Hermetic carbon-coated optical fibers: methods and applications

Eric Lindholm & Jie Li
OFS Specialty Photonics
November 5, 2008
Hermetic carbon-coated fibers

- Optical fibers
- Reliability
- Carbon deposition process
- Issues for consideration
Optical Fibers
Optical fibers

- Light guides
  - Information is carried by light

- Glass
  - Some plastic - short distance communication

- Advantages of optical fibers
  - High bandwidth
  - Low loss
  - Electromagnetic immunity
  - Small size/light weight
  - Safer
  - Environmentally friendly
**Telecommunication fibers**

- 99% of the optical fiber market is telecommunication fibers

- Singlemode – long haul \( \approx 25\text{km} \)
- Multimode – short haul \( \approx 2\text{km} \)

- Fiber is well protected in Kevlar-strengthened cables and rarely sees significant stress
Specialty fibers

• Used for special applications

• High-stress applications
  • Tensile stress
  • Bending stress
  • Torsional stress

• Adverse environments
  • Water
  • Solvents
  • High operating temperatures
  • Elevated pressures

Fibers require enhanced protection
Specialty fibers - Geophysical

Multimode fiber
Carbon / polyimide coat

Fiber is deployed down stainless steel tube during oil well completion for distributed temperature sensing

Environment:
Pressurized steam
Hydrogen gas
Solvents
Specialty fibers - Aerospace

**FlightGuide™ Cables**
Graded-index multimode
Carbon/Polyimide/Silicone/ETFE Fiber
Used in: F-22, Commanche, F-18, Space Station
Qualified: for F-16 and EA-6B

- Small size + EMI immunity
- Fiber placed into tight bends
- Temperature extremes, thermal shock, vibration
- High reliability required
Specialty fibers - Sensors

Structural sensors
Embedded in concrete, asphalt, other building materials to monitor stress and/or failure.

Engineering Lessons From the New, Reopened Minnesota Bridge
Reliability
Mechanical reliability

- Stresses
  - Tensile
  - Bending
  - Torsional/twisting

- However, glass is stronger than steel when segregated from water

- Water eats glass

\[
\sigma_{\text{tension}} = \frac{F}{A}
\]

\[
\sigma_{\text{bending}} = E \left( \frac{r}{R} \right)
\]

\[
\sigma_{\text{Torsion}} = G \varepsilon_{\text{Torsion}}
\]
Relative strengths of materials

Cross-Section area: $1.9 \times 10^{-5}$ inch$^2 = 1.23 \times 10^{-3}$

d = 125µm

Fiber

Steel

Copper

1 lbf (0.45 kgf)

15 lbf (6.8 kgf)

5 lbf (2.27 kgf)
Corrosion of silica in water

\[ \text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{SiOH} + \text{HOSi} \]

Hydrolysis of silica: water breaks the silicon-oxygen bond

Dissolution of silica accelerates crack growth and may cause degradation of strength.
Water-glass interaction

- Michalske & Frieman (1983)
- Strained crack tip bond susceptible to water attack
- Water-assisted crack growth weakens fiber
Effect of aging on glass surface morphology

- Atomic Force Microscope Images -

Unaged  aged in DI-Water for a month

From IWCS course notes “Fiber Design Considerations for Adverse Environments” by Hakan Yuce
Effects of water

• **Fatigue**: a.k.a. moisture-assisted sub-critical crack growth under stress. Strength drop due to crack propagation under applied stress in the presence of moisture.

• **Aging**: Degradation in fiber strength in the absence of stress is related to corrosion on the glass surface by an aggressor (almost always water).
Fatigue factor and fiber lifetime

Power law: \( t_f = \left( \frac{\sigma_p}{\sigma_a} \right)^n \)

where:
- \( t_f \) = Time to failure (seconds)
- \( \sigma_p \) = Prooftest stress
- \( \sigma_a \) = Application stress
- \( n \) = Fatigue factor or stress-corrosion factor

We want to increase the "n" value for greater reliability.

Non-hermetic fiber: \( n \approx 20 \)
Hermetic fiber: \( n > 100 \)

See Weiderhorn model for fiber lifetime:
\[ t_f = B S_{int}^{n-2} \sigma^{-n} \]
Predicted time to failure vs. fatigue factor

Non-hermetic → 20% $\sigma_p$
Hermetic → 80% $\sigma_p$
Hermetic carbon layer

- Applied via CVD reaction between glass and hydrocarbon gas
- Layer is typically 300-500Å in thickness
- Carbon is strongly bonded to silica with Si-C bond
- Amorphous, cross-linked graphite structure
- Black, shiny and opaque
- Electrically conductive → thickness is determined from linear resistance
- Hermetic to water: no strength degradation due to effects of aging or fatigue (n-value > 100)
- Resists HF attack
- Hermetic to H₂ (to a limit)

\[ R = \frac{\rho}{\pi \cdot D \cdot T} \]

where:
- \( R \) = Electrical resistance (kΩ/cm)
- \( \rho \) = Carbon layer resistance (Ω•cm)
- \( D \) = Fiber diameter (μm)
- \( T \) = Carbon layer thickness (Å)
Aging behavior of fibers in water

Carbon deposition process
Carbon deposition

- Hot glass + hydrocarbon gas = chemical vapor deposition
- Remove boundary layer around glass fiber
- Introduce hydrocarbon gas (in absence of O₂)
- Thermal decomposition of the hydrocarbon occurs on glass surface in a pyrolytic reaction
- Reaction temperature around 700-1000°C
- Disordered graphite platelets/"ribbons" accumulate from crosslinking of unsaturated bonds in carbon
- A minimum thickness is required until the fiber is hermetic and free of pinholes
• Disordered platelets, ribbons, “crystallites”

• Unsaturated bonds lead to crosslinking of carbon structure

• Fiber is hermetic when microvoids are eliminated

Carbon thickness vs. fatigue and hydrogen protection

"Hermetic product performance: Ensuring the Uniformity of the Carbon Layer" – Tuzzolo, Allegretto, Urruti of Corning, IWCS proceedings 1993
Fiber Draw

- Glass is melted and pulled from furnace
- Size is controlled by adjusting pulling speed at capstan
- Polymer coating added for protection – carbon layer too thin to protect fiber on its own
Fiber Draw with carbon reactor

- Retained heat of fiber drives reaction
Carbon reactors

- High draw speed = long reaction zone
- Reaction chambers
  - Gas inlet
  - Unreacted gas/reaction byproducts exhaust
  - Atmospheric reaction
- Different hydrocarbon gases employed
- Concurrent gas flow vs. counterflow
- Soot generation is a concern
Nitrogen purge to exclude O$_2$ and strip boundary layer

Exhaust

Reactant gases
Bell Labs reactor

- Small inside diameter in reaction zone
  - 9” long with inside diameter of 0.4”
- Fast draw speeds (>10m/s) = longer reaction zone

- Reactant gases:
  - Acetylene – C\textsubscript{2}H\textsubscript{2}
  - Benzene – C\textsubscript{6}H\textsubscript{6}
  - Molecular chlorine gas
    - H\textsubscript{2} scavenger
    - Contributes to carbon elongation → improve strength and resistance to hydrogen ingress

- Hermetic fiber (n>200) at high speed
Carbon reactors

- Low speed reactor (< 1m/sec)
- Greatly reduced reaction zone
- Jets are used to introduce hydrocarbon gas
  - Strip away boundary layer
  - Concentrate the pyrolytic reaction
OFS Specialty low-speed reactor

• Reactor is attached directly to draw furnace

• Fiber is not exposed to atmospheric water

• Process can be sensitive to speed / temperature changes because reaction zone is very small

• Glass directly below neckdown is most reactive (broken Si-O bonds)
Carbon reactors

- Open-air LCVD reactor
- CO2 laser used as heat source
- Inert and reactive gases introduced coaxially
- Exhaust on top
- Hermetically coat fiber splices

Issues for consideration
Issues for consideration

- Reactor designs
- Fiber temperature
- Hydrocarbon gases
- Gas additions
- Gas flow
- Challenges for carbon deposition

Hermetic carbon coating
Generic carbon reactor

Fiber temperature

• Fiber needs to drive CVD reaction for good bonding

• “In general, too low a temperature will produce a somewhat sooty non-hermetic coating, while too high a temperature can produce a predominantly diamondlike structure which is transparent, non-conductive, and also non-hermetic.”

• For desired carbon deposition, fiber temperature should be between 700-1000°C. (Depends on reactant gas)

• Temperature can be estimated from natural cooling equation.

Fiber temperature below neckdown at varied draw speeds

\[
\frac{T_f - T_a}{T_{fin} - T_a} = \exp\left(-\frac{4ht}{\rho \cdot c \cdot D}\right)
\]

Fiber Draw with carbon reactor

- Generally speaking, want reactor close to the furnace while maintaining optimum temperature range
  - Maximize reactivity
  - Minimize exposure to atmospheric water
Reactor with concurrent flow

Maximum fiber temperature


“Deposition of hermetic carbon coatings on silica fibers” – Huff et.al., AT&T Bell Labs, Material Research Soc. 1990.
Deposition rate in reactor

- Maximum deposition where fiber is hottest

“Deposition of hermetic carbon coatings on silica fibers” – Huff et al., AT&T Bell Labs, Material Research Soc. 1990.
Reactant gases

Organic gases

Aliphatic hydrocarbons:
- Methane
- Ethane
- Propane
- Butane
- Pentane
- Hexane

Aromatic hydrocarbons:
- Acetylene
- Benzene
- Toluene

Halogenated hydrocarbons
- Chloromethane
- Chloroethane
- Dichloromethane

Halogens:
- Chlorine
- Bromine
- Fluorine

Carrier gases:
- Nitrogen
- Argon
- Helium

n.b. patent #5,354,348
Reactant gases

• Hydrocarbon gases = carbon supply = building blocks
  • Thermal decomposition breaks down carbon-hydrogen bonds and unsaturated bonds reform in carbon matrix

• Chlorine gas is used as a hydrogen scavenger
  • Contributes to carbon elongation
  • Improves strength
  • Better protection from H₂ ingestion

• Halogenated hydrocarbons = “best of both worlds”

• Inert carrier gases help to strip boundary layer, accelerate gas flow and minimize soot buildup
Increasing energy to break carbon triple bond in acetylene gas $\text{H-C\equiv C-H}$ to form amorphous, hermetic carbon layer.

Carbon layer resistance vs. gas addition ratio

12% addition of “A” increased carbon thickness by 40%

Low speed carbon deposition process for hermetic optical fibers – Lindholm, et.al., IWCS 1999.

• Counterflow of gases
Countercurrent gas flow

• Fiber (substrate) is hottest at top of reactor = point of most deposition

• Huang & Chiu found that, in a counterflow reactor, distribution of surface reaction species is higher at inlet due to conversion of precursor gas*

• In parallel flow model, reactive gases concentrate near reactor exit where the fiber is coldest

• Counterflow may also be more efficient due to better stripping of boundary layer

- Counterflow of gases
  - Concentration of reactive gases
  - Counterflow strips boundary layer → turbulent flow preferable?
Challenges for carbon deposition

- Hermeticity to water = mechanical reliability

- Hermeticity to hydrogen = optical reliability
  - Most carbon layers are completely hermetic to H$_2$ up to $\approx$150°C
  - At temperatures $> 150$°C, diffusion of H$_2$ increases
  - Want to increase thickness and decrease permeability

$$\tau_i = \frac{\delta^2}{6 D_c}$$

where:
- $\tau_i$ = time for first molecule of H$_2$ to diffuse through carbon layer
- $\delta$ = carbon thickness
- $D_c$ = diffusivity of H$_2$ in carbon layer
Thicker layer = more $H_2$ protection

Nakamura et. al. showed increasing graphite platelet size enhances $H_2$ protection by creating tortuous route for diffusion

Biswas et. al. noted that chlorine increases carbon’s elongation

Figure 7. Model of structure of the carbon coatings


Issues for consideration

Parameters:
- Reactor designs
- Fiber temperature
- Hydrocarbon gases
- Gas additions
- Gas flow

Models:
- Numerical heat transfer and temperature modeling
- Gas flow patterns
- Energy of pyrolytic reactions

Goal: Hermetic carbon layer with high strength and low \( \text{H}_2 \) permeability
Questions

Eric A. Lindholm
Senior Product Development Engineer
860-678-6678
Email: elindholm@ofsoptics.com