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PREPARATION AND CHARACTERIZATION OF PROPERTIES
OF OXYNITRIDE GLASSES AND FIBERS

July 1989

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ABSTRACT

→ It has been shown that the substitution of nitrogen for oxygen in oxide glass structures enhances bond strength, which results in glasses having outstanding properties. These oxynitride glasses have higher elastic moduli, tensile strength, hardness, and better corrosion resistance than oxide glasses. Previous work at MTL demonstrated techniques for making significant quantities of these oxynitride glasses. It was also recognized that these glasses had the potential to be formed into glass fibers. Such glass fibers would have potential applications in high-performance composites. This final report summarizes research and development efforts conducted by GEO-CENTERS, INC. during the period from April 1986 through August 1988 on the preparation and characterization of properties of oxynitride glasses and glass fibers.

Initial work concentrated on glasses in the Y-Si-Al-O-N system. Properties of the yttrium oxynitride glasses include elastic moduli to 165 GPa and micro-hardnesses up to 10.4 GPa. These Y-Si-Al-O-N glasses, however, have relatively high densities (3.6 to 4.0 g/cc). Other lower density (2.6 to 3.0 g/cc) systems were also investigated. These systems include M-Si-Al-O-N, where M = Mg, Ca, Li, and Zr. Also, a method was developed for the continuous drawing of oxynitride glass fibers from these glasses with properties the same as those of the parent glasses.

Discussed in this final report are the results of the research efforts. Indications show that oxynitride glasses and glass fibers have considerable potential as high-performance engineering materials.

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1.0 INTRODUCTION:

The addition of nitrogen into common oxide glass systems has been shown to enhance many properties, including hardness, corrosion resistance, strength, and elastic modulus. The replacement of oxygen by nitrogen in the glass structure leads to a tightening of the glass network due to the formation of more bonds and cross-linking than would be present in a similar oxide glass. These properties are essential for glass fiber applications. Glass fibers with these improved properties could find use in many applications, including high-strength resin matrix composites. Previous work at MTL demonstrated that Y-Si-Al-O-N glass fibers could be produced with elastic moduli approximating the exceptionally high values (140 to 186 GPa) obtained for the parent glasses. While these moduli are more than double those of ordinary glasses, the Y-Si-Al-O-N glasses have relatively high densities (3.6 to 4.0 g/cc). The modulus/density ratio is, however, still impressively high (50% higher than ordinary glass). In addition, literature reviews produced convincing evidence that the substitution of nitrogen for oxygen increases elastic modulus for many glass systems, including M-Si-Al-O-N systems in which M = Li, Mg, or Ca, which also produce low density (2.6 - 2.7 g/cc) glasses. The objective of this research effort was to identify systems in which the modulus/density ratio is as high as possible, optimize critical glass fiber properties, and demonstrate the feasibility of forming small diameter, high quality, high specific modulus glass fibers from those systems.



2.0 PREPARATION OF OXYNITRIDE GLASSES

2.1 Li-Si-Al-O-N System

Figure 1 is a molar plot of the $\text{Li}_2\text{O}-\text{AlN}-\text{Si}_2$ system with points L5 to L11 representing compositions that were being studied when work on this contract was initiated. Composition L5 was initially chosen for further experimentation. Several melts were performed on glass batches of this composition. Starting materials consisted of Li_2CO_3 , AlN , and SiO_2 . Melting was performed in BN-lined graphite crucibles in a N_2 atmosphere at 1600°C . It was observed during these experiments that the evaporation of Li from such melts during processing contaminates the furnace. Attempts to avoid this problem by melting in a larger, contamination-resistant furnace, however, were unsuccessful; the quenching rate was found to be too slow to avoid devitrification. Crucibles were then designed and ordered to allow for glass melting to be performed in the induction-heated furnace, which is easy to clean and can be cooled very quickly.

In order to analyze samples of the prepared glasses, rectangular slabs, approximately $3/16"$ x $1/8"$ x $1-3/4"$, were cut from a prepared sample with a diamond saw. The specimens appeared somewhat devitrified and also contained inclusions and imperfections. It was then decided to systematically explore the potential glass forming region in the $\text{Li}_2\text{O}-\text{AlN}-\text{SiO}_2$ system. Points L12 to L25 on Figure 1 are subsequent compositions that were produced and examined for glass forming characteristics. Each point has been classified as either glass, crystalline, or intermediate. Points were randomly selected on the plot, and from the molar percentages of each component, batch calculations were made to determine the weight, in grams, of each component. The total weight of each

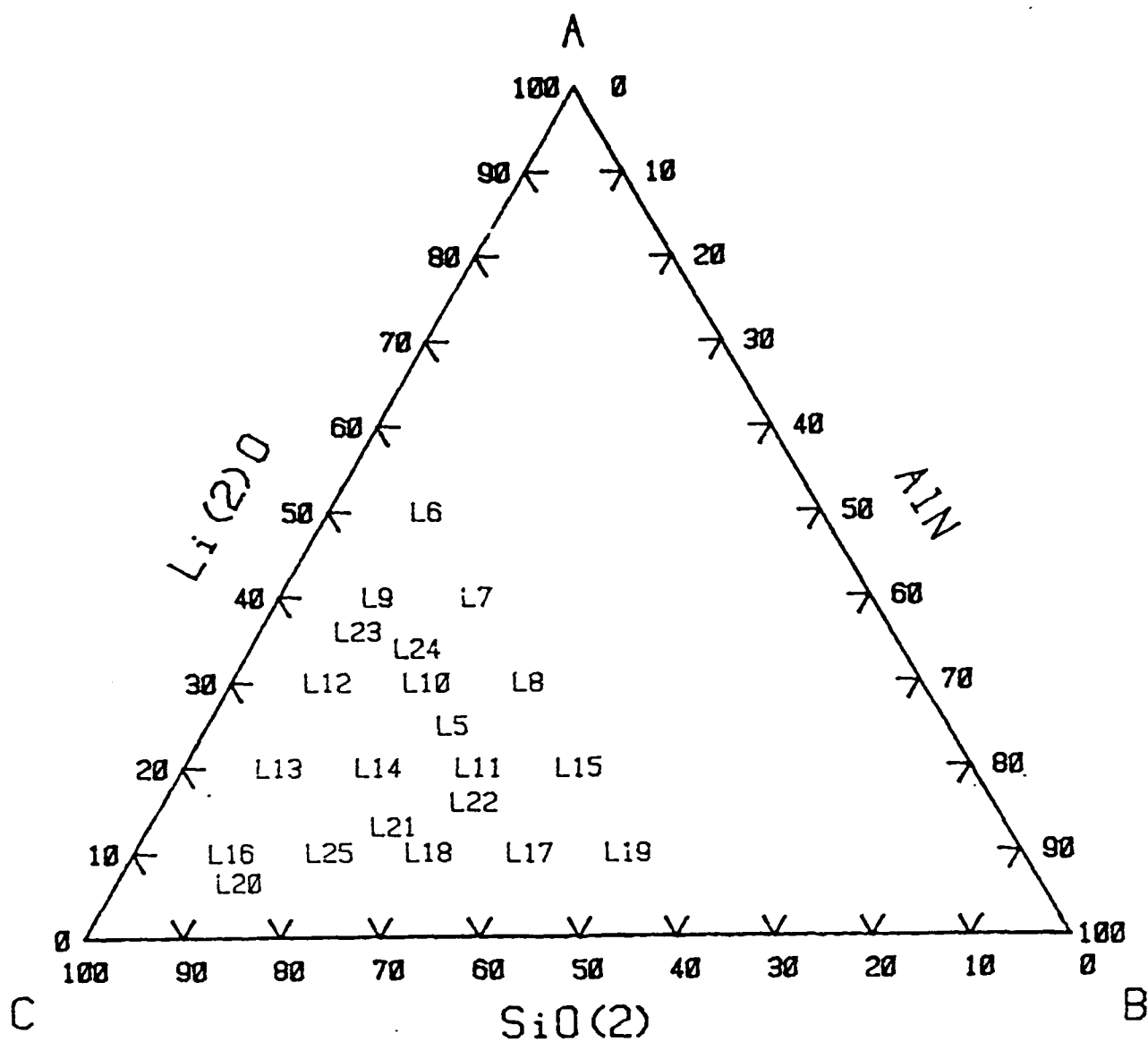


FIG. 1 MOLAR PLOT OF LI GLASSES

crystalline
glass
intermediate

batch was approximately 10 grams. Each component was individually weighed out on a top loader scale to the nearest hundredth of a gram. The AlN was Cerac-200 mesh, 99% pure, stored in a vacuum desiccator. The SiO₂ was obtained from a dried silica slip made at MTL. The Li₂CO₃ was Puratonic Grade 1, batch number S.84462. The weighed powders were placed in plastic screw top bottles with 50 ml methanol and three Al mixing balls. The containers were then mixed overnight. After thorough mixing, the solutions were poured into beakers and placed into a drying oven overnight, set at approximately 75°C. After the powders were dried, they were isostatically pressed at 20,000 psi, crushed, and stored in plastic containers.

The powders were melted in BN pellet holders. Each holder has three reservoirs capable of holding approximately 0.3 grams of powder. The holders were loaded into a graphite crucible and placed in the induction furnace, where melting was performed in a N₂ atmosphere. The powders were heated to approximately 1550°C, held for 2 minutes, then cooled as quickly as possible to room temperature. The samples were then removed, evaluated, and characterized.

It was determined that the Li-Si-Al-O-N glasses had a tendency to devitrify and crystallize when heated after the initial melt from a powder. Under close microscopic examination, small inclusions could be seen dispersed throughout the glasses. These inclusions may be serving as nucleation sites, crystallizing when the glasses are remelted and cooled. Thus, these glasses were determined to be inappropriate for fiber drawing consideration. A more detailed description of this Li-Si-Al-O-N research is presented in Reference 1.



2.2 Oxynitride E Glass Compositions

Experiments were also performed on a "E" glass composition. The basic E glass formula is an industry standard for the production of continuous glass fibers. E glass is a calcium-magnesium-alumino-borpsilicate containing trace amounts of Na_2O , K_2O , and Fe_2O_3 , and its density is approximately 2.53 g/cc.

Initially, a basic E glass was produced. The E glass components were weighed on a top loader scale and 100 g of the powder was placed in a plastic screw top bottle with 175 ml acetone and 6 Al mixing balls. The container was then mixed overnight. After thorough mixing, the solution was poured into a beaker and placed into a drying oven overnight, set at approximately 75°C. After the powder was dried, it was isostatically pressed at 20,000 psi, crushed, and stored in plastic containers. Then, approximately 15 g of the powder was loaded into a BN-coated graphite crucible and placed into the induction furnace. The furnace was then run to 1300°C in 15 minutes, held at 1300°C for 30 minutes, then quenched. The melting was done in a nitrogen atmosphere.

The next step was to incorporate nitrogen into the system to enhance the critical properties. The nitrogen was introduced by substituting Si_3N_4 for SiO_2 on an equivalent basis. The silicon nitride substitution (approximately 7.5 wt. percent) significantly increased the melting temperature, to 1650°C with 30 minutes required for melting.

These first oxynitride E glass compositions had a tendency to devitrify and crystallize when used for fiber drawing. A literature review suggested the amount of B_2O_3 in a glass composition

affects the firing characteristics when nitrogen is added to the system. Reduced B_2O_3 oxynitride glass compositions were prepared, which had improved melting characteristics. When the B_2O_3 amount was decreased, a slight increase in density was noticed.

The best oxynitride E glass produced was a composition made without the addition of B_2O_3 . This composition designated EN3A was fired in a nitrogen atmosphere at $1650^\circ C$ for 30 minutes. The resulting glass looked very good and was semi-transparent when thinly sliced. There was, however, some evidence of small metallic balls present. The density of this glass was approximately 2.68 g/cc. This composition contained approximately 4.74 atomic % nitrogen. This glass composition was scaled up and a 50 g puck of glass was made. The glass was crushed and use for experimentation to draw glass fibers.

Two other experimental oxynitride E glasses were also produced. In the first one, the atomic percent of nitrogen was increased to 6.83%. This glass looked very good, and was also semi-transparent when thinly sliced. It still also had the small metallic balls present. There was only a very slight increase in density to 2.70 g/cc. This glass was not successful when used for fiber drawing experiments. The second experimental composition contained 9.29 atomic % nitrogen. This resulting glass did not look as good as the other glasses. It was a light gray color that was not transparent, and seemed devitrified.

2.3 Zr-Si-Al-O-N System

Work was also performed on the melting and formation of zirconium oxide and oxynitride glasses. The addition of zirconium to sodium silicate glass compositions has been shown to enhance

alkali resistance. Corrosion-resistant fibers made from these compositions have applications such as fiber reinforcements for portland cement. A zirconium oxide glass was produced, and nitrogen was incorporated into the system to see whether or not critical properties (elastic modulus, strength, corrosion resistance, etc.) can be enhanced further.

Nitrogen was added to the oxide glass system in the form of silicon nitride powder. It was determined that the best way to incorporate the silicon nitride to the system was to melt the oxide glass powder, crush the resulting glass into a fine powder, then dry mix the silicon nitride into the crushed glass. The zirconium oxide glass powders were melted in BN coated graphite or BN crucibles, in a nitrogen atmosphere. They were melted at 1300°C. The resulting oxide glasses were quite transparent, had no metallic inclusions, but seemed to have bubbled quite a bit. The glass had an approximate weight loss of 7%. The density of the glass was approximately 2.67 g/cc.

After the oxide glass was crushed, approximately 5 atomic percent nitrogen was added in the form of powdered silicon nitride. The zirconium oxynitride glass powders were melted in BN coated graphite or BN crucibles in nitrogen atmosphere, to 1600°C. The resulting glass was a dark gray color, not very transparent, with some metallic balls present. There were also certain areas of the glass that seemed to have crystallized or devitrified. There was only about 1% weight loss, and the density of the glass was approximately 2.78 g/cc. This composition had approximately 4.99 atomic % nitrogen.



Another zirconia composition was formulated which contained 6.65 atomic % nitrogen (the previous composition contained 4.99 atomic % nitrogen). This new glass was made the same way as the first composition, melting the oxide components of the glass first, then adding the nitrogen to the system in the form of powdered silicon nitride dry mixed with the crushed oxide glass. The oxide glass was melted in a BN-coated alumina crucible in a nitrogen atmosphere at 1300°C. The weight loss of the oxide zirconium glass was approximately 15%. The density was 2.68 g/cc. The nitrogen zirconium glass was melted in a BN-coated alumina crucible in a nitrogen atmosphere at 1600°C. The weight loss of the oxynitride glass was approximately 5%. An accurate density of the glass was not obtainable. Although parts of the resulting oxynitride composition were glassy, a large portion of the glass seemed devitrified or decomposed. This particular composition did not seem to promising.

2.4 Oxynitride S Glass Compositions

Experiments were performed on an "S" glass composition. S glass is a commercially available magnesium-alumino-silicate composition designed for high strength applications. It is quite refractory and must be worked with at relatively high temperatures (1500° - 1600°C). The oxide S glass was fired in a BN-coated alumina crucible in a nitrogen atmosphere at 1600°C. There was approximately 2.43% weight loss and the density was 2.45 g/cc. The resulting glass looked quite good with a brownish color and a few bubbles. There were a few scattered small black specks, but they did not look metallic.

Two oxynitride S glass compositions (labeled NS1 and NS2) were made, contained 2.97 and 4.97 atomic % nitrogen, respectively. Both compositions were fired in a BN-coated alumina crucible in a nitrogen atmosphere at 1600°C. NS1 had a weight loss of less than 1%, while NS2 had a weight loss of 1.5%. Both glasses had densities of approximately 2.50 g/cc, although this may not be completely accurate due to amount of bubbles scattered throughout the glass. The glasses looked very good; quite glassy with a dark brown color. There was fairly extensive bubbling in both glasses and there were a few scattered, small black specks that did not look metallic, however.

After reviewing the work performed on NS1 and NS2, it was found that these nitrogen S glasses were formulated from the wrong oxide composition. The mole % of the components were mistaken for the weight %. The formulation used was (in weight %); 68.68% SiO₂, 15.57% Al₂O₃, and 15.75% MgO. Although this composition resulted in a good quality glass, it was not the correct "S" glass composition.

The correct "S" glass composition is (in weight %); 65% SiO₂, 25% Al₂O₃, and 10% MgO. A glass composition based on this oxide formula, containing 5.52 atomic % nitrogen, was made and designated NS7. This composition formed a fairly good glass, but had a tendency to form many bubbles. Although the glass seemed to fully melt at 1500°C, a temperature of 1650°C produced a glass with fewer bubbles. Another composition (also based on the new "S" formula) NS8 containing 2.72 atomic % nitrogen was also made. This lower nitrogen glass looked better than the 5.52 atomic % nitrogen glass. There were fewer bubbles and the overall appearance and glass quality was better. The optimum firing temperature was approxima-



tely 1550°C. A density measurement 2.45 g/cc was obtained. A higher nitrogen composition (7.77 atomic %) NS11 was also tried. It appeared as though this nitrogen content was too high for this composition. All test firings of this formulation were not glassy, were light gray in color, and had many bubbles.

In a related literature review, R. Wursirika² reported a high strength glass in this system with 9.91 atomic % nitrogen. This composition was made and designated as NS5 and NS 6. The resulting samples obtained from this composition did not look good. They had a light gray color and seemed divitrified. There were quite a few bubbles and metallic balls. Several different firing temperatures were used, all with the same results.

An experimental composition between the new "S" glass and the Wursirika glass compositions on the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ phase diagram was also formulated. NS9 was made to have 2.53 atomic % nitrogen, and NS10 had 6.91 atomic % nitrogen. The NS9 samples looked quite good. They were very glassy, had only a few bubbles, and did not have as many metallic balls or divitrified patches. The density was approximately 2.62 g/cc and the optimum firing temperature seemed to be 1500°C. The NS10 samples did not look as good. They were a little "cloudy" and under high microscopic examination, fine particles (possible nucleation sites) could be seen. There were some bubbles toward the tops of the samples and small metallic balls present. The density was 2.68 g/cc.

Figure 2 is a phase diagram (in mole %) of the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ system. The compositions above were derived from this diagram. Points are chosen in the known glass forming region, and then nitrogen was introduced into the system by substituting Si_3N_4 for



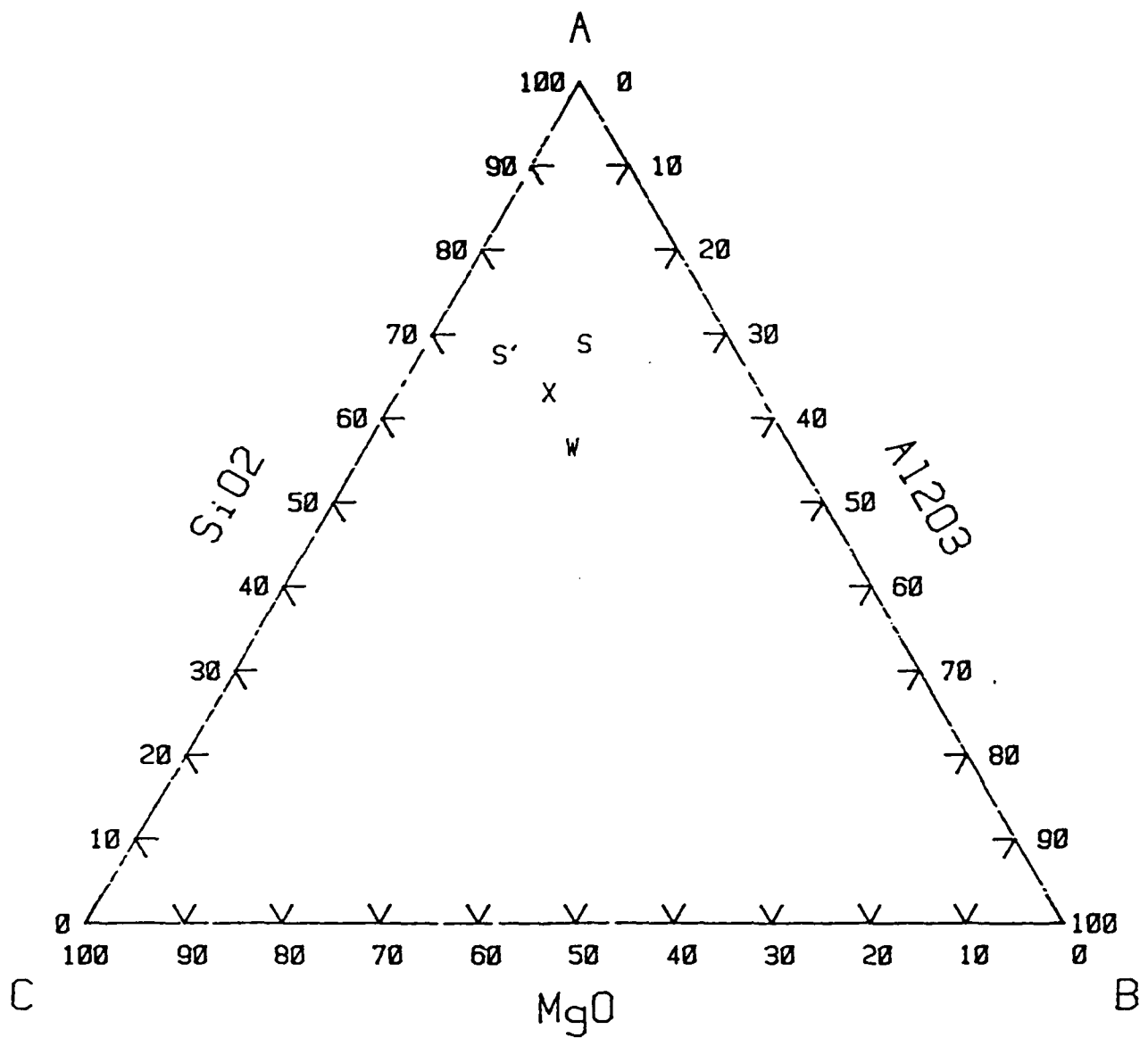


Figure 2. Mg-Si-Al-O-N Oxide Diagram

SiO₂ on a molar basis. The amount of atomic % nitrogen contained in each sample is determined by the amount of Si₃N₄ substituted for SiO₂. Each point on the diagram represents a certain composition that may or may not have several different forms containing varying nitrogen amounts. Point "S" represents NS7 (5.51 atomic% nitrogen), NS8 (2.72 atomic % nitrogen), and NS11 (7.77 atomic % nitrogen). Point S' represents the mistaken S compositions NS1 (2.97 atomic % nitrogen), and NS2 (4.96 atomic % nitrogen). The X point represents the experimental compositions NS9 (2.53 atomic % nitrogen), and NS10 (6.91 atomic % nitrogen). Point W represents the Wursirika composition.

2.5 Ca-Si-Al-O-N System

A composition in the Ca-Si-Al-O-N system was also chosen for study. The composition, designated SKAN4, was taken from a paper by S. Sakka et. al.³ It has 10.11 atomic % nitrogen. The resulting glass looked quite good. Although the outside had a grayish crust, the inside was very glassy, had virtually no bubbles, and was quite transparent. The optimum firing temperature seemed to be 1650°C, and the density was approximately 2.84 g/cc. Although this glass looked promising, there was a substantial weight loss (10-15%) that will have to be investigated.

2.6 Y-Si-Al-O-N System

Some experimentation was also performed on a glass in the Y-Si-Al-O-N system. A previously formulated "B" glass (13.3 atomic % N₂) composition was modified in an attempt to produce a glass in the Y-Si-Al-O-N system with a higher nitrogen content, yet still retain fiber forming characteristics. Initially, MgO was tried as

a modifier. This proved to be unsuccessful, with the resulting material looking quite crystallized and being quite brittle. Next, CaO was used to modify the Y-Si-Al-O-N glass composition. The resulting glass looked quite good, being fairly transparent. The density of the modified glass was approximately 3.71 g/cc. The melting point of the glass was approximately 1650°C.

2.7 Glass Preparation Under Specialty Atmospheres

During all of the above experimental glass melting, certain changes were made in an effort to reduce thermal decomposition which is believed to contribute to the formation of metallic Si balls and decrease the quality of the formed glasses. One such effort was to replace the graphite crucibles, previously used to melt the glasses, with either BN or Al₂O₃ crucibles. Molybdenum was also substituted for graphite as a susceptor material in the induction furnace. It was anticipated that using these crucible materials would help to minimize thermal decomposition by making melting conditions less reducing than with graphite. In spite of this effort, however, the formation of the metallic balls was not prevented.

Using a specialty atmosphere during glass melting was also tried. A mixture of 90% nitrogen, 5% carbon dioxide, and 5% carbon monoxide was used in experimental glass melts. The mixture was designed to produce an oxygen pressure high enough to suppress the thermal decomposition reaction of the glasses, but low enough as not to oxidize the molybdenum susceptor.

Several melts were performed using the "a" glass composition. Each melt was made using molybdenum as a susceptor, and the temperature the glasses were being held at was approximately

1600°C. Most melting was performed in BN-coated BN crucibles, with approximately 5g of crushed glass or glass powder being used for each run. One melt was performed in an uncoated alumina crucible, and, as expected, the glass reacted with the crucible. One 25g batch was melted successfully in a BN-coated alumina crucible. The main variable that was changed was the time the samples were being held at the maximum temperature. Melts were held anywhere from 10 to 60 minutes.

There seemed to be a slight improvement in some of the glasses based on the amount of time the glasses were held at temperature. The longer the samples were held, the better they looked, i.e., the resulting glasses seemed to have slightly better transparency and a reduce number of metallic inclusions. The metallic inclusions seem to float to the top of the glass sample. The white powder that formed on the tops of the glass samples and sometimes on the sides of the silica furnace tube was found to be amorphous by x-ray diffraction. Weight losses and densities of specimens melted in the new atmosphere were the same as previous glass melts in pure nitrogen. There did not seem to be much difference in the final glasses whether unfired glass powder, crushed glass powder, or large chunks of glass were used in the experimental melts.

Two melts with the "a" composition (AlN is used instead of Si_3N_4 as the nitrogen source in the glass) were performed. The "a" glass was fired at 1600°C using a rolled molybdenum sheet susceptor in a pure nitrogen atmosphere, and also the $\text{CO}_2/\text{CO}/\text{N}_2$, 5/5/90 atmosphere. A BN-coated BN crucible was used for melting. There did not seem to be much difference between the resulting glasses from the two different atmospheres. They both had small metallic inclusions concentrated at the top of the samples. The glass fired

in the $\text{CO}_2/\text{CO}/\text{N}_2$, 5/5/90 atmosphere, however, had more of a white crust on the top of the sample. Both melts had the normal weight loss and densities.

A few melts were performed using the "B" glass composition (13.3 atomic % nitrogen). There did not seem to be any significant difference between the samples fired in pure nitrogen and the samples fired in the $\text{CO}_2/\text{CO}/\text{N}_2$, 5/5/90 atmosphere. All of the fired samples had the normal weight loss and densities.

Two experimental melts were performed with the oxide "S" glass in the $\text{CO}_2/\text{CO}/\text{N}_2$, 5/5/90 atmosphere using a molybdenum susceptor. The glasses were heated to 1600°C and held for 45 minutes. The outside of the fired samples were a swirling light blue color, which could be due to some kind of oxidation of the molybdenum. The blue swirling, however, was only around the outside of the glass. The inside of the samples had some areas that had black swirling clouds, and some areas that seemed quite transparent.

One experiment was performed with oxynitride glass NS2. The glass was heated to 1600°C and held for 45 minutes. The resulting glass was not improved. There was white crust on top of the sample, and some milky swirls in the sample. There were quite a few metallic balls present, especially around the top of the sample. All of the S glass melts had the normal weight losses and densities.

One melt was performed with an oxide "E" glass in the $\text{CO}_2/\text{CO}/\text{N}_2$, 5/5/90 atmosphere using a molybdenum susceptor. The glass was heated to 1300°C and held at a temperature for 45 minutes. There was slight evidence of a blue color (possible molybdenum oxidation). There were small metallic balls on the top



of the sample. Inside there were light black swirls that were concentrated towards the bottom of the sample. There were also quite a few bubbles throughout the glass. The resulting glass had the normal weight loss and density.

Although slight differences could be observed in certain cases, it was concluded that the specialty atmosphere did not significantly improve the quality of the glasses. It is believed that the oxygen partial pressure of the specialty gas mixture was not enough to suppress thermal decomposition of the experimental glasses.

3.0 PREPARATION OF OXYNITRIDE GLASS FIBERS

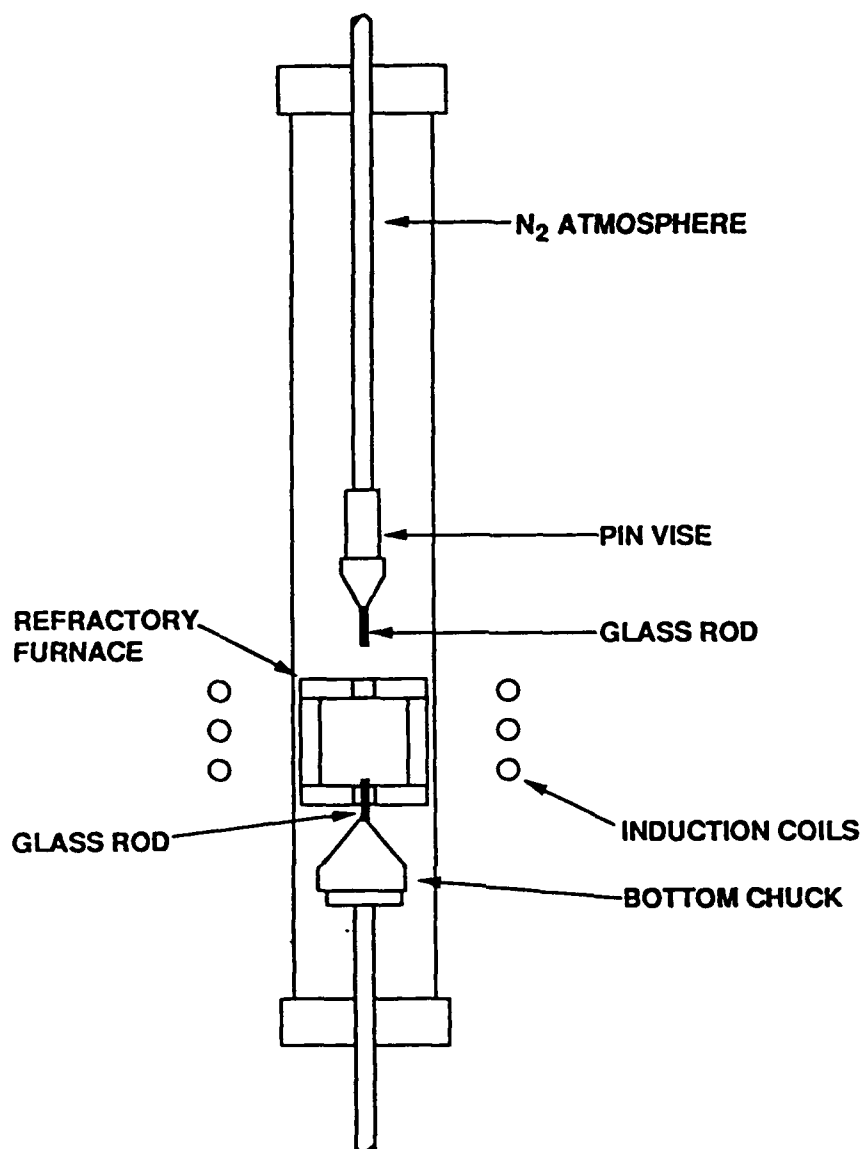
3.1 Development of Fiber Drawing Apparatus

The formation of oxynitride glass fibers from previously made glass compositions was performed in two distinct stages of development. The first stage involved "stretching" heated glass preforms, and the second stage involved drawing the fibers from a glass melt.

Initial work required modification of the existing fiber drawing set-up to improve the fiber drawings capability. A schematic diagram of the apparatus is presented in Figure 3. The most significant modification of the furnace involved shortening the length of the refractory furnace and the induction coil. The diameter of the modified furnace is 1-3/4 inches and is 1-3/4 inches long. The hot zone is 5/8 of an inch long and the induction coil length was reduced from 4 inches to 1-1/4 inches. The smaller furnace area makes it easier to melt only the desired portion of the glass and also makes it easier to align the glass preforms for more efficient fiber production. An added benefit is that the shorter work area allows the use of shorter pieces of glass for fiber drawing.

The previous method employed for fiber drawing used Al_2O_3 or SiC rod "dipsticks" to fuse to the glass, and at the precise viscosity, pull up to draw a fiber. With this method, however, it was difficult to get the glass to wet to the dipstick, and the molten glass often fell off. A possible reason for this was that either the thermal conductivity or the thermal expansion coefficient of the dipstick and the glass rod were dissimilar. To eliminate this problem, the glass rods were prepared with a smaller diameter (~5mm) so they could be mounted from above in a pin vise





SKETCH OF FIBER DRAWING UNIT

FIGURE 3

attached to the sliding metal rod. In this way, the glass rod in the bottom fixture could be fused to a glass rod of the same composition from above. This configuration was made possible because the reduction in furnace size eliminated the requirements for a long dipstick. The best "stretching" method for successful fiber formation was to start with a glass rod long enough for one end to be attached in the bottom chuck and the other in the pin vise. This method eliminated the need for the initial melting of two glass rods to fuse them together. Thus, there only had to be one initial heat up to soften the glass to a point where a fiber could be drawn.

Several successful fiber pulls were achieved using Y-Si-Al-O-N "a" glass, and $\text{Li}_2\text{SiAlO}_3\text{N}$ glass preforms. An example of the formation of a $\text{Li}_2\text{SiAlO}_3\text{N}$ fiber is as follows. Two pieces of $\text{Li}_2\text{SiAlO}_3\text{N}$ glass were loaded into the induction unit and fused together in a nitrogen atmosphere. The temperature of the glass was measured with an optical pyrometer. Temperature readings were only approximations, due to the difficulty in focussing directly on the glass. The glass sample melted at approximately 1350°C , cooled to 900°C , and then re-heated and a fiber stretched at approximately 1325°C . The fiber drawn was 10" long, with an average thickness of approximately 1mm with the ends closer to the glass rods being thicker.

All of the fibers formed from this method had severe limitations. One of the biggest limitations was that only a small fiber could be produced, due to the space limitations of the furnace. A 10 to 20 inch fiber would be the longest possible fiber. Also, only small sections have a uniform thickness, and the average diameters of the fibers were very large. The formed fibers also seemed to have striations, or ridges on the surface. In summary,

fibers formed by this method were short in length, had large diameters, and poor overall fiber quality. These conclusions led to the next stage of fiber development, fiber drawing from the melt.

The induction unit was modified so that it would be possible to pull fibers from a glass melt. Pulling fibers from a melt involves heating the desired glass composition in a specially designed crucible that has a nozzle centered in the bottom of the crucible. When the glass reaches the correct temperature and viscosity, it will begin to flow through the nozzle and form a glass bead at the nozzle tip. After the glass bead has formed, it must be "started" in order to begin fiber formation. At this point, an Al_2O_3 rod is used to touch the glass bead and, by pulling down, drawing a fiber from the melt. Pulling fibers from a glass melt enables the formation of more uniform, continuous fibers with less chance of crystallization or contamination.

In order to accommodate this fiber pulling method, a new induction coil was made so that the hot zone, where the glass is melted, could be moved to a higher position. The hot zone was raised so that there would be as much space as possible below the crucible for fiber drawing. The new hot zone location provided about 24" of available working length for fiber drawing. Having the crucible located in the higher position also made it possible to view the nozzle tip when the crucible was heated. This facilitated aligning the Al_2O_3 rod to the glass bead when attempting to pull a fiber.

Another major modification was to incorporate into the system an optical pyrometer with a microprocessor-based digital process controller. An IRCON MODLINE two-color ratio pyrometer was mounted

above the furnace so it could be pointed directly into the crucible where the glass is melted. The pyrometer senses radiation emitted by the heated glass, and supplies an electrical signal proportional to the temperature to an indicator unit. The front panel display of the indicator provides the temperature of the glass melt in degrees Celsius. The signal is also fed to a MICRICON 823 microprocessor controller in a feedback loop in order to control the output of the induction unit either according to a pre-set program or allowing for manual operation. The manually operated pyrometer that was previously used to measure temperature still was used as a back-up, or to double-check the IRCON pyrometer.

The configuration provided for greatly improved temperature control of the glass-forming hot zone region. This is essential when drawing fibers from a melt because precise temperature control is needed to achieve the correct viscosity for the glass to flow. Using a microprocessor to control the furnace also increases the reproducibility of any glass melting, or of a fiber drawing run. A BN crucible was fabricated for melting the glass samples. The cylindrical crucible was approximately 3 cm long, with an I.D. of 1.8 cm and an O.D. of 2.5 cm. A nozzle located in the bottom center of the crucible extended 2 mm below the bottom. The nozzle had an I.D. of 4 mm, and an O.D. of 6 mm.

Several initial fiber drawing experiments were performed using previously formed glasses prepared in the Y-Si-Al-O-N system. Approximately 10 grams of crushed glass was placed in the crucible. The crucible was inserted into a graphite susceptor, placed into the refractory furnace, and mounted in the induction unit. The glass was heated in a N₂ atmosphere up to its melting point, between 1500°C - 1600°C. Exact melting point temperatures were difficult to determine due to atmospheric interference (smoke,

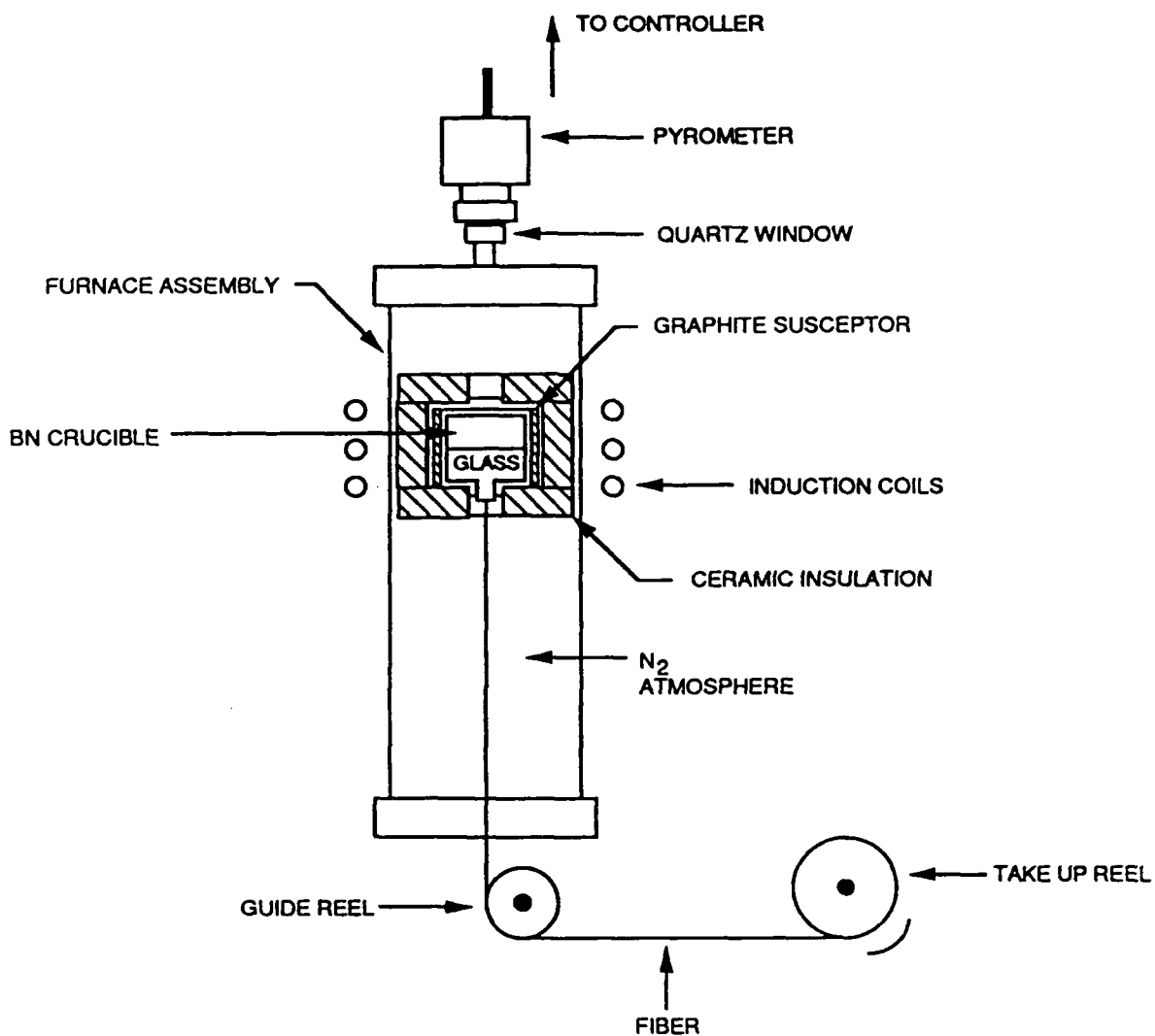
etc.). The main objective was to form a glass bead at the end of the crucible nozzle, which would then be touched with an Al_2O_3 rod mounted in a pin vise from below. Once the glass bead was touched, the Al_2O_3 rod is drawn down, pulling a fiber from the crucible.

Some of the first fiber drawings were attempted before the induction unit was interfaced with the controller. These attempts were unsuccessful due to lack of precise control of the temperature and viscosity range. One attempt was made after the controller was successfully interfaced with the induction unit. The glass was initially brought to a temperature of 1350°C . Then every 5 minutes the temperature was raised 10 degrees. At each step the crucible was examined to see if the glass was ready to be pulled. At 1500°C , the glass was at the correct temperature and viscosity to facilitate the drawing of a fiber. A fiber approximately 18" long was drawn. Optical analysis of the fiber did not indicate evidence of crystallization, a problem in previous attempts to form fibers by pulling from rods.

More modifications were made to the induction furnace system to better accommodate bottom fiber pulling from a melt. The glass tube on the induction unit was shortened to approximately 25" and the bottom fixture was raised. This modification created more space below the assembly to manipulate the alumina pull rod when attempting to start a fiber pull. The extra space also facilitates the potential winding of a continuous fiber coming from the bottom of the crucible, out the bottom of the assembly, and eventually onto a take-up spool. Figures 4 & 5 are sketches of the fiber drawing and fiber winding set-ups.

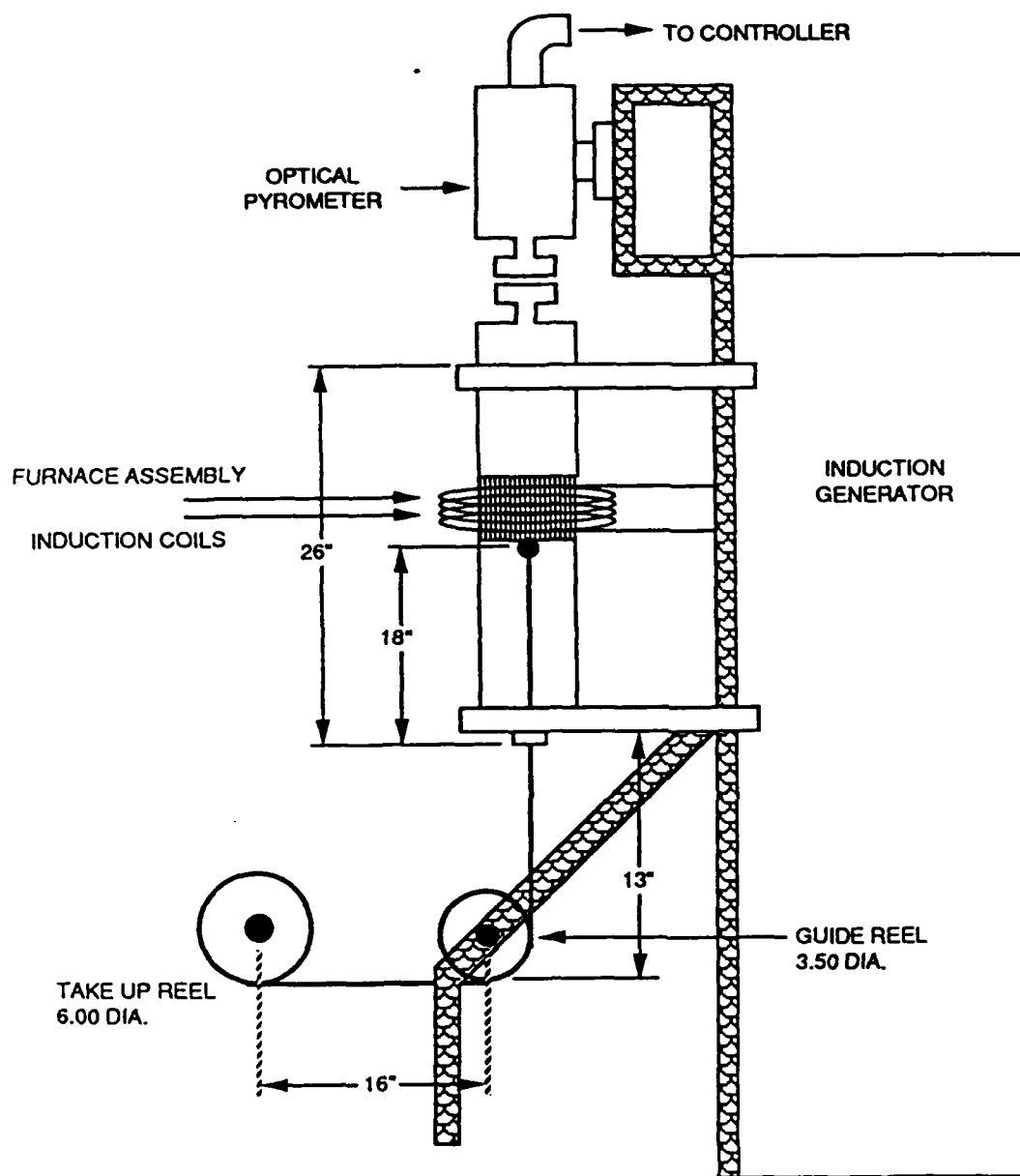
After extensive experimentation with drawing fibers from a melt, success was achieved; a continuous fiber was started and the

FIBER DRAWING



SKETCH OF FIBER DRAWING UNIT

FIGURE 4

**SKETCH OF FIBER WINDING SET-UP****FIGURE 5**

drawing process sustained. Previously formed Y-Si-Al-O-N glass was crushed into chunks using a metal mortar and pestle. Approximately 6.5 g was loaded into a BN crucible. The cylindrical crucible was approximately 3 cm long, with an I.D. of 1.8 cm, and an O.D. of 2.5 cm. A nozzle located in the bottom center of the crucible extended 2 mm below the bottom. The nozzle had an I.D. of 4 mm, and an O.D. of 6 mm.

The loaded crucible was then placed in a BN shell, surrounded with a zirconia cylindrical shell and alumina end caps, and placed into the induction unit. The furnace was then evacuated, back-filled with nitrogen, evacuated again and then a steady nitrogen flow was started.

Using the Micricon controller, the temperature was brought to approximately 1342°C in 20 minutes. Then under manual operation the power output was set to 20% and the temperature increased to 1380°C. At this time, a glass bead was starting to form at the crucible nozzle. When it was certain that the glass flow had started through the nozzle, the power output was cut to 0% and the temperature dropped to 1330°C. Output power was again increased to 18% to bring the temperature to around 1350°C. This seemed to be the optimum drawing temperature.

The glass bead that had formed at the crucible nozzle was then touched with the alumina pull rod and a glass fiber was drawn down until it got knocked off at the fitting at the bottom fixture of the assembly. At this point the output power was dropped to approximately 15% and the temperature decreased to 1335°C. Then the Swage-Lok fitting at the bottom of the fixture was removed to make the opening bigger to better accommodate the passage of the fiber.



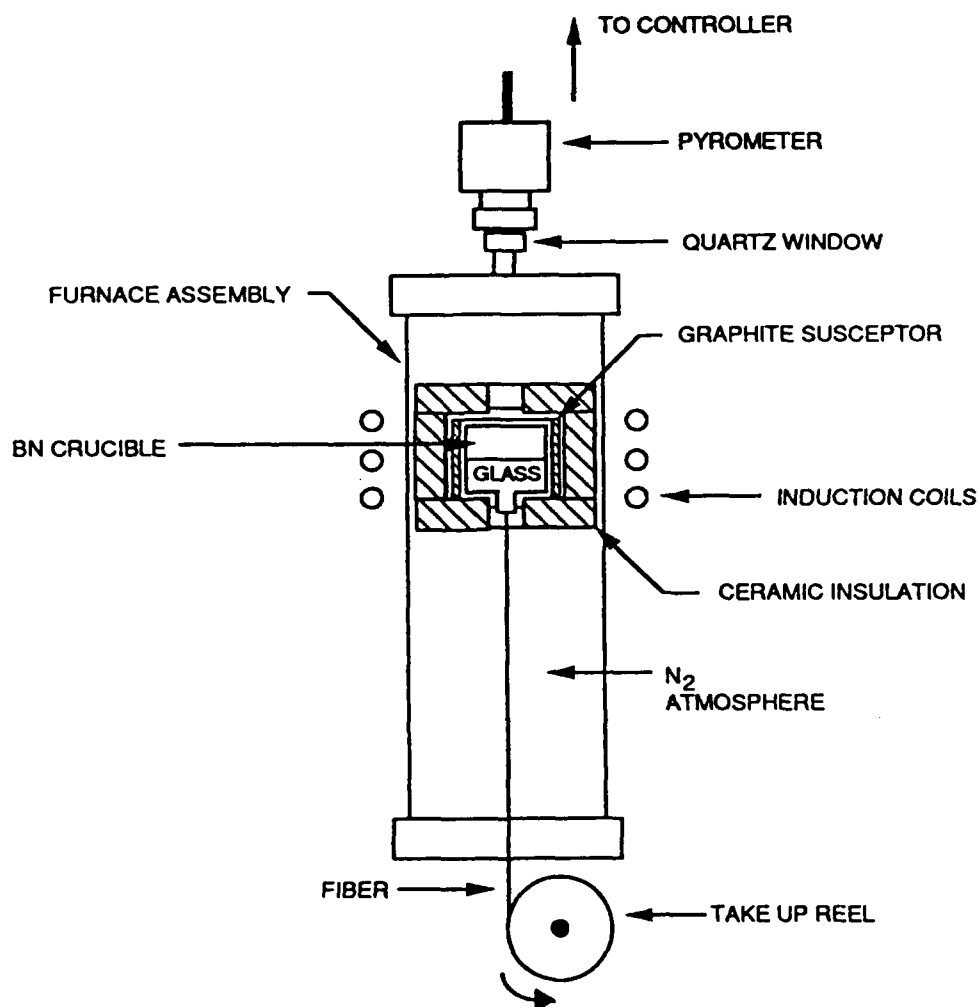
Output power was then resumed to 18% and the temperature climbed back up to 1350°C. The fiber (which was still attached to the crucible nozzle) started to descend through the bottom fixture opening. When enough of the fiber had passed through, it was taken by hand around a guide spool and attached to a take-up reel. The take-up reel, which was attached to a variable speed laboratory motor, was started and the fiber wound around the reel for approximately 8 minutes. The fiber eventually became too thin to sustain, and broke off at the nozzle tip. Over 100 yards was estimated to have formed.

The average fiber diameter was approximately 68 microns with the fiber at the beginning of the pull having a larger diameter and the fiber at the end of the pull having a slightly smaller diameter. It looked as though there might be some evidence of some crystallization within the fiber and there also was some kind of particles clinging to the surface of the fiber at various sections of the fiber. The fiber looked more transparent than the parent glass.

Various process and equipment modifications were made as necessary to facilitate the drawing of small diameter, high quality, high specific modulus glass fibers from those systems. Because the guide reel was a location where frequent fiber breakage occurred, the system was modified to eliminate the guide reel and wind directly onto the take-up reel. This modification facilitated both starting and sustaining a fiber pull. Figures 6 and 7 are sketches of the fiber drawing and fiber winding set-ups. A clear path from the crucible nozzle to the take-up reel minimizes the chance of strength limiting defects being introduced to the surface of the fiber by abrasion of the fiber as it passes through furnace fittings.

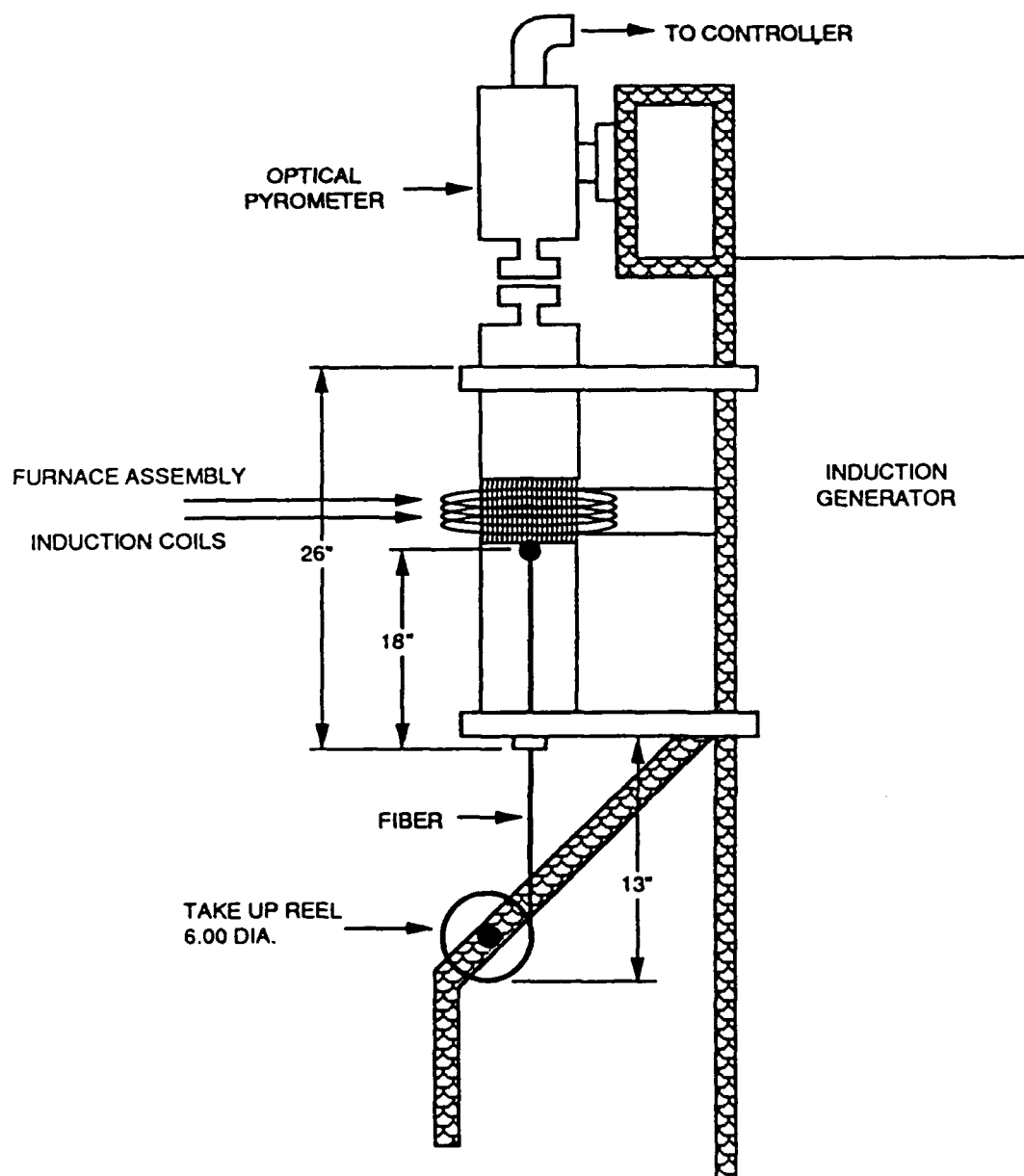


FIBER DRAWING



SKETCH SHOWING THE ORIENTATION OF ESSENTIAL COMPONENTS OF THE FIBER DRAWING UNIT.

FIGURE 6



SKETCH SHOWING THE PATH OF THE DRAWN FIBER
DURING THE WINDING PROCEDURE.

FIGURE 7

It was determined that in order to obtain smaller diameter fibers, the drawing rate had to be increased. In order to draw faster, the winding system had to be more stable so that it would not vibrate too much at higher speeds, causing fiber breakage. First, custom made shafts were mounted in the take-up spools, and the spools were then spin balanced. This helped the spools to rotate more evenly at higher speeds. Then a new motor system was installed. A 1/15 h.p. d.c. synchronous motor with a speed controller was permanently mounted in place of the laboratory motor previously used. This motor is heavier and will produce a more steady rotation of the take-up spool at higher speeds. The same take-up spool is used and is mounted in a drill chuck attached to the motor shaft. A magnetic transducer and a digital readout for the monitoring of the take-up spool speed was also installed.

Also custom designed molybdenum fiber drawing crucibles were used in the induction furnace, which eliminated the use of a graphite susceptor. In some instances, rolled molybdenum sheet was used as a susceptor, using the BN fiber drawing crucibles. The molybdenum crucibles also have the advantage of being more durable.

3.2 Oxynitride Glass Fiber Compositions

Several continuous fiber pulls have been completed with many different compositions. The following will describe representative fiber pulls for each composition.

Y-Si-Al-O-N "a" glass was used for many fiber drawings. Previously formed oxynitride glass containing (in weight %) 6% Al, 18.9% Si, 39.8% Y, 32.2% O, and 3.2% N was used as feed-stock for fiber drawing. The glass was crushed into small pieces and 6 grams of the crushed glass were loaded into the molybdenum crucible

nozzle. The crucible was loaded into the furnace assembly and heated to 1550°C, at which temperature the glass was molten, and a drop of molten glass observed at the nozzle tip. The alumina dipstick was then inserted into the furnace through the bottom fitting to contact the glass drop and withdrawn to start a fiber that remained attached to the tip of the dipstick as the latter was pulled out of the furnace through the bottom fitting. The fiber was then broken off near the end of the dipstick, and the fiber tip attached to the takeup reel with a piece of cellophane tape, after which the motor was started to wind the fiber on the takeup reel. Winding continued for about 8 minutes at a speed of approximately 550 r.p.m. to produce a continuous fiber estimated to be from 1400 to 1500 m long.

Examination of short lengths of the fiber showed that it was uniform and 20µm in diameter containing a few pores and fine (5µm) metallic (silicon) inclusions. Analysis of polished cross-sections of the fiber pieces by wavelength dispersive spectroscopy showed that the chemistry of the fiber was the same as that of the bulk glass, and also the same as the nominal starting composition.

The Ca-Y-Si-Al-O-N glass ("b" glass, 13.3 atomic % N₂) was also used for fiber drawing attempts. Short fibers were easily formed around 1400°C. A continuous fiber pull could not be sustained. The fibers that were formed seemed to be of very good quality. The difficulty in drawing a continuous fiber seems to be that the fiber tends to break when the winding starts due to the fibers' increased stiffness. Long lengths of fiber of this composition could not be produced.



A fiber drawn from previously formed oxynitride glass similar to commercial "S" glass, but containing N. The glass NS2 composition (in weight %) was: 8.0% Al, 33.4% Si, 9.5% Mg, 45.6% O, and 3.5% N. The basic procedure as described above was used. The crucible contained 10 grams of crushed glass that was heated to 1550°C for fiber-drawing. Winding for 7 minutes at about 500 r.p.m. produced a continuous fiber estimated to 1000-1200 m long. The fiber was very uniform in cross-section and 35 μ m in diameter, the oxynitride S glasses were well suited for fiber drawing, producing high quality uniform fibers.

A fiber was drawn from previously formed oxynitride glass similar to commercial "E" glass, but containing N. The glass EN3A, consisted of (in weight %) 28.5% Si, 8.7% Al, 2.2% Mg, 14.8% Ca, 0.2% Na, 0.1% K, 0.1% Fe, 42.4% O, and 3.1% N. The BN crucible was loaded with 5 grams of crushed glass and a fiber drawn using the basic procedure with the glass at a temperature of 1350°C. Winding for 5 minutes at approximately 300 r.p.m. produced a continuous fiber estimated to be 400-500 m long. The fiber was uniform but somewhat tapered over its length, with a maximum diameter of 50 μ m. The oxynitride E glasses also had good fiber forming characteristics.

Some limited fiber drawing was performed with zirconium oxide and oxynitride glasses, using the old motor system. Zirconium oxynitride fiber formation was easily achieved. Fiber formation started at approximately 1320°C. After first winding the fiber slowly, the temperature and winding speed were slowly increased. The fiber wound at the maximum winding speed on the lower gear ratio of the laboratory motor at 1351°C for approximately 20 minutes. The fibers got thinner as time went on, and averaged out to be approximately 70 microns in diameter.

Fibers were also formed from the zirconium oxide glass. Again, the fibers formed quite easily. Fiber formation began at approximately 1250°C. Then the temperature was decreased to 1223°C. The fiber was wound at maximum speed of the lower gear ratio of the laboratory motor for approximately 7 minutes. The average fiber diameter was approximately 45 microns. This fiber seemed quite resilient and bendable.

3.3 Property Data for Oxynitride Glass Fibers

Some limited fiber testing was performed on some selected fiber samples. The following is the procedure used to measure elastic modulus. First, an instrument was used to measure the sonic velocity in a given length of fiber. Then the density of the fiber was obtained by using a micrometer to get the dimensions of a section of the fiber, then weighing the fiber to get the mass. The density measurements were made with the assumption that the fiber dimensions were uniform. In the case that the fiber dimensions were obviously not uniform, densities of the bulk glass were used. The sonic velocity and the density were then used in a formula to calculate the elastic modulus.

$$E = (1.45 \times 10^5) p c^2$$

where E = Elastic modulus in psi
 p = Density of fiber
 c = Longitudinal sonic velocity

Table 1 contains a summary of the results of the elastic modulus measurements.

Tensile strength testing was also performed on various fibers. An Instron Model 1123 testing machine with a 5 N load cell was used for the testing. Samples were prepared in accordance with the ASTM

TABLE 1. ELASTIC MODULUS OF GLASS FIBERS

<u>SPECIMEN</u>	<u>DENSITY (g/cc)</u>	<u>AVERAGE OF ELASTIC MODULUS IN GPa (psi)</u>
Normal E Glass	2.57	83 (12 Million)
Oxynitride E Glass EN3A	2.80	100 (14.5 Million)
Y-Si-Al-O-N "a" Glass	3.71	138 (20 Million)
Zr Oxide Glass	2.67	95 (13.7 Million)
Zr Oxynitride Glass	2.75	101 (14.6 Million)
*Ca-Y-Si-Al-O-N modified "b"	3.72	152 (22 Million)

*limited testing performed

D339-75 tensile strength testing procedures. Much time was spent becoming familiar with the testing procedure and choosing the best materials for sample preparation. It was found that standard graph paper and DUCO adhesive worked the best for sample preparation and minimized fiber slippage during testing.

Several different Y-Si-Al-O-N "a" fibers were tested. It was found that aging and fiber handling play significant roles in fiber strength degradation. Fibers that were formed several months ago and stored in air on the reel had an average tensile strength of 64,667.0 psi. Fibers that were formed several months ago and stored on the reel in a zip lock plastic bag had an average tensile strength of 83,876.8 psi. Fibers that were formed during this reporting period and tested immediately had an average tensile strength of 117,719.7 psi.

Oxynitride "S" fibers (NS2) were also tested immediately after fiber drawing. Fibers that were cut from the reel and tested had an average tensile strength of 82,168.9 psi. The fibers that were taken directly from the nozzle (not wound on the reel) had an average tensile strength of 98,567.0 psi. A different batch of NS2 fibers that were recently formed and taken from the reel had an average tensile strength of 86,648.2 psi. Also, some Spectran optical fibers with the resin coating burned off were tested and had an average tensile strength of 36,474.0 psi.

It was easily determined that aging and fiber handling cause the fibers to weaken. The more the fibers are handled, the greater chance of introducing strength limiting defects. When the fibers are wound on the reel, they are constantly abrading against each other. A resin coating applied to the fibers as they are formed would decrease the amount of defects introduced to the fibers due to handling.

Also, EDX and WDS spectroscopy was conducted on the fibers. The results of this analysis indicated that the compositions of the parent glasses and the fibers formed from these glasses were essentially the same.

Corrosion tests were also performed on zirconium oxide and oxynitride glass fibers. Fibers from the zirconium oxide and the oxynitride fibers were cut into 3 inch lengths. The respective fibers were gathered into two different bundles and one end of each bundle was dipped in rubber cement to secure the fibers. The weight of the oxide bundle was 0.0093 g and the weight of the oxynitride bundle was 0.0088 g. Two different solutions of 10 pH were made by mixing 35 ml distilled water with 1 drop of a 6% NaOH solution. Then each fiber bundle was placed in a separate vial with the NaOH solution. The vials were capped and placed in a 37°C water bath. Valid results were not obtained due to experimental error. The caps on the vials containing the fibers in the NaOH solution became loose, allowing the solutions to mix with the surrounding water bath, which altered the pH of the solutions.

4.0 GENERAL SUMMARY

The general scope of work for this research project was carried out. Oxynitride glasses of various compositions were prepared and analyzed. An existing fiber drawing apparatus was modified, and the fiber drawing capability greatly improved. Continuous glass fibers were produced from scaled up oxynitride glass compositions. Formed fibers were characterized and evaluated (including elastic modulus and tensile strength measurements). From the information gathered during this research, it is clear that there is great potential for high specific modulus oxynitride glasses and glass fibers. It is believed that with additional

experimentation and testing, oxynitride glasses and glass fibers can be developed into a commercially and industrially valuable product.

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