Journal of the European Ceramic Society 19 (1999) 2543–2550
© 1999 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
PII: S0955-2219(99)00120-X
0955-2219/99/$ - see front matter

Growth and Crystallization of YAG- and Mullite-composition Glass Fibers

J. K. R. Weber,[a]* B. Cho,[a] A. D. Hixson,[a] J. G. Abadie,[a] P. C. Nordine,[a] W. M. Kriven,[b] B. R. Johnson[b] and D. Zhu[b]

[a]Containerless Research, Inc., 906 University Place, Evanston, IL 60201, USA
[b]Department of Materials Science and Engineering, University of Illinois Urbana-Champaign, Urbana, IL 61801, USA

Abstract

This paper describes a new process to synthesize crystalline oxide fibers for high temperature structural applications. Strong and chemically homogeneous precursor fibers of 5–40 μm diameter were made at rates of up to 1·6 m s^{-1} by glass fiber pulling techniques from undercooled molten oxides. The precursor fibers were heat treated at temperatures up to 1873 K to make crystalline fibers with controlled grain size and properties. Tensile strengths of the precursor fibers were up to 5–6 GPa (900 ksi) for YAG- ($Y_3Al_5O_{12}$) and mullite- ($Al_6Si_2O_{13}$) compositions. Research to optimize fiber compositions and crystallization processes, and to scale up precursor fiber production is discussed. © *1999 Elsevier Science Ltd. All rights reserved.*

Keywords: YAG, glass fibers, fibers, strength, mullite.

1 Introduction

Current technology for fiber synthesis is limited in the composition of materials from which fibers can be formed, the quality and diameters of the fibers that can be obtained, and the compatibility with coating and matrix materials that may be used in composites.[1–5] The relatively high cost of oxide fibers available for composite materials also makes research and development very expensive.[6]

It was recently shown that glass fibers can be drawn from molten oxides which are deeply undercooled to increase the melt viscosity.[7,8] By working with deeply undercooled melts, the new technique allows glass fibers to be made from materials which form 'fragile' liquids and have very low viscosity — less than 0·1 Pa s — at temperatures close to the equilibrium melting point.[9,10] Oxides of interest for high temperature structural applications such as mullite[7] ($Al_6Si_2O_{13}$) and yttrium aluminum garnet or YAG[8] ($Y_3Al_5O_{12}$) can be drawn into glass fibers in this way. Also, the high mutual solubility of many molten oxides would allow a uniform distribution of dopants or additives to be incorporated in the fibers.

Results presented later show that crystallization of mullite- and YAG-composition glass begins to occur at approximately 1200 K when the glass is heated at a rate of 2·5 K min^{-1}. The temperature at the onset of crystallization increases about 20 K when the heating rate is increased to 40 K min^{-1}. Containerless processing experiments on molten oxides achieve deep undercooling and spontaneous crystallization of the metastable liquid at somewhat higher temperatures, leading to crystal growth rates of 5–10 cm s^{-1}.[11] Since the glass fiber heating rate can be increased to several 1000 K s^{-1} by rapidly inserting the fiber into a hot furnace, crystallization can be performed over a wide range of temperatures up to the softening point of the glass fiber. The wide temperature range available for crystallization allowed control of crystal nucleation and growth rates, hence the morphology and properties of the product can be controlled and optimized.

2 Experimental

The approach to synthesis of crystalline oxide fibers comprised two steps: (i) pull glass fibers from the undercooled molten oxides, and (ii) crystallize the glass fibers by heat treatment. Table 1 presents the compositions which were investigated. Materials were synthesized from 99·999% pure elemental oxide powders (Cerac, Inc., Milwaukee, WI),

*To whom correspondence should be addressed. e-mail: weber@containerless.com

Table 1. Compositions of oxide materials investigated in fiber processing research

Aluminium oxide (mol%)	*Yttrium oxide (mol%)*	*Comment*
62·5	37·5	From crushed single crystal and mixed powders
63·5	36·5	From mixed alumina and yttria powder
62·5	36·5	+1 mol% Nd_2O_3
62·5	36·5	+1 mol% Er_2O_3
Aluminum oxide (mol%)	*Silicon dioxide (mol%)*	
60	40	From Kyoritsu mullite
58	42	From mixed alumina and silica powder
62	38	From mixed alumina and silica powder
59	40	+1 mol% Y_2O_3
55	40	+5 mol% Y_2O_3
60	39	+1 mol% TiO_2
60	35	+5 mol% TiO_2
60	39	+1 mol% ZrO_2
60	35	+5 mol% ZrO_2

Kyoritsu mullite[12] ($Al_6Si_2O_{13}$) or crushed single crystal YAG ($Y_3Al_5O_{12}$). Powder mixtures were formed into spheroids by laser hearth melting.[13] Effects of substituting cations in the mullite and YAG compositions were also investigated.

2.1 Formation of undercooled melts

In order to obtain the viscosity required to support fiber pulling, the molten oxides were undercooled below the liquidus temperature. Nucleation of the undercooled liquid was avoided by using containerless melting in an Aero-Acoustic Levitator[14] or Conical Nozzle Levitator[15] which completely eliminated contact with a solid container. In this way, the liquids could be deeply undercooled and/or cooled to form glass by reducing the heating power.

Preliminary levitation, melting and cooling experiments were performed to establish conditions under which specimens formed glass. Glass formation showed that a large increase in viscosity occurred below the melting point and that conditions which permit fiber pulling could be achieved. Material was levitated in pure argon, oxygen, or air and heated with a continuous-wave CO_2 laser beam. An automatic optical pyrometer measured the apparent temperature of the specimen at rates up to 100 Hz. Rapid cooling of the liquid was obtained by blocking the laser heating beam, and either glass formation or nucleation of crystalline materials were observed as the liquid cooled. The heat released upon nucleation and rapid crystallization of the liquid produced a rapid temperature rise (recalescence) followed by cooling of the solid material. Glass formation resulted in smooth cooling to room temperature without any discontinuity in the measured temperatures.

2.2 Fiber synthesis

The apparatus and procedure used to make most of the fibers from levitated melts is described in Ref. 8. The levitated samples were completely melted and the heating laser beam was blocked so that the drop undercooled. Fibers were pulled from the drop by rapidly introducing and withdrawing a 100 μm diameter tungsten wire stinger at a preselected temperature. Fiber pulling was performed under transient cooling conditions at pulling rates of 50–160 cm s^{-1}. Batches of 10–20 fibers up to 50 cm in length were pulled from each composition.

2.3 Crystallization

X-ray diffraction analysis confirmed that the bulk glass synthesized in the containerless experiments and the as-pulled fibers were free of detectable crystalline phases. Differential thermal analysis (DTA) experiments were performed on crushed bulk glass at heating rates from 2·5 to 40 K s^{-1} in a Netzsch STA 409 Simultaneous Thermal Analyzer.

Bulk glasses were formed from pure mullite compositions and with substituted titanium, yttrium or zirconium. The glass was annealed at 1473 K for 3 h and examined by X-ray diffraction.

Fibers were crystallized by heat treatment at temperatures above the onset temperature for crystallization and below the melting point of the crystalline solid. All of the heat treatment experiments were performed in air. Two heat treatment methods were used.

In the first method, several fibers were placed in a furnace at ambient temperature and heated at a rate of about 10 K min^{-1} to preselected maximum temperatures of 1273–1473 K. The fibers were held at the process temperature for periods of 1–4 h, and then cooled at a rate of approximately 20 K min^{-1}.

In the second method, fibers were mounted on a ceramic lance and rapidly heated by inserting the lance into a tube furnace which was preheated to temperatures of 1373–1873 K. The fibers were held in the furnace for 5–30 s and then rapidly removed and cooled to ambient temperature.

2.4 Characterization

The as-pulled glass fibers were first inspected with a 5× hand lens and their length was measured. In identifying the optimum temperature range and pulling rate for each composition, some fibers were formed that showed defects, variations in fiber diameter, and opaque regions. These fibers were not evaluated further.

Long fiber sections which showed no visible defects were identified using a video microscope

inspection technique. Fibers were mounted on a computer-controlled translation stage and scanned under the field of view of the 175× microscope. A video record of the image was reviewed to select sections of the fiber for property testing and crystallization experiments.

The strength of uniform-diameter glass fibers was measured using a fixture developed for high-modulus, single-filament materials. The fiber diameters were 5–40 μm and the gauge length was fixed at 23 mm, 580–4600 times the fiber diameter. Tests were performed in an Instron 1205 tensile testing machine equipped with a high sensitivity load cell and operated under computer control. Tensile tests were performed using a cross-head speed of 5 μm s^{-1}. Diameter measurements were obtained with an optical microscope prior to tensile testing.

Bend tests were performed on the crystalline fibers to determine the minimum bend radii at which fracture occurred.

Transmission electron microscopy (TEM) was used to examine selected fibers. A new technique for mounting small cross sections of monofilaments for TEM examination was developed. Specimens were made by bonding several 0·5 mm lengths of fiber into a zirconia disk which had an inside diameter of 140 μm and an outside diameter of 2·5 mm. Fiber sections were placed into the mount and set in epoxy resin. The resulting disks were polished and thinned to approximately 1–2 μm using a tripod polisher and diamond lapping film. Polished disks were mounted on a copper grid and thinned in a Gatan 600 Duo Mill ion mill with a liquid nitrogen cooled stage. TEM analysis was performed in Philips EM420 and CM12 microscopes.

3 Results

The following sections present the results of glass fiber synthesis experiments, characterization of the glass fibers, and investigation of crystallization of the glass fibers.

3.1 Fiber synthesis

Fibers could be pulled from mullite-composition melts in the apparent temperature range from 1600–1750 K, 425–575 K below the mullite liquidus temperature. The longest and best quality fibers were obtained at temperatures of about 1700 K. YAG-composition glass fibers were pulled in the apparent temperature range from 1600–1660 K, approximately 600 K below the equilibrium melting point of YAG.

X-ray diffraction studies of mullite-composition materials containing titanium, yttrium or zirconium showed that crystalline material was formed by annealing bulk glass at 1473 K for 3 h. Compositions containing 1–5 mol% titanium and 1 mol% yttrium or zirconium were single phase, had the mullite structure, and had unit cell dimensions that were slightly larger than the values for high purity mullite. The material with 5 mol% yttrium showed a higher background spectrum indicating the presence of amorphous phases. The material with 5 mol% zirconium contained mullite and zirconium silicate ($ZrSiO_4$).

The following guidelines were established for the fiber pulling process.

1. Material needs to be completely melted so that no residual nuclei remain in the liquid. This can be accomplished by superheating the levitated drops 50–100 K above the liquidus temperature.
2. Molten alumina–silica materials have a greater glass forming tendency in an oxygen atmosphere than in argon.
3. Molten alumina–yttria materials have a greater glass forming tendency in an argon atmosphere than in oxygen.[8]
4. Substitution of up 5 mol% yttrium for aluminum and up to 5 mol% zirconium or 1 mol% titanium for silicon in the mullite composition enhances glass formation and improves the quality of fibers pulled from the undercooled melt.
5. Addition of excess alumina or substitution of neodymium oxide for yttrium oxide in the YAG-composition enhances glass formation and improves the quality of fibers pulled from the undercooled melt.

The influence of dopants was significant at concentrations of 1 mol% and considerable at 5 mol%. Longer and more uniform diameter mullite-composition fibers could be pulled from the melts which contained substituted yttrium. Zirconium substitution decreased the temperature range for fiber pulling and increased the quality of the fibers. Fibers less than 5 cm long were obtained from these compositions. Material with 5 mol% titanium substituted for aluminum produced short and brittle fibers, with large diameter variations, which often fractured when they were bent slightly.

3.2 Glass fiber properties

Process conditions that resulted in defect-free sections of fiber with uniform diameters, smooth surfaces and no visible changes in appearance along the fiber over lengths of 5–30 cm were identified. Even the best fibers had defects near their ends, since the fiber pulling occurred in a transient process in which significant changes in the liquid temperature occurred as the fiber was pulled.

Figure 1 presents video microscope images of mullite- and YAG-composition glass fibers. Test

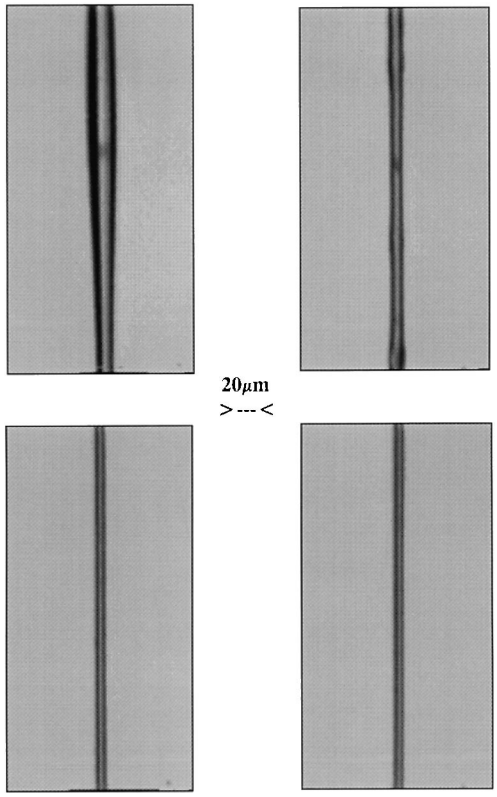

Fig. 1. Video microscope images of glass fibers. Left: mullite-composition; right: YAG-composition with 1 mol% Nd_2O_3 substituted for Y_2O_3. The top figures show characteristic defects. In mullite, regions with smoothly increasing diameter occurred along the length of the fiber. In YAG defects were localized regions where the fiber diameter changed over a distance of a few micrometers. The lower pictures show smooth sections of the fiber with uniform diameters. The scale is marked on the figure.

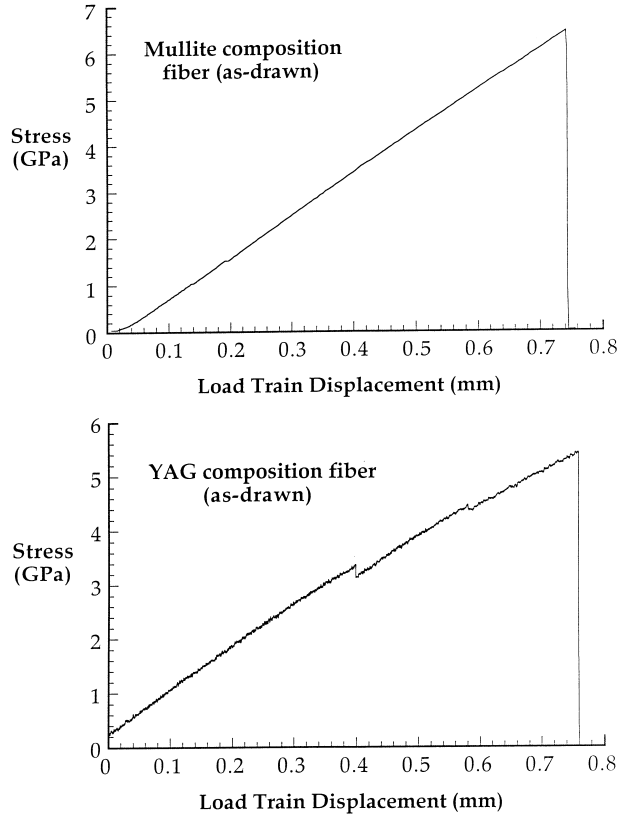

Fig. 2. Typical plots of stress versus load train displacement for selected glass fibers. Above: mullite-composition; below YAG-composition with 1 mol% neodymia substituted for yttria.

specimens were cut from uniform-diameter sections of the fibers for mechanical property testing, crystallization experiments and examination by SEM.

Figure 2 presents selected stress versus elongation plots for the glass fibers. The measurements recorded total cross-head displacement, including the load-train compliance and any movement between the fiber and the mounting, so that modulus cannot be derived from the results. Average tensile fracture strengths were $5{\cdot}6 \pm 0{\cdot}7$ GPa for the mullite-composition glass fibers and $5{\cdot}0 \pm 0{\cdot}3$ GPa for the YAG-composition fibers (with 1 mol% neodymia substituted for yttria). Both YAG- and mullite-composition glass fibers had reproducible mechanical properties. Smooth and uniform diameter mullite-composition glass fibers occasionally fractured at a stress on the order of 2 GPa. Slight movement of the fiber in the mount resulted in 'steps' in the stress-elongation plot for some fibers — see Fig. 2 for example.

3.3 Transmission electron microscopy

Figures 3 and 4 show TEM images from a mullite-composition fiber which had a tensile fracture strength of about 2 GPa, considerably less than the $5{\cdot}6 \pm 0{\cdot}7$ GPa which was obtained on other fibers. Figure 3(A) and 3(B) show regions of the fiber which contained crystallites (the dark areas) which were in the diffracting condition. The crystallites were equiaxed, had dimensions on the order of 20–50 nm, and were distributed throughout the fiber section. Figure 4(A) shows a crystallite which is approximately 75 nm across, Fig. 4(B) is the corresponding convergent beam electron diffraction pattern from this region. The diffraction pattern confirms that crystalline regions were present in the fiber. Additional TEM analysis using selected area diffraction confirmed that the crystalline material was mullite.

3.4 Crystallization

The DTA experiments performed at the slowest heating rates of 2·5 K min^{-1} indicated the onset of bulk glass crystallization at approximately 1233 K for mullite-composition glass and at 1188 K for YAG-composition glass. The data showed that the onset temperature increased with the heating rate and the rate of crystallization increased with temperature.

Rates of crystallization of the undercooled melt determined by observing recalescence were 3·5–15 cm s^{-1} at apparent temperatures of 1500–1800 K for the mullite composition and 1·4–6 cm s^{-1} at

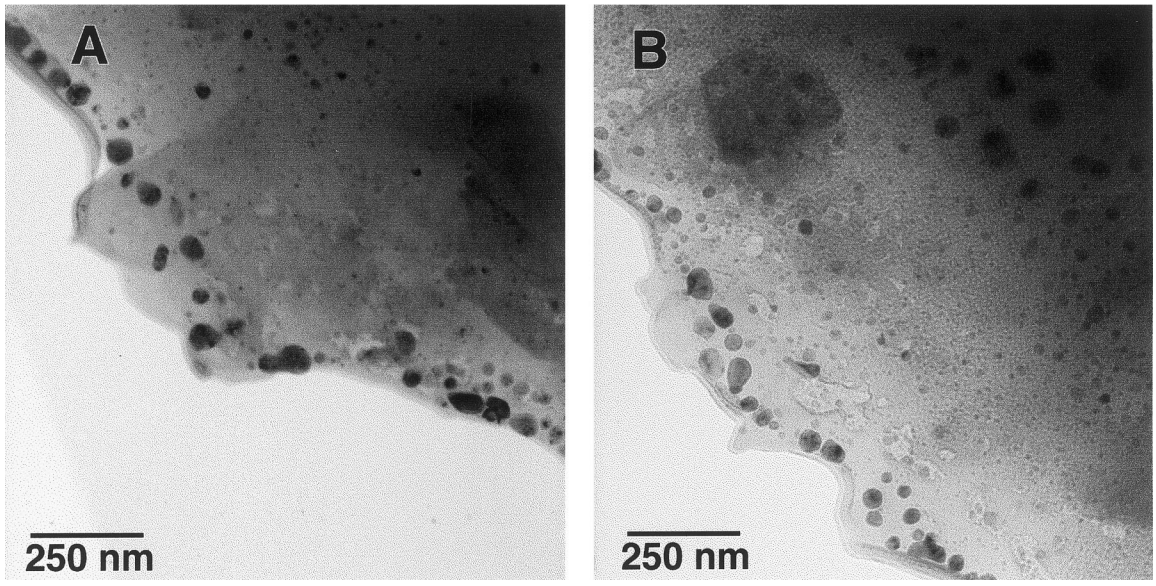

Fig. 3. (A) and (B) Bright field TEM images of an as-drawn mullite-composition glass fiber which fractured at low tensile stress. The dark areas are crystallites which were present in the fiber section.

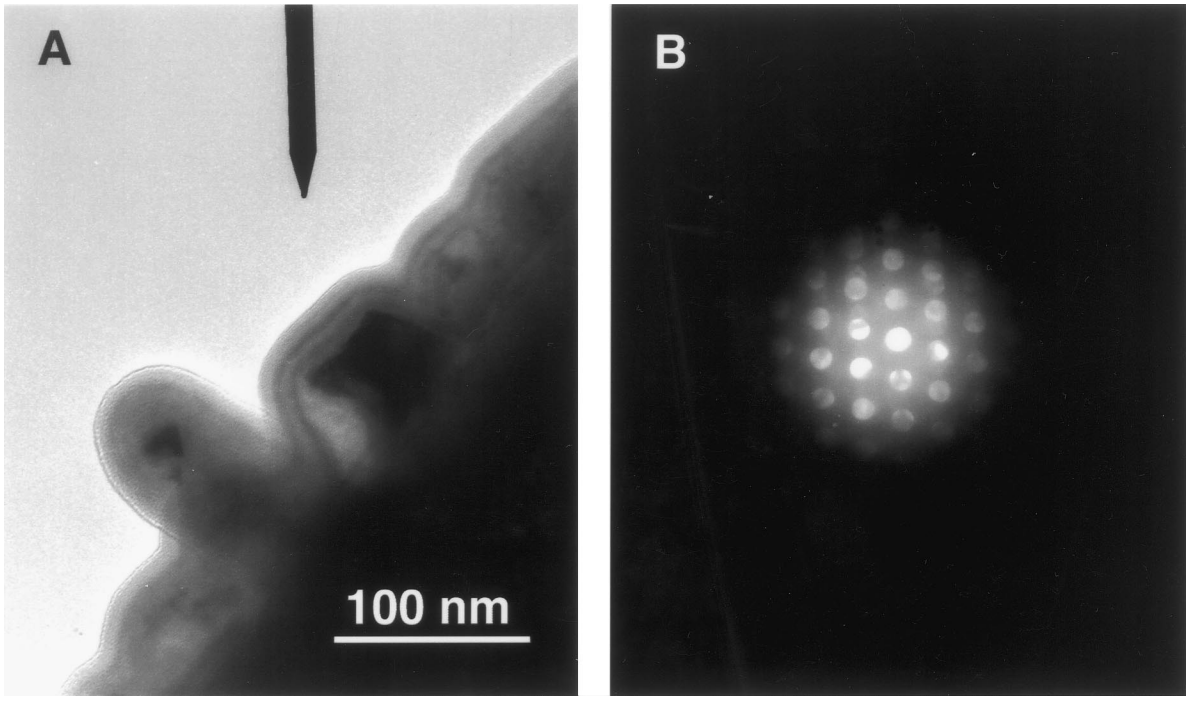

Fig. 4. (A) Bright field image of section containing a crystallite; (B) convergent beam electron diffraction image of the crystallized region.

1400–1900 K for molten YAG. The experiments with undercooled melts also demonstrated that nucleation of crystals occurs at a negligible rate in the melt at apparent temperatures above 1500 K for the mullite composition and above 1400 K for the YAG-composition.

The SEM micrographs in Figs. 5 and 6 show fibers crystallized under rapid heating conditions. Figure 5 shows longitudinal views of YAG and mullite fibers after rapid heating of the glass fibers to 1573 and 1873 K for 30 s. Figure 4 is of etched sections of mullite fibers crystallized by rapid heating to 1373 and 1673 K for 30 s followed by cooling to ambient temperature in air. The figures indicate that the grain size was rather large for the crystalline YAG fibers, on the order of 5–10 μm. Porosity is also visible in the YAG fibers. The mullite-composition glass fibers crystallized to produce dense crystalline material with grain sizes in the range 0·5–1 μm.

3.5 Properties of crystalline fibers

Crystallization of the glass fibers produced stresses that resulted in curved crystalline fibers. Some of the fibers were curled with several bends of variable radius from 2–10 mm, these were not tested.

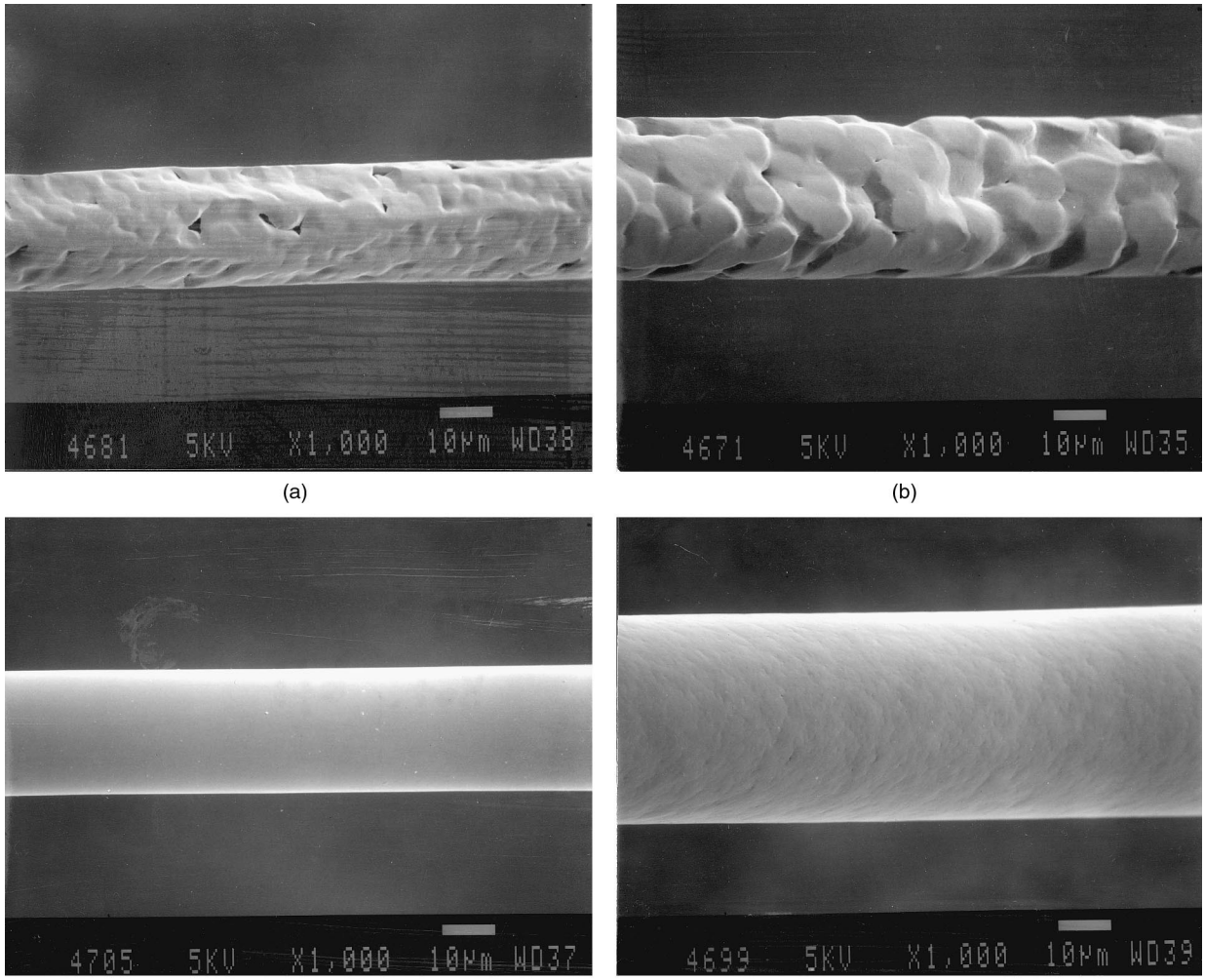

Fig. 5. SEM pictures of longitudinal views of YAG (top) and mullite (bottom) composition fibers which were crystallized by rapid heating to (left) 1573 K and (right) 1873 K and soaking for 30 s.

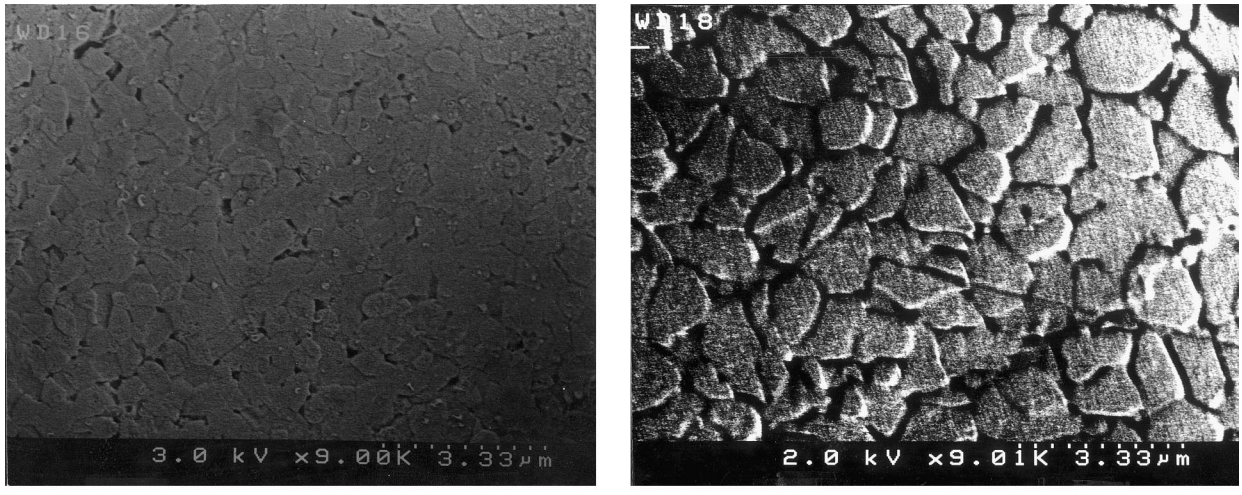

Fig. 6. SEM images of etched cross-sections of mullite fibers processed at (left) 1623 K and (right) 1873 K for 30 s.

Reproducible tensile testing of the crystallized fibers was not possible with the Instron tensile testing machine.

The tensile strength of crystallized mullite fibers was estimated by bending the fibers between the anvils of a vernier caliper. Short sections of crystallized fiber could be bent to a radius of approximately 2 mm. The minimum radius to which a fiber bent without fracture was used to calculate the tensile strain in the outer part of the curved region.

Thus for a fiber of 10 μm radius, a minimum bend radius of 2 mm corresponds to a strain of 0·5%. Using a modulus of elasticity of 360 GPa for mullite,[16] a tensile strength of 1·8 GPa is deduced.

4 Discussion

The intrinsic properties of crystalline oxides present many opportunities for application in high temperature technology. The realization of these applications would be enhanced if ceramic materials, including fibers for ceramic–ceramic composites, can be made with properties approaching the intrinsic values.

The glass fibers pulled from undercooled melts have highly reproducible properties and can be formed at high rates. The fiber pulling process creates uniform property fibers with smooth surfaces which are defined by surface tension of the liquid acting in the region where the fiber is drawn from the molten liquid. The fibers contain minimal flaws and exhibit high and reproducible values of the tensile fracture strength. TEM analysis of glass fibers which had high tensile strength indicated that they were free from crystallinity.[7] TEM analysis of mullite-composition glass fibers with decreased mechanical properties revealed that they contained nanocrystalline regions. The process by which nanocrystals are formed in some of the fibers has not been identified.

The fiber making process also allows selected additives and dopants to be added to the fibers and control of fiber diameter through changes in the fiber pulling conditions. These fibers are thus considered to be suitable precursors for investigating the production of ceramic oxide fibers by controlled crystallization of the glass.

The results demonstrate that high mechanical properties can be achieved in short sections of the crystalline fibers, as seen in the elongation results from bend tests. X-ray diffraction analysis of crystallized glass indicated that at least 1 mol% of cations can be substituted in the mullite crystal lattice and that they change the lattice parameter. Continuing work is emphasizing the study of dopant effects and control of the thermal processing on the microstructure and properties of the crystalline fibers.

The extremely rapid heat transfer that occurs from a hot ambient gas to the thin fibers allows heating rates of several thousand K s^{-1} when a fiber is inserted into a furnace. Since the levitated liquids can be formed into bulk glass at cooling rates of a few hundred K s^{-1}, it appears that the glass fibers can be heated to high temperature without nucleating crystals during the heating step. This observation explains the grain sizes observed in fibers that were rapidly heated to crystallize at high temperatures. The grain size increases with temperature, indicating that growth was enhanced relative to nucleation at the higher process temperatures.

5 Conclusions

The process of forming glass fibers from undercooled melts greatly expands the range of materials which can be made into fibers. The glass fibers have high strength, reproducible properties, and can be produced with a uniform distribution of additives. The fiber making process is inherently fast and potentially inexpensive and it can provide a source of materials for high temperature structural applications. Ongoing research is directed to scale up glass fiber production and optimize the fiber crystallization process.

Acknowledgements

This research was supported by the US Air Force Office of Scientific Research under an STTR and the US National Science Foundation. Work at University of Illinois at Urbana-Champaign (UIUC) was also supported by the AASERT Program. TEM was performed at the Center for Microanalysis of Materials in the Materials Research Laboratory at the UIUC. Earlier experiments on undercooled melts were supported by NASA. SEM photographs of rapidly crystallized fibers were taken by B.C. as part of his senior year project in Materials Science at Northwestern University under the direction of Professor Vinayak Dravid. We thank Mr William Jellison for assistance in the research.

References

1. Loewenstein, K. L., *The Manufacturing Technology of Continuous Glass Fibers*, 3rd ed. Elsevier, Amsterdam, 1993.
2. Pollock, J. T. A., Filamentary sapphire. *J. Mat. Sci.*, 1979, **7**, 787–792.
3. Haggerty, J. S., Menashi, W. P. and Wenckus, J. F., Apparatus for forming refractory fibers. US Patent 4,012,213, March 1977.
4. Sayir, A. and Farmer, S. C., Directionally solidified mullite fibers. *MRS Symp. Proc.*, 1995, **365**, 11–20.
5. Richards, E. A., Goodbrake, C. J. and Sowman, H. Z. G., Reactions and microstructure development in mullite fibers. *J. Am. Ceram. Soc.*, 1991, **74**, 2404–2409.
6. National Material Advisory Board. *Ceramic Fibers and Coatings — Advanced Materials for the Twenty-first Century*. (NMAB-494). National Academy Press, Washington, DC, 1998.
7. Kriven, W. M., Jilavi, M. H., Zhu, D., Weber, J. K. R., Cho, B., Felten, J. J. and Nordine, P. C., Synthesis and microstructure of mullite fibers grown from deeply

undercooled melts. In *Ceramic Microstructure Control at the Atomic Level*, ed. A. P. Tomsia and A. Glaeser. Plenum, New York, 1996, pp. 169–176.
8. Weber, J. K. R., Felten, J. J., Cho, B. and Nordine, P. C., Glass fibers of pure and erbium or neodymium-doped yttria-alumina compositions. *Nature*, 1998, **393**, 769–771.
9. Angell, C. A., Formation of glasses from liquids and biopolymers. *Science*, 1995, **267**, 1924–1935.
10. Debenedetti, P. G., *Metastable Liquids*. Princeton University Press, Princeton, New Jersey, 1997.
11. Weber, J. K. R., Anderson, C. D., Krishnan, S. and Nordine, P. C., Solidification behavior of undercooled liquid aluminum oxide. *J. Am. Ceram. Soc.*, 1995, **78**, 577–582.
12. Mizuno, M. and Saito, H., Preparation of highly pure fine mullite powder. *J. Am. Ceram. Soc.*, 1989, **72**, 377–382.
13. Weber, J. K. R., Felten, J. J. and Nordine, P. C., New method for high purity ceramic synthesis. *Rev. Sci. Instrum*, 1996, **67**, 522–524.
14. Weber, J. K. R., Hampton, D. S., Merkley, D. R., Rey, C. A., Zatarski, M. M. and Nordine, P. C., Aero-acoustic levitation — a method for containerless liquid-phase processing at high temperatures. *Rev. Sci. Instrum*, 1994, **65**, 456–465.
15. Weber, J. K. R. and Nordine, P. C., Containerless liquid-phase processing at high temperatures. *Microgravity Science and Technology*, 1995, **VII**, 279–282.
16. Kriven, W. M., Palko, J. W., Sinogeikin, S., Bass, J. D., Sayir, A., Brunauer, G., Boysen, H., Frey, F. and Schneider, J. High temperature single crystal properties of mullite ($3Al_2O_3{\cdot}2SiO_2$). *J. Eur. Ceram. Soc.*, 1999, **19**(13–14), this issue.