

PROCESSING OF COLLOIDAL SILICA SOL-GEL BODIES FOR OPTICAL FIBER APPLICATIONS

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A colloidal sol-gel process suitable for optical fiber applications has been developed. Fumed silica is dispersed in a high pH liquid, mixed with an ester and cast into a precision mold to form a large tubular shape. The ester hydrolyzes to form an acid, which gradually lowers the pH and causes gelation. The gelled body is removed from the mold and dried. The dried gel is heated to remove remaining organic residues and then purified at temperatures up to 1000 °C in halogenated gases to remove hydroxyls and metal oxide impurities including break inducing refractory metal oxide particles. The body is then sintered to dense, transparent, pure silica glass. These multi-kilogram bodies have been successfully used to overclad fiber preform core rods containing the core and immediate cladding glass.

The tubes have the needed dimensional precision for this demanding application. Optical fiber drawn from these preforms meets the quality standards of modern communications fiber.

INTRODUCTION

Sol-gel technology has elicited major research interest in the past 5 or more decades with thousands of publications on the chemistry and potential applications including optical fibers.^{1,2} In this study we have concentrated on the use of colloidal sols to fabricate large bodies for applications in optical fiber.

Optical fiber preforms manufactured by the Modified Chemical Vapor Deposition (MCVD) technique,³ yields highly pure immediate cladding and core glass deposited in a fused silica substrate tube. The MCVD process can be extended to large fiber preforms by depositing a large core and then overcladding the collapsed MCVD "core rod" with a large tube of pure fused silica. This overcladding silica can make up greater than 90% of the mass of a final preform.

When drawn into fiber, the overcladding silica is positioned beyond the core and immediate deposited cladding glass and a very minute fraction of the optical power passes through it. Nevertheless, there are stringent demands

on the properties of the overcladding glass tube. It must be free of undesirable impurities, which could diffuse into the core during the overcladding and fiber draw processes. It must be free of refractory metal oxide particles such as ZrO_2 and Cr_2O_3 , which can result in break inducing mechanical flaws within the fiber. Finally the tube must be of precise dimensions to accommodate the MCVD core rod and to keep the core precisely centered within the fiber to meet current industry standards.

It is the fabrication of the overcladding tubes which is the object of our research on silica sol-gel technology. Sol-gel processing offers the potential for fabricating these tubes in a "net shape" casting process using low cost starting materials. The challenges have been outlined: bodies must be large (multi-kilogram), pure and of precise dimensions.

PROCESS CHEMISTRY

For successful utilization of this colloidal sol-gel silica process, chemistry has paid a large role in both forming the gel and in purification of the dried gel.

Gel Chemistry: A colloidal sol-gel process was chosen over an organo-metallic route based on the need for very large bodies. Large drying shrinkages associated with organometallic gels would necessitate unacceptably long drying times. As a source of particulate silica, fumed silica produced by burning chlorosilanes was chosen due to its purity and relatively low cost. Of the fumed silicas, the lowest surface area (largest particle size) silica commercially available ($50 \text{ m}^2/\text{g}$) was chosen to enable ease of dispersion into sols of high silica content.

To provide sol stability with time and to lower the sol viscosity, tetramethylammonium hydroxide (TMAH) was used to bring the pH of the sols to >13 . This base was chosen over alkali metal hydroxides to avoid alkali contamination and over ammonium hydroxide because of the inability of ammonium hydroxide to fully dissociate and yield the needed high pH values. Sols stabilized with TMAH can be made with silica concentrations on the order of 50% by weight with low viscosity ($<100 \text{ cp}$) and long shelf life (>1 month).

To effect gelation of these sols, the pH must be lowered to <10 where the surface charge on the silica particles is lowered and weak bonds form. Adding an acid to the sol does cause gelation but in a very uncontrolled fashion. The acid quickly reacts with the sol at its point of introduction and results in an inhomogeneous curdled mix of gel and sol which cannot be molded. To allow uniform, time controlled reduction in the pH, a hydrolyzable ester is used. Methyl formate (MF) is a convenient example of an ester, which slowly reacts with water to produce formic acid and methyl alcohol. Depending on

the concentration of base, temperature of the sol, amount of added ester and the type of ester, gelation of these sols occurs in 5-30 minutes after adding the ester. This allows adequate time to uniformly mix the ester and cast the sol into molds before gelation.

Purification Chemistry: Dried gels consist of interpenetrating networks of pores and silica. This is an ideal medium for gas phase reaction to remove undesirable impurities since no part of the silica is more than a few tens of nanometers from a gas accessible surface. Purification of porous silica bodies produced by "soot" deposition methods such as VAD (vapor axial deposition) or OVD (outside vapor deposition) is commonly done using chlorine gas. This treatment removes hydroxyls from the silica surfaces and also reacts with impurity metals such as many optically absorbing transition metals to form relatively low vapor pressure metal chlorides, which are then transported away by the gas stream.

Such chlorine chemistry forms a part of this sol-gel process as well. However, for application in fiber preform overcladding tubes it was also necessary to remove break-inducing particles such as ZrO_2 . Modern fiber drawing must be done with a minimum of fiber breaks which either disrupt the drawing process or lead to poor yields of usable fiber. The goal of this project has been to have fewer than one break per million meters of fiber drawn attributable to the sol-gel derived overcladding tubes. Since a $1\text{ }\mu\text{m}$ particle can cause a break at 100 Kpsi proof testing and a $0.25\text{ }\mu\text{m}$ particle can cause a break at 200 Kpsi proof testing, it was necessary that the concentration of these particles be less than one part in 10^{15} by mass. Undesirable refractory metal oxide particles are inevitably present in raw materials or are inadvertently introduced during processing. This challenge stood as one of the major hurdles in making a viable sol-gel silica process for fiber overcladding tubes.

In the normal chlorine treatments of porous silica, either the reaction rate with refractory metal oxides is too slow or the volatility of the reaction products are too low. To circumvent this, it was found that the introduction of thionyl chloride (SOCl_2) into the gas stream at 600-900 °C reacts with the refractory metal particles to form volatile products.

THE PROCESS⁴

Sol Preparation: Fumed silica (Degussa OX-50) is mixed with water using a high shear mixer to effect a maximum dispersion of agglomerates. The silica powder is added stepwise to a water solution of TMAH during the dispersion. Concentrations of silica from 46 to >50 wt % can be used. The sol is aged for several hours where the pH decreases as some silica is dissolved. The sol is then centrifuged at 4000 times gravity as a first step in removing large impurity particles. The centrifugation step can remove large silica

aggregates but more importantly, it removes relatively large refractory metal oxide particles which are more dense than silica and generally of larger particle size than the silica which is an average particle size of about 57 nm. The sol is then stable and can be stored if needed before further use.

Just prior to casting an ester such as methyl formate (MF) is added to lower the pH. The sol is vacuum deaired to remove dissolved gasses and any bubbles within the sol.

Casting: Successful fabrication of net shape precision tubes requires precision molds. Depending on the desired tube size, metal molds were used with inside diameters greater than 10 cm and lengths up to 2 m. End caps for the tubular molds were designed to concentrically position a metal mandrel rod in the mold assembly. The mixed sol was pumped into the molds with care taken to avoid air bubble formation in the sol. The sol spontaneously gels as the ester hydrolyzes. The gel is aged for several hours prior to demolding.

Demolding: After aging, the gel network contracts slightly by syneresis and expels pore liquid. The mandrel rod is first removed from the mold assembly while vertical. The mold with the gel body is rotated to a horizontal position where the gel body is pushed onto a set of rolls for transfer to the drying chamber.

Drying: The wet gel bodies on the supporting rollers are transferred to a drying chamber. The chamber incorporates a flowing atmosphere of filtered air of controlled temperature and relative humidity. To avoid non-uniform drying and consequent warpage, the bodies are slowly rotated on the supporting rolls. Depending on the body dimensions, drying is completed in 3-8 days at temperatures below 100 °C.

Purification: Tubes taken from the drying chamber contain a few percent of water and organic reaction products from the organic base. The bodies are placed in a furnace with a sealed muffle. The remaining water and organic components are removed by heating to 400 °C in atmospheres of controlled oxygen content designed to avoid explosion hazards from oxidation of the organics. Any remaining carbon residue is removed later by heating to higher temperatures in a more oxidizing environment. Other treatments in the purification chamber utilize Cl_2 and SOCl_2 to remove hydroxyl ions, transition metal impurities and refractory oxide particles in the temperature range of 500-1000 °C. After cooling, the purified tubes are stored in a dry atmosphere to avoid water contamination.

Sintering: The purified tubes are then raised through a 1450-1550 °C hot zone in a silica muffled vertical furnace with a flowing atmosphere of He. The helium gas diffuses quickly through the silica glass structure and allows the collapse of closed pores to form transparent silica glass.

OVERCLADDING TUBE AND FIBER PROPERTIES

Tube Characterization: Depending on the silica concentration in the sol, the total shrinkage from mold dimensions to silica glass dimensions is 35-40% linear. Despite this contraction, the reproducibility of the shrinkage is assured by the uniformity of silica concentration within the sol and the ability to reproduce a desired silica concentration. Using this process, the following tube dimensional precision has been achieved.

OD variation	$\pm 0.6\%$
ID variation	$\pm 0.7\%$
Average concentricity/OD	$0.15 \pm 0.03\%$
Maximum ovality/OD	$0.08 \pm 0.06\%$
Straightness	$0.59 \pm 0.33 \text{ mm/m}$

Concentricity is the displacement of the center of the ID from the center of the OD. Ovality is the difference between the maximum and the minimum OD measurements on a tube. Straightness is the maximum deviation of the outside surface from an ideal straight cylinder.

These tubes meet the demands of the overcladding process for fiber preform manufacture. They are used to fabricate preforms using MCVD core rods from which optical fiber is drawn.

Fiber Loss: Spectral measurements on experimental preforms showed that losses as low as 0.333 dB/km could be achieved. The losses seen are comparable to those for preforms made using conventional silica glass.

Fiber Break Frequency: With centrifugation of sols and thionyl chloride purification, it was shown that breaks caused by particulates within the sol-gel derived glass met the <1 break per 1000 km of fiber.

SUMMARY

We have demonstrated that a colloidal sol-gel process incorporating commercial fumed silica can be used to produce large overcladding tubes for optical fiber preform fabrication. Key to the successful demonstration were several innovations. A fumed silica product of relatively low surface area was used to produce sols with high solids content. This minimized drying shrinkage and permitted the practical drying of multi-kilogram bodies without cracking. The utilization of a slowly hydrolyzing ester permitted the timely gelation of a cast sol, which was otherwise stable against gelation. The ability to fabricate large precision molds and control the silica content of sols permitted the casting of bodies which sintered to precision dimensions. Studies of the drying process enabled maximizing the drying rate consistent with uncracked bodies. Finally, utilization of sol centrifugation and halogenated gas purification of dried gel

bodies resulted in purity levels which permitted the use of these tubes in overclad MCVD fiber preforms yielding fiber of desired optical and mechanical performance.

This colloidal sol-gel process has been demonstrated for a demanding application in optical fiber technology. The ability to make large bodies of precision size in a net shape process using commercially available raw materials makes the process appealing for fabricating fused silica bodies for other applications. Also, the potential ability to incorporate dopants into the porous body using gases or liquids opens further opportunities for using a modified process in making low cost optical fiber.

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Discussion

R.E Newnham: Drawing of silica fibers is an anisotropic process. Therefore radial and longitudinal strains must be different. Does this lead to strain birefringence and optical problems?

J. MacChesney: The draw of silica fiber is carried out at $>2000\text{ }^{\circ}\text{C}$ using an applied tension. This results in a longitudinal strain which would not produce birefringence in an isotropic material (glass) of perfect radial geometry. But in "real" optical fiber, there are: core, clad and overclad. All have slightly different composition, viscosities, and expansion coefficients. There is anisotropy induced in manufacture by asymmetry of these elements, and in draw by variation in the cooling conditions around the fiber, resulting in variation in fictive temperatures. Birefringence is to expected.

As a result, two distinct HE_{11} polarization modes with distinct phase and group velocities exist. These give rise to polarization mode dispersion (PMD) and polarization dependent loss (PDL). In long systems, PMD increases as the square root of length. It is minimized by twisting the fiber during draw. PDL is introduced by the presence of optical (system) elements: isolators, filters, etc. This is minimized by control of the properties of system components.

G. Messing: The gelation of silica preforms was done by first adjusting the pH to 11 and then dropping it. The gelation point at 8.5 suggests precipitation is the critical process since SiO_2 gels at pH 2-3. Have you considered simply adjusting the pH to acidic side thus inducing flocculation.

D.W. Johnson, Jr.: We have found that the isoelectric point of these sols moves to higher pH using organic bases. While the gelation does take place while the pH is > 7 , we have not found that precipitation of dissolved silica plays a significant role in the gelation process. In fact, the pH reduction with the hydrolysis of the ester is fast enough that the dissolved silica precipitates homogeneously as small particulates. The evidence for this is twofold. Firstly, the surface area of the dried gel is raised above that of the starting fumed silica due to the precipitated fine silica particles. Secondly, we find no evidence for the formation of necks at particle contact points where the free energy would be minimized were the kinetic constraints not operative. The gelation is therefore due to the collapse of the electrical double layer as the pH decreases. Finally, for sols stabilized at high pH, it is not possible to adjust the pH to the acidic side to cause flocculation without rapid gelation which would interfere with pouring the sol into a mold.