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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 m^2/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 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