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Crystallization of Mg-containing phases in ß′-Si-Al-O-N ceramics

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The microstructures of β'-Si–Al–O–N ceramics of base composition $Si_4Al_2O_2N_6$ with large MgO additive (6 to 7 wt %) have been compared in the hot-pressed and sintered conditions. In both ceramics Mg shows only a small solubility in β' crystals and is mainly segregated in a "matrix" phase. In hot-pressed materials this is an Mg–Al-silicate glass whereas in sintered materials, inhomogeneities in composition and internal cavities are believed to catalyse its crystallization as the spinel phase ($MgAl_2O_4$ with partial Si substitution). A minor phase in sintered ceramics is the 15R "polytype" of the AlN structure.

1. Introduction

In a previous paper, describing the evolution of a single-phase hot-pressed Si–Al–O–N ceramic [1], the importance of solid-solubility of the components of a liquid-phase sintering addition (e.g. MgO, SiO_2) was discussed in relation to the problem of avoiding residual grain-boundary phases. For β'-Si–Al–O–N ceramics having compositions given by the general formula $Si_{6-x}Al_xO_xN_{8-x}$, derived from the substitution of Al and O in the β-Si_3N_4 crystal, it is possible that Mg forms a series of solid solutions corresponding to its substitution for Si or Al given by the composition surface $Si_{6-x}Al_{x-s}Mg_sN_{8-(x+s)}O_{x+s}$ indicated in Fig. 1.

In this paper the question of Mg solubility is explored for a series of compositions with varying MgO additive level, based on the $x = 2$ Al substitution level in β' crystals. The observation of limited solubility and of a partitioning of Al between β' and a substantial volume of, initially liquid, second phase has motivated the exploration of pressureless sintering as an alternative fabrication route for two-phase ceramics based on the β' structure. The microstructure of these sintered Si–Al–O–N ceramics has been studied by electron microscopy, diffraction and X-ray microanalysis.

2. Mg solubility in β'

Hot-pressed ceramics prepared (at 1800° C) from appropriate mixtures of the four components Si_3N_4, AlN, SiO_2 and Al_2O_3 together with variable amounts of MgO (2 to 7% by weight) were sectioned and ion-beam thinned for electron microscope examination. An increasing volume fraction of matrix glassy phase, surrounding β'

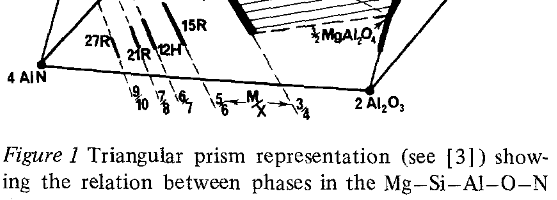

Figure 1 Triangular prism representation (see [3]) showing the relation between phases in the Mg–Si–Al–O–N system which are stable at hot-pressing/sintering temperatures of 1700 to 1800° C (β', 15R etc.) and terminal compounds (Si_3N_4, AlN etc.) used in the ceramic processing. The shaded plane represents the crystal substitution of Mg on Si (or Al) sites in β' given by the general formula $Si_{6-x}Al_{x-s}Mg_sN_{8-(x+s)}O_{x+s}$.

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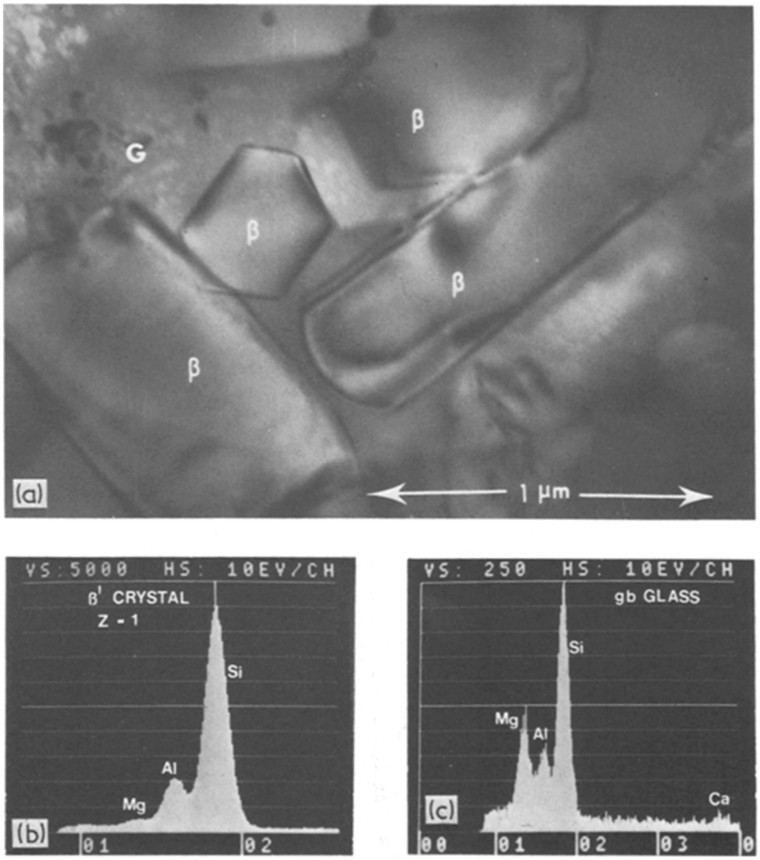

Figure 2 (a) Transmission electron micrograph (TEM) of a hot-pressed ($x = 2$) β'-Si–Al–O–N containing 7%MgO. X-ray microanalysis spectra (EDAX) from β' and glassy phases are shown in (b) and (c) with vertical scales 5000 and 250 counts, respectively.

crystals, was observed with increased MgO concentration. Fig. 2a, from the 7% MgO material, is an example of the typically faceted hexagonal prism β' morphology formed in the presence of a large silicate liquid content. Energy dispersive X-ray spectra (Fig. 2b and c) confirm that nearly all Mg ions and part of the Al ions are segregated to the liquid silicate during hot-pressing. X-ray lattice parameter measurements on β' confirm that the crystals have an Al substitution level $z = 1$. (There is a progressive decrease in Al substitution level with increased MgO additive and hence with amount of liquid silicate.)

Hence the Mg solubility in β' appears to be small (just detectable above background to the EDAX spectrum) i.e. solid solutions do not extend very far to the Si_3N_4–spinel join in Fig. 1. However, these materials with large liquid silicate volume may be readily hot-pressed to theoretical density and, because of the additional observation of "spinel" ($MgAl_2O_4$) X-ray diffraction lines, similar ceramics have been prepared by pressureless sintering.

3. Sintered microstructures

Powder charges for sintering were prepared by colloid milling mixtures of Si_3N_4, AlN and Al_2O_3 in proportions corresponding to the $x = 2$ β' substitution level with ~ 6 wt % MgO. This composition is similar to one of the hot-pressed series analysed above and lies on the β'-spinel ($MgAl_2O_4$) join (Fig. 1). The dried powders were preformed by cold isostatic pressing in rubber envelopes at a pressure of $140\,MN\,m^{-2}$. The preforms were sintered in a bed of boron nitride within a graphite crucible and r.f. susceptor using a thermal cycle of 1 h to 1800° C, 1 h isothermal sintering, then "furnace" cooling by switching off the r.f. power.

The microstructure contains two main phases; β' in faceted hexagonal prism morphology and a crystalline "matrix" of spinel. The phases are difficult to distinguish in randomly oriented sections because of their fine distribution and are best imaged in bright or dark field (Fig. 3a and b) when the spinel matrix is multiply diffracting (Fig. 3c or d). This is facilitated by the unexpected property of the spinel having constant orientation over many β' grain spacings. The mean β' grain size is smaller than in single-phase hot-pressed materials [1], indicating the grain-growth inhibiting effect of the initially liquid second phase. There is also a rounding of β' grain corners and incursions of spinel phase into their faceted surfaces, a property less noticeable when the matrix is non-crystalline (Fig. 2).

The cubic spinel phase is positively identified via series of electron diffraction patterns recorded with different goniometer angles (Fig. 3c and d). Its lattice parameter is measured from such patterns as 8.2 Å, which is slightly larger than the pure $MgAl_2O_4$ value of 8.08 Å. Also, fine-probe X-ray analysis (Fig. 3f) indicates a partial substitution of Si such that the ratio $(Al + Si)/Mg \approx 2$. There is a further indication of substitution from the irradiation damage which appears as a fine "speckled" contrast on long exposure to the electron beam (Fig. 3b). This is not a feature of unsubstituted spinels [2]. It is probable that a substitution of Si for Al in the spinel is accompanied by the substitution of N for O, to maintain charge balance as in β' crystals.

β' crystals show a small Mg solubility, similar to hot-pressed materials, but a variable and generally higher Al substitution level up to $x \sim 2$ (Fig. 3e).

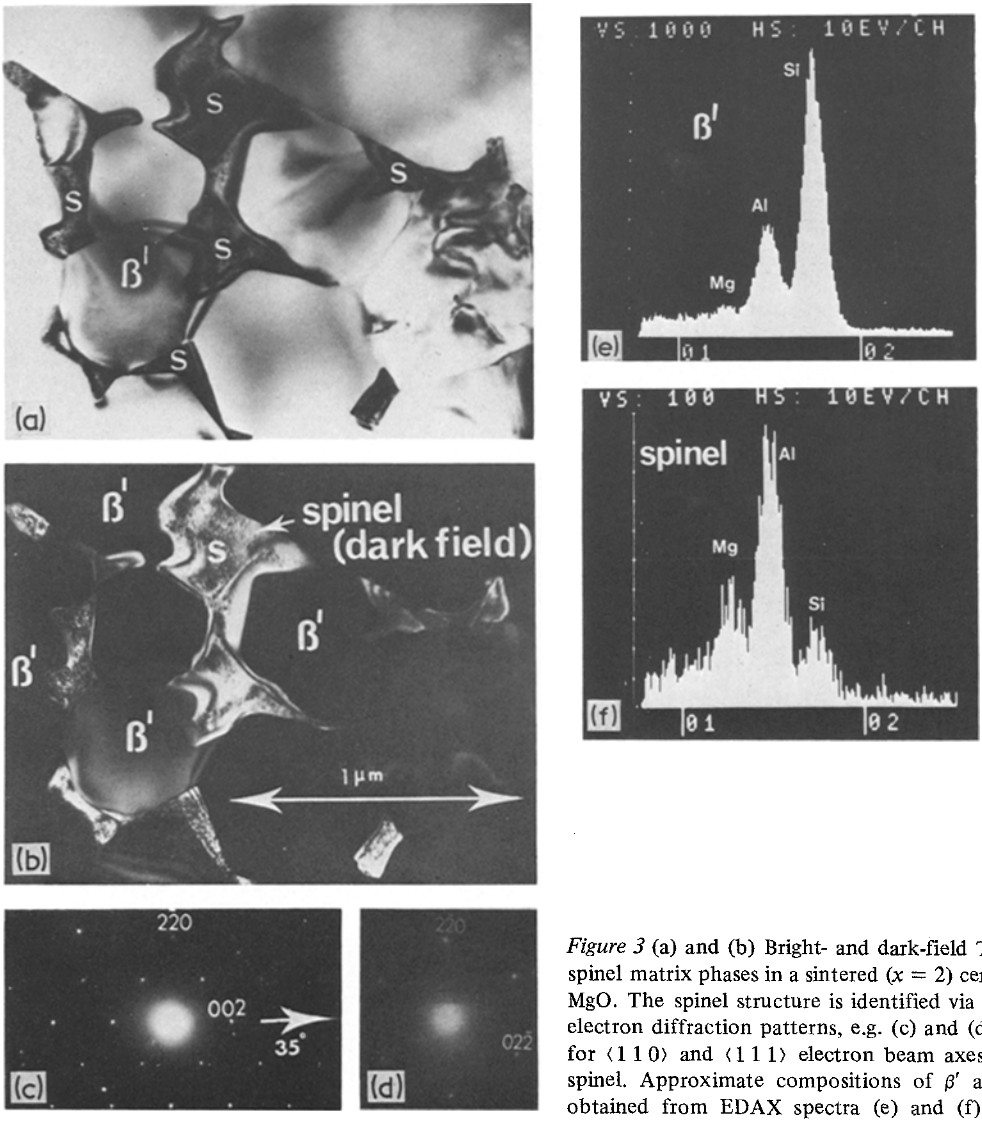

Figure 3 (a) and (b) Bright- and dark-field TEM of β' and spinel matrix phases in a sintered ($x = 2$) ceramic with 6% MgO. The spinel structure is identified via a sequence of electron diffraction patterns, e.g. (c) and (d) are patterns for ⟨1 1 0⟩ and ⟨1 1 1⟩ electron beam axes in the cubic spinel. Approximate compositions of β' and spinel are obtained from EDAX spectra (e) and (f) with vertical scales 1000 and 100 counts, respectively.

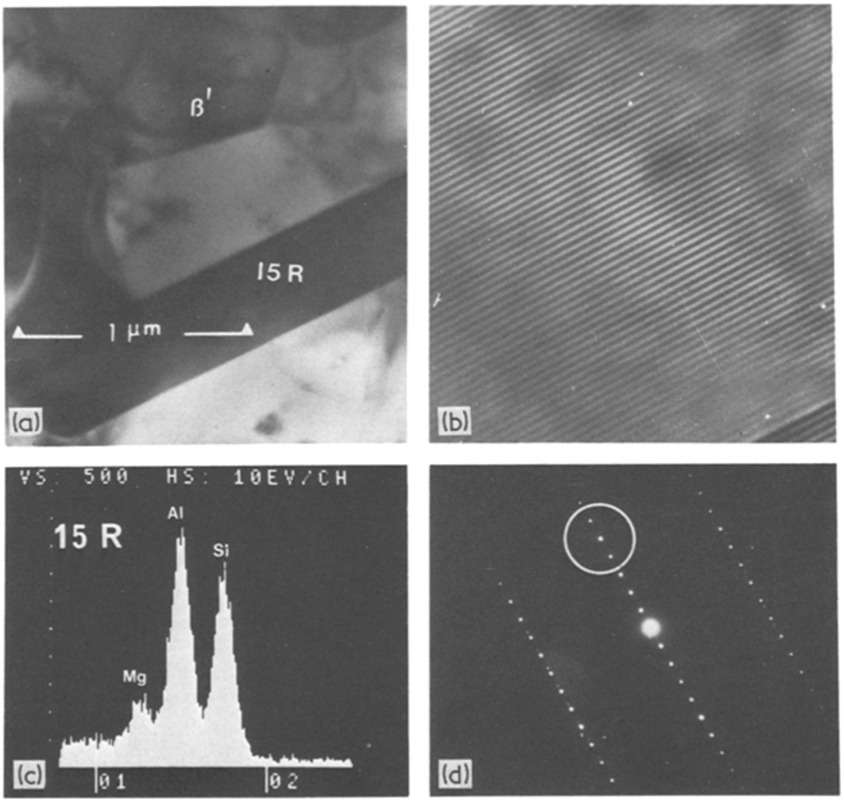

Figure 4 The sparsely distributed 15R "polytype" phase, identified via its plate-like morphology (a) and ~ 1.5 nm spacing lattice image (b) recorded using the set of systematic reflections ringed in (d). The EDAX spectrum (c) from 15R shows a Mg solubility higher than for β' (vertical scale 500 counts).

Interspersed with β' grains is a sparse distribution of isolated plate-shaped crystals (Fig. 4a) which may be identified via electron diffraction or "lattice" imaging (Fig. 4b and d) as the 15R "polytype" of the AlN "wurtzite" structure [3, 4]. The lattice image, spacing ~ 14 Å, was recorded in dark field using three reflections from the systematic row of $0 0 l$ reflections (Fig. 4d). The "polytypes" occur at nearly constant metal/non-metal atom ratio M/X, but with variable composition along these lines of constant M/X (Fig. 1). The analysed composition is variable and usually has an Si/Al ratio greater than given in diagrams such as in [3]. The Mg solubility in 15R is much greater than in β', which may be important in achieving single-phase structures in ceramics based on the polytypes to which MgO sintering additives are made.

4. Discussion

A comparison of β' and matrix-phase morphology (Figs. 2 and 3) indicates that β' in both hot-pressed and sintered ceramics grows within a liquid-"silicate" sintering medium following solution of α-Si_3N_4, as previously descibed [1, 5]. Minor differences in thermal cycle (probably a slower specimen cooling rate in the sintered ceramic) and inhomogeneities in composition due to differences in initial mixture (three components in place of four) have encouraged, (i) nucleation and growth of isolated 15R polytype crystals in place of β' during sintering, and (ii) crystallization of the matrix phase during the later stages of sintering or on cooling from 1800° C. A spinel phase is the expected crystalline product since it dominates the liquidus surface of the MgO–Al_2O_3–SiO_2 phase diagram above ~ 1600° C and has been detected within the glass-forming matrix of Fig. 2. Nucleation of crystallization is catalysed at free surfaces, possibly enhanced via surface composition change due to loss of Si and O to the vapour phase as SiO. Internal cavities in sintered ceramics behave similarly and are present during the cooling process, final densities being ~ 3.04 to 3.10 g cm^{-3} compared with a theoretical density of ~ 3.13 to 3.15 g cm^{-3}, for the estimated β'/spinel fraction. This may explain the low crystallization-nucleation density which results in large volumes having a constant orientation (Fig. 3). In an homogeneous matrix one would expect that the β'-matrix interfaces would act as efficient heterogeneous nucleation sites and produce a spinel "grain" size comparable with that for β'.

A preliminary survey of these Si–Al–O–N ceramics in the as-sintered condition shows moduli of rupture of 300 to 350 MN m^{-2}, which are inferior to those for hot-pressed ceramics and probably cavity-dominated. High-temperature creep, which is usually an intrinsic property of the microstructure (i.e. not "critical flaw" dominated), shows a strain rate at ~ 1230° C and 55 MN m^{-2} slightly inferior to that for HS 130 Si_3N_4 but much improved in relation to the HS 110 grade. These properties have been easily surpassed in sintered Si–Al–O–N ceramics recently prepared with large Y_2O_3 additions. The evolution of microstructure in these materials will be described in a separate publication.

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