New Optical Sensor Suite for Ultrahigh Temperature Fossil Fuel Applications

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ABSTRACT

Accomplishments during the first six months of a program to develop and demonstrate technology for the instrumentation of advanced powerplants are described. Engineers from Prime Research, LC and Babcock and Wilcox Research Center collaborated to generate a list of potential applications for robust photonic sensors in existing and future boiler plants. From that list, three applications were identified as primary candidates for initial development and demonstration of high-temperature sensors in an ultrasupercritical power plant. In addition, progress was made in the development of materials and methods to apply high-temperature optical claddings to sapphire fibers, in order to improve their optical waveguiding properties so that they can be used in the design and fabrication of high-temperature sensors. Through refinements in the processing steps, the quality of the interface between core and cladding of the fibers was improved, which is expected to reduce scattering and attenuation in the fibers.

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1 INTRODUCTION

The goal of this project is the research and development of advanced, robust photonic sensors based on improved sapphire optical waveguides, and the identification and demonstration of applications of the new sensors in advanced fossil fuel powerplants, where the new technology will realize improvements in process control and monitoring. The advantages of fiber optic sensors over electronic sensors, particularly in environments where the electronic sensing materials can not withstand the rigors of the harsh conditions, are well known. Typically, advanced power generation systems operate at higher temperatures and pressures than traditional power plants. Traditional sensor technology for measuring temperature, pressure, flow and strain will not survive the harsh conditions anticipated in these plants. Furthermore, these plants will require more extensive process monitoring and condition assessment to maintain optimum performance and minimize maintenance costs. An effective means is required to reduce the complexity and cost of connecting the larger number of sensors to a central data acquisition platform. Therefore, one of the goals of the program is the identification of all potential applications in supercritical boiler plans where photonic sensors can be used for process control and monitoring.

For the ultrahigh-temperature environment found in current and future power generation facilities, new materials for the optical sensors will be required. Previous efforts to utilize sapphire fiber sensors that can theoretically operate above 1650° C (3000° F) have been limited because the fiber itself does not lend itself to incorporation in the known sensor techniques, due to its unclad and multimode construction. Another goal of this program is the development of high-temperature, ceramic claddings for sapphire fibers to improve the waveguiding properties of sapphire fibers and facilitate their use in photonic sensor systems.

Current efforts towards improvement of sapphire fibers focus on creating cladding in sapphire (aluminum oxide single crystal, Al_2O_3) fibers by dip-coating the fibers in a a mixture of magnesium oxide (MgO) powders and magnesium aluminate spinel ($MgAl_2O_4$) powders to form a coating on the sapphire fibers. The technique involves dip coating a sapphire fiber in a suspension of MgO and spinel powders, drying the coating, then firing at elevated temperature to react the MgO powder with the sapphire fiber and to densify the coating.
The overall reaction for the process is given by the chemical equation:

$$MgO + Al_2O_3 = MgAl_2O_4$$

which proceeds rapidly at 1750°C (3182° F).

The coated fibers are then fired at high temperatures to facilitate the reaction between the MgO in the coating and the Al_2O_3 in the fibers by ion diffusion, and create a cladding consisting of $MgAl_2O_4$ surrounding the sapphire core. As a result, the diameters of the sapphire fibers are reduced and the number of modes propagating in the sapphire fibers is also reduced.

2 EXECUTIVE SUMMARY

The objective of this program is to enable revolutionary improvements in the efficiency and output of fossil fueled power plants through the development of new, robust photonic sensors based on improved sapphire fibers, and of the application of those sensor systems to monitoring and process control of the powerplants. Specific objectives include the integration of new high-temperature optical sensor technology into future fossil fuel power plant facilities, resulting in improved performance and efficiency, and reduced emissions. The key research objectives involve the development of new processing methods to produce the ultrahigh temperature clad and writable sapphire fiber, identification of applications within advanced boiler plants for new ultrahigh-temperature photonic sensors, and the demonstration of prototype sensors for fossil fuel power plants.

Specific tasks within the program include (1) identifying all the applications within a next-generation fossil fuel power generation plan where ultrahigh temperature sensors are needed, (2) identifying which types of sensors are most applicable in each location within the facility, (3) developing a reproducible process for creating chemically modified sapphire fiber to be used in the sensors, and (4) demonstrating success through laboratory and field measurements at ultrahigh temperatures.

During the reporting period, progress was made in two main areas: identifying applications, locations, and specifications for high-temperature optical sensors in power plant systems, and in development of high-temperature claddings for improved sapphire fibers with enhanced optical properties.

Under a subcontract to Prime Research, Babcock & Wilcox Research Center convened a team of engineers to consider possible applications of photonic sensors in existing and future boiler plants. In addition, a meeting was held at Alliance, OH between representatives of B&W and Prime Research to discuss the results of the B&W study, and to brainstorm other possible applications where robust sensors could be used to good advantage for controlling or monitoring power plants. Issues that were identified as potential barriers to increased use of instrumentation in advanced plants include limited materials for typical conditions (which include corrosion, corrosion, and reducing atmospheres), very high temperatures due to oxygen firing, need for improved models, difficulty in interfacing with existing control systems, and resistance of customers to pay for sensors and controls.

Four classes of measurements within supercritical boiler plants were identified as desirable for monitoring and control the plants. These include temperature measurement for thermal barrier coatings, in-situ strain measurements on superheater tubes, measurement of steam flow in membrane walls and tube banks, and dynamic pressure measurements for monitoring of combustion dynamics. Three specific locations were identified as primary candidates for sensor development in this program: the furnace water wall (tube temperature, feet flux, water flow), secondary superheater tubes (tube temperature, steam temperature, strain), and burners (temperature of burner components).

Methods for applying magnesium aluminate spinel coatings to sapphire fibers to function as optical claddings were researched. Magnesium alumina spinel is well-suited for cladding of sapphire fibers due to its high melting temperature, refractive index slightly less than that of sapphire, and coefficient of thermal expansion closely matched to that of sapphire. Application of spinel coatings involves dipping the sapphire fiber in a slurry of spinel and magnesium oxide powders, firing the slurry on the fiber, and then sintering the coating to densify it on the fiber.

An investigation was undertaken in which certain parameters such as the firing profiles, the slurry dipping procedures, the atmosphere of firing, the particle sizes of the powders, and a slurry compositions were systematically varied. A total of 37 samples were prepared and tested. Results indicate that a smooth interface between the sapphire core and spinel cladding can be achieved through a carefully tailored firing procedure in argon atmospheres. In addition, it was found that the core diameter of the sapphire fiber can be reduced by a specified amount through the addition of a specified proportion of magnesium oxide in the slurry. We have successfully fabricated spinel clad sapphire fibers with reduced cored diameters and smooth core/cladding interface with promising light guiding properties.

3 EXPERIMENTAL PROGRESS

During the reporting period, progress was made in two main areas: identifying applications, locations, and specifications for high-temperature optical sensors in power plant systems, and in development of high-temperature claddings for improved sapphire fibers with enhanced optical properties.

3.1 Requirements definition study

On March 23, 2004, a meeting was held at Babcock Wilcox Research Center to discuss possible applications of advanced photonic sensors for instrumentation of current and future boiler plans. Russell May represented Prime Research as program PI. B&W representatives present were Tom Flynn, Stan Vecci, Jeff Sarver, Bruce Young, Ralph Bailey, Greg Nakeneczny, Dennis McDonald, and Tim Fuller. In advance of the meeting, the B&W representatives convened to discuss instrumentation needs and possible sensor applications. The objective of the meeting was to identify all potential sites within the existing/near term boiler designs and planned future supercritical boiler designs where new technology optical sensors could be used for process monitoring and condition assessment. Currently, supercritical steam boilers generally rely on indirect and calculated measurements. Advanced sensors and controls are needed to monitor process conditions directly to increase process efficiency, reliability, availability and detect early signs of failure [1].

Results of the meeting and the B&W study are described in detail below in Section 4.1.

3.2 Development of high-temperature optical cladding for sapphire fibers

The spinel slurry is prepared by dissolving a powder mixture of MgO powders (EMD Chemical Inc., formally EM Science, Gibbstown, NJ; average particle size ≈ 15 μm) and $MgAl_2O_4$ powders (Baikowski International, Rayleigh, NC; average particle size ≈ 3 μm) in a solvent consisting of isopropyl alcohol (2-propanol, Jade Scientific, Canton, MI), propylene glycol methyl ether (1-methoxy-2-propanol from Fluka, Milwaukee, WI), polyvinylpyrrolidone (Aldrich Chemical Company, Milwaukee, WI), and polyethylene glycol (SPI supplies, West Chester, PA). To maintain its homogeneity, the slurry is constantly stirred in a beaker covered with parafilm on a hot plate using a magnetic spinning bar.

After the slurry is prepared in a beaker on a hot plate with magnetic stirring, the slurry is poured into a 250 c.c. polypropylene bottle for ball milling. The bottle is filled to about 50% in volume with alumina grinding media as shown in Figure 1 (a). The grinding medium is in a cylindrical shape ¼ inch long and ¼ inch in diameter. For best milling efficiency, more isopropyl alcohol is added into the bottle to the level just covering the grinding media. The bottle is then placed and fastened using rubber bands in a porcelain container for ball milling as shown in Figure 1 (b). The ball miller is made by US Stoneware (East Palestine, OH). The ball milling step is critical in achieving a slurry with fine particle sizes and uniform and homogeneous thickness (viscosity).

(a) **(b)**

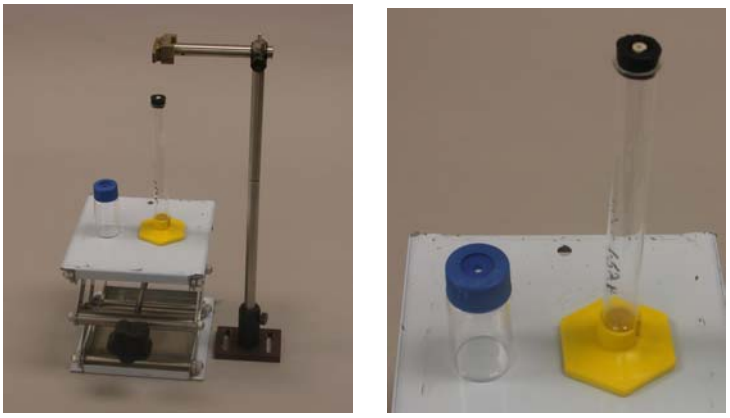
Figure 1. (a) The 250 c.c. polypropylene bottle half filled with grinding media (right) and the porcelain container (left) for ball milling; (b) The container on the ball milling machine ready for milling.

After ball milling, the slurry is poured back to a beaker without a parafilm cover and is stirred using a spinning bar on a hot plate. In this process, the additional isopropyl alcohol gradually evaporates and the slurry slowly gets thicker and thicker. When the desired slurry thickness is reached, it is ready for fiber dipping.

Before dipping, the 150 μm diameter sapphire fiber (Photran LLC, Poway, CA) is cleansed with hydrochloric acid, deionized water, and finally isopropyl alcohol. The fiber dipping is performed using the experimental apparatus shown in Figure 2 (a) and (b). The fiber is clamped vertically using the stand shown in Figure 2 (a). The vertical orientation of the fiber is critical in creating a coating with uniform thickness. A graduated cylinder

or a small glass bottle is used to contain the slurry. The cylinder or the bottle sits on a small lab jack. The dipping is achieved by raising and lowering the cylinder or the bottle using the lab jack. Several dips are needed to form a thick enough coating on the fiber, and the overall time of the dipping procedures may take from several minutes to tens of minutes. In order to maintain a constant viscosity of the slurry during dipping, the cylinder or the bottle is capped, and a small hole is drilled in the stopper of the graduated cylinder or in the cap of the bottle as shown in Figure 2 (b); as a result, the fiber can pass through the hole while the evaporation of the solvent, i.e., isopropyl alcohol, in the slurry is minimized. To increase the uniformity of the coating thickness along the length of the fiber, a smooth motion of the platform of the lab jack with a constant speed is required. Since maintaining a constant speed by manually adjusting the height of the lab jack using the turning knob is not easy, so only best efforts are made to achieve this goal.

The step-by-step slurry preparation and fiber dipping procedures are described in Appendix 1. The dipped fibers are finally fired in either a Thermolyne 46100 high-temperature furnace or Thermolyne 48000 furnace (Thermolyne, Dubuque, Iowa). The former is referred to as the "Large Furnace" and the latter the "Small Furnace" in the firing profiles illustrated in Appendix 2.



(a) **(b)**

Figure 2: The experimental apparatus for the dipping of fibers

4 RESULTS AND DISCUSSION

Results of the requirements definition study to identify potential applications for process monitoring and control with advanced photonic sensors, and of the investigation and development of robust, high-temperature claddings for sapphire fibers, are described below.

4.1 Requirements definition study

B&W has developed designs for advanced ultrasupercritical steam boiler systems that will operate at steam conditions of 760° C (1400 °F) and 4500 psig and cycle efficiencies up to 50%. Most likely portions of the boiler will be operated at alternating oxidizing

and reducing atmospheric conditions, as well as under severe slagging and fouling conditions. New alloy steels will be required to withstand the operating conditions. The long term mechanical properties of these materials under these operating conditions are not well characterized. Although traditional measurement sensors such as Type K thermocouples, pressure transducers, heat flux, flow, and strain measurements may be applied, they suffer from rapid failure rates and currently require that all the sensor leads be routed individually to the data acquisition system. Current techniques for protecting these leads are costly and expensive to install.

4.1.1 General applications and requirements

The following issues were identified as general barriers to efficient and cost effective process monitoring and condition assessment in advanced power plants [1,2].

- Very high temperatures – Oxygen firing (increasing O_2 concentration to 27-28%) results in adiabatic flame temperatures (1650° C (3000 °F)) higher than occur in combustion with air as the oxidant. These conditions are similar to operating temperatures (1371-1650°C (2500-3000 °F)) anticipated in high-temperature heat exchangers associated with the indirectly-fired cycle systems. High temperatures and ash deposition in generating banks of tubes present challenges for sensor stability and reliability.
- Models – analytical models coupled with input from robust sensor systems show promise for optimization of plant efficiency and emissions, but development of accurate models is required.
- Interfaces must be compatible with existing plant distributed control system and plant information systems.
- Materials
    - Potential of failure due to harsh environmental conditions.
    - High temperature thermowells for harsh conditions (erosion, corrosion, reducing atmosphere) are required.
- Cost barriers: Customers still buy on the basis of initial cost and won't pay for sensors/controls. Cost must be minimized. Current development costs for advanced sensors are prohibitive without government support, especially given the price customers are willing to pay to implement the technology.

At the 2002 NETL Sensor and Control Program Roadmapping Workshop, workshop participants acknowledged that many of the sensors and control system issues stemmed from a lack of suitable sensor materials [1]. Besides development of robust sensors, the DOE workshop identified the need for advancements in control systems and system integration. Participants observed that sensor technology is currently limiting rather than control system or system integration technology.

The demand for advanced sensors and control systems is usually driven by more stringent regulation than by gains in efficiency. In general, if a specific sensor need is identified, then the sensor could be developed and the control system integrated. Problems arise

from the lack of knowledge of the end users' needs and the inability to convey the benefits of better measurement and monitoring systems. The extreme conditions anticipated in B&W's ultrasupercritical boiler concepts will drive the need for new sensor technology, because it is well known that existing sensors will not be able to withstand the harsh conditions.

4.1.2 Requirements specific to ultrasupercritical boiler plants

A process schematic for an ultrasupercritical boiler system concept is illustrated in Figure 3 below [3].

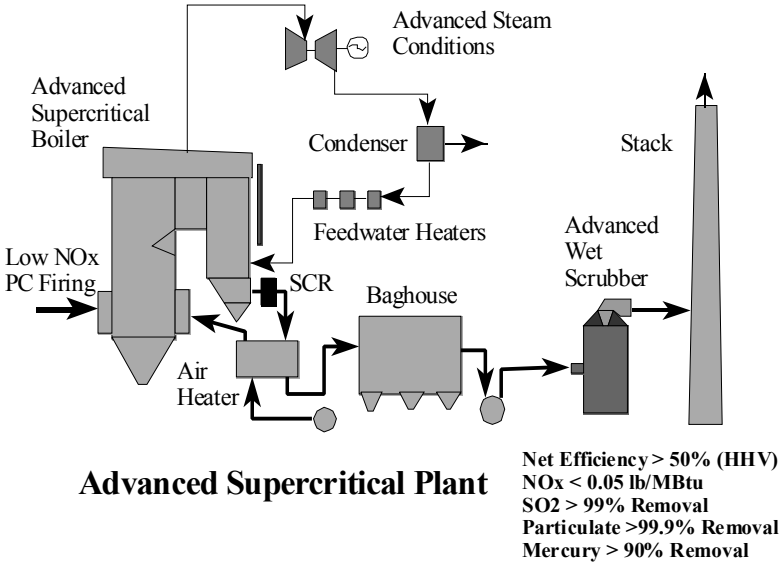


Figure 3. B&W Vision for Advanced Supercritical PC Rankine Cycle

Four classes of measurements within supercritical boiler plants were identified as desirable for monitoring and control of the plant. These classes are:

- Thermal barrier coating temperature measurement – B&W may require thermal barriers on materials for oxygen-firing burner designs due to high temperatures.
- Strain – in-situ strain measurements on ultrasupercritical steam generation secondary superheater tubes.
- Flow measurement –steam flow in membrane walls and tube banks.
- Combustion stability – dynamic pressure measurements at high temperature, for sensing combustion dynamics. B&W uses Flame Doctor™ to monitor conventional pulverized coal combustion flames, but will require advanced sensor technology to monitor and control the next generation of smart burners (i.e., burners that auto-adjust to coal quality changes and load changes).

In measuring water-cooled or steam-cooled furnace wall temperatures, high temperature burner components, and superheater tube temperatures (Figure 4), special protection must be provided because of the destructive high temperature furnace atmosphere and, in some cases, the accumulation and shedding of ash and slag deposits. For example, special provisions must be made to protect the leads between the point of measurement and the exit from the boiler setting for superheater tubes. Traditionally, this is done by containing the sheathed thermocouple in stainless steel tubing that is welded to the superheater tube. This maintains the sheath and protection tubing at a temperature approximately equal to the temperature of the superheater tube. Additional cooling of the stainless steel protection tube is frequently required. An approach to both simplify this installation and reduce the cost is required to allow for more extensive and more reliable monitoring of superheater surfaces.

Advanced once-through supercritical boiler designs are more sensitive to inaccuracies in predictions for heat flux. Further, performance of these units is more sensitive to variations in the furnace heat flux during operation. Therefore, accurate measurement of furnace heat flux is essential for the design and operation of advanced steam cycle boilers. Measurement of heat flux at more locations in the boiler will also likely be required to obtain the spatial resolution required to design the boiler and operate the boiler close to optimal conditions. Also, staging combustion to achieve low NO_x emissions tends to move the more intense combustion zone upward in the furnace, which will influence furnace tube material selection.

B&W currently uses chordal thermocouples (chord-drilled holes) or heat flux buttons to measure surface temperatures and heat flux on heat absorption surfaces such as membrane walls or generating banks [4]. Measuring the temperature gradient through a tube wall is a means of determining the heat flow rate through the wall and of detecting the accumulation of certain types of external or internal deposits. Deposits on the internal surface of the tube can cause a significant increase in the tube temperature, possibly causing thermal stress beyond the yield strength of the tube material. A temperature differential between the external and internal surface of 38° C (100 °F) above the baseline difference is sufficient to justify chemical cleaning. Chordal thermocouples and heat flux buttons are expensive to install and maintain, so their use is often limited in large utility boilers. The chordal thermocouple requires a pressure part weld, and must be fabricated in the shop to precisely determine the location of the thermocouple location at the surface and depth within the tube wall.

Protection of pressure parts from excessive thermal stresses or overheating is also critical. Most periodic maintenance of pressure parts is performed during scheduled outages. Steam-cooled, thick wall headers such as those found on superheaters and reheaters are subject to cyclic thermal stresses as well as creep fatigue. Strain and temperature measurements are needed to calculate creep fatigue and predict remaining life.

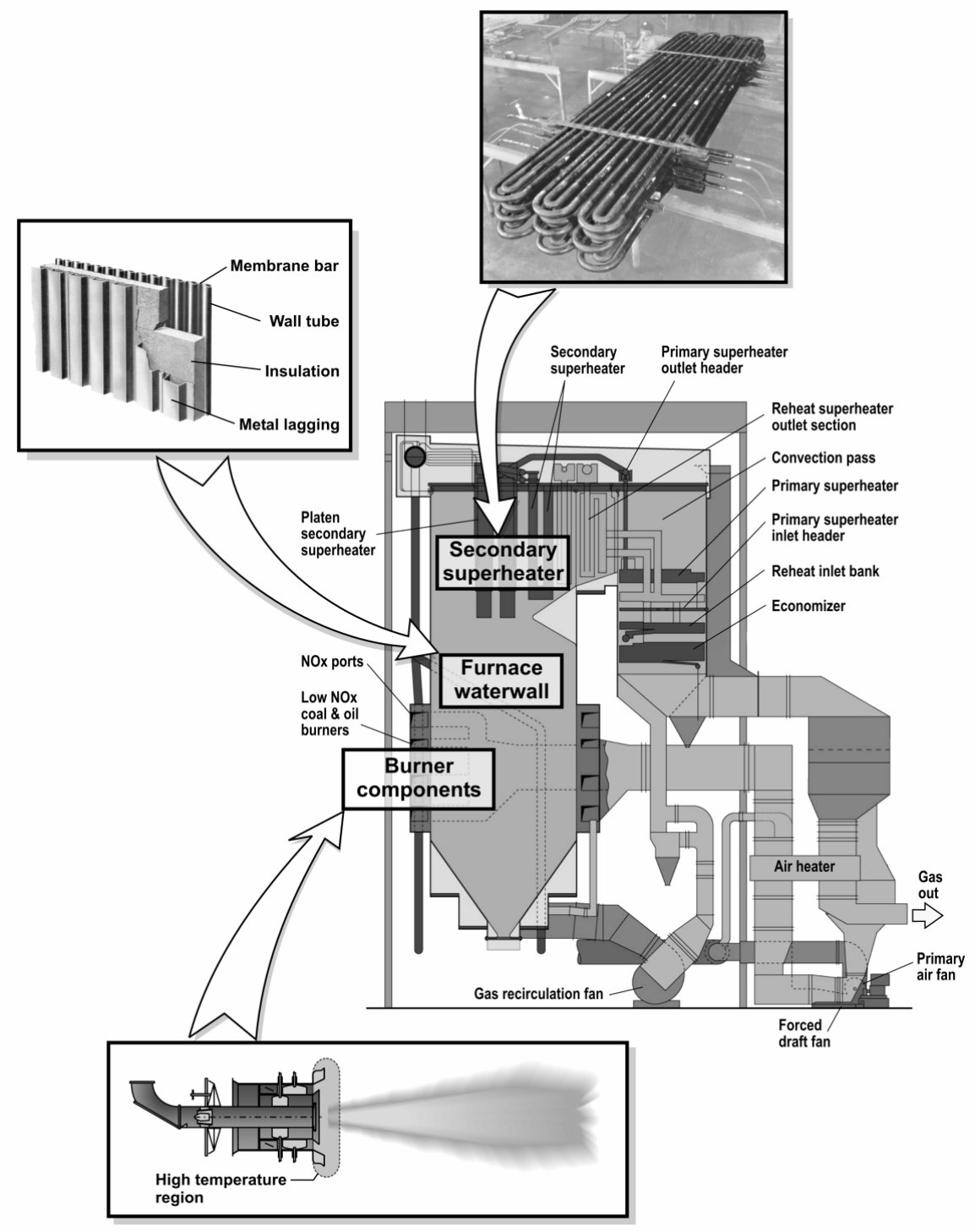


Figure 4. Typical Monitoring Points on a Boiler

Advanced low mass flux, supercritical vertical tube boiler designs require good measurement of steam temperature and flow through membrane walls to direct redistribution of flow to hot spots. This is a potential opportunity to combine advanced sensors and smart materials. For example, orifices that open and close at the discharge end of the tube to compensate for changes in steam conditions could be installed. The restriction orifices would open when steam conditions are hot relative to other legs, thereby preferentially increasing the water flow through the tubes that experience higher heat fluxes.

Customers are considering burning natural gas and coal in the same unit to address the restrictions in the Ozone Transport Rules (OTR). Existing low-NO_x coal burners cannot achieve the NO_x reduction that is possible with natural gas. An advanced dual-fuel burner capable of burning coal and natural gas in combination or individually is needed. Advanced control techniques may make it possible to achieve low NO_x emissions and fuel flexibility in a single burner.

The following applications for high temperature optical sensors within the advanced B&W plants were identified.

Temperature

- Thermal wells for pulverized coal combustors.
- Thermal wells for coal gasifier (1010-1150°C (1850-2100 °F)) suitable for corrosive reducing atmosphere (350 psi-900 psi).
- Primary stage for slagging gasifier 1427° C (2600 °F).
- Burner components (oxygen firing) employing staged combustion 1371-1650°C (2500-3000 °F), reducing conditions, oscillating reducing/oxidizing conditions.

Pyrometer Measuring and Monitoring

Pyrometry enables both surface temperature measurements and integrity monitoring in real time.

- Combustor tiles and liners such as those on cyclone boilers. The cyclone barrels operate under slagging combustion conditions (1538-1650° C (2800-3000 °F)), atmospheric pressure, and oscillating oxidizing/reducing atmosphere.
- Boiler burner vanes and superheater tubes can reach temperatures up to 760° C (1400 °F) at atmospheric pressure and oxidizing conditions.
- Boiler tube cladding is used for corrosion, erosion and oscillating oxidizing/reducing atmospheric conditions. Gas temperatures up to 1650° C (3000° F) may be experienced.

Strain

- Strain measurements on ultrasupercritical steam generation secondary superheater tubes may be required. Steam conditions inside the tubes in advance cycle boilers may reach 760° C (1400 °F) and 4500 psi. Strain measurements in the range 0.1-1.0% may be required for process monitoring and condition assessment. The team would couple pressure, temperature and strain measurements to perform condition assessment of leading secondary superheater tubes.

Heat Flux

- B&W uses heat flux sensors to measure heat flux in the furnace and confirm model predictions and assess fouling on boiler wall. Water or steam blowers can be operated based on the measured heat flux. The current approach (i.e. chordal thermocouples) limits how many of these sensors can be installed, due to the cost of running all the wires back to the control room for data acquisition.

Flow

- Steam flow in ultrasupercritical steam generating banks of tubes could be measured. The steam flow could be adjusted to optimize steam conditions for most efficient steam turbine/generator power production.

Flame Monitoring and Character Method

- Advanced burner diagnostic techniques may require nonlinear signal processing of optical sensor signal to monitor flame stability and characterize performance. Nonlinear signal processing of optical, temperature, acoustic, microwave, etc. could be coupled with chaos-based perturbation control to enhance combustion performance. B&W may be developing a "smart burner" as part of its "smart boiler". The smart burner would be characterized by fuel flexibility (wide range of coal ranks, natural gas and oil), adaptive control system, and ultra-low NO_x emissions achieved. The burner may include partial oxygen firing and internally-staged combustion.

From this range of possible applications, three locations within the next generation ultrasupercritical plant were identified as primary candidates for sensor development. The sensor applications and operating conditions are summarized below in Table 1.

Table 1. Summary of Typical Applications and Operating Conditions for Advanced Sensors

Location	Measurement	Fluid/Material	Gas Temp. °C (°F)	Metal Temp. °F	Steam Temp. °F	Steam Pressure psi	Steam Flow 10^3 lb/h-ft^2	Strain %	Heat Flux 10^6 Btu/h-ft^2	Atmosphere
Furnace Waterwall	Tube temperature, heat flux, water flow	T23 or T92	1371-1650 (2500-3000)	Up to 510 (950)	Up to 482 (900)	5000 +	400-1900	0.1-1.0	0.08-0.15	Oxidizing/ Reducing
Secondary Superheater Tubes	Tube temperature, steam temperature, strain	Austenitic Stainless Steel Croloy (Cr/Mo) or Haynes (Fe/Ni/Cr/Co) Alloys	1093-1371 (2000-2500)	871 (1600)	760 (1400)	5000 +	400-1500	0.1-1.0	0.02-0.04	Oxidizing
Burners	Metal temperature of burner components - vanes, coal pipe, mixers	Carbon Steel, possibly stainless steel alloys with oxygen firing.	1371-1650 (2500-3000)	815 (1500)	N/A	N/A	N/A	0.1-1.0	N/A	Oxidizing

4.2 Development of high-temperature optical cladding for sapphire fibers

The magnesium alumina spinel ($MgAl_2O_4$) clad sapphire (aluminum oxide, Al_2O_3) fibers with reduced core diameters and optically smooth cladding/core interfaces capable of light guiding have been successfully fabricated. The light guiding ability is qualitatively observed using an optical microscope (Nikon Optiphot-100) and is judged by the degree of smoothness of the cladding/core interface. The cross sections of the clad fiber are shown in Figures 5(a), (b), (c) and (d) below. The fiber is fired at 1600°C (2912° F) for 30 minutes in argon. The detailed firing profiles are illustrated in Appendix 2.

In Figures 5(a) and (b) the sapphire fiber is dipped for 14 times in the spinel slurry, while in Figures 5(c) and (d), 17 times. The details of the slurry preparation and dipping procedures are described in Appendix 1. In the case of the fiber with 14 dips, the core diameter is reduced from 150 μm to about 75 μm, and in the case of 17 dips, to about 50 μm. It is apparent in most of the figures that the core part of the fiber is significantly brighter than the cladding part, which indicates the light guiding ability of the core. Especially in Figure 5(b), a certain kind of pattern of brightness exists within the core, which possibly represents the mode patterns of light propagation in the core.

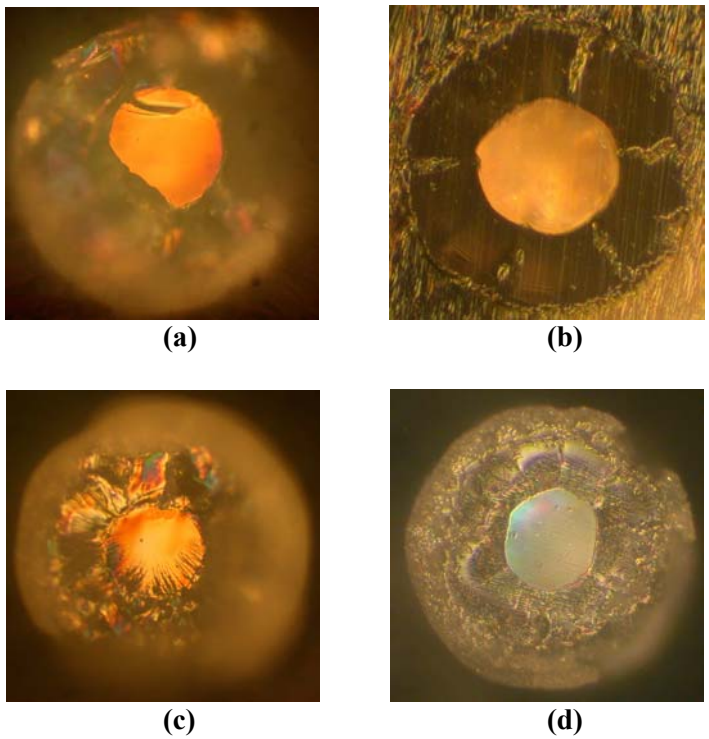


Figure 5: the fractured (a) and polished (b) cross sections of the clad sapphire fiber with 14 dips in the slurry, and the fractured (c) and polished (d) cross sections of the clad sapphire fiber with 17 dips in the slurry. (Both from the same sample with sample I.D. 14(17)s).

An investigation was undertaken in which certain parameters such as the firing profiles, the slurry dipping procedures, the atmosphere of firing, the particle sizes of the powders, and the slurry compositions were systematically varied. A total of 37 samples have been prepared as of the date of this report. The names of the samples, the dates on which the samples were dipped and fired, the firing atmosphere, the firing profiles, the type of powders, and the number of dips for all samples are summarized in Appendix 3.

The preliminary results show that to achieve an optically smooth $MgAl_2O_4$-spinel-cladding/Al_2O_3-sapphire-core interface, a carefully tailored firing procedure in argon (whose profile depends on the type of powders and the number of dips, i.e., the thickness of the slurry) is required. The suspected key mechanism at play is the crystalline grain growth of the polycrystalline spinel at the cladding/core interface. The results supporting this assumption in terms of the effects of firing profile, the firing atmosphere, the powder particle size, and the thickness (viscosity) of the slurry will be presented in the following sections. The issue of high-temperature stability of this materials system will be explored thereafter, and followed by the presentation of some results on the chemical composition analysis of the clad fibers using EDS technique. Finally the problems and difficulties encountered and their mitigating strategies will be discussed.

4.2.1 The effects of firing profile

An optimal firing profile completes the reaction between the slurry coating and the sapphire fiber, while minimizing the grain growth of the polycrystalline spinel at the cladding/core interface. Over-firing causes the spinel grains at the cladding/core interface to grow, resulting in a rough interface which contributes to the scattering of light at this interface, thus diminishes the capability of light guiding in the core.

An extreme case of over-firing is shown in Figure 6 below. This sample was fired in air at 1650°C (3000° F) for 16 hours. The flower-shape cladding/core interface presumably results from the growth of the $MgAl_2O_4$ spinel grains at the interface. In similar over-fired clad samples, depth profiling of the cross sections was performed by polishing the clad fiber ends in 25 μm steps. The results indicate that the cladding/core interface patterns change dramatically from one cross section to another along the lengths. Since the spinel grain size is presumably smaller than 25 μm, the assumption is that the interface pattern actually reveals the spinel grain structures at the cladding/core interface, which vary drastically in a 25 μm interval along the length of the fibers.

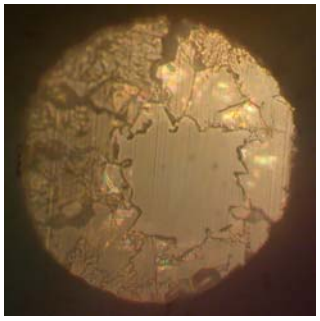


Figure 6: The cross section of a spinel clad sapphire fiber fired in air at 1650°C (3000° F) for 16 hours (Sample I.D. 6e).

4.2.2 The effects of firing atmosphere

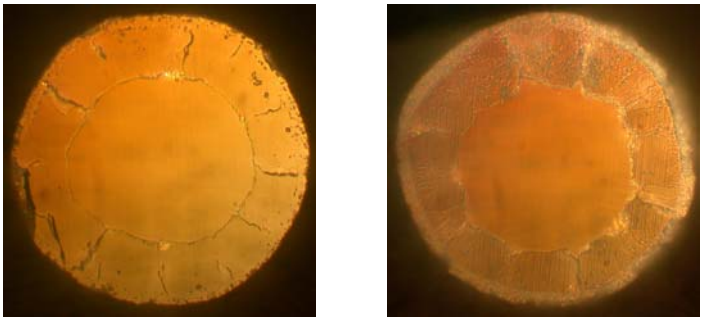
From various tests, it was observed that the firing in argon under current firing profiles seems to slow down the spinel grain growth compared to samples that were fired in air, judging from the smoothness of the cladding/core interfaces of the samples. In general, the samples fired in argon possessed smoother interfaces compared to the ones fired in air. This implies that the oxygen in air must have played an important role in the spinel grain growth process.

4.2.3 The effects of powder particle size

The important role the particle size in the slurry coating plays in the smoothness of the cladding/core interface is a function of the dependence of the spinel grain growth on the reactivity of the powders, i.e., the finer the particle sizes of the powders in the slurry, the

more reactive the powders, and the more rapid the spinel grain growth at the cladding/core interface.

Two samples were prepared using slurries with different powder particle sizes. In one sample, the slurry was prepared using fine powders; these powders were prepared by hand-grinding the original MgO and $MgAl_2O_4$ powders for 1 to 2 hours, followed by extensive ball milling for several days. In the other sample, the slurry is a mixture of the fine and the coarse powders; the coarse powders are the original powders with only about 30-minute ball milling. The exact portions of mixture between the fine and the coarse powders are not available; however, the ratio is believed to be close to 1:1. The two samples were both fired in argon at 1600°C (2912° F) for 1 hour. The exact firing profiles are illustrated in Appendix 4. The numbers of dips are comparable for both samples, in the range from about 20 to 30 dips. Figure 7 (a) and (b) show the cross sections of these samples. As shown in both figures, the cladding thickness is comparable in both cases, which implies that the amounts of powders in the coatings are comparable in both cases. Note that the cladding/core interface in Figure 7(a) is much smoother than that in Figure 7 (b); it indicates that the firing profile is close to optimal for the sample shown in Figure 7(a), which is prepared using the slurry with a mixture of coarse and fine powders. On the other hand, based on the assumption that the finer powders are more reactive, for the sample shown in Figure 7 (b), which is prepared using the fine powders only, the same firing profile is excessive and promotes re-configuration of the cladding/core interface configuration caused by additional grain growth of the spinel grains. This results in an undesirable rough interface.



(a) **(b)**

(b)

Figure 7: (a) The cross section of the clad fiber prepared using the slurry with a mixture of coarse and fine powders (Sample I.D. (20-35)o), and (b) the sample prepared using the slurry with the fine powders only (Sample I.D. 19(25)r). Both samples are fired in argon at 1600°C (2912°F) for 1 hour with a 10°C/minute heating rate and a 5°C/minute cooling rate.

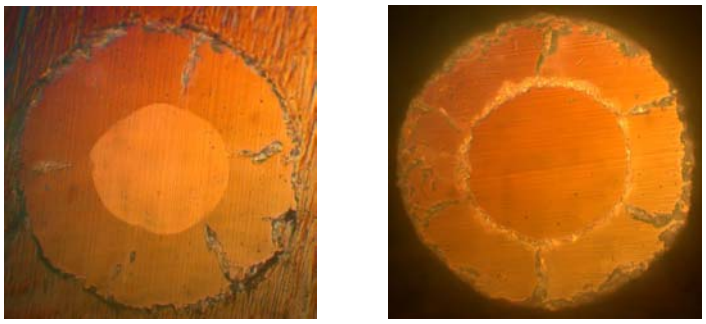
4.2.4 The effects of the slurry thickness (viscosity)

The preliminary results indicate that the ability to achieve a smooth core/cladding interface depends also on the slurry thickness (viscosity), which dictates the number of dips required to obtain a cladding with certain thickness. When all other experimental conditions (such as the powder particle size, firing profile, and the firing atmosphere) are

the same and the cladding thickness is comparable for two samples, the thinner the slurry (i.e., the larger the number of dips required to obtain the cladding thickness), the more reactive the dipped coating surrounding the fiber, and the lesser degree of firing is needed. This assumption is best illustrated by the following results.

Efforts were made to reproduce the clad fiber (Sample I.D. 14(17)s) which had previously demonstrated promising light guiding properties, as depicted in Figure 5. The same batch of fine-powder slurry was used to prepare the new sample (Sample I.D. 30t); however, this time the slurry was thinner than the one used to prepare sample 14(17)s, due to the additional amount of isopropyl alcohol added. The new sample was dipped 30 times while sample 14(17)s was dipped 14 times. The same firing profile of sample 14(17)s (as illustrated in Appendix 2) was used to fire the new sample, except that the argon flow rate for the new sample was greater (148 bubbles per minute, instead of the 84 bubbles per minute used for sample 14(17)s).

Figures 8(a) and (b) show the cross sections of sample 14(17)s and the new sample, respectively. As shown in Figure 8(b), the core/cladding interface of the new sample is much rougher than that of sample 14(17)s as shown in Figure 8(a). This implies that the firing profile optimal for achieving a smooth core/cladding interface in sample 14(17)s is excessive for the new sample, presumably due to its more reactive coating structure.



(a) **(b)**

Figure 8: (a) the cross section of sample 14(17)s, and (b) that of the new sample (Sample I.D. 30t). Both samples are fired in argon for 30 minutes at 1600°C (2912° F), and the heating and cooling rates are both 15°C (27°F) per minute. Sample 30t is prepared with a thinner slurry than that in the case of sample 14(17)s.

The suspected mechanism at work is that the coating structure created by the thinner slurry with a larger number of dips is denser in its packing. The powder particles move more freely in thinner slurry, and these particles can accommodate themselves more freely in successive dips to fill the voids existing on the surface of the coating, thus creating a denser coating structure, which is more reactive compared to a coating structure with a lot of voids, which is suspected to be the case when thicker slurry is used to prepare the sample.

4.2.5 The figh temperature stability of the clad sapphire fiber

Preliminary tests were performed to examine the high temperature stability of the fabricated fiber sample 14(17)s. The results indicate that the configuration of the core/cladding interface at the end face of the polished sample begins to change after the sample is heated to 1500°C (2732° F) for about 1 day. This may imply a degradation of light guiding ability of the clad fiber after prolonged operation in this temperature range. Further investigation is needed to clarify whether this phenomenon is due to the surface effects at the end face or it is a bulk behavior through the whole fiber. More data is needed to establish a guideline for the operation at elevated temperatures.

The sample was first heated at 1300°C (2372° F) for 22 hours, and the cross section of the sample was examined under an optical microscope. Then the sample was further heated to 1400°C (2552° F) for 22 hours and to 1500°C (2732° F) for another 22 hours, and after each heat treatment, the sample was examined again under an optical microscope. The results are shown in Figure 9. As shown in Figures 9(a), (b) and (c), there are no appreciable changes in the core/cladding interface after sequential heat treatments up to 1400°C (2552° F). However, as can be seen in Figure 9(d), significant changes occur at the interface after the heat treatment at 1500°C (2732° F) for additional 22 hours; further investigation is needed to interpret the newly formed patterns of the interface shown in Figure 9(d), in particular to determine if the changes are present only on the end-face surface of the fiber or within the body of the fiber.

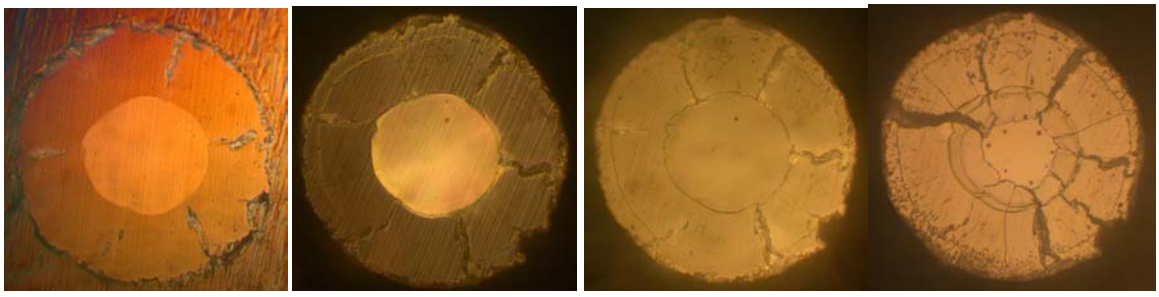


Figure 9: (a) the original sample 14(17)s before the high temperature heat treatment, and (b) the same cross section end face after the treatment at 1300°C (2372° F) for 22 hours, and (c) after additional treatment at 1400°C (2552° F) for 22 hours, and (d) after additional treatment at 1500°C (2732° F) for 22 hours. The heating and cooling rates in all heat treatments are 10°C per minute.

4.2.6 The EDS chemical analysis

Some clad sapphire fiber samples were examined using energy dispersive X-ray spectroscopy (EDS) at the Chemistry Department of Virginia Tech, to determine the chemical compositions in the core and cladding of the fibers. The preliminary results (Figure 10) show that the atomic ratio between the magnesium and the aluminum in the cladding parts is 0.16, which translates to a spinel composition of $0.23MgO{\cdot}0.77Al_2O_3$. This result in general lies within the ball park of the composition predicted from the

MgO-Al_2O_3 phase diagram (Figure 11) for the spinel formed at 1650°C (3000° F) from Al_2O_3, which is about $0.33MgO{\cdot}0.67Al_2O_3$. The reason for the discrepancy between the $0.23MgO{\cdot}0.77Al_2O_3$ in our case and the prediction $0.33MgO{\cdot}0.67Al_2O_3$ is not clear at this moment and is still under investigation. However, the fact that the cladding thickness ceases to increase at a certain point following prolonged firing supports the hypothesis that the MgO reacts with the sapphire until the spinel composition reaches the one on the phase boundary close to the point "c" in Figure 11, and the reaction continues until all the MgO in the dipped coating is depleted, and at that point the reaction ceases to proceed [5]. This conclusion implies that the cladding thickness can be well controlled by the amount of the MgO in the dipped coating, i.e., the thickness of the dipped coating, and the firing temperature. However, this conclusion is supported by consideration of the equilibrium phase diagram of the magnesium aluminates spinel ($MgO - Al_2O_3$) system, which treats the system in equilibrium only. Additional testing will be required to evaluate the effect of kinetics on the high temperature stability of the spinel coatings.

One typical EDS output for the cladding section of one fiber is shown in Figure 10 below. The fiber analyzed in the plot is sample 2b. As shown in the figure, there are prominent peaks representing Al, Mg, Au, Fe, and O. The first two elements and the O belong to the spinel; the Au comes from the Au coating evaporated on the surface of the fiber before the EDS examination; the Fe peaks occur from time to time due to the scattering of electrons from the sample holder. By comparing the areas under the Al and Mg peaks and after taking into account the adjustment factors for Al and Mg, the relative atomic ratio between Mg and Al is calculated to be 16%. The complete data of sample 2b and 8 other samples are listed in Appendix 6. For all samples, the core parts consist of almost pure alumina. A general expression of spinel composition can be written as $(1-x)MgO{\cdot}\ xAl_2O_3$, and the atomic ratio between Mg and Al is $(1-x)/2x$. If the atomic ratio between Mg and Al, i.e., $(1-x)/2x$, is 0.16, then x is 0.76. The MgO-Al_2O_3 phase diagram is shown in Figure 11 below. As depicted by the vertical dotted line in the figure, the x value for the spinel formed from Al_2O_3 at 1650°C (3000° F), the firing temperature of sample 2b, is about 0.67. As mentioned in the previous paragraph, the discrepancy of the value 0.67 predicted from the MgO-Al_2O_3 phase diagram and the calculated value of 0.76 for sample 2b is not clear at this moment.

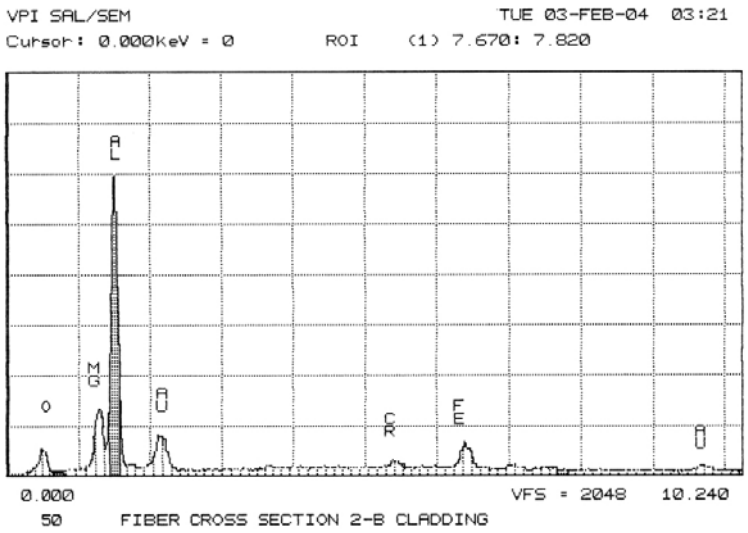


Figure 10: A typical EDS result at the cladding part of the fiber

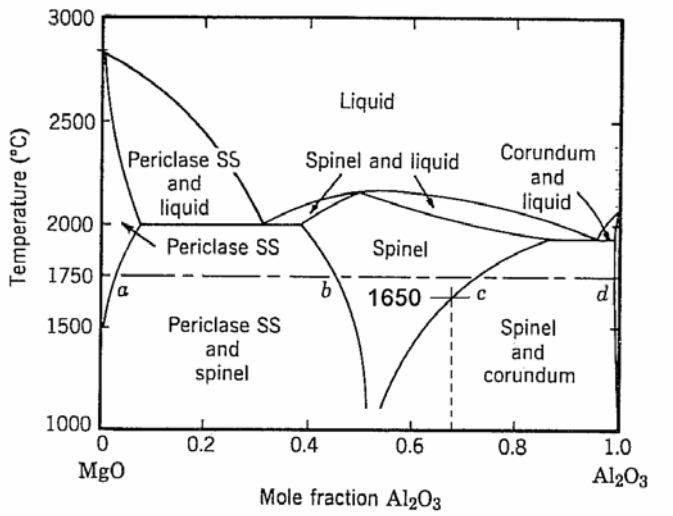


Figure 11: The MgO-Al_2O_3 phase diagram [5]

5 CONCLUSION

During the six-month reporting period documented in this report, progress was made in identifying locations within for work plants where application of robust sensors can be used to implement process control and monitoring in order to improve plant efficiency, and in development of high-temperature optical claddings for sapphire fibers to improve their optical performance and permit their use in interferometric sensor schemes.

Locations and requirements of the advanced photonic sensors for monitoring and process control in the advanced ultrasupercritical boiler plants were investigated and identified

through studies and discussions and Babcock and Wilcox Research Center. Specific measurements identified as critical for next-generation boiler plants include temperature measurement of thermal barrier coatings, in-situ measurements of strain in steam generation secondary superheater tubes, steam flow in membrane walls and tube banks, and dynamic pressure measurements for high temperature sensing of combustion dynamics. Three locations were chosen as primary candidates for sensor development during the program: the furnace water wall, the secondary superheater tubes, and burners.

Methods for applying magnesium aluminate spinel coatings to sapphire fibers to function as optical claddings were researched. Application of spinel coatings involves dipping the sapphire fiber in a slurry of spinel and magnesium oxide powders, firing the slurry on the fiber, and then sintering the coating to densify it on the fiber.

An investigation was undertaken in which certain parameters such as the firing profiles, the slurry dipping procedures, the atmosphere of firing, the particle sizes of the powders, and a slurry compositions were systematically varied. A total of 37 samples were prepared and tested. Results indicate that a smooth interface between the sapphire core and spinel cladding can be achieved through a carefully tailored firing procedure in argon atmospheres. In addition, it was found that the core diameter of the sapphire fiber can be reduced by a specified amount through the addition of a specified proportion of magnesium oxide in the slurry. We have successfully fabricated spinel clad sapphire fibers with reduced cored diameters and smooth core/cladding interface with promising light guiding properties.

5.1 Problems encountered and mitigating strategies

1. In almost all the optical micrographs shown in this report, there exist radial cracks originating from the core/cladding interface towards the surface of the clad fiber. These cracks degrade the mechanical integrity of the fibers and make the fibers fragile. The cracks are generated by the joint effects of the shrinkage of slurry coating during firing and the 47% expansion in volume as sapphire is converted to spinel [6]. This expansion is due to, in part, the fact that spinel has a lower density compared to that of sapphire; the specific density of sapphire is 3.98 g/cm^3, and that of spinel is 3.60g/cm^3. As the Mg ions diffuse from the coating into the fiber, successive layers of spinel are formed starting at the surface of the original fiber; the layers of spinel formed closer to the surface are under tensile stresses exerted by those spinel layers formed subsequently within the outer layers. If the spinel layers closer to the surface are not strong enough, fractures could occur in them under the existing tensile stresses.

   One strategy to mitigate this problem is to improve the mechanical properties of the converted spinel by using nanoscale MgO (130 m^2/g, 13 nm calculated diameter, Sigma-Aldrich, Item #: 549649) and sub-micron high-purity $MgAl_2O_4$ powders (10 m^2/g, sub-micron diameter, 99.985%, metals basis, Alfa Aesar, Item #: 40110) to prepare the slurry. Preliminary results show that spinel cladding

prepared with nanosized particles seems to be stronger and there are no cracks formed in the spinel cladding for a sample prepared using this slurry. Figure 12 illustrates a fiber with thin spinel cladding prepared with nanoscale powders. In this case, no cracks are evident in the cladding.

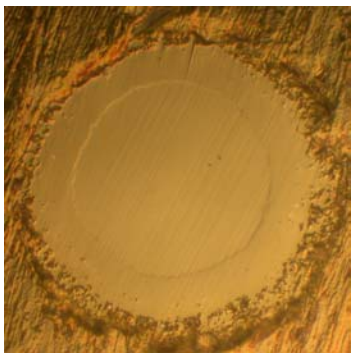


Figure 12: The polished cross section of sample 34x prepared using nano powders.

Another possible way of mitigating the problem of cracking is to implement vapor-phase deposition of MgO, which reacts with the sapphire upon heating to form magnesium aluminate spinel. In sapphire fibers with diameters in the range of millimeters, spinel cladding with no visible cracks have been successfully fabricated by Navias et al [6]. Figure 13 below shows one of these clad fibers fabricated using this technique.

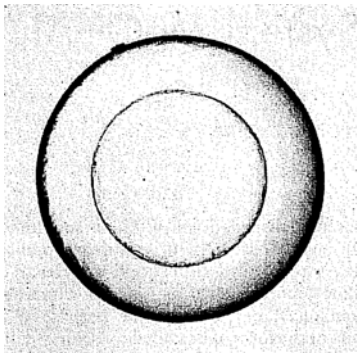


Figure 13: A spinel clad sapphire fiber fabricated using vapor deposition technology by Navias, et al. [6] The diameter of this fiber is 3.8 mm, about 25 times larger than the fibers that are currently been used in this project.

2. Another area warranting additional study is the high temperature stability of the spinel/sapphire material system. Preliminary results indicate that the maximum temperatures for prolonged operation of the clad fibers are below the range of 1500º C (2732° F). The way to mitigate this problem has to do with the inhibition of spinel grain growth at elevated temperatures. If the spinel grain growth at the core/cladding interface can be inhibited, the smoothness of the interface, i.e., the

light guiding ability, of the fibers can then be maintained. Further investigation is needed to identify the standard methods for grain growth inhibition and evaluate their validity in the current project.

6 REFERENCES

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[4] Steam: Its Generation and Use. Published by The Babcock & Wilcox Company, Barberton, OH, U.S.A. Edited by S. C. Stultz and J. B. Kitto. 1992.

[5] W. D. Kingery, H. K. Bowen and D.R. Uhlmann, "Introduction to Ceramics", John Wiley & Sons, 1976, p.133.

[6] Louis Navias, "Preparation and Properties of Spinel Made by Vapor Transport and Diffusion in the System $MaO-Al_2O_3$", Journal of the American Ceramic Society, v.44, n.9, 1961, p.434.

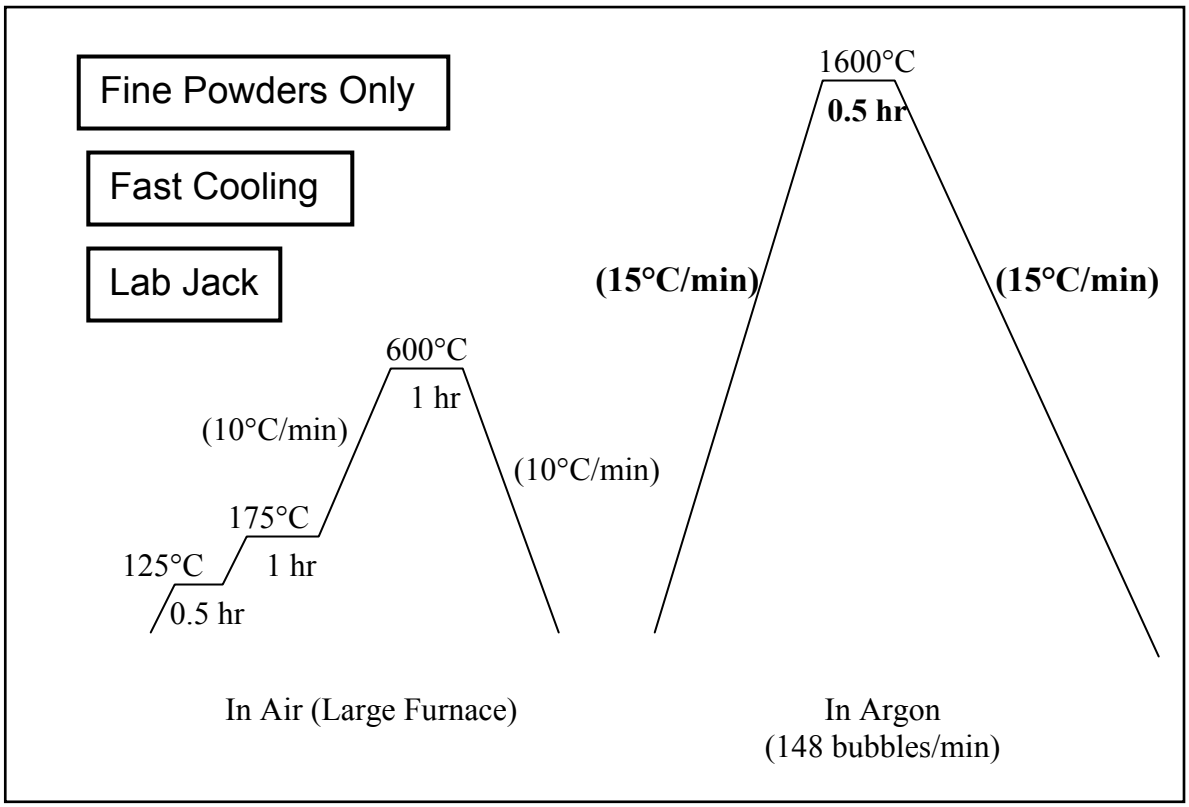
Appendix 1: The slurry preparation and fiber dipping procedures

1. Powder Preparation:
   1.1. MgO powders are hand-ground in a mortar using a pestle for 1 to 2 hours. During the grinding isopropyl alcohol is added to the mortar to form a paste. After grinding the powder slurry is poured into a polypropylene bottle (250c.c.) with alumina grinding medium filled to about 50% in volume of the bottle. More alcohol is added to cover the grinding media if needed. The jar is rotated using a ball mill at a speed of 60 to 70 turns per minute for a few days to further break down the particles.
   1.2. $MgAl_2O_4$ powders are also ground using the same steps described in step 1.1.
   1.3. 4.45 g of MgO powders (75 wt. %), and 1.49 g of $MgAl_2O_4$ powders (25 wt. %) are mixed in a beaker.

2. Slurry Preparation:
   2.1. A bath of 24.97 g of isopropyl alcohol (90.2 wt. %), 2.04 g of propylene glycol methyl ether (8.2 wt. %, Fluka 1-methoxy-2-propanol), 0.3 g of polyvinylpyrrolidone (1.2 wt. %) and 0.12 g of polyethylene glycol (0.4 wt. %) is prepared in a beaker on a hot plate. The bath in a beaker is covered with parafilm and is stirred using a magnetic stir bar on a hot plate for about 10 minutes. The polyvinylpyrrolidone crystals are fully dissolved at the end of stirring.
   2.2. The powder prepared in step 1 is added to the solution bath, one small scoop at a time. The spinning magnetic bar is also used to enhance the dissolution of the powders.
   2.3. The slurry is poured from the beaker into a polypropylene bottle (250c.c.) with alumina grinding medium filled to about 50% in volume of the bottle. More alcohol is added to cover the grinding media if needed. The jar is rotated using a ball mill at a speed of 60 to 70 turns per minute for a few days to mix the slurry thoroughly and to further break down the particles. After ball milling, the slurry is stirred in a beaker using a magnetic spin bar until the desired viscosity is reached.

3. Application of slurry (dipping processes):
   3.1. The slurry was transferred to a graduated cylinder or a small test tube for dipping. To prevent the slurry from drying, the cylinder or the test tube is capped, and a small hole is drilled in the cap to let the fiber pass through. The cylinder or the test tube sits on a small lab jack.
   3.2. Before dipping, the fibers are first cleaned with isopropyl alcohol using Kimwipe, and then the fibers are immersed in HCl for 1 minute, followed by in deionized water for 1 minute and finally in isopropyl alcohol for another 1 minute. The fiber is then clamped vertically to a sample holder.
   3.3. The fiber is dipped by slowly raising the graduated cylinder containing the slurry with a lab jack until the desired length of the fiber is immersed in the slurry. Then the cylinder is slowly lowered to complete the dipping. This procedure is repeated for multiple dipping. There is a 10 to 15 seconds interval between each dipping for the slurry coating on the fiber to dry.

Appendix 2: The firing profile of sample 14(17)s



(Note: The first firing profile in air is designed to remove water and the binder in the spinel slurry coating.)

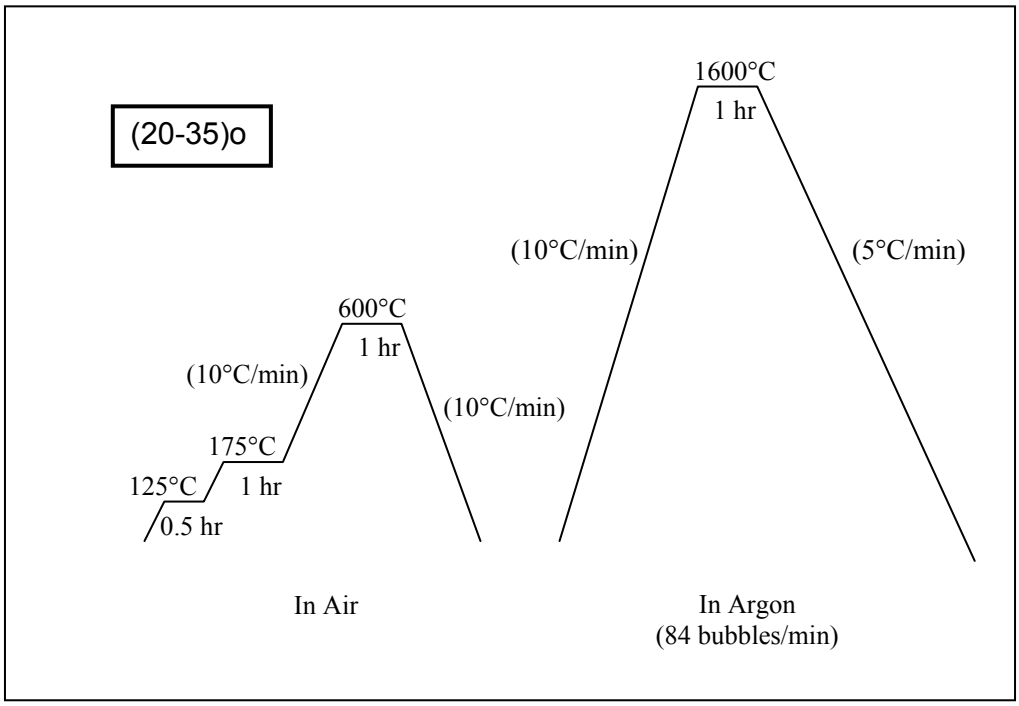
Appendix 3: The preparation conditions of all samples

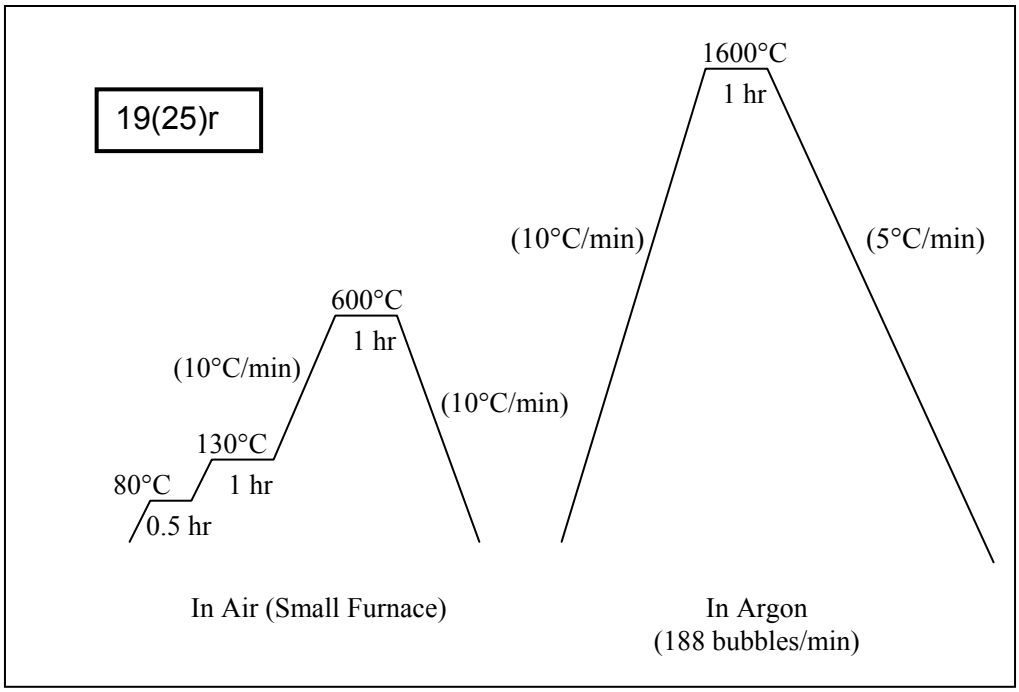
Sample I.D.	Date Dipped	Date Fired	Atmos-phere	Firing Profiles**	Powder type***	# of dips****
Sp-1	11/26/03	12/4/03	Air	0.5 h in at 1750°C	Coarse	1
Sp-2	11/26/03	12/4/03	Air	0.5 h at 1750°C	Coarse	2
Sp-3	11/26/03	12/4/03	Air	0.5 h at 1750°C	Coarse	3
1a	1/23/04	1/23/04	Air	2.5 days at 1650°C (Furnace cooled)	Coarse	1
2a	1/23/04	1/23/04	Air	2.5 days at 1650°C (Furnace cooled)	Coarse	2
4a	1/23/04	1/23/04	Air	2.5 days at 1650°C (Furnace cooled)	Coarse	4
1b	1/26/04	1/26/04	Air	16 hr at 1650°C (10°C/min. cooling rate)	Coarse	1
1b-1*	1/26/04	1/26/04	Air	16 hr at 1650°C (10°C/min. cooling rate)	Coarse	1
2b	1/26/04	1/26/04	Air	16 hr at 1650°C (10°C/min. cooling rate)	Coarse	2
3b	1/27/04	1/27/04	Air	16 hr at 1650°C (Furnace cooled)	Coarse	3
4b	1/27/04	1/27/04	Air	16 hr at 1650°C (Furnace cooled)	Coarse	4
8	1/20/04	1/20/04	Air	16 hr at 1650°C	Coarse	8
12	1/20/04	1/20/04	Air	16 hr at 1650°C	Coarse	12
2c	2/20/04	2/24/04	Air	16 hr at 1650°C (10°C/min. heating and cooling rate)	Fine	2
3c	2/20/04	2/24/04	Air	16 hr at 1650°C (10°C/min. heating and cooling rate)	Fine	3
4c	2/20/04	2/24/04	Air	16 hr at 1650°C (10°C/min. heating and cooling rate)	Fine	4
6e	3/3/04	3/3/04	Air	16 hr at 1650°C (10°C/min. heating and cooling rate)	Fine	6
10f	3/9/04	3/9/04	Air	4 hr at 1700°C (10°C/min. heating and cooling rate)	Fine	10
4(8)g-1	3/10/04	3/10/04	Air	2 hr at 1700°C (10°C/min. heating and 5°C/min. cooling rate)	Coarse + Fine	4
4(8)g-2	3/10/04	3/10/04	Air	2 hr at 1700°C (10°C/min. heating and 5°C/min. cooling rate)	Coarse + Fine	8
12(17)h-1	3/11/04	3/11/04	Air	2 hr at 1700°C (10°C/min. heating and 5°C/min. cooling rate)	Coarse + Fine	17
12(17)h-2	3/11/04	3/11/04	Air	2 hr at 1700°C (10°C/min. heating and 5°C/min. cooling rate)	Coarse + Fine	12
20(24)i-1	3/12/04	3/12/04	Air	1 hr at 1700°C (10°C/min. heating and 5°C/min. cooling rate)	Coarse + Fine	24

20(24)i-2	3/12/04	3/12/04	Air	1 hr at 1700°C (10°C/min. heating and 5°C/min. cooling rate)	Coarse + Fine	20
6(10)l	3/28/04	3/28/04	Argon	1 hr at 1600°C (10°C/min. heating and 5°C/min. cooling rate)	Coarse + Fine	6 & 10
20(26)m	3/29/04	3/29/04	Argon	4 hr at 1600°C (10°C/min. heating and 5°C/min. cooling rate)	Coarse + Fine	20 & 26
12(17)n	3/30/04	3/30/04	Argon	1 hr at 1600°C (10°C/min. heating and 5°C/min. cooling rate)	Coarse + Fine	12 & 17
(20-35)o	3/31/04	3/31/04	Argon	1 hr at 1600°C (10°C/min. heating and 5°C/min. cooling rate)	Coarse + Fine	20 to 35
20(25)p	4/1/04	4/2/04	Argon	1 hr at 1600°C (5°C/min. heating and 1°C/min. cooling rate)	Coarse + Fine	20 & 25
40(50)q	4/3/04	4/3/04	Argon	1 hr at 1600°C (5°C/min. heating and 1°C/min. cooling rate)	Fine	40 & 50
19(25)r	4/6/04	4/6/04	Argon	1 hr at 1600°C (10°C/min. heating and 5°C/min. cooling rate)	Fine	19 & 25
14(17)s	4/12/04	4/12/04	Argon	0.5 hr at 1600°C (15°C/min. heating and 15°C/min. cooling rate)	Fine	14 &17
30t	4/15/04	4/15/04	Argon	0.5 hr at 1600°C (15°C/min. heating and 15°C/min. cooling rate)	Fine	30
50u	4/20/04	4/20/04	Argon	10 min. at 1600°C (15°C/min. heating and 15°C/min. cooling rate)	Fine	50
35v	4/21/04	4/21/04	Argon	10 min. at 1600°C (15°C/min. heating and 15°C/min. cooling rate)	Fine	35
70w	4/21/04	4/21/04	Argon	2 min. at 1600°C (15°C/min. heating and 15°C/min. cooling rate)	Nano	70
34x	4/22/04	4/22/04	Argon	2 min. at 1600°C (15°C/min. heating and 15°C/min. cooling rate)	Nano	34

* Sample 1b-1 and Sample 1b are sections broken from the same dipped and fired sapphire fiber.
** Each fiber is dried at 80°C for 15 minutes and at 130°C for another 15 minutes in air. For samples treated in argon, another heating step at 600°C for 1 hour in air was added to remove the binder.
*** Coarse: MgO (15μm) and $MaAl_2O_4$ (3 μm); Fine: after hand grinding for a few hours and ball milling for a few days; Nano: MgO (130 m^2/g, 13 nm diameter) and $MgAl_2O_4$ (10 m^2/g, submicron diameter).
**** If there are two numbers for one sample, such as (x & y), x<y, it means that the bottom part of the fiber is dipped y times and the upper part of the fiber is dipped x times.

Appendix 4: Heating profiles of sample (20-35)o and 19(25)r





(Note: There exists slight difference in the above two firing profiles in the first heating stage to remove the water and the binder. However, the high temperature sintering steps, which are more influential to the results, are exactly the same in both firing profiles.)

Appendix 5: Results of EDS chemical analysis for 9 samples

Sample Name	Surface		Fractured cross section (Core)		Fractured cross section (Cladding)	
	Mg (at %)	Al (at %)	Mg (at %)	Al (at %)	Mg (at %)	Al (at %)
4a	15	85	4	96	15	85
2a	22	78	1	99	23	77
1a	22	78				
4b	15	85	1	99	15	85
3b	15	85				
2b	16	84	1	99	16	84
1b	24	76				
8**	***23***	***77***			***22***	***78***
12**	***53***	***47***			***31***	***69****

***** A large amount of suspected phosphor contamination exists in both surface and cross section EDS data.
****** In samples 8 and 12, the sapphire fibers are fully converted to spinel before the reaction between the slurry coating and the sapphire fiber is completed. This causes the Mg at% of these samples in the cladding parts significantly higher than those of the other samples.