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13. ABSTRACT (Maximum 200 words) Optimal ceramic reinforced CMS's and MMC's are the key to the success of many Air Force programs because of the significant promise these lightweight, high strength materials offer for meeting projected performance and protection requirements for a wide variety of aerospace applications. This Phase I program has explored methods of producing continuous yttrium aluminum garnet (Y3Al5O12) and mullite (3Al2O3.SiO2) fibers. In Task 1, synthesis reactors have been constructed with 12 l and 50 l capacities that will enable us to produce up to 2 kg of precursor compounds in a single reactor directly from Al(OH)3 and/or SiO2. In Task 2, fiber processing properties were optimized. We can produce 3 m/min of 30 um ave. dia. Fiber and spool it. This translates to 180 m/h. We have initiated efforts to optimize the spinning process to meet the expectations of Phase II work to produce 10s m/h of multi-fiber tows suitable for manufacture of ceramic/ceramic composites. In Task 3, Fiber properties for hand drawn fibers produced in earlier studies showed bend strengths as 1.9 Gpa (assuming e=280 Gpa), but tensile tests on continuously processed fibers have yet to be done. Phase I goals will be to refine the processing steps necessary to produce larger quantities of fibers, with better control of fiber diameters, pyrolysis treatments and finally mechanical properties. We also expect to extend our efforts to improve the mullite fiber system. We must learn to cure these fibers as they are being spun and then conduct pyrolysis studies.				
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# Low Cost, YAG and Mullite Fibers by Continuous Extrusion and Pyrolysis of Metal Carboxylate Precursors

## Final Report

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## Introduction

Optimal ceramic fiber reinforced CMCs and MMCs are key to the success of many Air Force programs because of the significant promise these light weight, high strength materials offer for meeting projected performance and protection requirements for a wide variety of aerospace applications. Hence, the availability of high quality ceramic fibers is also key to many Air Force programs. In particular, there is a critical need for high-modulus, refractory oxide fibers and matrices that will survive extended service at temperatures of 1500°C.

In this current program, Advanced Modular Powder Systems, working in concert with the Laine group at the University of Michigan, and in part with Tal Materials, Inc (an AMPS business partner) has explored methods of producing continuous yttrium aluminum garnet ( $Y_3Al_5O_{12}$ ) and mullite ( $3Al_2O_3 \cdot SiO_2$ ) fibers. The objectives of the proposed work and highlights of the program are briefly described below as a function of the original statement of work.

1. Task 1. Scale-up and economical production of YAG and mullite precursors. Our initial goal in Task 1 was to scale up syntheses of precursors to 500 g quantities. Because of an overlap with a Tal Materials NSF SBIR Phase I Program, we were able to synthesize up to one Kg quantities which were originally the goal set for Phase II. In joint work, AMPS and Tal Materials have constructed 12 l and 50 l synthesis reactors that will enable us to produce up to 2 kg of precursor compounds in a single reactor directly from  $Al(OH)_3$  and/or  $SiO_2$ .

2. Task 2. Fiber properties optimization through studies of process variables. Aluminum formate and aluminum and silicon alkoxides prepared in Task 1 were used to spin single, continuous fibers, and for the first time tows consisting of four YAG fibers. Original goals for spinning rates for YAG fibers were 10s m/h single filament. As of this point in the program, we can produce 3 m/min of 30  $\mu$ m ave. dia. fiber and spool it. This translates to 180 m/h. We still have problems with breaking and the green fibers cannot be directly pyrolyzed into ceramic fibers because of the need for a very long, low temperature cure. Mullite fibers can also be melt spun but no work was done to optimize this process to date. We have initiated efforts to optimize the spinning process to meet the expectations of Phase II work to produce 10s m/h of multi-fiber tows suitable for manufacture of ceramic/ceramic composites.

3. Task 3. Fiber property Characterization. Fibers properties for hand drawn fibers produced in earlier studies showed bend strengths as high as 1.9 GPa (assuming  $E = 280$  GPa), but tensile tests on continuously processed fibers have yet to be done. Continuous green and low temperature cured fibers have been characterized by SEM. High temperature mechanical properties are scheduled as a part of our Phase II efforts.

### **Background**

Although intense efforts have targeted the development of nonoxide silicon carbide (SiC), silicon nitride ( $\text{Si}_3\text{N}_4$ ) and silicon-carbide-nitride (SiCN) fibers with tensile strengths of  $\approx 3.0$  GPa and  $E = 400$ - $420$  GPa,<sup>1-20</sup> these fibers continue to suffer from low oxidation resistance and excessive creep at high temperatures. An additional drawback is the high cost. For example, Nicalon costs ca. \$500/Kg and Sylramic fibers are available for \$10,000/Kg. Nicalon and Tyranno fibers do not survive heating in an inert atmosphere at  $>1100^\circ\text{C}$  for more than a few hours. Even the nearly phase pure SiC Sylramic fibers degrade oxidatively at similar temperatures. Lipowitz et al report that Sylramic fibers lose 50% of their tensile strength on heating in air for 40 h at  $1200^\circ\text{C}$ . Thus, CMCs made with Sylramic fibers cannot offer useful service at  $1500^\circ\text{C}$ . It appears that only oxide ceramic fibers may meet the high temperature, strength and creep resistance requirements. However, achieving the proper microstructure still remains an incredible challenge.

Most commercial oxide fibers (produced currently or produced in the past) are alumina based. Saffil fibers (dia.  $\approx 3$   $\mu\text{m}$ , 5%  $\text{SiO}_2$ , ICI Ltd.) are produced from  $\text{AlCl}_3$  or  $\text{Al}(\text{O}_2\text{CCH}_3)_3$ / polysiloxane precursors.<sup>21</sup> Sumika  $\text{Al}_2\text{O}_3$  fibers (dia.  $\approx 17$   $\mu\text{m}$ , 50%  $\text{SiO}_2$ , Sumitomo Ltd.) are produced from alkylpolyaluminumoxane/silicate ester precursors.<sup>22</sup> Nextel (3M) fibers (312, 440, 610 and 720, dia. = 10-12  $\mu\text{m}$ ) are made using Al-monoacetate or formoacetate/ $\text{SiO}_2$  hydrosol precursors.<sup>23-26</sup> 3M's patents describe methods of producing  $\text{Al}_2\text{O}_3$  precursor fibers from solutions of Al monoacetate (or Al formoacetate), lactic acid (or DMF),  $\text{SiO}_2$  hydrosol and small amounts of boric acid ( $\approx 2$  wt.%) or a hydrous iron ( $\approx 0.6$  wt.% Fe) in  $\text{H}_2\text{O}$ .<sup>27,28</sup> Pyrolysis ( $>1000^\circ\text{C}$ ) of the extruded precursor fibers leads to composite microstructures consisting of mixtures of micro (nano) crystalline  $\text{Al}_2\text{O}_3$  with mullite, silica-boria, or aluminosilicate mixtures.

These fibers offer tensile strengths of 1-2 GPa and elastic moduli of 200-400 GPa. The higher values are typical of fibers closer to phase pure  $\text{Al}_2\text{O}_3$ . Unfortunately, none of these fibers offer utility above  $\approx 1200^\circ\text{C}$  mostly because of their poor creep properties. Others degrade because of excessive grain growth on heating to anticipated use temperatures. These poor properties arise because all the above fibers are nanocomposites of crystalline and amorphous (segregated) phases. They melt or creep severely below alumina's m.p. ( $2054^\circ\text{C}$ ) because of low melting second phases, e.g.  $\text{SiO}_2$ ,  $\text{B}_2\text{O}_3$ , or mullite. Nextel 440 (70 wt. %  $\text{Al}_2\text{O}_3$ /28 wt. %  $\text{SiO}_2$ /2 wt. %  $\text{B}_2\text{O}_3$ ) melts at  $\approx 1700^\circ\text{C}$ . Nextel 610 fibers ( $\approx 99$  wt.%  $\text{Al}_2\text{O}_3$ / $\approx 1$  wt.%  $\text{SiO}_2$ , grain size  $\approx 0.1$   $\mu\text{m}$ ) have a microstructure consisting of  $\alpha$ - $\text{Al}_2\text{O}_3$  (major phase) with nanocrystalline mullite (at grain boundaries).<sup>23</sup>

To date, no commercial fibers offer utility at  $1500^\circ\text{C}$  because they lack oxidative stability, creep resistance or suffer from excessive grain growth. Moreover, none of the available fibers is cost effective. On a performance basis; only phase pure, full dense, microcrystalline  $\alpha$ - $\text{Al}_2\text{O}_3$  and yttrium aluminum garnet (YAG) may offer the high temperature stability, good-to-excellent creep resistance and strength required for CMCs that will see extensive use at  $1500^\circ\text{C}$ . If cost projections can be realized, these materials are the best hope for achieving high quality, low-cost fibers.

If cost were not an issue, then single crystal fibers would provide the ultimate in properties. Corman's work on compressive creep of single crystal YAG shows that at  $1700^\circ\text{C}$  and at an applied stress of 100 MPa, the creep rate is  $2 \times 10^{-9} \text{ s}^{-1}$ .<sup>29</sup> Single crystal  $\text{Al}_2\text{O}_3$  creeps at a rate of  $2 \times 10^{-8} \text{ s}^{-1}$ , under analogous conditions.<sup>30</sup> Both materials are stable to  $>1500^\circ\text{C}$ , and as single crystals they offer tensile strengths  $> 3$  GPa and elastic moduli  $\leq 500$  GPa. These values are fiber diameter (flaw size) dependent. Unfortunately, as currently produced, single crystal fibers are extremely expensive and technically difficult to mass produce. Currently the next best alternatives are the polycrystalline analogs. Thus, polycrystalline YAG ( $\approx 3 \mu\text{m}$  grain size) stressed at 75.5 MPa ( $1400^\circ\text{C}$ ), creeps at  $2.5 \times 10^{-6} \text{ s}^{-1}$  vs.  $7.5 \times 10^{-6} \text{ s}^{-1}$  found for polycrystalline  $\text{Al}_2\text{O}_3$  ( $\approx 3 \mu\text{m}$  grain size).<sup>31-33</sup>

The objective of the current research program has been to develop continuous, low-cost, high strength YAG fibers. At the U of M, we learned to process fully dense, polycrystalline, 15-30  $\mu\text{m}$  dia. YAG fibers using very inexpensive precursors. Preliminary data indicate that these YAG fibers offer bend strengths as high as 1.9 GPa based on an estimated elastic modulus of  $\approx 280$  GPa. As

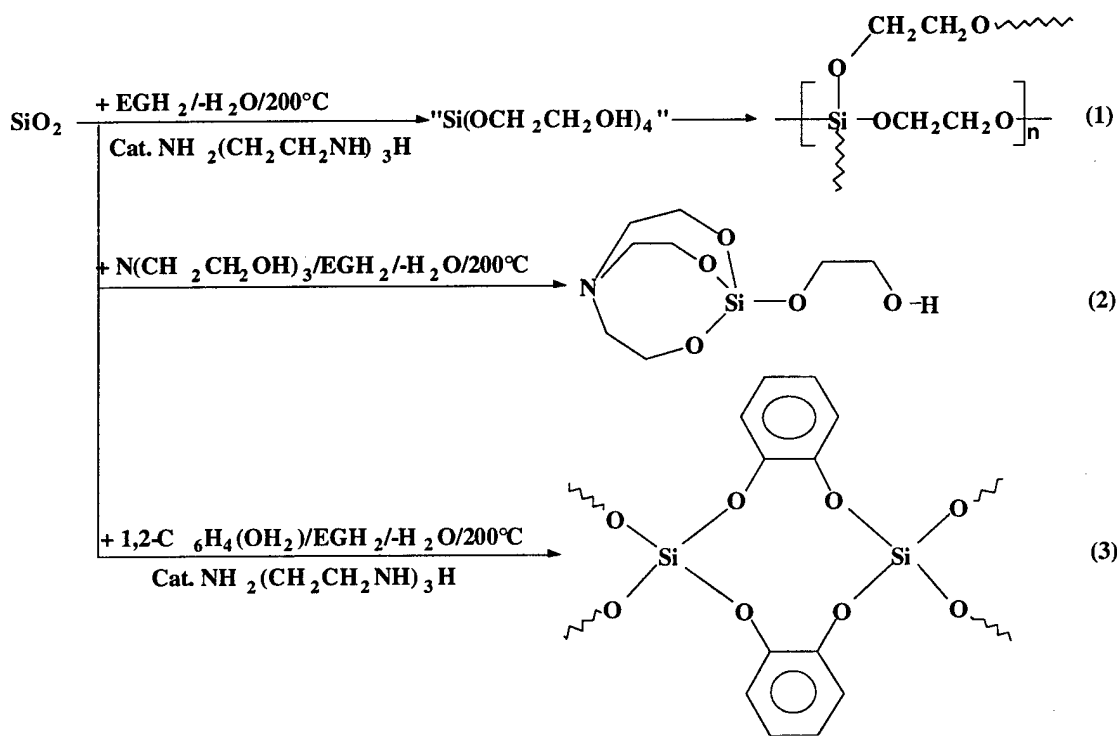
discussed below, the inexpensive precursors will serve as a basis for the work proposed here. We are working with AMPS and Tal Materials, to commercialize these fibers. We are using Tal's methods of making low cost precursors. These methods are licensed from the University of Michigan.

As part of Phase I, Task I studies, we worked with the University of Michigan and Tal to scale up low cost precursor syntheses. The scientific basis for the work in Task 1 is presented below.

### Task 1. Low cost precursor chemistry.

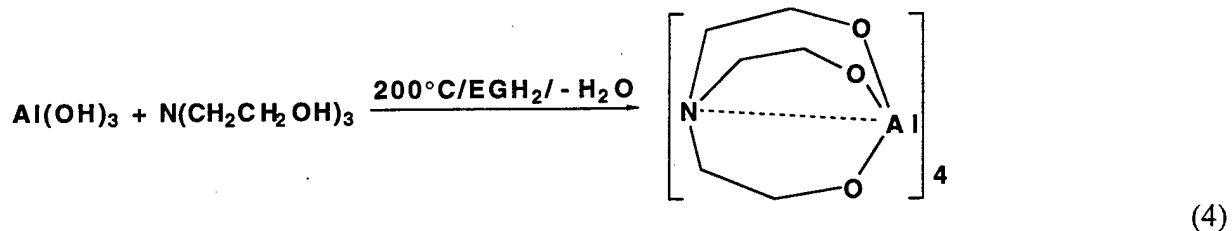
Based on a discovery in the Laine group that ethylene glycol (EGH<sub>2</sub>) reacts with SiO<sub>2</sub>/base to give alkali and alkaline glycolato silicates; <sup>36-38</sup> a set of routes was developed to produce neutral siloxanes. <sup>39-43</sup>

Thus, high boiling (b.p. >200°C) amines can be used either in catalytic or stoichiometric quantities, respectively, to dissolve SiO<sub>2</sub> in EGH<sub>2</sub> at reasonable rates. The products can be the spiro-siloxane [Si(eg)<sub>2</sub>], silatranes or aryloxysilanes. <sup>39</sup> The reaction (2) silatrane, is a water soluble silica



precursor that is a major component in our mullite fiber precursor synthesis, when mixed with the alumatrane analog made as follows. <sup>39,44-50</sup>

Alumatrane. Based on reaction (2), TEAH<sub>3</sub> was reacted with Al(OH)<sub>3</sub> to give (6 h) alumatrane (>95 % yield):

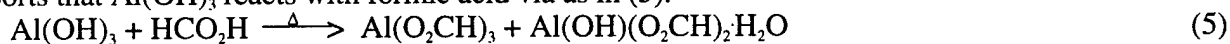


(TEAl)<sub>4</sub> was made previously, but not from Al<sub>2</sub>O<sub>3</sub>, [AlO(OH)]<sub>n</sub> or Al(OH)<sub>3</sub>, and was well characterized.<sup>47</sup> The found TGA ceramic yield is 29.0 % vs. 29.4 % calc. for Al<sub>2</sub>O<sub>3</sub>. (TEAl)<sub>4</sub> is quite unique. Most Al alkoxides hydrolyze rapidly in atmospheric moisture mandating a strictly anhydrous work environment. In contrast, solid (TEAl)<sub>4</sub> is stable in laboratory air (humidity) for weeks.<sup>48-50</sup> Tal Materials, in an NSF funded SBIR program proved that (TEAl)<sub>4</sub> could be synthesized, with 95-98 % conversions, from spacerite (Al(OH)<sub>3</sub> which costs \$2/kg) and represents an important cost advantage that was anticipated, but not proven.

Combinations of the silatrane, (TEAl)<sub>4</sub> and group I and II metal alkoxides can be used to provide processable precursors to aluminosilicates<sup>45</sup> especially mullite, one of the fiber materials of choice here. To our knowledge there are no other examples of aluminosilicate precursors produced this way. Still another possible alumina precursor was based on aluminum carboxylates.

Aluminum carboxylates may provide low cost opportunities as precursors because many of them are air and moisture stable and can be made processable (see below). One critical issue is the need to make these precursors without using Al metal, AlR<sub>3</sub> (R = alkyl), AlCl<sub>3</sub> or Al(OiPr)<sub>3</sub>.<sup>51-55</sup>

The literature on aluminum carboxylate syntheses is relatively plentiful. A 1933 Gmelin citation<sup>53</sup> reports that Al(OH)<sub>3</sub> reacts with formic acid via as in (5).



Thus, one direct route to carboxylates exists. Unfortunately, reaction (5) appears to work only with freshly prepared (amorphous) Al(OH)<sub>3</sub>, made from AlCl<sub>3</sub> or Al(OiPr)<sub>3</sub>. Thus, the real question is can naturally occurring or feedstock materials be used instead.

Work by Barron et al suggests that boehmite, [AlO(OH)]<sub>n</sub>, available naturally and from the Bayer process, may offer the required solution.<sup>56,57</sup> Barron reports that refluxing boehmite with carboxylic acids generates particles consisting of a small "boehmite-like core" decorated with carboxylate groups, reaction (12). Analytical evidence indicates the z ≥ 1.



IR reveals the presence of Al bound hydroxyl groups and a unique, bridging carboxylate. Longer chain acid modified materials, R = pentyl, heptyl or methoxyethyl, are soluble in organic solvents and offer processability. Preliminary MW data suggest polymers with 20-30k Da.

We find quite different results using gibbsite as the starting material. We noticed, in working with processable aluminum isobutryates,  $\text{Al}(\text{O}_2\text{CiPr})_3$ , that it is highly susceptible to hydrolysis to  $\text{Al}(\text{OH})(\text{O}_2\text{CiPr})_2$ .<sup>58</sup> Recognizing that  $\text{H}_2\text{O}$  is a byproduct of (6), we used acetic anhydride to trap water formed, or distilled the reactant carboxylic acid (b.p.  $>100^\circ\text{C}$ ) to codistill any  $\text{H}_2\text{O}$  generated. The result is complete conversion of  $\text{Al}(\text{OH})_3$  to anhydrous  $\text{Al}(\text{O}_2\text{CH})_3$ , free of  $\text{Al}(\text{OH})(\text{O}_2\text{CH})_2$ . Gibbsite (Catapal/Dispal from Vista Chem., Spacerite from Alcoa, Inc.) reacts to give pure  $\text{Al}(\text{O}_2\text{CH})_3$  with trace amounts of acetic anhydride. If the formate is refluxed in pure anhydride, it appears that some  $\text{O}_2\text{CCH}_3$  groups are introduced. The ceramic yields (to  $\text{Al}_2\text{O}_3$ ) of these products range from 27-33 wt. % vs 32 wt. % theory for  $\text{Al}(\text{O}_2\text{CH})_3$ . The theoretical ceramic yield for  $\text{Al}(\text{OH})(\text{O}_2\text{CH})_2$  is 37 wt. %.

$\text{Al}(\text{O}_2\text{CH})_3$ , on dissolution in boiling water, transforms to a cold water soluble compound (1 g/10 mL). Thus, low-cost gibbsite can be used to make a water soluble, alumina precursor. Working in conjunction with AMPS and Tal Materials, we learned to make Kg quantities of  $\text{Al}(\text{O}_2\text{CH})_3 \cdot 3\text{H}_2\text{O}$  in about 6 h using 80% formic acid as the reactant, and solvent for Spacerite which is crystalline gibbsite,  $\text{Al}(\text{OH})_3$  available from Alcoa for \$0.80-0.90/lb depending on quantities (to one ton). The resulting formate can be used to make spinnable YAG precursor.

### Task 2. Spinning studies

Although, in earlier studies, we developed an extrudable YAG precursor,<sup>59</sup> no efforts were made to develop a system that was continuously spinnable such that the fibers could be spooled. Thus, we were surprised by the difficulties in making materials with the correct rheology. A typical spinning dope is as follows:

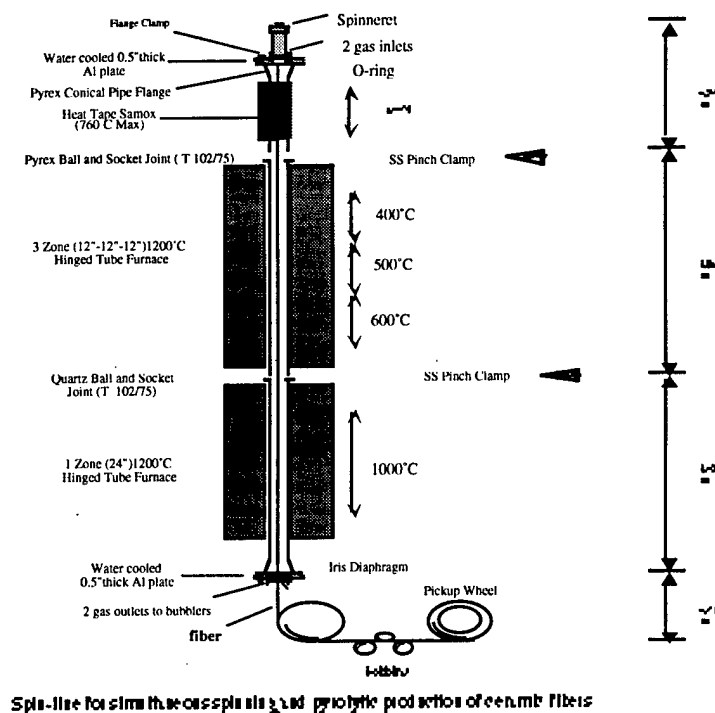
#### Spinnable YAG ( $\text{Y}_3\text{Al}_5\text{O}_{12}$ ) formulation

**A. Synthesis of Precursor.** To make 3:5 stoichiometric YAG precursor solutions, 40.178 g of  $\text{Y}(\text{O}_2\text{CCH}_3)_3 \cdot 4\text{H}_2\text{O}$ , and 30g of aluminum formate,  $\text{Al}(\text{O}_2\text{CH})_3 \cdot 3\text{H}_2\text{O}$ , were dissolved in about 900 mL DI water. The mixture was heated with stirring. Initially, the mixture was cloudy. After a few

minutes, the mixture became a clear and colorless solution. When the mixture began to boil, 20.13 g of formic acid, 13.65 g of ethylene glycol and 6.11 g of isobutyric acid were added separately to stabilize the solution. The solution was evaporated to about 80 mL and the viscosity increased significantly. To obtain a clear solution with suitable viscosity, evaporation in the last few minutes was followed carefully to determine when to stop heating. Sometimes, when the solution was evaporated to  $\approx$  100 mL, a white precipitate formed. In these cases, 300 mL boiling water was added to dissolve the precipitate and the solution was concentrated again as the procedure described above. The final precursor was a transparent and viscous gel.

**B. YAG/PVP Formulation.** In a beaker, 200 mL DI water was heated to boiling. Then the boiling water was added to another beaker containing 15-20 g of YAG precursor. The YAG precursor dissolved in the boiling water and the solution was boiled further. Then PVP was added. The PVP solution used was a mixture contained 0.25 g K30, 0.25 g K90, 0.25 g K120 and 11 g water (the values are for molecular weight of the PVP). The grams of PVP were 0.3 wt. % the weight of YAG precursor. Then YAG/PVP solution was evaporated to about 20 mL. The final solution was a clear, viscous gel suitable for spinning.

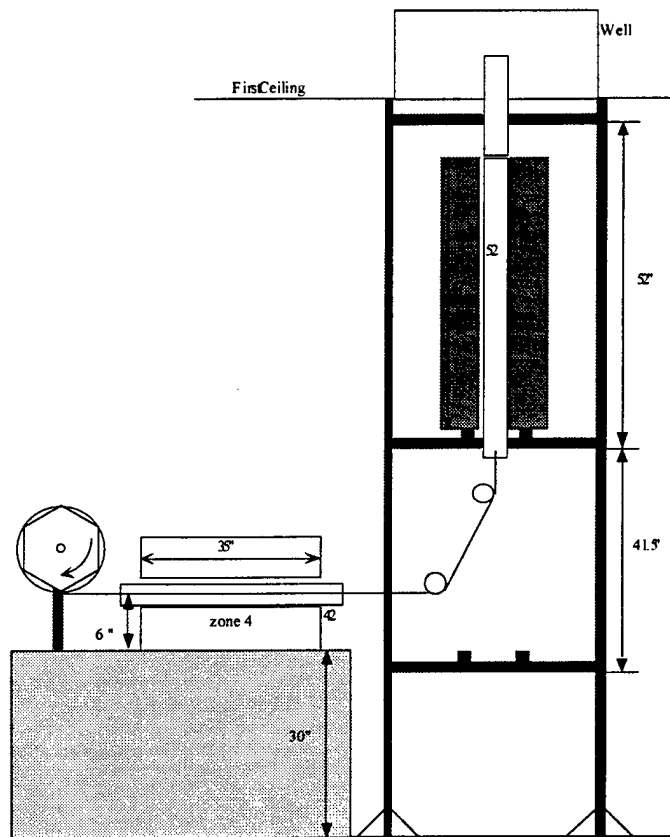
The above formulation is the result of about nine months of trial and error. One might assume that it should be straightforward to make a spinnable solution, but it turns out that the spinning environment is extremely critical to successful spinning. For example, we find that when it rains, we cannot spin good fibers. This is obviously a humidity problem. We tried to adjust the spinning environment by enclosing the spinning tower in a plastic curtain. This works better but makes spinning more difficult. Figure 1 shows the spin tower as originally built. We recently had to modify this



**Figure 1. Spinning tower--original design.**

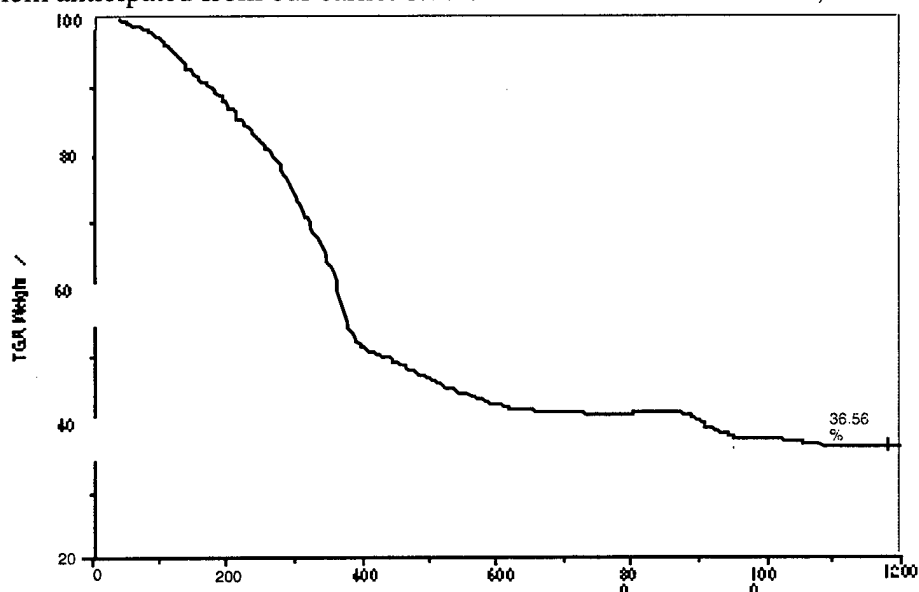
tower because we found that having an extra furnace in line did not help with spinning. Thus, we introduced a bend as shown in Figure 2 below. We normally do not use the second furnace. We have finally been able to spin single fibers and spool them. In the space of two weeks and with further precursor modification, we learned to first spin fibers at 2m/h with diameters of 60  $\mu\text{m}$ . Then we learned to heat them to  $\approx 135^\circ\text{C}$  during spinning to cause them to self draw to about 30-40  $\mu\text{m}$  and to dry them enough to be spooled. Thus, within the last three weeks we have been able to spool fibers and also to draw them. At this point we can now spin, draw and spool fibers with average diameters of 30  $\mu\text{m}$  at a rate of 3m/min or 130 m/h to be conservative. About 15% of the time we can get diameters down to 20  $\mu\text{m}$ . Making 20  $\mu\text{m}$  green fibers 100 % of the time represents a near term goal.

In very recent work, we have been able to spin multiple fiber tows using a spinneret with four holes. We find that again there are multiple engineering problems to overcome. For example, sometimes only two or three rather than four fibers will extrude. Sometimes the fibers contact each other before drying sufficiently and then weld together. Other times fibers extrude faster out of one spinneret than the others. All of these are engineering problems that can be resolved in Phase II.



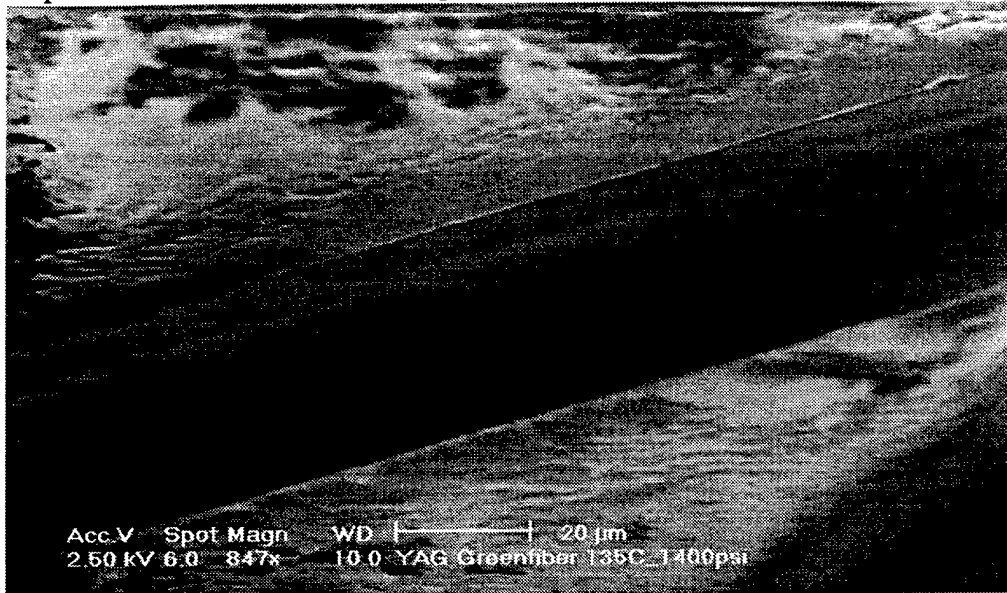
**Figure 1. Spinning tower--modified.**

We found that once spun and spooled, these fibers could not be heated rapidly enough to allow in situ pyrolysis --at least not for the size spin tower we had constructed. The reason is that the fiber exteriors cure and densify too rapidly and produce "french bread-like" fibers on heating. This was a potential problem anticipated from our earlier studies and from the TGA below,<sup>59</sup> which shows the



**Figure 3. YAG Fiber TGA**

tremendous mass changes that occur in the 150-300°C region. Thus, we were forced to conduct very careful heat treatment studies. At this point, we must spool the green fibers (Figure 4) and then cure them (on the spools under tension) at low temperatures (< 200°C) for long periods of time prior to



**Figure 4.** Green YAG fiber cured to 120°C/5 h.

converting them to dense ceramic fibers. After long term low temperature curing, we are now exploring the processing between 200° and 700°C where the final residual carbon contents are lost. We hope to achieve the properties obtained in the earlier studies with much shorter fiber segments as detailed in Reference 59. We have conducted numerous trials of various heating schedules in the 200°-1400°C. The following section summarizes our recent efforts in this area.

### **Heat treatment**

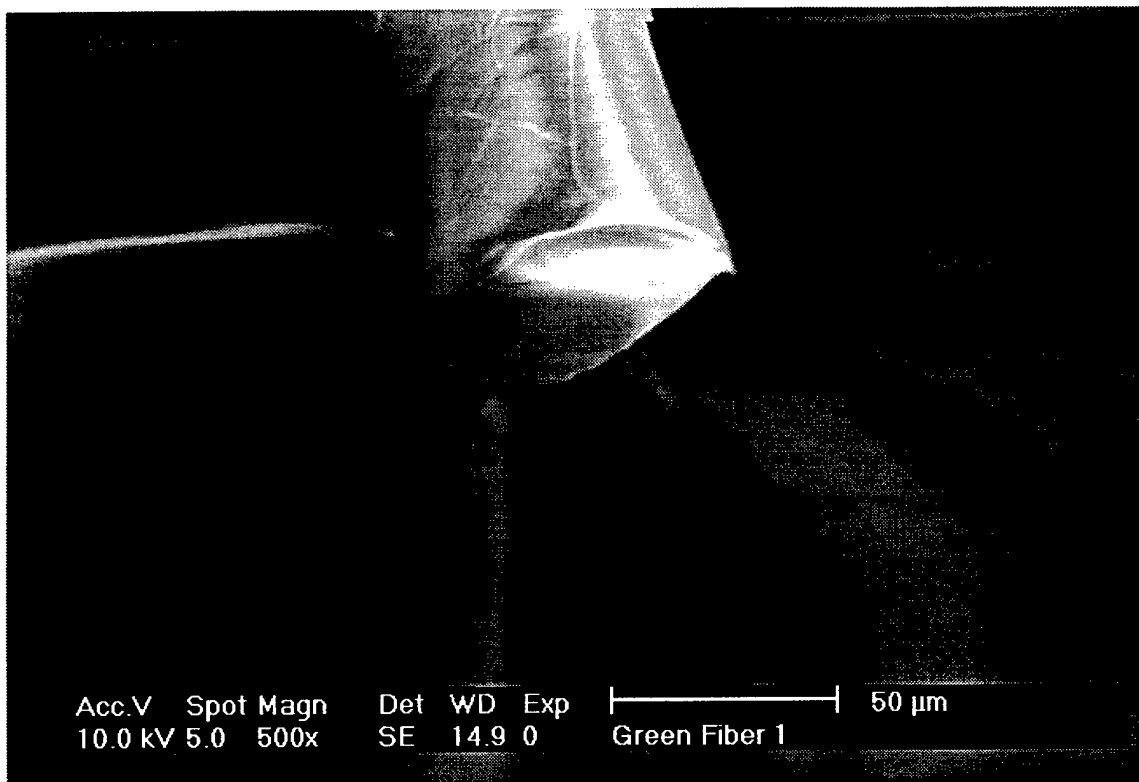
The diameter of our latest green fibers are about 50μm. See Figure 5. Green fibers pyrolyzed at 1°C/min to 1400°C (2 h) were found to be porous, Figure 6. The Figure 3 TGA analysis of green fiber shows three mass loss regions. The first one is from 50°C to 300°C. The second mass loss is around 400°C and the third mass loss is around 900°C.

Fibers heated at 200°C (20 h) → 300°C(10 h) → 400°C (2 h) were porous, see Figure 7.

Increasing the time at 200°C and 250°C made some improvements, see Figure 8. Fibers processed with longer treatment times at 200°C were dense, see Figure 9. Heat treatment at 250°C was also

necessary. Fibers tended to be porous if not treated at 250°C, see Figure 10. Generally, heat treatment of 200°C/30 h and 250°C/10 h was necessary. A heating rate of 0.5°C/min was used. With faster heating rates, e.g. 1°C/min, fibers were more porous. See Figures 11 to 14.

Different heating schedules were used to heat the fibers to 900°C. See Figures 15 to 18. Fibers heated at 5°C/min from 400° to 900°C had fewer pores and cracks than those heated at 15°C/min. Once apparently dense fibers were produced at 900°C, efforts were made to produce fully dense and crystalline fibers at 1500° and 1600°C. The 900°C fibers (Figures 17 and 18) were heated at 30°C/min and at 15°C/min to 1500°C/2h leading to fully dense fibers as shown in Figures 19 and 20. Figures 21 to 24 show fibers heated at 30°C/min and at 15°C/min to 1600°C/2h.



**Figure 5.** Green fiber.

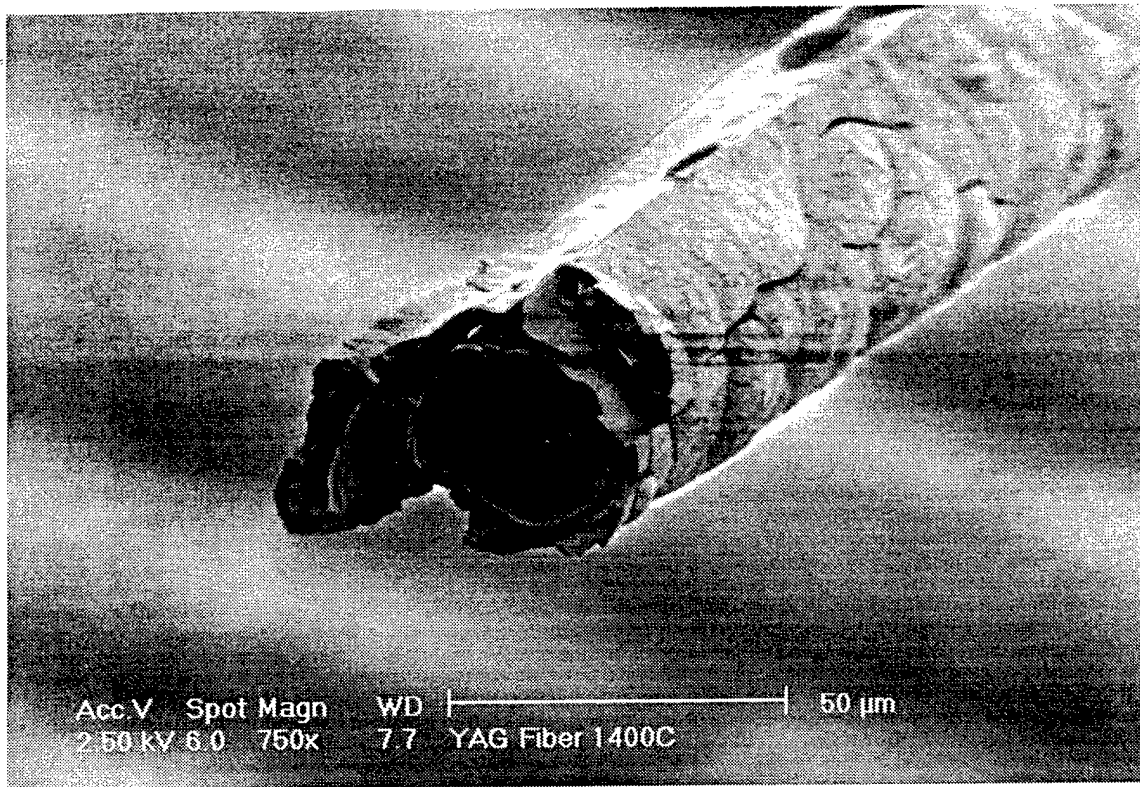


Figure 6. Heated at 1°C/min to 1400°C/2hr.

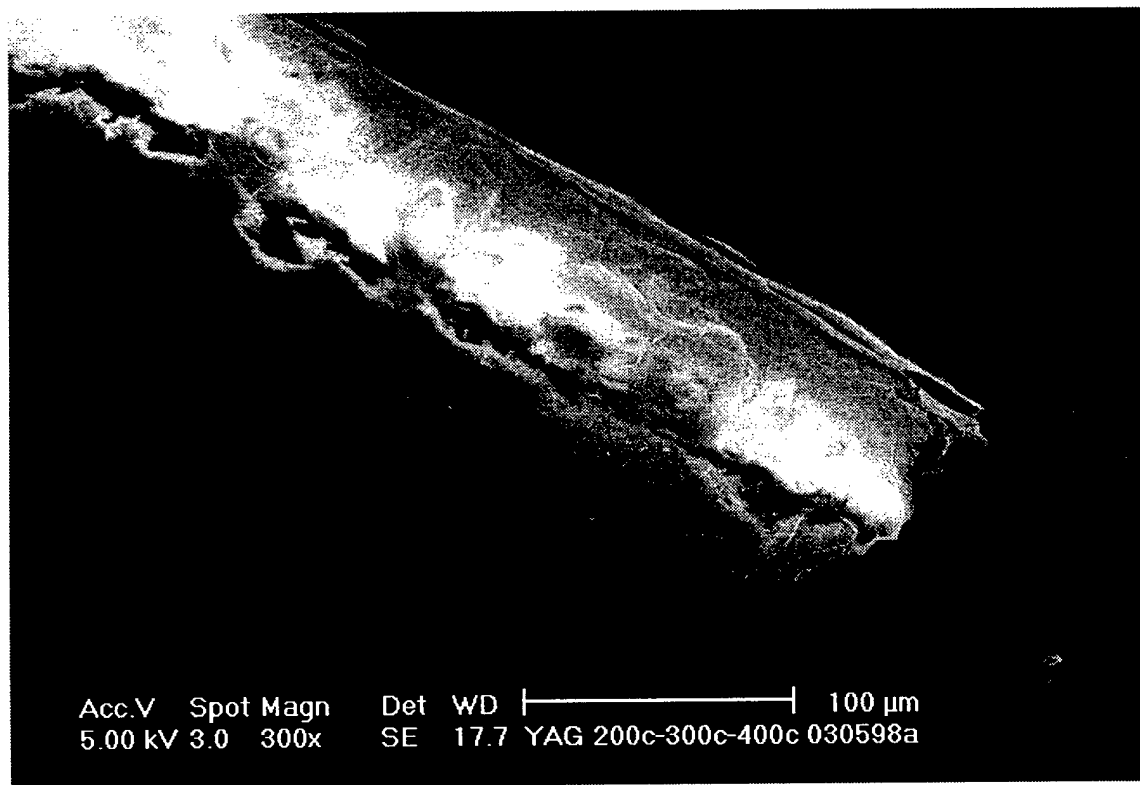
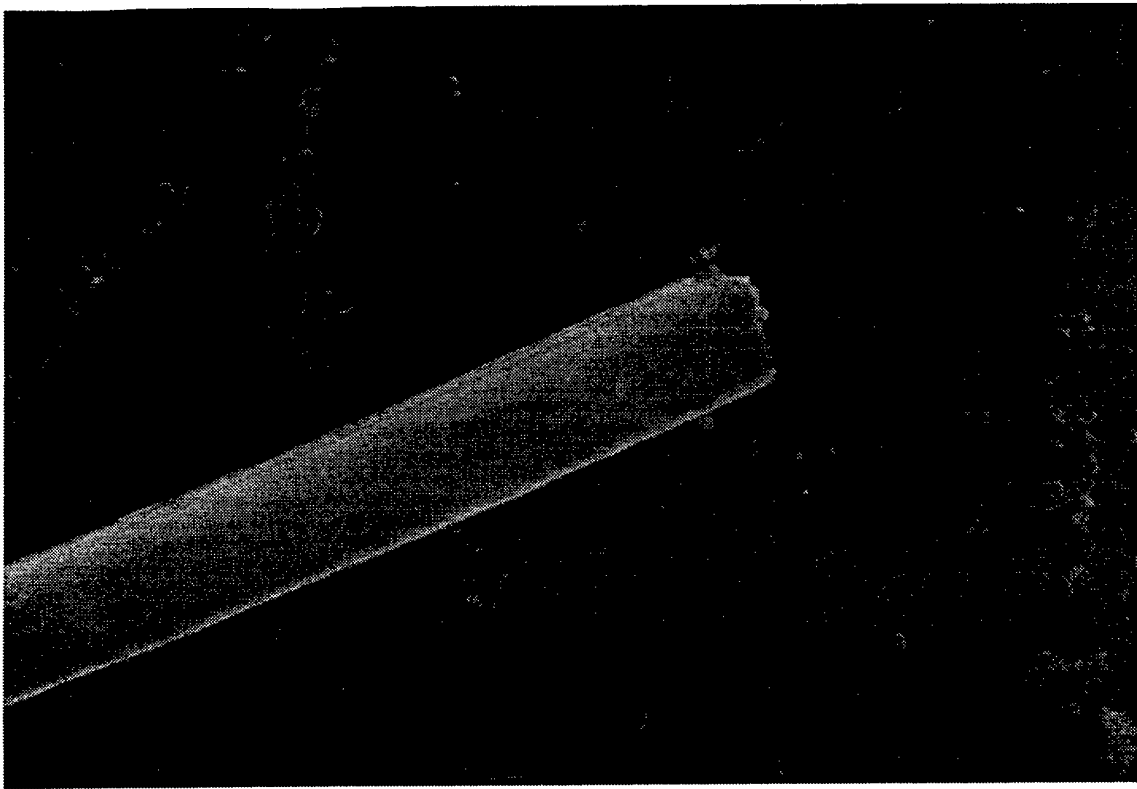
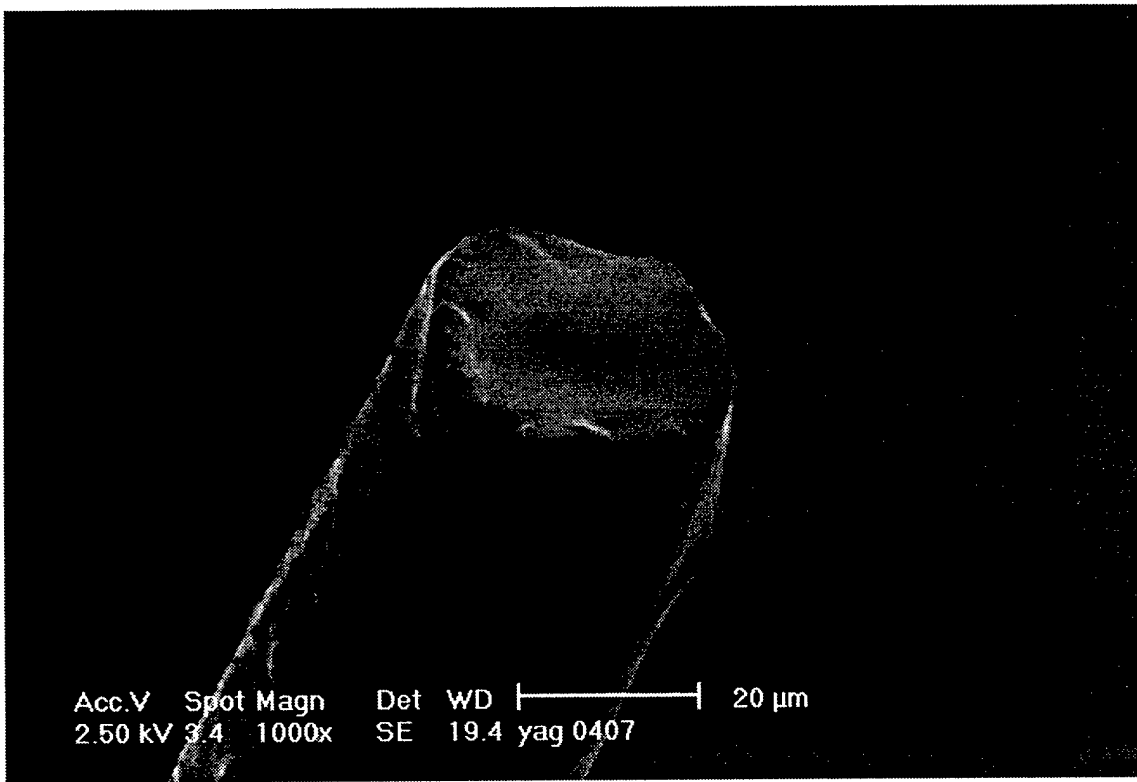


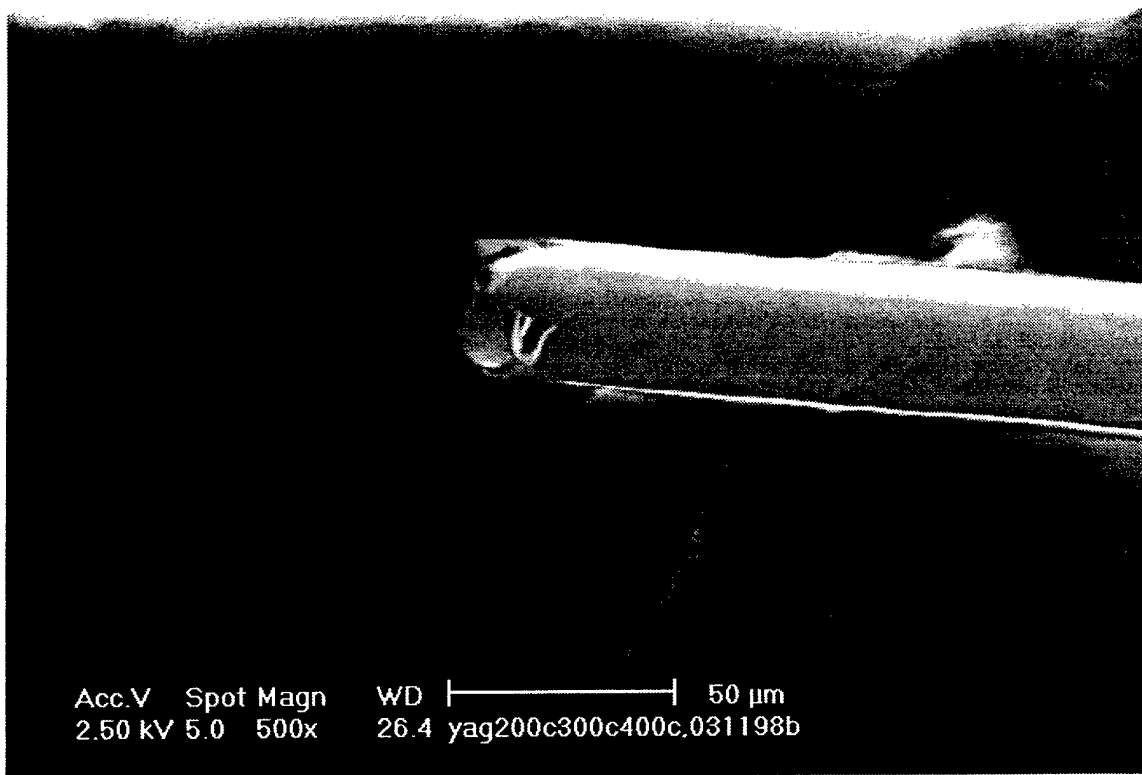
Figure 7. Heated at 1°C/min to 200°C/20hr, 0.5°C/min to 300°C/10hr, 0.5°C/min to 400°C/2hr.



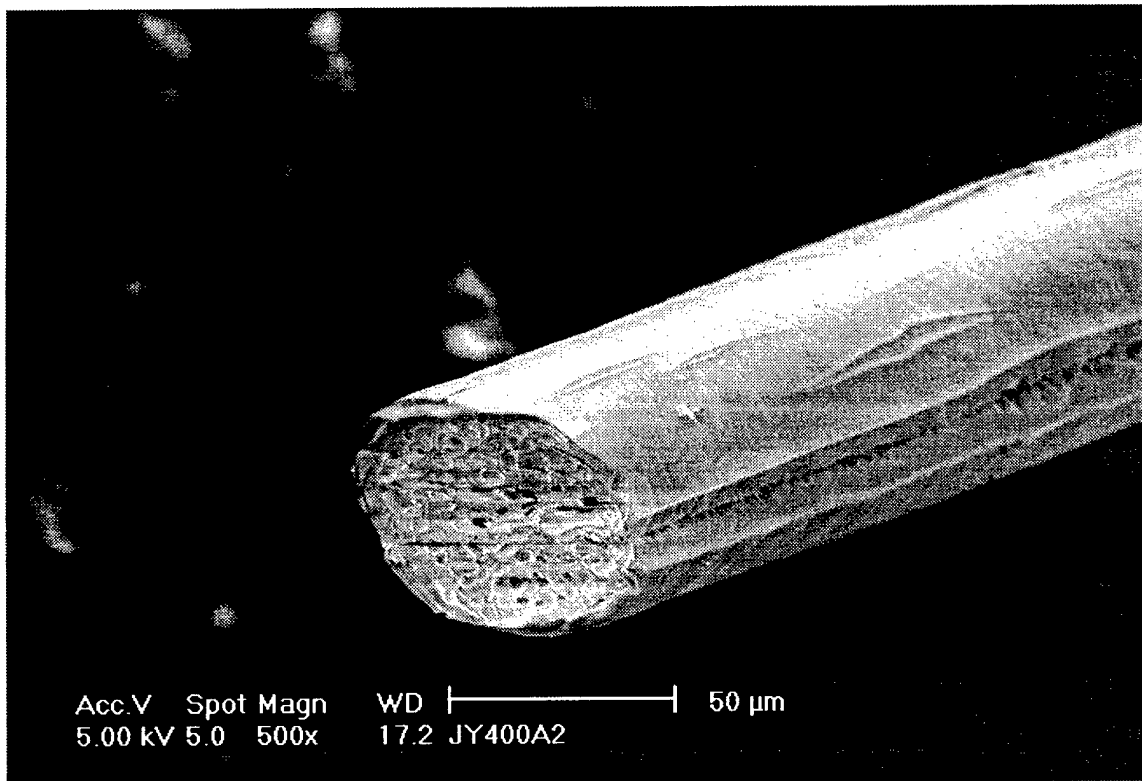
**Figure 8.** Heated 1°C/min to 200°C/30 h, 0.5°C/min to 250°C/10 h, 0.5°C/min to 300°C/10 h, 0.5°C/min to 400°C/2 h.



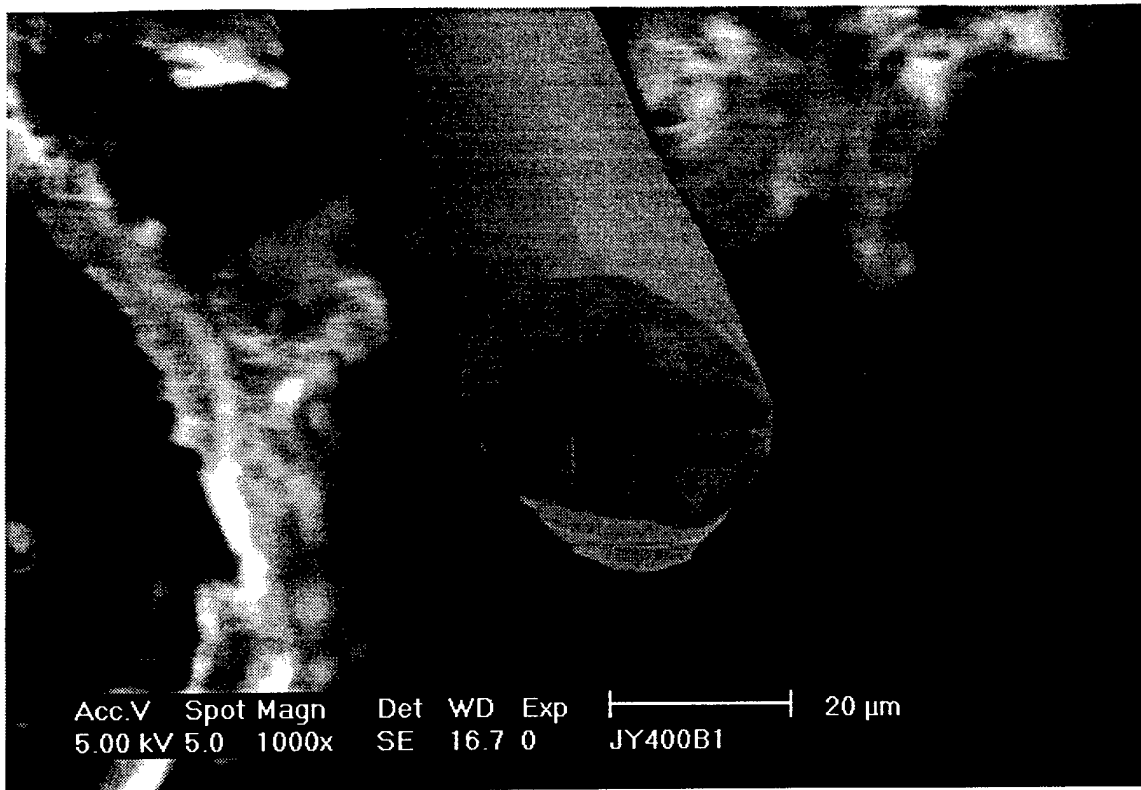
**Figure 9.** Heated at 0.5°C/min to 200°C/50h.



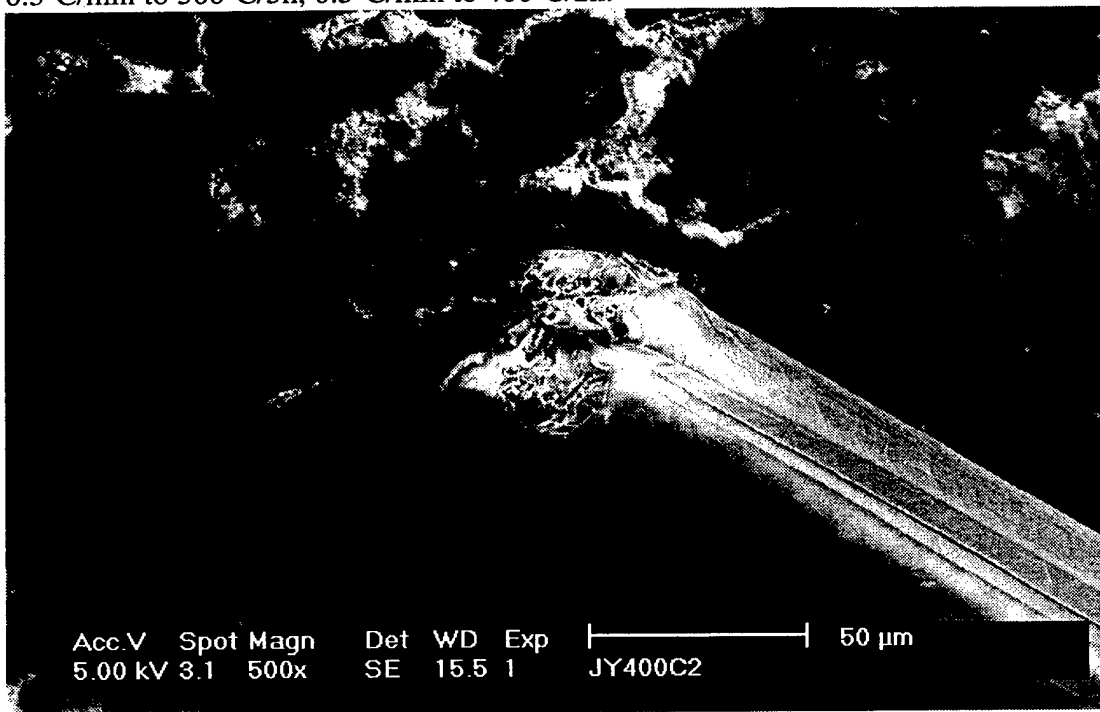
**Figure 10.** Heated at 1°C/in to 200°C/50h, 0.5°C/min to 300°C/10h, 0.5°C/min to 400°C/2h



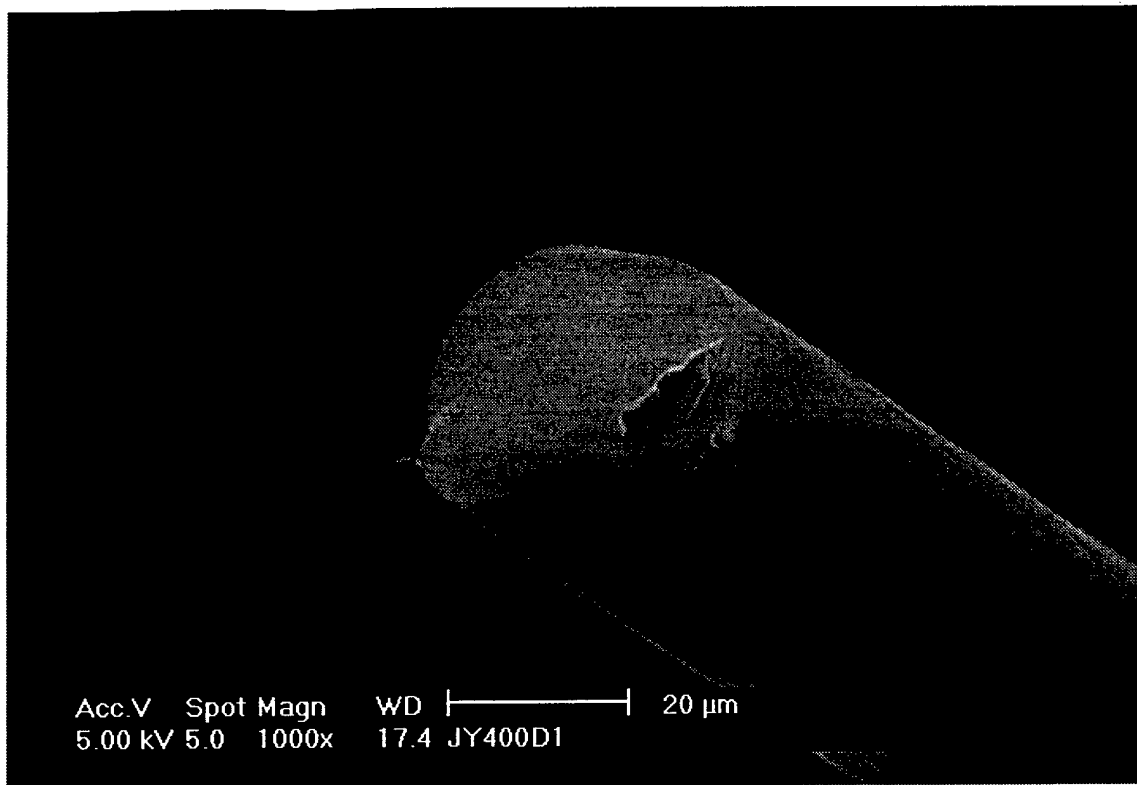
**Figure 11.** Heated at 0.5°C/min to 200°C/30h, 1°C/min to 250°C/10h, 1°C/min to 300°C/5h, 1°C/min to 400°C/2h.



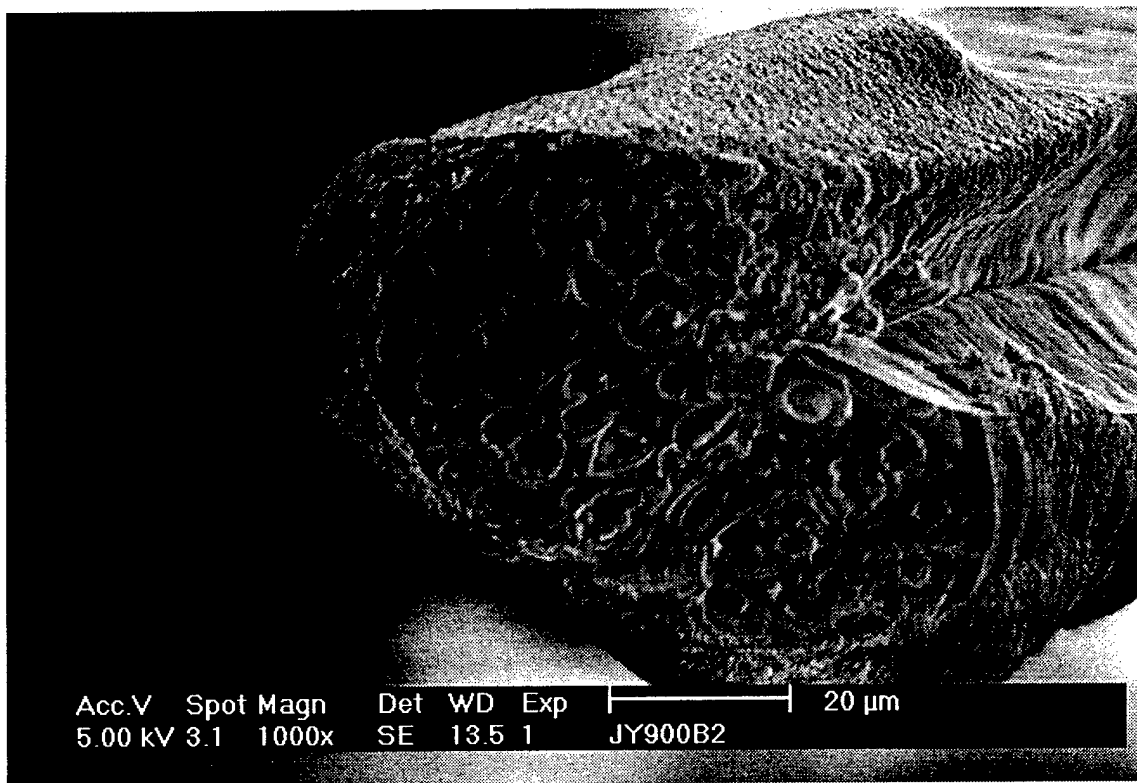
**Figure 12.** Heated at 0.5°C/min to 100°C/10h, 0.5°C/min to 200°C/30h, 0.5°C/min to 250°C/10h, 0.5°C/min to 300°C/5h, 0.5°C/min to 400°C/2h.



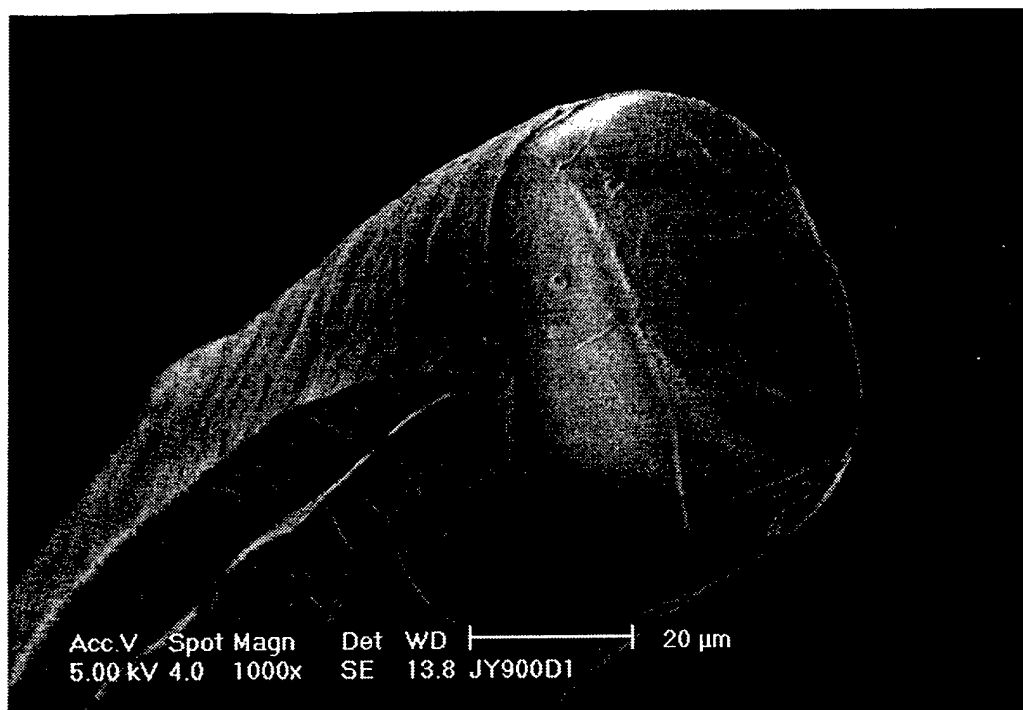
**Figure 13.** Heated at 1°C/in to 100°C/10h, 1°C/min to 200°C/30h, 1°C/min to 250°C/10h, 1°C/min to 300°C/5h, 1°C/min to 400°C/2h.



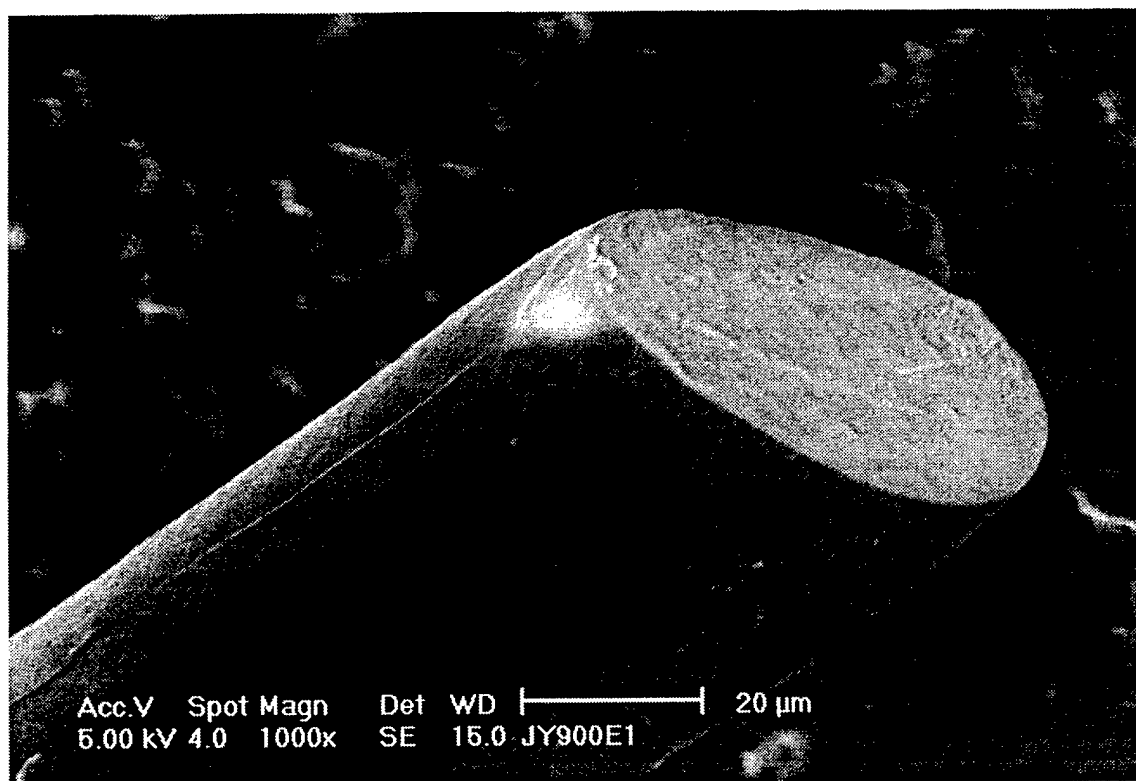
**Figure 14.** Heated at 0.5°C/min to 200°C/30h, 0.5°C/min to 250°C/10h, 0.5°C/min to 400°C/10h.



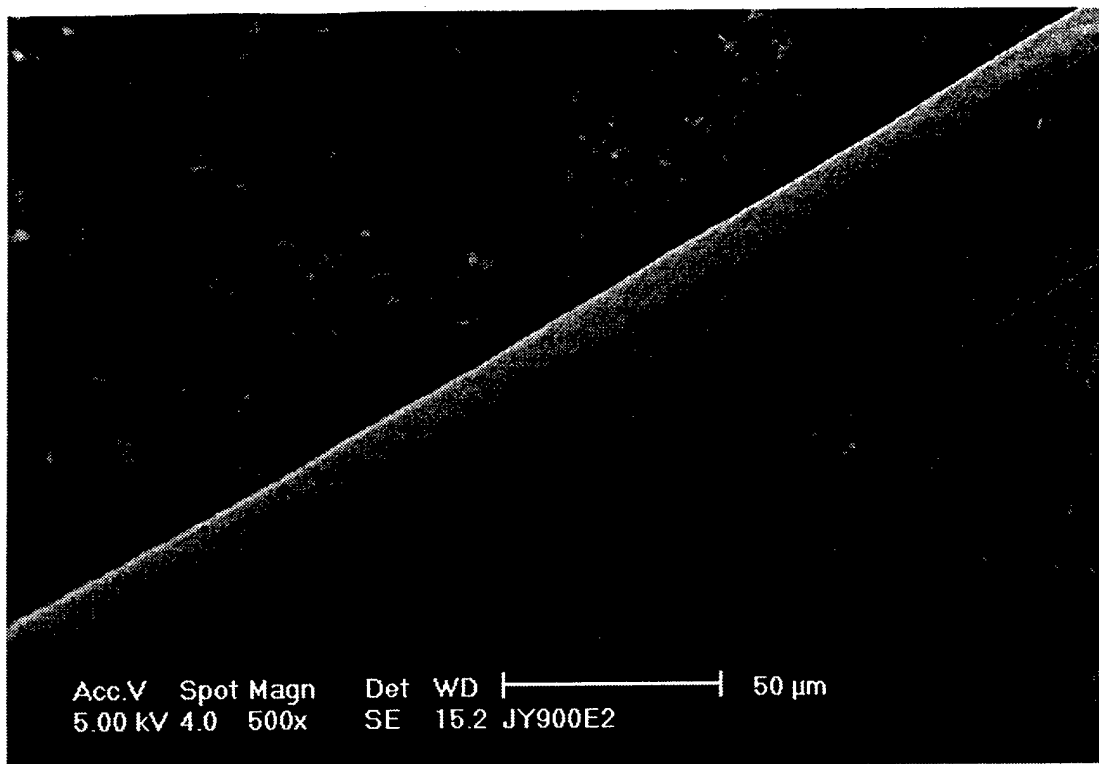
**Figure 15.** Heated at 0.5°C/min to 100°C/5h, 1°C/min to 200°C/30h, 1°C/min to 250°C/10h, 1°C/min to 300°C/5h, 1°C/min to 400°C/5h, 15°C/min to 900°C/2h.



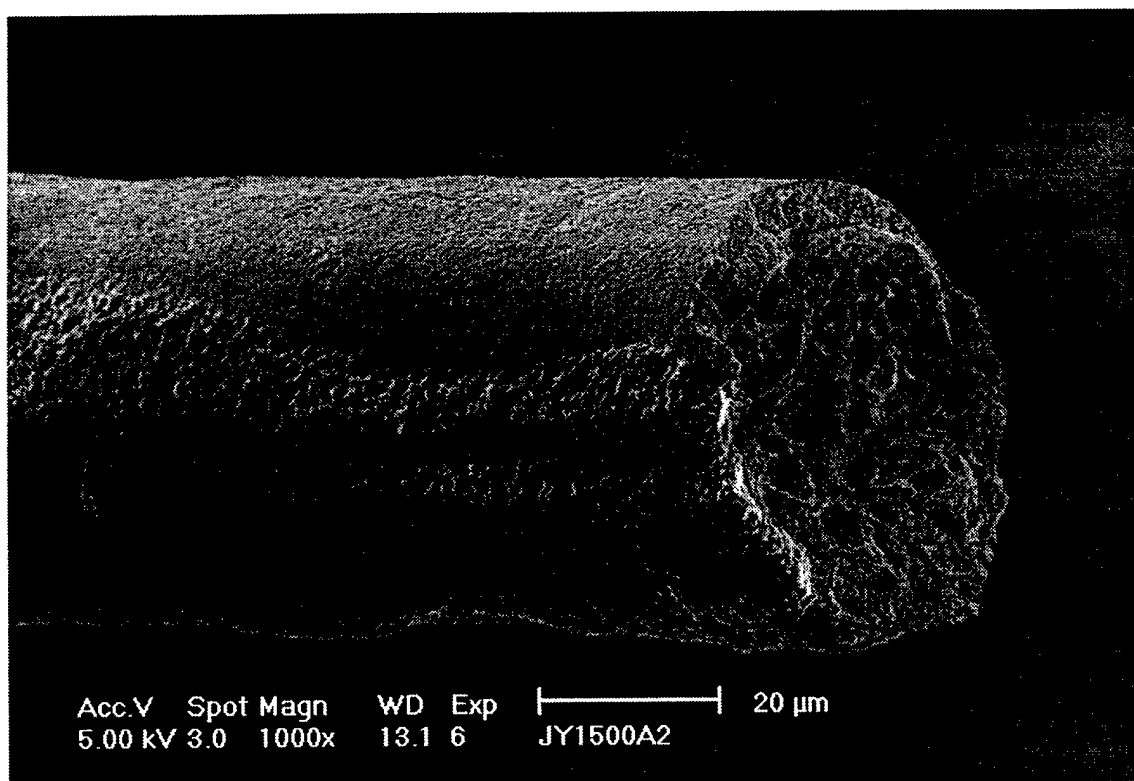
**Figure 16.** Heated at 0.5°C/min to 100°C/10h, 0.5°C/min to 200°C/30h, 0.5°C/min to 250°C/10h, 0.5°C/min to 300°C/5h, 0.5°C/min to 400°C/2h, 5°C/min to 900°C/2h.



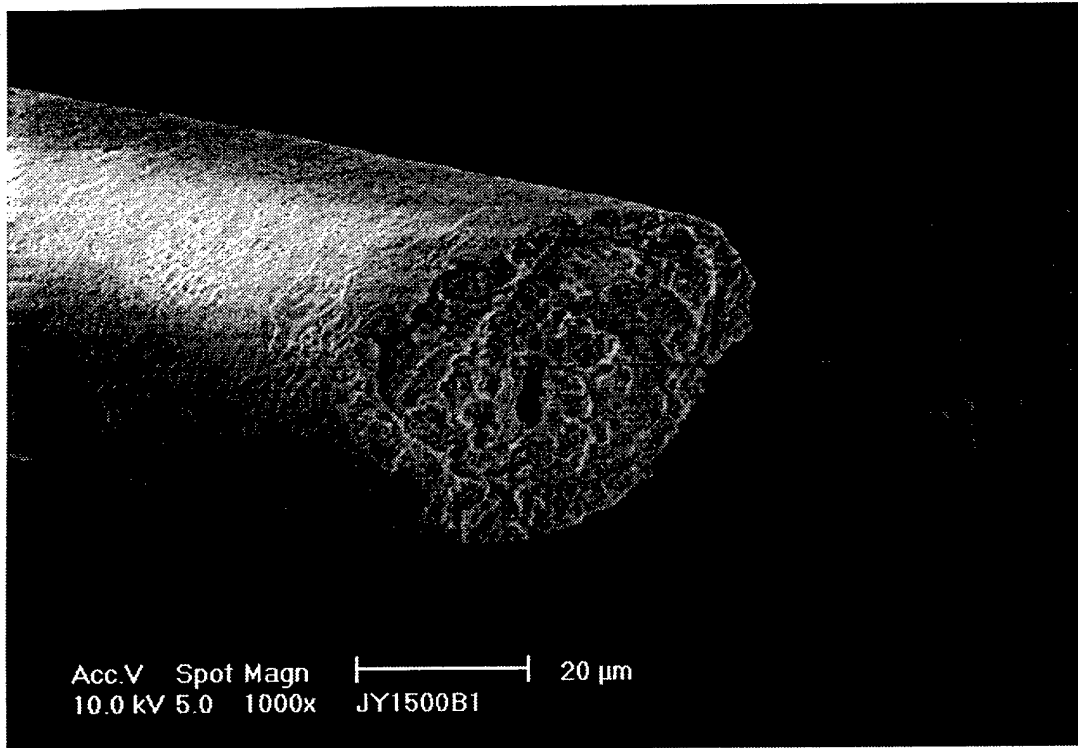
**Figure 17.** Heated at 0.5°C/min to 200°C/30h, 0.5°C/min to 250°C/10h, 0.5°C/min to 400°C/10h, 5°C/min to 900°C/2h.



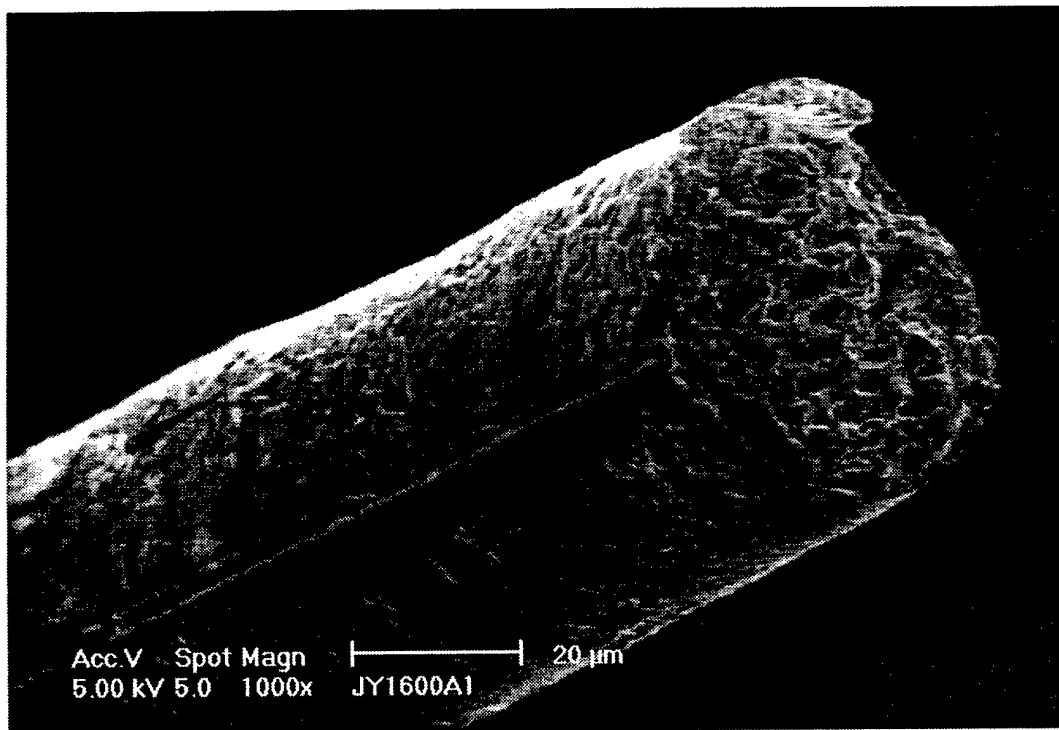
**Figure 18.** Heated at 0.5°C/min to 200°C/30h, 0.5°C/min to 250°C/10h, 0.5°C/min to 400°C/10h, 5°C/min to 900°C/2h.



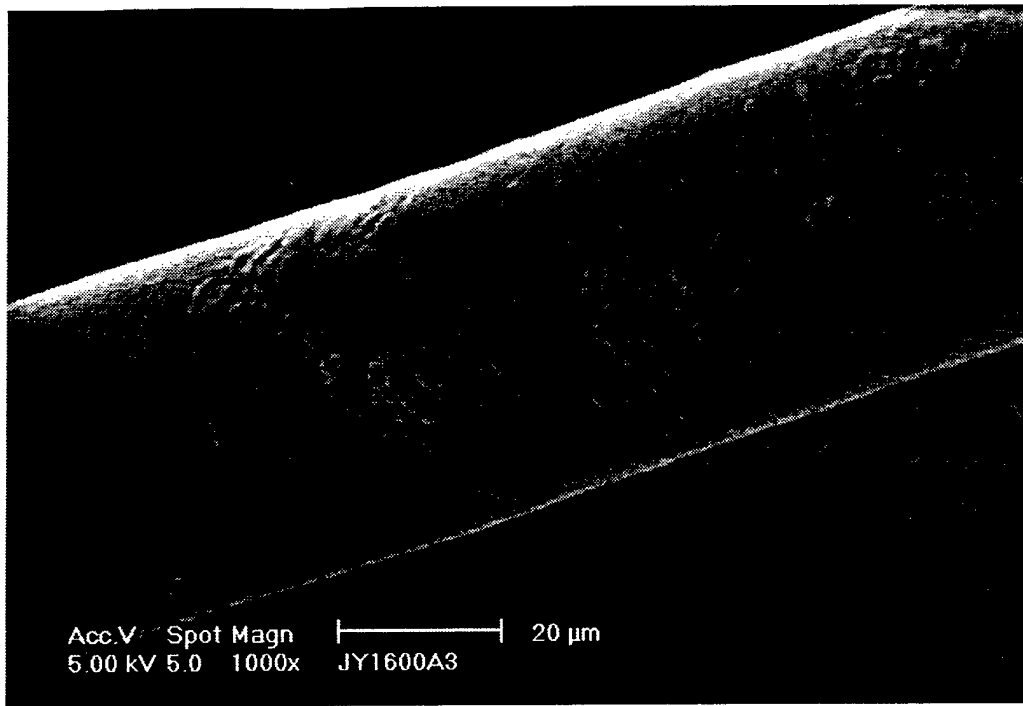
**Figure 19.** Heated at 0.5°C/min to 200°C/30h, 0.5°C/min to 250°C/10h, 0.5°C/min to 400°C/10h, 5°C/min to 900°C/2h, 30°C/min to 1500°C/2h.



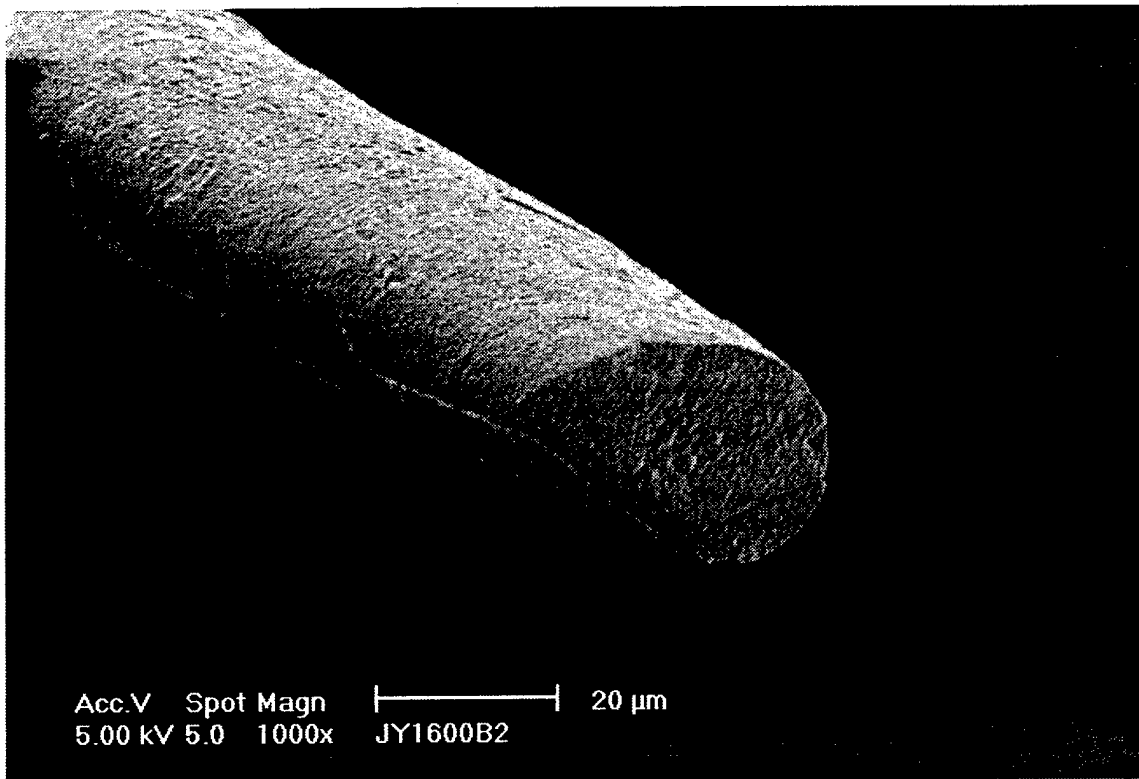
**Figure 20.** Heated at 0.5°C/min to 200°C/30h, 0.5°C/min to 250°C/10h, 0.5°C/min to 400°C/10h, 5°C/min to 900°C/2h, 15°C/min to 1500°C/2h.



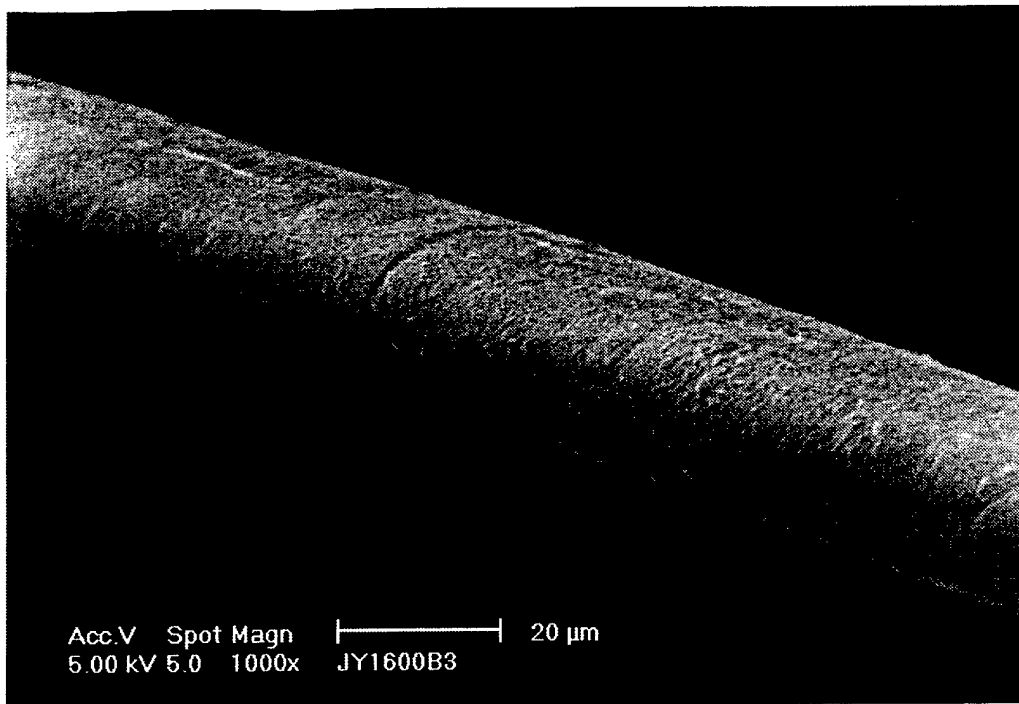
**Figure 21.** Heated at 0.5°C/min to 200°C/30h, 0.5°C/min to 250°C/10h, 0.5°C/min to 400°C/10h, 5°C/min to 900°C/2h, 15°C/min to 1600°C/2h.



**Figure 22.** Heated at 0.5°C/min to 200°C/30h, 0.5°C/min to 250°C/10h, 0.5°C/min to 400°C/10h, 5°C/min to 900°C/2h, 15°C/min to 1600°C/2h.



**Figure 23.** Heated at 0.5°C/min to 200°C/30h, 0.5°C/min to 250°C/10h, 0.5°C/min to 400°C/10h, 5°C/min to 900°C/2h, 30°C/min to 1600°C/2h.



**Figure 24.** Heated at 0.5°C/min to 200°C/30h, 0.5°C/min to 250°C/10h, 0.5°C/min to 400°C/10h, 5°C/min to 900°C/2h, 30°C/min to 1600°C/2h.

The 1600°C fibers heated at both 15°C/min and 30°C/min appear to be nearly fully dense. However, they do not show the excessive grain growth that we observed previously for stoichiometric YAG fibers.<sup>59</sup> The reasons for this are not clear; it may be that the stoichiometry is not correct (we are checking that) or the heat treatments result in lower grain sizes. The results in reference 59 suggest that fully dense fibers with grain sizes smaller than  $\approx 0.5 \mu\text{m}$  should provide good-to-excellent bend and tensile strengths ( $\approx 2.0 \text{ GPa}$  or better). At this point, we must now learn to produce longer lengths of 1600°C fiber to conduct mechanical properties studies. We hope to get some of the testing done by Dr. G. Morescher at NASA Lewis. This work will go beyond the Phase I time limits but must be done to prove the quality of the fibers. Our goals are to achieve mechanical properties such as found for the hand drawn and partially extruded fibers shown below.

Phase II goals will be to refine the processing steps necessary to produce larger quantities of fibers, with better control of fiber diameters, pyrolysis and post pyrolysis treatments and finally mechanical properties. We also expect to extend our efforts to improve the mullite fiber system. We must learn to cure these fibers as they are being spun and then conduct pyrolysis studies.

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