-treatment for 3 h at 1575°C.

mutually exclusive, and whereas sialon ceramics can be pressureless-sintered to full-density at ≈1750°C, the eutectic temperature of ≈1350°C in the final ceramic represents a maximum temperature for strength retention. On the other hand, silicon nitride ceramics (i.e. materials which contain no aluminium) can retain their properties up to higher temperatures, but require pressure-assisted techniques for densification. Given the choice between a silicon nitride and a sialon ceramic, most manufacturers would in general prefer a sialon, because of the ease of densification; the challenge then remains of finding ways of achieving improved refractoriness of the resulting sintered materials. A considerable amount of know-how exists on the conversion of residual glass in sialon ceramics into crystalline grain-boundary phases.

For most sialon ceramics, conventional grain boundary devitrification is carried out between 1200 and 1400°C, i.e. below the eutectic temperature of the system, in the same way as for producing glass-ceramics [17]. This process, in most cases, involves a phase transformation from a low density glass to a high den-

sity crystalline phase or phases and often creates small pores at interfaces as a result of volume reduction after devitrification. Another limitation of this below-eutectic temperature (BET) heat-treatment method is that many suitable crystalline phases have to be excluded from consideration in grain boundary designs simply because their compositions are outside the glass forming region. The system itself selects which phases are stable, even though depending on the devitrification temperature, there is some choice of the final product. As a general rule, the resulting phases are either pure oxides (e.g. $Y_2Si_2O_7$, YAG, mullite in the Y-Si-Al-O-N system), or oxynitrides of high O:N ratio. Although various crystalline grain boundary phases have been studied, there has not been one that satisfies the combined requirements of refractoriness and chemical and environmental stability above 1350°C, a critical temperature for engine applications. In the different systems explored, YAG ($Y_3Al_5O_{12}$) has been one of the best possibilities as an intergranular phase for commercial ß-sialon [28] and α-β-sialon composites [29]. For ß-sialon-YAG materials, creep properties are significantly improved up to 1300°C compared to ß-sialon glass materials, but due to oxidative degradation above this temperature as the YAG reacts with SiO_2 to form a low melting liquid giving poor high-temperature creep properties, the ceramic is limited to operating temperatures below 1350°C [30]. Recent work on microstructural tailoring of YAG-containing α-β-sialon composites containing very limited amounts of residual glass at the grain boundaries after devitrification, has shown that the oxidative reversion of YAG to the liquid state still makes the materials unlikely to perform beyond 1350°C [31].

A route for increasing the refractoriness of these materials is to replace the oxide/oxynitride phases produced during devitrification with alternative phases of higher N:O ratio which have compositions on the nitrogen-rich side of the eutectic in these systems. This principle is well-known in oxide systems, and for example in the CaO-SiO_2 system, compositions on the SiO_2-rich side of Ca_2SiO_4 exhibit liquid phase at temperatures above ≈1450°C, whereas compositions on the CaO-rich side of Ca_2SiO_4 exhibit partial melting at ≈2000°C [32]. In composite ceramics containing CaO and SiO_2, for good refractoriness it is important to adjust the CaO:SiO_2 ratio to lie in the correct phase region.

In nitrogen ceramic systems, very little work has been carried out on oxynitrides with high N:O ratio. The only promising phase of this type in M-Si-Al-O-N systems (M = Y, Ln), is nitrogen melilite of formula $M_2Si_{3-x}Al_xO_{3+x}N_{4-x}$. Recent work has established that the melilite composition which exhibits maximum Al + O substitution (M′) in the low atomic number rare earth nitrogen melilites ($x = 1$ in the above formula) corresponds very closely to the maximum solubility limit of nitrogen in M-Si-Al-O-N liquids in these systems [33–36]. By careful control of starting composition, it is therefore possible to sinter a sialon composition such that it retains a grain-boundary liquid of this composition, which after subsequent crystallization can be converted into M′. The resulting sialon-M′

microstructure would be expected to show good refractory properties, because the eutectic in this system is close to the M' melting point and experiments have shown this to be ∼1750°C. In fact, previous work has shown that the M' phase crystallizes out of grain boundary liquid at temperatures above the eutectic temperature (AET) and in the range 1450–1650°C [33–35]. Since the nitrogen content of the liquid at these temperatures is high, it is possible to convert essentially all of it into M'. The principle of crystallising liquid into crystalline grain boundary phases (as compared with

(a)

(b)

(c)

Figure 4 Back scattered SEM images of Sm_2O_3 densified α-β sialon ceramic after (a) sintering at 1800°C for 2 h, (b) Below Eutectic Temperature (1350°C for 24 h) heat treatment and (c) Above Eutectic Temperature (1500°C for 8 h) heat treatment.

devitrifying glass) has not been explored fully, but has the advantage that the process is much faster and with careful selection of starting compositions, can be arranged to give a negligible amount of residual liquid phase.
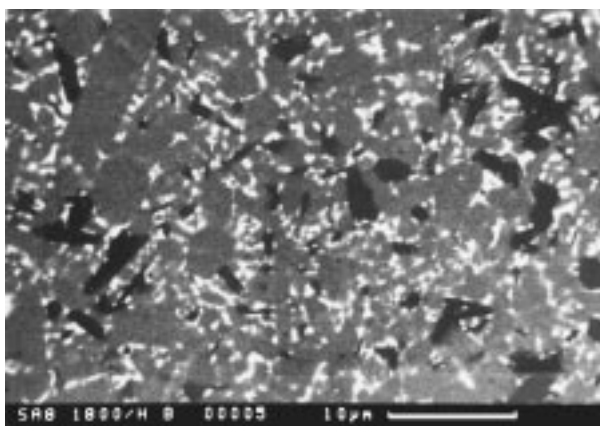
Fig. 4 shows back scattered SEM images of Sm_2O_3 densified α-β sialon ceramic after (a) sintering at 1800°C for 2 h, (b) BET (1350°C for 24 h) heat treatment and (c) AET (1500°C for 8 h) heat treatment.

The above process cannot be applied as easily to ß-sialon ceramics, because ß-sialon is not in equilibrium with the M'-phase at sintering temperatures. Therefore, recent work has focused on α-sialon ceramics and (preferably) mixed $\alpha + \beta$ sialon ceramics as the relevant matrix phase, in which M' is then produced as the grain-boundary phase. The additional advantage of the latter system, is that two phase α-β materials can be further tailored by selection of $\alpha : \beta$ ratio to give a pre-selected combination of mechanical properties.

An objection which might be raised, and perhaps the reason why so little work has been carried out on M (M') as a grain boundary phase for silicon nitride ceramics is that extensive previous studies showed that dense Si_3N_4 ceramics containing ≈15 vol% of yttrium nitrogen melilite show catastrophic cracking on oxidation at ≈1000°C [37]. Quantitative studies showed that this phenomenon arises because of the large amount of this phase in these materials, and also because of the 30% specific volume increase which takes place on oxidation. Further work has shown that the aluminium-containing M' phase exhibits much less specific volume change on oxidation than the Al-free M phase, because of the increased amount of mullite in the product compared with low density silica. Moreover, in the present materials, the volume of M' phase can be controlled to very small levels, because most of the densification additive is incorporated into the α-sialon phase, leaving a relatively small volume of grain boundary liquid to be crystallised into the M'-phase. Recent studies have shown no evidence of catastrophic cracking during oxidation of $\alpha + \beta$ sialon-M' ceramics at 1000°C. This is an important advantage of these materials, because during creep testing in air, oxidation resistance is also assessed. Creep testing of nitrogen ceramics is
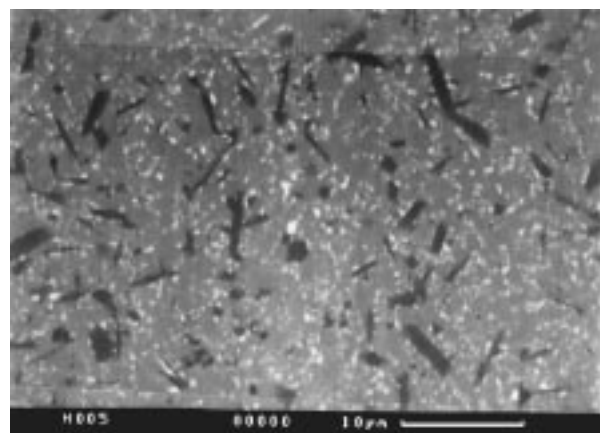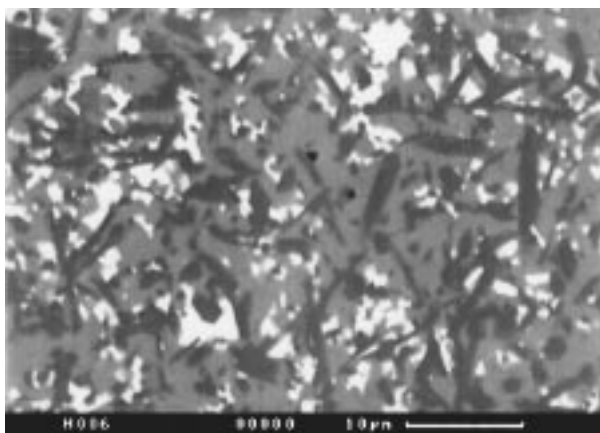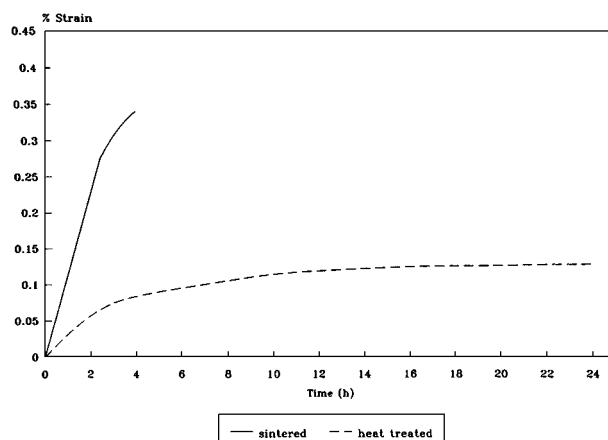

Figure 5 Creep strain versus time for Sm_2O_3 densified α-β sialon material after post sintering heat treatment.

normally carried out at temperatures up to $\approx 1350°$C, because residual glass in the sample is fairly soft at these temperatures, and eutectic liquid formation results in rapid fall-off in mechanical integrity. However, in the present case, heat treatment of the sample above the eutectic temperature results in very little residual glass, and creep measurements at 1600°C for 24 hours under 77 MPa, exhibited total creep strains of less than 0.12 (see Fig. 5). This is a formidable result, and confirms that these materials have definite promise for use at higher temperatures compared with more conventional sialon ceramics which contain alternative crystalline phases, and exhibit eutectic melting below 1400°C.

4. Conclusions

A better understanding of the phase relationships, stabilities of crystalline phases, microstructures and reaction chemistry in silicon nitride based ceramics has allowed improvement of high temperature mechanical performance and oxidation resistance in these systems by development of new heat-treatment techniques. Thus the heat treatment in vacuum or hydrogen of samples which have been densified with volatile cations (e.g. Mg) allows all the glass to be removed in gaseous form, whilst retaining densities in excess of 99% of theoretical. These materials offer improved hardness and oxidation resistance up to 1600°C and show no fall of mechanical properties in the range 1000–1400°C. Such ceramics exhibit the intrinsic properties predicted for silicon nitride when it was originally developed, but which have never been observed (apart from in selected CVD-based materials) because of the problem of grain boundary glass. In a similar way, above-eutectic temperature (AET) heat-treatment of Y, Ln densified sialon compositions has allowed the formation of essentially glass-free α-sialon + M$'$ and (α-β-sialon) + M$'$ ceramics which also show improved creep and oxidation resistance at temperatures of up to 1600°C. The development of these materials represents an important landmark in the improvement of processing techniques for nitrogen ceramics.

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