GLASS FORMATION AND CRYSTALLIZATION IN HIGH-TEMPERATURE GLASS-CERAMICS AND Si₃N₄

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The softening of glassy grain boundaries in ceramic matrix composites and silicon nitride at high temperatures reduces mechanical strength and the upper-use temperature. By crystallizing this glass to more refractory crystalline phases, a material which performs at higher temperatures may result. Three systems were examined: a cordierite composition with zirconia as a nucleating agent; celsian compositions; and yttrium silicate glasses both in bulk and intergranular in silicon nitride. For the cordierite compositions, a series of metastable phases was obtained. The crystallization of these compositions was summarized in terms of metastable ternary isothermal sections. Zircon formed at the expense of zirconia and spinel. In SiC composites the transformations were slower. In celsian, two polymorphs were crystallized. One phase, hexacelsian, which always crystallized, even when metastable, had an undesirable volume change. The other phase, celsian, was very difficult to crystallize. In yttrium silicate bulk glasses, similar in composition to the intergranular glass in silicon nitride, a number of polymorphs of Y₂Si₂O₇ were crystallized. The conditions under which these polymorphs formed are compared with crystallization in silicon nitride.

1. Introduction

The increased demand for high-temperature materials for aerospace applications has recently provided the impetus for the development of materials which can withstand higher operating temperatures. Potential uses include high-temperature structural materials for high-efficiency, high-performance engines in aerospace propulsion and power systems. The properties required in some applications also include oxidation resistance and the ability to withstand thermal cycling to these temperatures. Glass-ceramics and silicon nitride, which maintain their structural integrity above 1200 °C, are two materials which may meet some or all of these requirements.

Glass-ceramics, like ceramics in general, exhibit brittle fracture behavior. Improved mechanical behavior can be obtained if a second phase, capable of withstanding high tensile loads, can be embedded in the glass-ceramic matrix [1,2]. The use of materials at higher temperatures requires not only a refractory matrix composition, but also a microstructure which does not soften due to the presence of the glassy phase usually in the grain boundary of such systems.

Two ways to eliminate the glassy phase from the final microstructure are by crystallization [3–5] and by alteration of the glass composition to increase the ease of crystallization. The result is an improvement in the high-temperature properties, in particular, the mechanical properties such as creep and strength. Various models including microcrack growth and cavitation [6–9] have been proposed to explain this improved mechanical behavior at high temperature.

The results of crystallization of two glass-ceramic matrix compositions and of the glassy phase in silicon nitride densified by solution-reprecipitation are presented. Two key factors addressed are the complete crystallization of the glassy phase and the formation of metastable crystalline phases. The crystallization of metastable phases may not be desirable depending on the properties of these phases.

In general, crystalline phases melt at significantly higher temperatures than the softening temperature of a glass of the same composition. Superior properties may be obtained if the more refractory crystalline phases are formed. For example, the four-point flexural strength of hot-pressed silicon nitride, in which the intergranular
Glassy phase of a different composition was partially crystallized [3], showed a significant increase in strength and a higher temperature for the initiation of slow crack growth. Specifically, at 1275 °C the strength was 50% greater for the crystallized grain boundary and the temperature of initiation of slow crack growth was increased from 1200 to 1300 °C.

The final application of these materials will probably require the addition of a second phase in the form of fibers, whiskers or particulates to achieve desired properties. However, composite processing (except for one example) and an evaluation of the mechanical properties of these materials will not be presented in this paper.

Three examples in which the crystallization of an intergranular phase could significantly affect the properties of the matrix are discussed: (1) ceramic matrix composites based on metal alkoxide-derived cordierite compositions with and without SiC fibers; (2) melt-quenched barium-aluminosilicate compositions; and (3) silicon nitride with yttria added as a sintering aid.

1.1. Crystallization of intergranular glassy grain boundaries

The crystallization of an intergranular glassy grain boundary has been treated by Raj [10]. He concluded that it may not be possible to completely crystallize glass segregated at thin grain boundaries on the order of 10 Å or triple-junction nodes. These small volumes of glass may be thermodynamically stable due to strain energy arising from a volume change upon crystallization generating a hydrostatic stress which cannot be released by fluid flow. Experimental evidence for this conclusion is not possible since the optimum heat treatment that could result in complete crystallization may never be achieved.

Certainly, a number of microstructures have been reported in which complete crystallization of the grain boundaries has not occurred. What has been observed is that crystallization occurs first at triple-junction nodes with the very thin intergranular phase boundaries being the last portions of the microstructure to crystallize.

If complete crystallization of the glassy intergranular phase is not possible from a theoretical standpoint or if it cannot be achieved by heat treatment for a given system, the high-temperature properties are limited by this glassy phase, which softens in a temperature range determined by the glass composition. By altering the composition, the refractoriness may be increased. However, since most compositions are silicates with at least some additional oxides, the maximum temperature of use for such systems is not significantly higher than 1500 °C and in fact could be much lower. The addition of nucleating agents can increase the amount and ease of crystallization, but still may not lead to complete crystallization.

1.2. Zirconia/magnesium-aluminosilicate glass-ceramics

Cordierite, 2MgO·2Al2O3·5SiO2, glass-ceramics have higher mechanical strength than other glass-ceramics [2] and are able to withstand higher temperatures than other compositions, such as lithium-aluminosilicates. The microstructure of magnesium-aluminosilicates (MAS) contains minerals that form platy and elongated grains. The interweaving structure produces enhanced strength and toughness [11] over the same mineral phases developed with lower aspect ratios. Cordierite is an example of a mineral capable of forming such a microstructure.

Zirconia was used as a nucleating agent to avoid problems with TiO2, which has been shown to be detrimental in composite systems. The compositions were modified by the addition of Nb2O5. It has been shown [2] that Nb2O5 precipitates as NbC on or near the surface of the fibers. The NbC may then form a protective coating and a diffusion barrier between the fiber and the matrix.

Cordierite glass-ceramics were synthesized from metal alkoxides [12]. The general form of the reaction is

\[ M + n \text{ROH} \rightarrow M(\text{OR})_n + \frac{n}{2} \text{H}_2 \]

or

\[ M\text{Cl}_n + n \text{ROH} + n\text{NH}_3 \rightarrow M(\text{OR})_n + n\text{NH}_4\text{Cl}. \]
The advantage of the metal alkoxide synthesis method for this study was a lower processing temperature. By coating the fibers with a slurry of the matrix prior to hot-pressing, a composite was formed at temperatures lower than those required to process a glass frit. This avoided the degradation of the fibers [13]. In addition, precursor material in the form of fine-grained (<10Å) amorphous powders of higher purity than those from conventional processing [14] were obtained.

Since partially stabilized zirconia exhibits excellent fracture toughness and high strength, zirconia up to 30 wt% was added. In this study, however, the grain size of the zirconia was not optimized to obtain transformation toughening. Additional MgO was added to stabilize the high-temperature tetragonal form and prevent the transformation to the low-temperature, monoclinic form which results in microcracking due to the volume change.

1.3. Crystallization of barium-aluminosilicate glasses

Some of the most refractory ceramic matrix compositions are in the barium-aluminosilicate (BAS) system [15]. Celsian, BaO·Al₂O₃·2SiO₂, has a melting temperature of 1760°C. For use at high temperatures, complete crystallization of the glass is necessary. Any remaining silica rich glass will soften below the melting point of celsian, perhaps as low as 1200°C. Even with complete crystallization, compositions with cristobalite present would be expected to have poor room temperature mechanical properties because of the α-β cristobalite transition and the subsequent volume change during temperature cycling.

An additional problem in this system is that celsian has two polymorphs – celsian and hexacelsian. The high-temperature polymorph, hexacelsian, undergoes a rapid, reversible transformation at 300°C from the low-temperature hexagonal hexacelsian (β) to an orthorhombic form (α) with a volume change of 3% or greater. For BAS matrix compositions subjected to temperature cycling, this phase transformation in hexacelsian would be detrimental. Monoclinic celsian does not undergo such a volume change.

The details of the structures of hexacelsian and celsian and the kinetics of the transformation between these two polymorphs have been summarized [16]. Unfortunately, hexacelsian, the metastable phase below 1590°C, is always the first phase to crystallize at all temperatures. Further, the transformation to celsian is very slow. Without the addition of a mineralizer, such as Li₂O [17] or CaF₂ [18] or a nucleating agent, complete transformation of –200 mesh hexacelsian powder required 60 h at 1250°C [19]. Time-temperature requirements such as these would be unacceptable for composite processing.

1.4. Crystallization of yttrium silicates

Yttrium silicate compositions were studied in bulk, because such glasses were formed when yttria was used at NASA Lewis [20,21] as a sintering aid for the densification of silicon nitride. Silica present on the surface of the silicon nitride grains and formed by oxidation during processing, combined with the added silica and yttria. A silicate glass forms when these powders are sintered or hot-pressed at temperatures in excess of 1700°C. The solution-reprecipitation of the β-Si₃N₄ and subsequent densification is one common method of formation of dense silicon nitride. If the intergranular glassy silicate phase can be crystallized to form more refractory crystalline phases, an improvement of the high-temperature mechanical properties of silicon nitride is expected.

There are a number of crystalline phases in the Y₂O₃-SiO₂ system which are important in this study. Four polymorphs of Y₂Si₂O₇, designated α, β, γ and δ exist. The diffraction data for these polymorphs have been summarized by Liddel and Thompson [22]. The transformation temperatures, densities and the crystal class of each polymorph are given in fig. 1.

The structure of all polymorphs consists of Si₂O₅⁻ units with the Y³⁺ connecting these units. The volume change associated with the polymorphic inversions of Y₂Si₂O₇ is as large as 6.7% and may be significant in the crystallization of intergranular glassy grain boundary phases in silicon nitride [23,24]. Densities of these glasses have not been reported. The several polymorphs of YSiO₅...
have been discussed by Liddel and Thompson [22]. The existence of the 2Y2O3 • 3SiO2 phase as shown in the published phase diagram [25] has not been confirmed and, in fact, the existence of such a phase has been questioned [22].

The compositions studied were nominally cordierite in the stable phase fields of spinel and mullite. Five different cordierite compositions were synthesized from metal alkoxides. These compositions are shown in fig. 2 and are denoted MAS (2% ZrO2), ZMAS (25% ZrO2), ZCOR (15 and 25% ZrO2), ZSPIN (30% ZrO2).

For these syntheses, commercial grade tetraethoxysilane (TEOS), Si(OCH3)4, was used but the other alkoxides were synthesized from high-purity metals or anhydrous metal chlorides. The

Fig. 2. ZrO2/cordierite composites synthesized.
following reactions gave metal alkoxides of Mg, Al, Zr and Nb:

\[
\begin{align*}
\text{Mg} + 2\text{C}_2\text{H}_5\text{OH} & \rightarrow \text{Mg(OC}_2\text{H}_5)_2 + \text{H}_2, \\
\text{Al} + 3\text{C}_3\text{H}_7\text{OH} & \xrightarrow{82^\circ \text{C}} \text{Al(OC}_3\text{H}_7)_3 + \frac{3}{2}\text{H}_2, \\
\text{ZrCl}_4 + 4\text{C}_3\text{H}_7\text{OH} + 4\text{NH}_3 & \rightarrow \text{Zr(OC}_3\text{H}_7)_4 + 4\text{NH}_4\text{Cl}, \\
\text{NbCl}_5 + 5\text{C}_3\text{H}_7\text{OH} + 5\text{NH}_3 & \rightarrow \text{Nb(OC}_3\text{H}_7)_5 + 5\text{NH}_4\text{Cl}.
\end{align*}
\]

Quantities of metal alkoxides solutions to give the desired nominal composition were combined in a dry box, refluxed to give a homogeneous solution, and dropwise acid-hydrolyzed using water and nitric acid. The general reaction is:

\[
\text{M(OR)}_n + \text{H}_2\text{O} + \text{HNO}_3 \rightarrow \text{MO(OR)}_{n-2} + 2\text{ROH}.
\]

The mixture, after being stirred and allowed to stand overnight, was made basic with \(\text{NH}_4\text{OH}\). The resulting hydroxide slurry was concentrated to dryness by roto-evaporation and vacuum dried. The dried powder was ground in a \(\text{B}_4\text{C}\) mortar to comminute the larger agglomerates before calcining. The as-prepared fine powders, as well as the powder calcined at 500°C, were amorphous as determined by X-ray diffraction (XRD). The hydroxide slurry and calcined powder were used in the fabrication of the matrix and composites.

Matrix samples were prepared by vacuum hot-pressing the calcined material into 25-mm round discs under pressures up to 41.5 MPa (6000 psi) at temperatures up to 1500°C. The samples were X-rayed, chemically analyzed and the strength measured in four-point loading with the surface polished to 3 \(\mu\)m.

Composites were fabricated by slurry-coating fibers which were then dried and calcined to 450°C prior to vacuum hot-pressing. The final composite contained between 30 and 50 vol.% fibers. The continuous fibers were ceramic-grade SiC Nicalon® and approximately 13 \(\mu\)m in diameter.
2.2. Crystallization of barium-aluminosilicate glasses

Composition BASB in the celsian phase field shown in fig. 3 and a stoichiometric composition BASC were melted in a small commercial electric furnace with Mo electrodes at 2000–2100°C. Reagent grade BaCO₃, Al₂O₃ and SiO₂ were used. The liquid was roller quenched from flakes of homogeneous glass. The BSAB composition was melted with MoO₃ added as a nucleating agent. The as-batched composition was BaO: 39.0, Al₂O₃: 25.0, SiO₂: 35.0 and MoO₃: 1.0 wt%. The analyzed composition was BaO: 36.7, Al₂O₃: 26.2, SiO₂: 34.0 and MoO₃: 1.0 wt%. The crystal phases expected with complete crystallization were celsian, mullite and cristobalite for BASB and only celsian for BASC.

Heat treatments were performed in air using a programmable Linberg box furnace. The temperature was controlled to ±5°C. Samples were nucleated for 1 h at the following temperatures: 850, 900 and 950°C and grown for 4 h at 1080, 1150, 1220 and 1290°C. Additional heat treatments were 1 h at 800°C followed by 48 h at 1000°C. Details of the chemical analysis, XRD, and electron microscopy are given elsewhere [16,26]. Standard techniques were employed.

2.3. Crystallization of yttrium silicates

Reagent grade silica and yttrium oxide were ball milled for 4 h with silicon nitride grinding media in dry alcohol and dried. The powder was dry milled for 2 h then pressed into pellets and placed in tungsten crucibles for melting in a high-pressure nitrogen furnace [21,27]. Powders were melted at temperatures ranging from 1900 to 2100°C, depending on composition, and were held for 4 h under 50 atm nitrogen. Additional melts were also made in 1 atm nitrogen. No difference in properties or crystallization behavior was observed between these two melting conditions. It was necessary to break the crucibles to remove the melt. The X-ray diffraction patterns of the as-melted samples identified the crystalline phases formed on cooling. Additional heat treatments of as-melted material were carried out in air from 1100–1600°C and followed by phase identification by XRD and transmission electron microscopy (TEM).

The primary glass composition studied was the eutectic composition between SiO₂ and Y₂Si₂O₇ which is similar to the intergranular glassy grain boundary composition without nitrogen in the as-processed silicon nitride. This material has been designated as 6Y by NASA Lewis since it contains a 6.6 wt% yttria addition as the sintering aid. This composition lies in the oxidation-resistant Si₃N₄–Y₂Si₃O₇–Si₂N₂O₃ triangle.

The formulated and as-melted bulk glass compositions are given in table 1. The 1 indicates that the melt was made under one atm nitrogen and 50 denotes 50 atm nitrogen. Additional compositions melted ranged from 20–40 mol% Y₂O₃. This compositional range is centered around the lower temperature eutectic region shown in fig. 4, which is a modified version of the Y₂O₃–SiO₂ phase diagram [25] without the inclusion of the Y₂S₃ phase.

A small amount of tungsten was found due to the fact that the melts were made in tungsten crucibles. Less than 0.2% nitrogen was found, indicating that little nitrogen was dissolved in the melt as a result of the 50 atm nitrogen overpressure. The exact chemical analysis was difficult to
determine because the energy dispersive spectroscopy (EDS) system on the TEM had a Be window, which precluded soft X-rays such as those that arise from O or N.

3. Results

3.1. Zirconia / magnesium aluminosilicate glass-ceramics

Complete crystallization of the glassy phase was not attempted or confirmed. However, because of the ease of crystallization of these compositions and the presence of zirconia as a nucleating agent, nearly complete crystallization was probably achieved.

The crystalline phases developed were metastable but partially transformed to the equilibrium phases, as shown in fig. 5. A composition midway between cordierite and spinel with 30% zirconia, ZSPIN, crystallized at 600°C as spinel (Mg$_2$Al$_2$O$_4$), sapphirine (a spinel-type structure with the formula Mg$_7$Al$_3$Si$_3$O$_{16}$) and tetragonal zirconia. Crystallization at 1300°C or greater resulted in zircon and cordierite formation, with the amount of zircon increasing and zirconia decreasing with time.

The formation of zircon and cordierite was at the expense of sapphirine. The crystallization of zircon with a 20% density increase over sapphirine resulted in the formation of significant flaws and lower four-point bend strengths. The zircon for-
formation is consistent with phase formation in a glass-ceramic with 10 wt% ZrO₂ and magnesium-aluminosilicate composition between ZSPIN and ZCOR [28].

The ZCOR and ZMAS compositions contained primarily cordierite with tetragonal zirconia. At 1300 °C and above, zircon began to form as earlier work showed [28]. The zircon formation was not sensitive to modest variations in the zirconia or silica content. In addition to zircon formation, cordierite transformed from the μ to the α phase and sapphirine disappeared. Some tetragonal zirconia remained, since the reaction to form zircon was sluggish.

Not only was the amount of tetragonal zirconia decreased with the zircon formation, but also a portion of the tetragonal phase destabilized and monoclinic zirconia formed. The monoclinic zirconia formation at 1300 °C corresponded to the disappearance of sapphirine and the formation of spinel as the ternary component.

Spinel contains a higher magnesia content than sapphirine. A portion of the magnesia stabilizing the tetragonal zirconia probably reacted with s-
phirine, forming spinel and freeing silica for zircon formation.

With the addition of Nicalon® SiC fibers, the phase development was more sluggish with the transformation of $\alpha$ to $\mu$ cordierite and zircon formation retarded. This result suggests that phase transformations in the matrix may be altered, or at least slowed, as a result of the addition of a second, nonreacting phase. The major phases developed in the composites are shown in fig. 6. The matrix composition in the composites appeared to contain a higher silica content than the matrix material alone. Since the fibers used contained a significant $\text{SiO}_2$ fraction, the higher content silica matrix was not surprising.

3.2. Crystallization of barium-aluminosilicate glasses

In this study complete transformation of hexacelsian to celsian without the addition of a flux or a nucleating agent was never achieved. As-quenched BASB and samples nucleated below 950 °C were amorphous, as shown by XRD in fig. 7. Various heat treatments and the phase identification by XRD are also shown in fig. 7. Results of

Fig. 7. X-ray diffraction data for celsian compositions for heat treatments indicated with phase identification.
these heat treatments and others not shown indicate that regardless of the crystallization temperature hexacelsian always forms when MoO₃ is used as a nucleating agent. Further studies [26] have shown that stoichiometric celsian, BASC, does not crystallize as celsian with various heat treatments.

The microstructure of a heat-treated glass (BASB 13, fig. 7) is shown in fig. 8. Both hexacelsian grains, all with the same orientation, and mullite crystallized in the apparent grain boundaries. The single orientation of the grains may be the result of recrystallization or a slow growth rate. The phases were identified by EDS spectra.

With the addition of 5 wt% Li₂O to the BASB...
composition, the as-quenched sample was amorphous. When nucleated at 900 °C and grown at 1220 °C for 4 h, celsian crystallized as shown in fig. 7. The micrograph in fig. 9 shows the complex microstructure formed with the addition of the mineralizer, Li₂O. Bands of a Mo rich glass alternated with bands of mullite and bands of celsian. Although MoO₃ was added as a nucleating agent, it was not effective for the crystallization of celsian.

3.3. Crystallization of yttrium silicates

The bulk glass compositions, GS1 or GS50, similar to the intergranular glassy composition, have been shown [29] to have a minimal amount of nitrogen dissolved in the glass. In other studies [20,23] on the 6Y composition, no crystallization of yttrium containing nitrides was observed. Thus, the results of crystallization studies on bulk glass with minimal nitrogen content may be used to optimize crystallization of the intergranular glassy phase in silicon nitride.

In all cases, XRD results of the as-quenched melt indicated partial crystallization. Most of the melts contained δ-Y₂Si₂O₇. The quench rate obtained in these melts was not a rapid one: it was estimated to be 270 °C/min. The furnace did not permit a more rapid rate. In the bulk glass material, the γ or δ polymorphs were observed. The dif-

Fig. 9. Micrograph of celsian (C) with 5 wt% Li₂O showing Mo rich glass (G) and mullite (M).
ference was probably due to different quench rates in the two furnaces used.

In the as-processed silicon nitride, the crystalline phase formed was $\beta$ or $\delta$, depending on the heat treatment [24]. The difference between bulk glass samples and the glassy phase in silicon nitride may have been due to the presence of nucleating agents, perhaps silicon nitride itself, since in bulk glass samples with the addition of zirconia as a nucleating agent the $\beta$ polymorph is formed.

The $Y_2S_3$ composition did not crystallize when quenched in the bulk. All other compositions in this study were partially crystallized. Differential thermal analysis results showed an exothermic peak at $1400^\circ$C, corresponding to the crystallization of $Y_2Si_2O_7$. The previously observed [30] crystalline phase of the $Y_2S_3$ composition was not observed.

The results of these crystallization studies are shown in figs. 10–13. The $X_1$ denotes a polymorph of $YSiO_3$ and the $u$ an unidentified phase (fig. 13). The expected transformation temperatures are shown by the horizontal dashed lines with the expected phases shown on the right in each figure. When more than one phase is shown at a particular time and temperature, both phases were detected by XRD. The $\alpha$ phase was never observed. In the GS1 sample the melt was $\gamma$ as quenched and in the GS50 melt it was $\delta$. Over time at various temperatures polymorphic changes occurred, but not always the expected one. For example, the $\gamma$ phase formed in some cases instead of the reported stable phase $\beta$.
4. Discussion

4.1. Zirconia / magnesium-aluminosilicate glass-ceramics

Cordierite compositions with excess silica and 10 or 15 wt% zirconia crystallized as primarily cordierite and tetragonal zirconia with conversion to zircon at higher temperatures. These results can explained in terms of a simplified non-equilibrium isothermal ternary section (fig. 6). They suggest that the zircon formation is not sensitive to variations in zirconia and silica contents.

With MgAl₂O₄ being considered as a single component and with the aid of the ZrO₂-SiO₂ phase diagram [31], these compositions and their resulting phases can be illustrated semiquantitatively. Figure 6 illustrates the spinel-zirconia-silica non-equilibrium ternary isothermal section at 1250 and 1300°C. Sapphirine cannot be properly depicted as a component on the 1250°C metastable ternary. However, since at 1250°C a combination of spinel and sapphirine was present and structurally and compositionally they are very similar, sapphirine is included on the isothermal section with spinel. This modified ternary provides a useful tool in visualizing the phase development of these materials.

The composition ZSPIN was unable to form cordierite and spinel with tetragonal zirconia as shown in the metastable ternary section in fig. 6. This was without the formation of zircon. A slightly higher silica-content composition than ZSPIN may be out of the two-phase region between spinel and zirconia observed at 1250°C. Examination of the diagram implies that a metastable coexistence between spinel, cordierite, and zirconia could be achieved with a composition of slightly higher silica content than ZSPIN.

The matrix materials without SiC fiber densified most rapidly at 1200 through 1250°C. The final density depended upon the applied pressure and the rate of temperature increase or hold time in this temperature range. Compositions ZSPIN and ZCOR were the most extensively studied for densification characteristics. ZSPIN densified up to 95% of theoretical when hot-pressed at 10°C/min heating rate and 15 min at 1250°C under 7.6 MPa (1100 psi) applied pressure. Crystalline phase development appeared to be unaffected by the applied pressure when varied from 0 to 7.6 MPa (1100 psi).

Composition ZCOR was extremely difficult to densify. At 11.7 MPa (1700 psi) applied pressure, a 10°C/min heating rate and 15 min at top temperatures of 1250°C and 1300°C, the density appeared to be ~ 90% of theoretical. Although there may have been some glass remaining in the matrix which would have had a lower density than the crystalline phases, most of the deficiency in density was probably due to porosity. The addition of a flux to the matrix composition would probably aid in densification but would be detrimental to the high-temperature properties.

The phase development in the composites appeared to be sluggish compared to the matrix material without the fibers. Comparing the composite metastable ternary at 1300°C with that of the matrix only material (fig. 6), it is apparent that the α to β transformation is retarded and the zircon formation region is reduced in the composite materials.

4.2. Crystallization of barium-aluminosilicate glasses

Crystallization of celsian glass-ceramic matrices for composite applications requires not only the complete crystallization of the amorphous phase to avoid softening at high temperature, but also the crystallization of the celsian polymorph. The hexacelsian polymorph is always the first phase to form, even in a temperature range where it is the metastable phase. However, the large volume change at 300°C makes it unsuitable for composite applications.

In this system, unfortunately, the crystallization of cristobalite or hexacelsian will reduce both room and high-temperature mechanical properties. Complete crystallization of the BASC with a nucleating agent resulted in only celsian phase and no cristobalite.

4.3. Crystallization of yttrium silicates

The crystallization of metastable phases which exist above and below their thermodynamically
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stable temperature range was a common feature in this system. The polymorphic transformations were also sluggish.

A satisfactory explanation has not been given. It may be due to formation of nuclei on cooling from the melt or during reheating followed by growth. Crystallization from the bulk GS glasses never resulted in the $\alpha$ phase. Either the $\gamma$ or the $\delta$ phase formed in the melt of the GS1 or GS50 compositions with no $\beta$ formation. This formation is in contrast to the results [24] in the 6Y silicon nitride in which the $\beta$ phase readily formed in the triple point junctions. In addition, an increase in dislocation density has been found in the crystallized 6Y silicon nitride materials [24].

The reason for the appearance of dislocations is probably associated with a volume difference between the yttrium silicate glass and the first $Y_2Si_2O_7$ crystals formed or with volume differences between some of the $Y_2Si_2O_7$ polymorphs. Alternatively, differences in thermal expansion between the various phases may lead to stress in the system. The dislocation density however was reduced by annealing at 1500°C, thus minimizing the effect on mechanical properties.

Moreover, $Y_2Si_2O_7$ crystallizes at a single orientation over large distances in the microstructure [23,24]. This behavior may be due to the degree of ease of nucleating the second phase: the easier the nucleation, the less the chance of crystals growing around the $Si_3N_4$ grains. Since crystallization of $Y_2Si_2O_7$ was observed around several $Si_3N_4$ grains, it seems probable that complete crystallization of all the glass in that area had occurred even though the very thin intergranular regions were not illuminated in dark-field images.

5. Conclusions

For both the glass in a glass-ceramic matrix and as a grain boundary phase in silicon nitride, complete crystallization is required to prevent softening at higher temperatures. With complete crystallization, improvement in mechanical properties such as creep and strength is possible for composite or monolithic materials.

Crystallization studies on three different systems showed that the addition of nucleating agents and heat treatment can result in crystallization of the intergranular glassy phase. Studies on bulk glasses are useful for application to composite materials, but the transformations may be altered by the addition of other components, resulting in different crystalline phases or sluggish transformations. Volume changes upon crystallization or polymorphic changes of crystal phases formed must be considered in optimizing the properties at high temperatures or during thermal cycling.

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