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Nucleation and growth of β′-magnesium sialons and their composition limits

S. WILD, G. LENG-WARD
Department of Civil Engineering and Building, The Polytechnic of Wales, Pontypridd, Mid Glamorgan, UK

M. H. LEWIS
Department of Physics, University of Warwick, Coventry, UK

Previous reports on the solubility of magnesium in β′-sialons have been conflicting. The present work shows conclusively that crystalline magnesium sialons with the β silicon nitride structure do exist. They are formed by crystallization of magnesium sialon glasses at low temperatures. β″-magnesium sialon crystals nucleate on β′-sialon nuclei which are themselves formed by precipitation from Mg–Si–Al–O–N liquids at high temperatures. The current results suggest that β″-magnesium sialons exist only over a limited composition range within the 3M/4X plane of the Mg–Si–Al–O–N system, which is indicative of some form of ordering within the β″ structure. Although the compositions investigated in the present study are unstable with respect to forsterite above about 1000° C, the possibility of producing β″-magnesium sialons which are stable at much higher temperatures cannot be fully discounted at present.

1. Introduction

1.1. Densification of silicon nitride

Pure silicon nitride powder will not sinter at high temperatures. Therefore, in order to fabricate a fully dense, high-strength, body from silicon nitride it is necessary to employ liquid-phase sintering, the liquid frequently employed being a nitrogen-containing magnesium silicate. Such a mechanism was first suggested by Wild *et al.* [1] in their discussion of the role of magnesia additions in hot-pressed silicon nitride. They claimed that the magnesia reacts with surface silica on the α-silicon nitride powder to form forsterite which subsequently reacts with α-silicon nitride itself to produce a liquid magnesium silicate and β-silicon nitride. The liquid acts as a flux by which pores are removed during pressing and also provides a medium which facilitates diffusion and mass transport during the $\alpha \rightarrow \beta$ transformation.

Subsequent work has broadly confirmed this suggestion. From observations using TEM on thin films of hot-pressed silicon nitride with MgO additions Drew and Lewis [2] have shown that many β grains are adjacent to a small volume of non-crystalline phase. The amount of non-crystalline phase decreases with decreasing amounts of MgO additive and for small additions appears only at triple junctions of adjacent grains. The grain size of the β grains is of the order of 0.1 to 2 μm, although a small number of larger grains are also observed. These observations support earlier work of a similar nature by Evans and Sharp [3]. More recent work by Clarke and Thomas [4] employing high-resolution electron microscopy lattice-imaging studies also confirms the existence of a non-crystalline second phase which is heterogeneously distributed appearing especially at multiple grain junctions. Lou *et al.* [5], in a similar study, claim that the glassy phase forms a continuous grain-boundary film surrounding all of the grains.

The possibility of significant amounts of magnesium going into the solid solution in the β-silicon nitride has been discounted by Auger electron spectroscopy studies of hot-pressed silicon nitride fracture surfaces [6]. This shows

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the magnesium to be concentrated in the fracture surface, the concentration dropping off to zero after about 20 Å thickness, hence confirming that the magnesium is contained mainly in the grain-boundary glassy phase.

From their microstructural observations, Drew and Lewis [2] proposed a mechanism for the $\alpha \rightarrow \beta$ transformation whereby Si and N are transported from α grains through a silicate liquid phase to β nucleation sites at either α-liquid interfaces, or homogenously nucleated β grains. This type of mechanism was also proposed by Brook *et al.* [7] who concluded, from a study of densification and $\alpha \rightarrow \beta$ transformation rates, that both the densification and the $\alpha \rightarrow \beta$ transformation are controlled by diffusion through a grain-boundary amorphous phase.

All the discussion thus far has concerned hot-pressed silicon nitride. The presence of the reactive liquid phase should, however, promote sintering and densification without the application of pressure. It has been shown [8, 9] that densification can, in fact, be achieved by pressureless sintering although weight losses due to the volatilization of SiO and MgO can present serious problems.

1.2. β'-sialons

The range of high-temperature materials based on silicon nitride has increased considerably in recent years following initial investigations by a number of workers [10–12] which showed that Si and N can be replaced respectively by Al and O in β-silicon nitride producing a material of composition

$$Si_{6-z}Al_zN_{8-z}O_z, \qquad (1)$$

termed β'-sialon. The value of z can vary from 0 to 4. These materials are formed by either hot-pressing or reaction-sintering three-component mixtures of AlN, SiO_2, Si_3N_4 and Al_2O_3 in the appropriate proportions. Densification again appears to be influenced by the formation of a liquid phase at the reaction temperature [13] with a progressive reduction in the amount of second phase present as the balanced composition, given by the z-formula, is approached. Balanced compositions are, therefore, difficult to densify. Also the high viscosity of the liquid alumino-silicates means that very high temperatures ($> 1800°$ C) are required to promote rapid densification. Densification can, however, be achieved at lower temperatures by making small additions of MgO, which is found to enhance markedly densification by lowering the viscosity of the liquid phase. The α-silicon nitride $\rightarrow \beta'$-sialon transformation is similar to that discussed previously with the α phase dissolving in the liquid and precipitating as β'-sialon. Auger electron spectroscopy gives magnesium concentrations in the grain-boundary glassy phase somewhat lower than those predicted from the original magnesium concentration, suggesting either a loss of magnesium due to volatilization or a limited solubility of magnesium in the β'-sialon.

Clearly a liquid phase is essential at the firing temperature in order to achieve densification. Unfortunately, however, the presence of a glass, formed from solidification of the liquid phase during cooling, is undesirable owing to its deleterious effect on the high-temperature strength properties of the material.

An ideal situation (see Jack [10]), would be initial formation of a liquid phase to facilitate densification by liquid-phase sintering, followed by suitable heat treatment in order either to:

(a) incorporate the components of the liquid into solid solution in the silicon nitride; or

(b) crystallize out the grain-boundary glass as a multicomponent β' metal-sialon.

Two necessary criteria for achieving this goal are:

(i) the existence of a liquid phase with composition M_3X_4, where M is the cation component, and X is the anion component; and

(ii) the ability of the additional cations and anions to substitute for, respectively, silicon and nitrogen in the β-silicon nitride structure.

1.3. β' metal-sialons

There are a considerable number of reports of different cations replacing silicon in β-silicon nitride. Aluminium substitution is well established in the sialons but the Si–Al–O–N system does not satisfy the first criterion. That is the liquidus region in this system does not extend across the 3M/4X line (see Jack [14], and Naik *et al.* [15]). The only other cation which has been shown unequivocally to enter the β-silicon nitride lattice is beryllium [16], the oxide of which is highly toxic. In the five component Mg–Si–Al–O–N system there is an extensive liquidus region in the 3M/4X plane [14] but the evidence for the existence of β'-magnesium sialons is highly conflicting. Jack [14] claims primarily from X-ray diffraction analysis, that there is a significant degree of magnesium substitution in the β'-sialon structure whereas Gauckler [16] claims that magnesium substitution, if any, must be less than 1.5 at %. Work by Lewis *et al.* [17] on the crystallization of Mg-containing phases in β'-sialon ceramics tends to support Gauckler's findings. Using TEM and EDAX Lewis claims that Mg shows only a small solubility in β' crystals and is mainly segregated in a "matrix" phase.

In view of these currently conflicting reports, the present authors decided to make a more detailed study of the Mg–Si–Al–O–N system employing a wide range of different analytical techniques including TEM, EDAX, SEM, X-ray diffraction, and electron diffraction.

2. Experimental techniques

2.1. β'-magnesium sialon compositions

A comprehensive series of compositions were made up in the 3M/4X plane represented by the equation

$$\mathrm{Mg}_{m/2}\mathrm{Si}_{6-z+(m/2)}\mathrm{Al}_{z-m}\mathrm{O}_z\mathrm{N}_{8-z}. \qquad (2)$$

Each composition was prepared by grinding together (in an AGS agate mortar and pestle grinding machine) appropriate proportions of α-$\mathrm{Si_3N_4}$, $\mathrm{SiO_2}$, AlN, $\mathrm{Al_2O_3}$ and MgO. The mixed powders were compacted into 13 mm diameter cylindrical pellets at a pressure of $2.25\,\mathrm{MN\,m^{-2}}$. The weighted pellets were packed in boron nitride powder, contained in graphite crucibles, and were reacted in a static nitrogen atmosphere at 1650° C employing a platinum-wound alumina tube furnace. Each composition series consisted of compositions with a range of m values (Equation 2) but with a constant Al/Si ratio. Such a series is represented by a line in the 3M/4X plane. For example, the points M1 → M6 in Fig. 1 lie on the line Al/Si — 2/9.

2.2. Heat treatment

All specimens were reacted for various times at 1650° C. Rapid cooling by quenching into liquid nitrogen was employed, in order to freeze in the reaction temperature state and, to prevent crystallization and phase transformation during cooling. The quenched specimens were subsequently heat treated in a static nitrogen atmosphere for various times at temperatures ranging between 850 and 1200° C.

2.3. Phase characterization, elemental analysis and microstructure

Crystalline phases were characterized by X-ray powder diffraction analysis employing a Guinier-Hägg focusing camera. Microstructure and phase morphology were determined by scanning and transmission electron microscopy. Specimens for

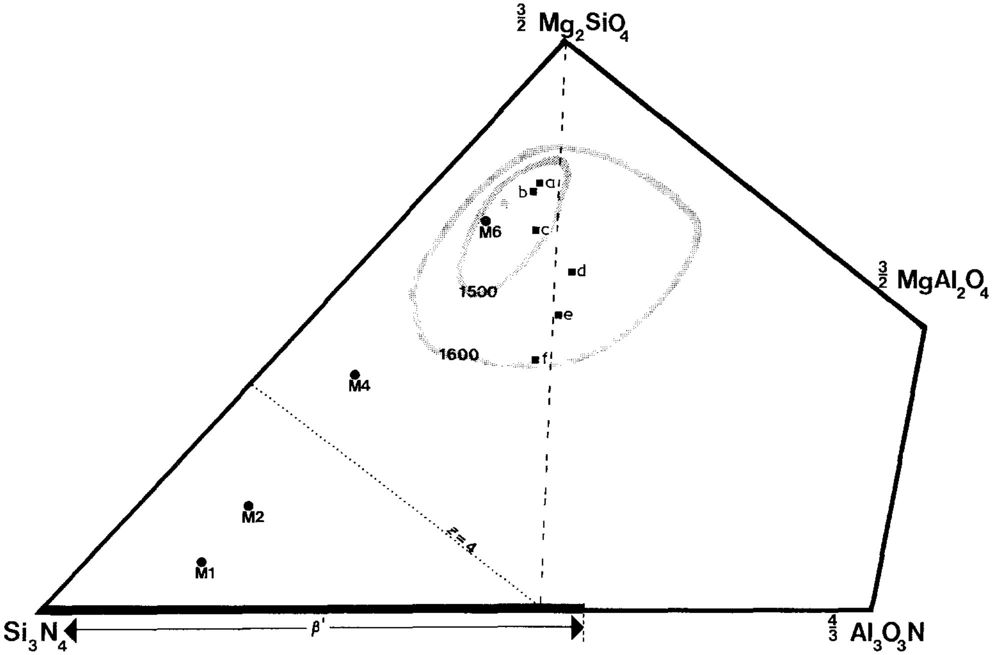

Figure 1 The 3M/4X plane in the Mg–Si–Al–O–N system showing: (i) the 1500 and 1600° C liquid isotherms and eutectic point; (ii) compositions M1, M2, M4, M6; (iii) β''-magnesium sialon compositions a to f.

SEM were, mounted in resin, polished to a 0.25 μm finish, and etched for a few seconds in a 2% HF solution. They were then vacuum-coated with a thin gold film prior to being examined in a Cambridge Stereoscan 150 electron microscope. Specimens for TEM were thinned down mechanically to a thickness of $\sim 50\,\mu$m prior to ion-beam thinning using 5 keV argon ions at an incident angle of 40°. The surfaces of specimens were evaporation-coated with a thin carbon film before being introduced into a JEOL 100C electron microscope. The microscope was fitted with an EDAX 707B energy dispersive analysis system which enabled elemental analysis to be carried out on areas as small as 0.4 μm diameter. Identification of crystalline components was achieved by employing selected-area diffraction. Elemental analysis of SEM specimens was also carried out at Harwell using the Cameca "Camebax" system. This system incorporates wavelength dispersive spectrometers sufficiently sensitive to give quantitative X-ray analysis of the very light elements such as oxygen and nitrogen as well as energy dispersive analysis for determination of the heavier metals such as magnesium, silicon, and aluminium.

3. Experimental observations and results

3.1. The progress of the reaction and the nature of the reactants at 1650° C

Fig. 1 shows the 3M/4X plane in the Mg–Si–Al–O–N system. The liquid isotherms are drawn from previously published data by Jack [14] plus data obtained in the present work. The eutectic temperature is estimated to be about 1430° C. Assuming no magnesium substitution, any composition within the triangle Mg_2SiO_4, Si_3N_4, $SiAl_2O_2N_2$ will consist, at 1650° C, of liquid, or liquid plus β'-sialon, or liquid plus forsterite, depending on the particular composition. Fig. 2 shows SEM photographs of reacted and quenched specimens with starting compositions M2, M4 and M6. As the composition moves closer to the eutectic the proportion of β'-sialon decreases and the proportion of liquid (i.e. glassy phase) increases as might be expected. The analytical results for these specimens confirm that the only phases existing at temperature are β'-sialon and liquid. Although the EDAX results of the β'-sialons do occasionally show evidence of some magnesium substitution (see Fig. 8) the levels of magnesium detected are so small as to be insignificant.

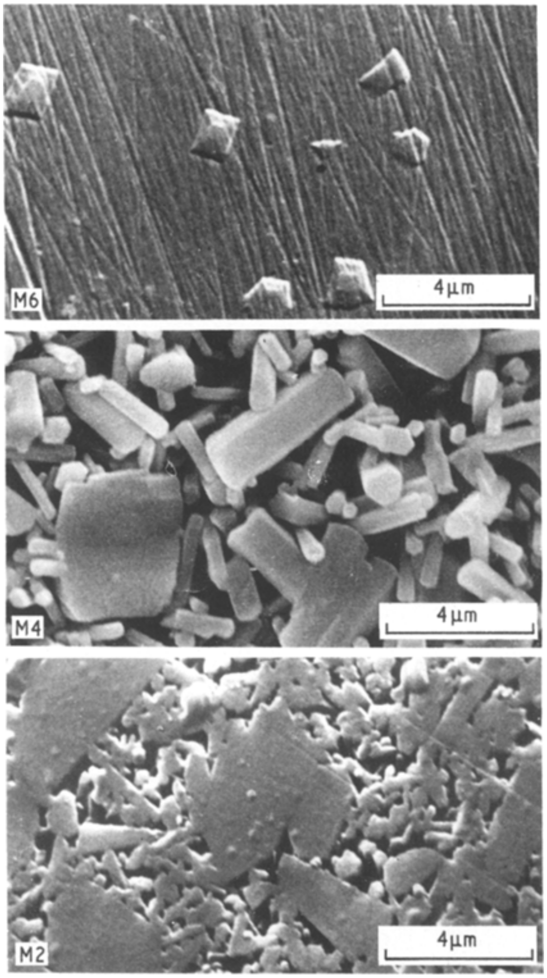

Figure 2 Scanning electron micrographs of compositions M2, M4, M6 reacted at 1650° C and quenched.

The progress of the reaction towards equilibrium may be deduced from the proportion and character of the reaction products existing at different reaction times. Initially an Mg–Si–Al–O liquid phase is formed containing a dispersion of α-Si_3N_4 particles which slowly dissolve in the liquid, and reprecipitate as β'-sialon. The first β'-sialon which crystallizes has a high z value and contains a high proportion of Al and O. As the reaction proceeds and more α dissolves in the liquid the Al and O concentrations of the liquid decrease and the N and Si concentrations increase, therefore the z value of the precipitating β'-sialon decreases. When all the α has dissolved in the liquid, equilibrium is achieved, and no further significant changes occur. This is illustrated by Fig. 3 which shows a plot of the proportion of β' (relative to α) and the a dimension of the hexagonal β' cell against time for composition M1.

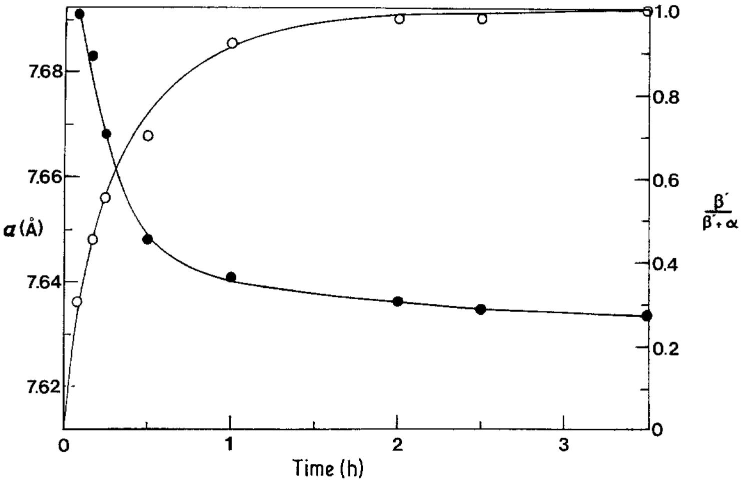

Figure 3 Plot of proportion β' (relative to α) (open circles) and the a dimension (full curcles) of the hexagonal β' cell versus time for composition M1, reacted at 1650° C and quenched.

The phases observed in the reaction product are very sensitive to cooling rate and the above observations apply only when extremely rapid cooling rates are employed. If very slow cooling rates are used further crystallization occurs during cooling and forsterite and/or spinel (depending on composition) crystallize out from the amorphous phase. The most interesting observations are made at intermediate cooling rates. In this case X-ray powder diffraction photographs show, including the β'-sialon diffraction lines, a very weak set of diffraction lines which are indexed on a hexagonal β structure with exceptionally large unit cell dimensions. Clearly this new β material termed β'', is formed during cooling at temperatures lower than those required to initiate the crystallization of forsterite from the glassy phase.

3.2. Characterization of the β'' material

Depending on the starting composition, the β'' material is found to exist with a wide range of hexagonal cell dimensions ($a = 7.764$ to 7.933 Å, $c = 3.047$ to 3.113 Å) indicating a range of composition. Fig. 4 shows a plot of a versus z for β'-sialon on which are superimposed the range of a values observed for β'' in the present study. Quite clearly β'' is not a β'-sialon with an unusually high Al and O content, as the cell dimensions are substantially greater than the maximum theoretical values for a hypothetical $z = 6$ β'-sialon. This evidence alone strongly indicates that β'' is, in fact, a magnesium sialon. Fig. 5 comprises TEM photographs of a thin section of rapidly cooled specimen (composition M5.5). Illustrated are hexagonal prism-shaped crystals dispersed in a glassy matrix and aligned with their c axes both parallel and perpendicular to the electron beam together with associated electron diffraction patterns of the crystals. Each crystal shows an inner strain-free core surrounded by a highly strained peripheral

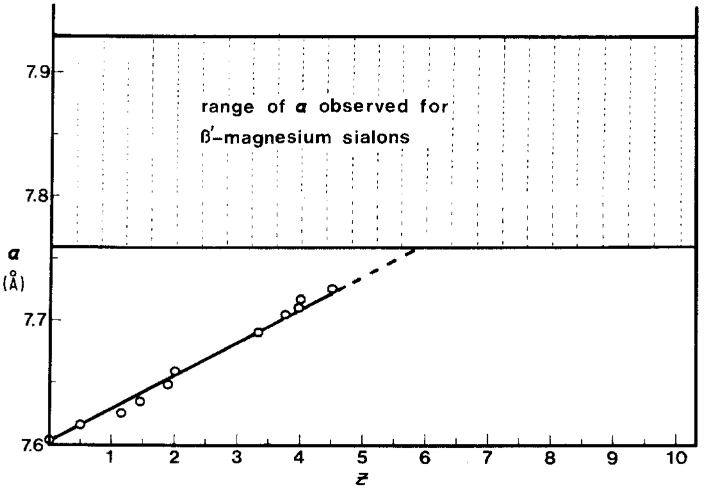

Figure 4 Plot of a dimension versus z for β'-sialons, showing the range of a dimensions for β''-magnesium sialons in the present study.

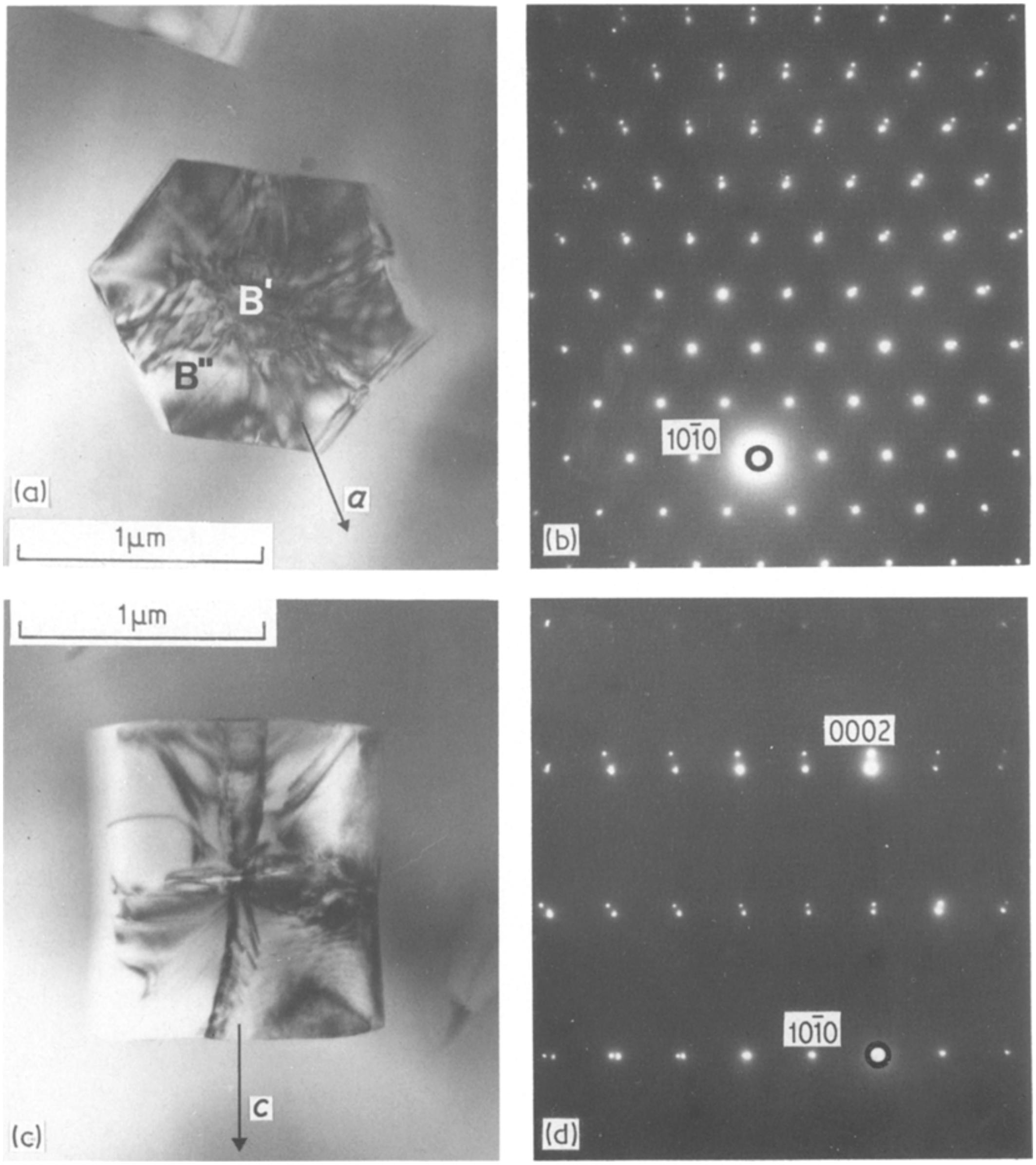

Figure 5 Transmission electron micrographs of hexagonal β''-magnesium sialon crystals containing β'-sialon cores with associated electron diffraction patterns. (a) electron beam parallel to *c* axis. (c and d) electron beam perpendicular to *c* axis.

region. The electron diffraction patterns show double spots which can be indexed on two β structures of small and large hexagonal cell dimensions. The electron diffraction data agree exactly with the X-ray data which for this particular specimen are:

$$\beta' (z \simeq 0) \quad a = 7.606 \quad c = 2.913\,\text{Å}$$
$$\beta'' \quad a = 7.815 \quad c = 3.070\,\text{Å}.$$

Unequivocal evidence that β'' is a magnesium sialon is provided by the EDAX results on the above crystals. Fig. 6 shows that the cation content of the inner core regions consist only of Si whereas the peripheral regions consist of Mg, Al, and Si. The matrix glass is of a similar cation composition to the β'' but contains relatively smaller proportions of Al and Mg.

3.3. Nucleation and growth of β''-magnesium sialon

Experimental observations made on a whole range

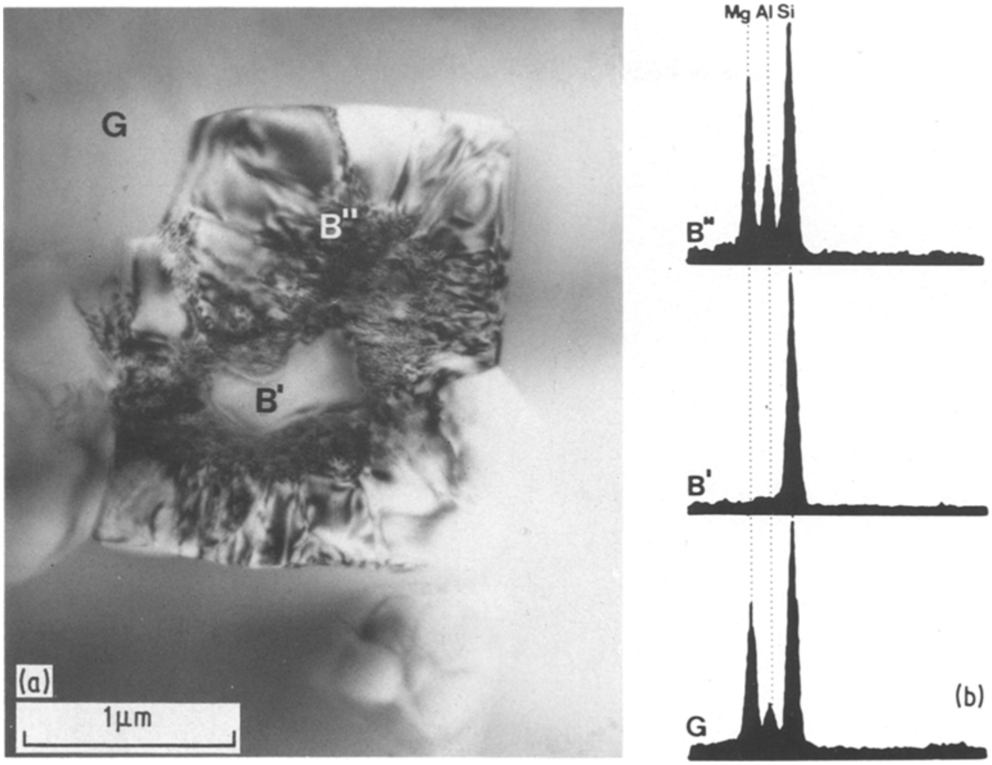

Figure 6 (a) Transmission electron micrograph and (b) associated EDAX analysis of β'', β' core and glass matrix.

of different β'' materials verify that β'' always forms in association with β'. The previous TEM results show that β'' occurs as an overgrowth on β' crystals and the results of experiments employing various cooling rates confirm that β'' is formed in the temperature region 850 to 1100° C by crystallization from the glassy phase. Clearly the β' crystals which precipitate from the liquid at the firing temperature are acting, at low temperatures, as nucleation centres for the formation and growth of β''-magnesium sialon (β'') from the glassy phase. If complete crystallization of the glassy phase can be achieved this material will form the basis of a self-nucleating nitrogen-glass ceramic.

The major conditions which govern the effectiveness of a nucleant as a crystal-growth promoter are given by Stookey [18] as (i) the interface energy between the glass and the nucleant must be low, and (ii) the crystal structure and the lattice parameters of the nucleant and the crystal phase to be developed should be as nearly the same as possible. In the present case, the mode of formation of the β' nucleant and its chemical similarity to the glass will ensure a low interfacial energy. Also the X-ray diffraction results indicate that the β' nucleant and the nucleating β'' phase are isostructural. The TEM observations show the β'' growing in identical orientation to the β' which, when considered with the X-ray data, suggests a highly coherent boundary between the nucleant and the nucleating phase. Thus the conditions necessary for effective nucleation are fully satisfied.

The rate at which crystal growth proceeds subsequent to nucleation is dependent on temperature and the degree of supersaturation. At low temperatures with large undercooling there is a high degree of supersaturation but viscosity is high and diffusion rates are low. At high temperatures the converse is true. This results in a limited temperature region for growth with the maximum rate of growth occurring at a temperature intermediate between the glass transition temperature and the melting point. In the present work specimens quenched from 1650° C were heat treated at temperatures between 850 and 1200° C for various times. After polishing and etching, the specimens were examined in the SEM in order to follow the development and growth of the β'' phase. Fig. 7 shows the development of microstructure (composition M6) with time at a fixed temperature

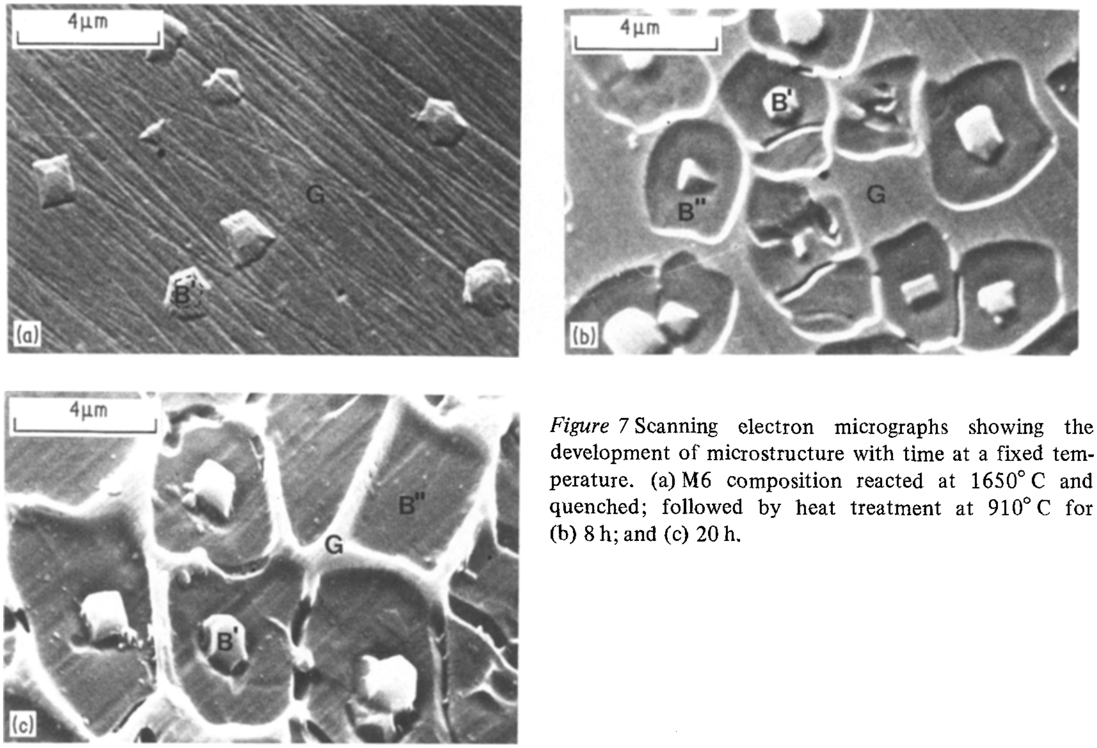

Figure 7 Scanning electron micrographs showing the development of microstructure with time at a fixed temperature. (a) M6 composition reacted at 1650° C and quenched; followed by heat treatment at 910° C for (b) 8 h; and (c) 20 h.

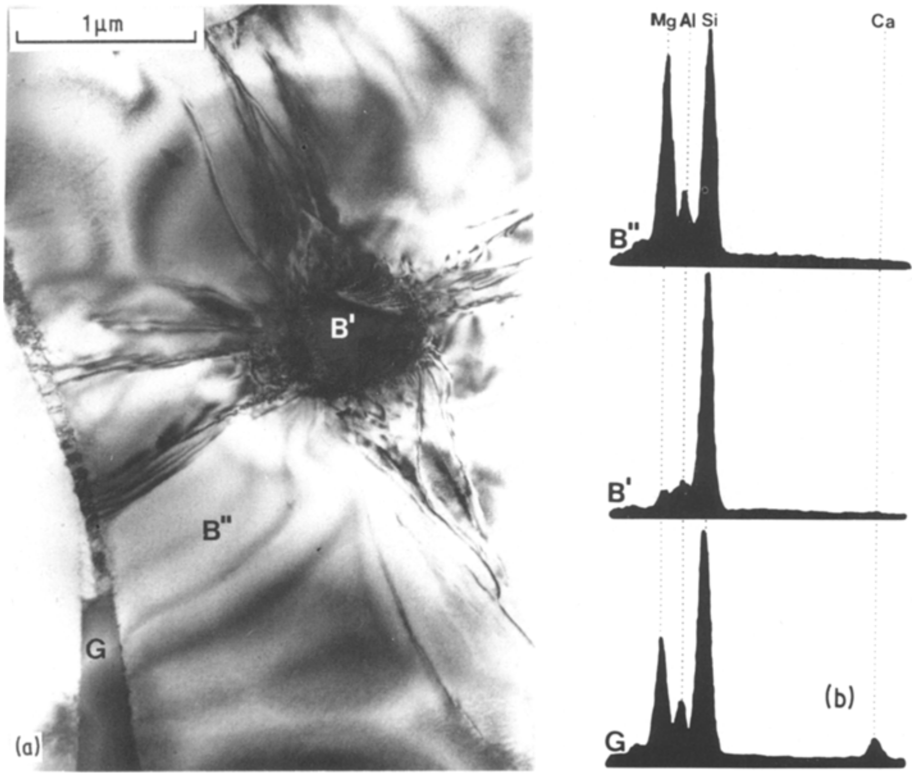

Figure 8 (a) Transmission electron micrograph and (b) associated EDAX analysis of M6 composition reacted at 1650° C, quenched and heat treated for 20 h at 910° C.

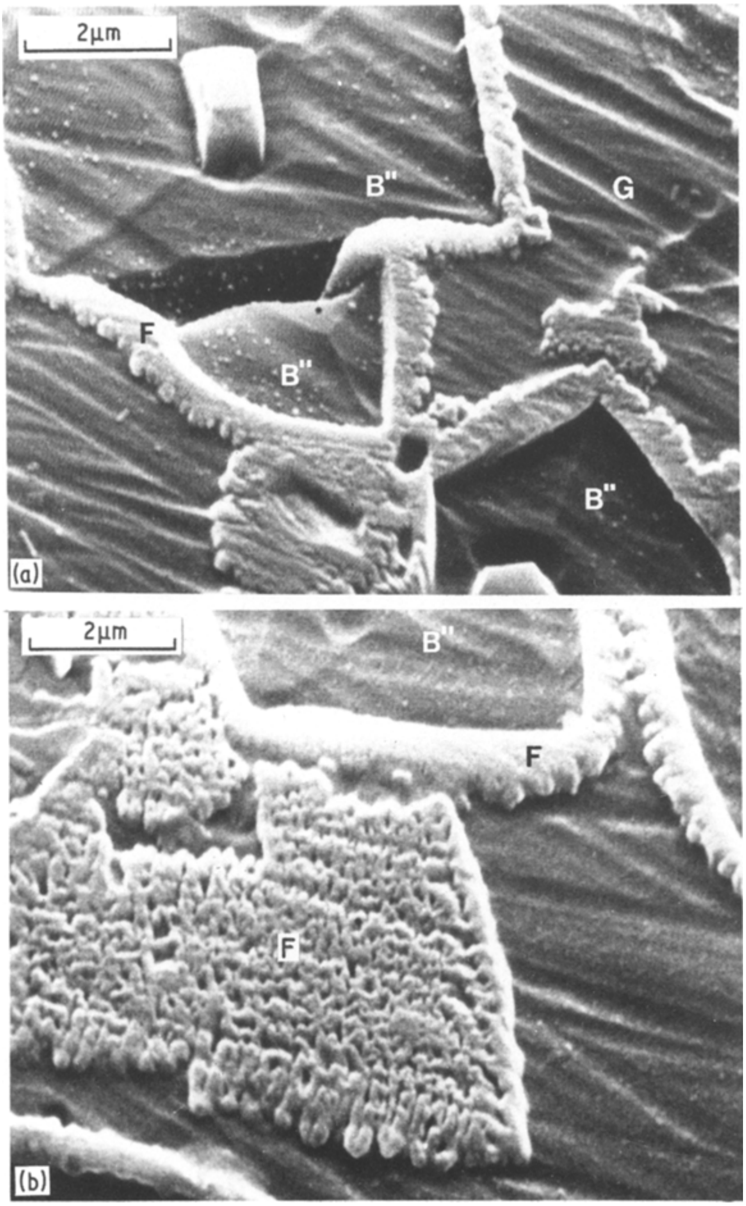

Figure 9 Scanning electron micrograph of M6 composition reacted at 1650° C, quenched and heat treated for 10 min at 1050° C, showing the development of β′-magnesium sialon (β″) and forsterite (F) in the glass.

(910° C). Each crystal consists of an inner core of β′ (~ 0.7 μm across), surrounded by a thin overgrowth of β″ (~ 0.6 μm thickness) which is formed during quenching, plus a further overgrowth of β″ which has developed during the low-temperature heat treatment. The growth rate in the initial stages is independent of time suggesting an interface-controlled growth mechanism. For longer heat-treatment times the growth rate declines and becomes insignificant after long periods (36 h), hence preventing complete crystallization of the glassy phase. A likely explanation for this decline in growth rate after long heat treatment times is a transition from interface-controlled growth to diffusion-controlled growth. This would, in turn, be brought about by (i) increasing impurity concentrations in the contracting glassy matrix; and (ii) increasing departure in overall composition between the advancing β″ phase and the contracting glassy matrix.

These latter effects are clearly demonstrated by the EDAX results (composition M6) presented in Fig. 8. Calcium impurity present in the starting materials is not incorporated into the β″ structure

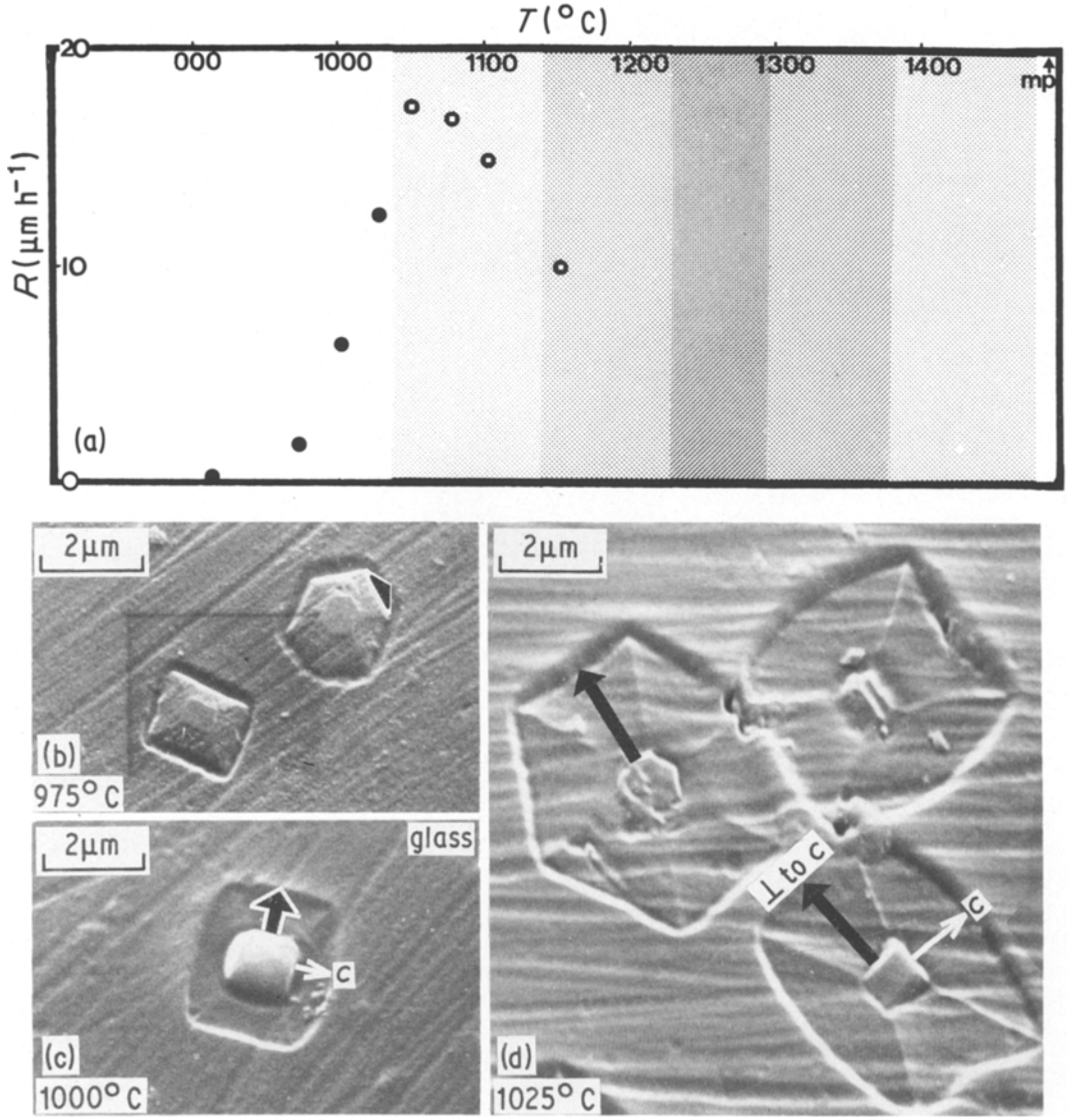

Figure 10 (a) Plot of observed growth rate perpendicular to the *c* axis, R, against temperature for β''-magnesium sialon (M6 composition). Region of forsterite formation shown schematically by shading. (b–d) Scanning electron micrographs showing the growth of β''-magnesium sialon crystals in a 10 min period at (b) 975° C (c) 1000° C and (d) 1025° C.

and becomes concentrated in the residual glass as crystallization proceeds. Also the proportion of magnesium in the residual glass is significantly lower than that detected in the β'' phase indicating that the initial glass composition was significantly different from the composition of the advancing β'' crystals.

During crystallization of glass ceramics there is commonly more than one crystallization product. There may, in fact, be a number of crystalline phases appearing simultaneously and, in addition, portions of the primary crystalline phase may begin to transform, by solid-state reaction, to a new structure type. This is, in fact, the case in the present work. Between 850 and 1025° C the only developing phase is β''. Above 1025° C forsterite begins to appear growing within both the glass and the β'' crystals. The origin of the forsterite nucleation sites is at present not confirmed although there is strong microstructural evidence (Fig. 9) that nucleation commences at the β'' crystal-glass interface.

Fig. 10a shows a plot of growth rate against temperature for β'', the maximum growth rate occurring at a temperature of 1050° C. Superimposed on this graph is the region of temperature

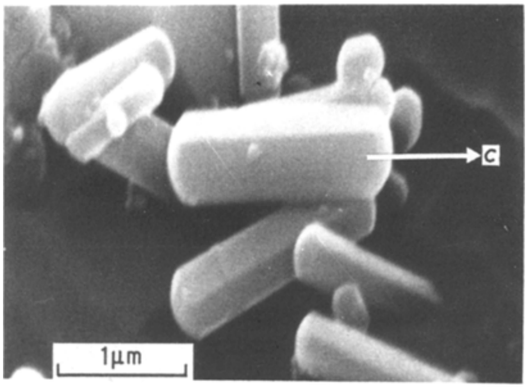

Figure 11 Scanning electron micrograph of β'-sialon crystals in glass matrix.

over which forsterite formation is observed (shaded area). It should be noted that the limiting growth rate of 17.4 μm h^{-1} at 1050° C may, in this particular case, be a result of the onset of forsterite formation inhibiting further growth and not as a direct result of increasing temperature. Fig. 10b shows the development of β'' crystals at various temperatures for a constant heat-treatment period. The necessity to quench from the reaction temperature in order to prevent forsterite formation is clearly explained by these results.

Another significant observation in relation to the growth of the β'' crystals is that growth rates are anisotropic. For example at 1000° C the growth rate perpendicular to the **c** axis is 6.4 μm h^{-1} and that in the **c** direction is 4.1 μm h^{-1}. This produces hexagonal prisms with a small aspect ratio. Also the prisms have flat tops and show pronounced faceting. This is in marked contrast to the β' crystals which are much longer in the **c** direction than in the **a** direction and thus have a much larger aspect ratio. They also show less pronounced faceting, exhibiting rounded ends (see Fig. 11).

3.4. The homogeneity range of β''-magnesium sialon

The observed variations in cell dimension for β'' confirm that it exists over a range of compositions. The composition of a particular β'' material is derived from the composition of the glass from which it has crystallized. This, in turn, depends upon the starting composition, the composition of the liquid phase at the firing temperature, and the cooling rate. As the observed crystalline phases formed at the reaction temperature all have composition 3M/4X then assuming negligible weight loss on firing (observed weight losses are $\simeq 2$ wt %) the composition of the residual glass will also have composition 3M/4X. Any composition in the 3M/4X plane is represented by Equation 2.

In the present work glasses, containing β'-sialon nuclei, prepared with various m and z values were heat treated to crystallize out the glass as β'' and were analysed using X-ray diffraction, TEM and EDAX. The EDAX results indicate that the β'' does not necessarily crystallize with the initial glass composition. For example, Fig. 8 shows the EDAX results for composition M6.

In this particular case the residual glass is richer in silicon and the β'' is richer in magnesium and aluminium in comparison with the initial glass.

One of the problems associated with quantitative energy dispersive analysis, is the degree of accuracy to which elemental concentrations may be determined, and the choice of suitable correction factors. In many systems preferential absorption of the elemental characteristic X-rays occurs, for example absorption of Mg–K X-rays by the Be window can present problems. It is therefore advisable to use suitable standards in order to check the reliability of the data obtained. In the present work a synthetic spinel was used to check the reliability of observed Mg/Al ratios and a synthetic forsterite was used for the Mg/Si ratios. In addition, it is not possible, using the present system, to determine directly oxygen and nitrogen concentrations. Therefore, overall compositions were determined indirectly by substituting observed Mg/Si/Al ratios into Equation 2. This procedure relies on the assumption that Mg enters the β structure in a substitutional manner and that all β'' compositions lie in the 3M/4X plane. In view of the report by Hampshire *et al.* [19] of the presence of interstitial magnesium in α'-sialons, the possibility of magnesium being incorporated in the β structure in an interstitial manner cannot be fully discounted. However, preliminary results from Harwell using the Cameca "Camebax" system to obtain a full analysis confirm, within the limits of error, that the β'' specimens prepared in the present work do, in fact, have compositions which lie in the 3M/4X plane.

Fig. 1 gives the compositions, calculated from the corrected EDAX data, of the different β'' materials examined in the present work and Table I gives the associated cell dimensions for a selection of these compositions. A significant factor of these results is the proximity of all the compositions to the Mg_2SiO_4–$Al_2SiO_2N_2$ join of the 3M/4X plane

TABLE I

Figure code	β''-sialon composition*					Hexagonal cell dimensions (Å)	
	Mg	Al	Si	O	N	*a*	*c*
a	3.20	0.67	2.13	7.07	0.93	7.875	3.105
b	3.10	0.66	2.24	6.86	1.14		
c	2.90	0.93	2.17	6.73	1.27	7.838	3.089
d	2.59	1.42	1.98	6.60	1.40		
e	2.31	1.64	2.06	6.26	1.74		
f	1.98	1.84	2.17	5.80	2.20		
$z = 4$ sialon		4.00	2.00	4.00	4.00	7.717	3.009

*Determined from corrected EDAX data for cations, using Equation 2.

suggesting, as previously stated, that β''-magnesium sialon may exist only over a specific composition region, i.e. that given by the equation

$$Mg_xAl_{4-x}Si_2O_{4+x}N_{4-x}, \quad (3)$$

where $x = m/2$.

4. Discussion

4.1. Complete crystallization of magnesium sialon glasses

The results of the present study show that it should be possible to produce a fully crystalline material consisting of β' plus β''-magnesium sialon. In order to achieve this, however, it is necessary to obtain much closer control of glass composition, and heat-treatment procedures. The maximum degree of crystallinity so far obtained is about 82% with 18% residual glass. The fact that impurities such as calcium are concentrated in the residual glassy phase and are not taken into solid solution in the β'' structure means that high-purity starting materials must be employed. The observation that β'' has an apparently limited composition range means that adjustments must be made to the relative proportions of the starting materials to allow for weight losses (~ 2 wt%) due to volatilization of SiO and MgO during firing. Also the liquid formed at the firing temperature must not only be within the composition range of β'' but must also contain a large number of small evenly dispersed β'-sialon nuclei. To achieve the appropriate liquid composition, whilst at the same time producing β'-sialon nuclei by precipitation from the liquid, requires very precise control of the system parameters. A simpler approach may be to produce a glass within the β'' composition range and then artificially seed the glass with $z = 4\,\beta'$-sialon nuclei. This should then ensure that on subsequent firing, the liquid phase produced will fall within the required limits of Equation 3.

4.2. The stability range of β''-magnesium sialon

The low-temperature heat-treatment programme has shown that above about 1025° C β'' is unstable with respect to forsterite for the particular compositions investigated. These compositions are, however, at present limited to values of x (Equation 3) between 2 and 3. This limit is imposed due to the fact that the maximum working temperature in the present work is 1650° C and at this temperature only a proportion of compositions along the Mg_2SiO_4–$Al_2SiO_2N_2$ join are fully liquid. To produce liquids with compositions of higher or lower values of x will require much higher firing temperatures. Also as the eutectic composition in the 3M/4X plane does not lie on, but is to the left of, the Mg_2SiO_4–$Al_2SiO_2N_2$ join, the cooling rates employed will have to be sufficient to freeze in the liquid composition as a glass and prevent crystallization during cooling. If this is not achieved, the glass composition will not lie in the required region.

The stability of β'' with respect to forsterite might be expected to increase with decreasing x. For example, $x = 0$ gives $z = 4\,\beta'$-sialon which is stable at temperatures well in excess of 1000° C. It may, therefore, be possible to produce β''-magnesium sialons which are stable up to much higher temperatures than those so far observed in the present study. It may also be possible to increase the stability of β'' by incorporating other cations as well as magnesium into the β' structure.

4.3. The crystal structure of β''-magnesium sialon

The following observations support the hypothesis that β''-magnesium sialons exist only over a narrow composition range.

(i) Although the present work clearly confirms that magnesium can be incorporated in the β'-

sialon structure there is no evidence of significant amounts of magnesium being taken up by the β'-sialon phase which is formed by precipitation from the liquid phase during firing.

(ii) β''-magnesium sialon does not necessarily crystallize with the composition of the surrounding glassy matrix even though the composition of the glass lies within the 3M/4X plane.

(iii) The results of energy dispersive analysis of the β''-magnesium sialons prepared in the present study give compositions which lie close to the Mg_2SiO_4–$Al_2SiO_2N_2$ join in the 3M/4X plane.

The existence of these apparently narrow composition limits strongly suggests some form of ordering of the different atom types within the β'' structure. A similar suggestion was made by Wild *et al.* [20] for $z = 4$ β'-sialons. They interpreted the results of X-ray and infra-red absorption studies of β'-sialons in terms of an ordered structure at the $z = 4$ composition and suggested an ordering scheme for the cations similar to that found in phenacite (Be_2SiO_4). This suggestion is now further supported by the present work. Taking the β''-sialon composition as $Mg_xAl_{4-x}Si_2O_{4+x}N_{4-x}$, then when $x = 0$ the composition gives a $z = 4$ sialon. As x increases Mg replaces Al in its preferred crystallographic site and simultaneously O replaces N.

A second aspect of the present work which lends support to β'' having an ordered structure is the observation of distinctly different crystal morphologies for β'-sialon and β''-magnesium sialon. The relatively low growth rate in the ***c*** direction and the distinct faceting of the surfaces perpendicular to the ***c*** direction might be expected if β'' has a similar ordering scheme to phenacite, because of the layered arrangement of the different cation types in this particular direction. However, owing to the simularity in X-ray scattering factors for the three different cations, direct and positive confirmation of ordering will be achieved only by the employment of alternative techniques such as neutron diffraction.

5. Conclusions

The present study confirms that:

(1) β''-magnesium sialons exist;

(2) they are formed by crystallization of magnesium sialon glasses in the temperature region 850 to 1100° C;

(3) they nucleate on β'-sialon nuclei which are themselves formed by precipitation from Mg–Si–Al–O–N liquids at high temperatures;

(4) the particular β''-magnesium sialon compositions investigated in the present work are unstable with respect to forsterite above 1025° C;

(5) β''-magnesium sialon crystals show faceted interface growth, the growth rate in the ***c*** direction being smaller than that in the ***a*** direction thus producing crystals of low aspect ratio;

(6) the unit-cell dimensions of β''-magnesium sialons are substantially greater than those of β'-sialons. The currently observed range is

$$a = 7.764 - 7.933\,\text{Å},\ c = 3.047 - 3.133\,\text{Å}.$$

The results of the present study indicate that:

(1) β''-magnesium sialons occur over a narrow range of composition within the 3M/4X plane and are therefore likely to have an ordered structure;

(2) by careful control of composition, impurity levels, and heat-treatment procedures, it should be possible to produce a fully crystalline β''-magnesium sialon.

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