Report Title: DOE Sapphire Project

Type of Report: Semi-Annual Report

Report Period Start Date: October 1, 1999

Report Period End Date: March 31, 2000

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Date Report was issued: March 2000

DOE Award Number: DE-FC26-99FT40685

Name and Address of Submitting Organization:

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Introduction

Since this is the first report for this project an extensive background section follows on the theory of operation of the single crystal sapphire sensor technology which will be developed and field tested at the Wabash River Coal Gasification Facility.

Background of the Single Crystal Sapphire Temperature Sensor

Single crystal sapphire optical fibers have a high melting point (above 2050° C), possess good mechanical properties and are expected to have excellent corrosion resistance. While silica-based optical fiber sensors have shown great promise for measuring temperatures (and other physical parameters) below 800° C, at higher temperatures the devices degrade rapidly. The degradation mechanisms fall into two general categories either crystallization of the silica cladding region occurs or diffusion of the germanium dopant (used to establish the refractive index gradient between the core and the cladding) from the core region into the cladding changes the waveguiding properties of the fiber. Many useful devices have been fabricated from silica-based optical communications grade fibers. Interferometers are attractive because interference between reflected light waves from adjacent surfaces allows discrimination of the distance between the reflecting surfaces on the order of angstroms. Thus, very precise measurements of the separation distance (or change in separation distance) between adjacent reflecting surfaces is possible. This in turn, allows very sensitive determination of changes in the physical environment of the sensor for any signal that perturbs the distance between the reflecting surfaces.

As mentioned above, the long term performance of the sensor in any operating is a function of the temperature of operation and the properties of the material used to fabricate the sensor. In many industrial applications an equally important parameter is the corrosion resistance of the sensor. For coal gasification environments, alkali, sulfur, silica, steam, transition metals, and a host of other corrosive agents are present to a greater or lesser extent depending upon the source of the coal and the operation of the gasifier unit. For temperature sensors which must operate in the high temperature sections of the gasifier unit, the corrosion can be especially severe. As part of this program, a high priority has been placed on characterizing the performance of the single crystal sapphire fibers in the coal gasification environment. These measurements are being carried in conjunction with our industrial partner, Dynegy. For sensors that will operate in a region where slag buildup will occur, it is imperative that immersion tests in the actual coal slag material be performed at sufficiently high temperatures to ensure durability of the sensor.

There are several different types of interferometric techniques which have been used with optical fibers to measure physical parameters. One type of interferometer is the Fabry-Perot and sensors have been developed to take advantage of this technique. Fiber Fabry-Perot sensors are highly sensitive to temperature, mechanical vibration, magnetic fields, and acoustic waves¹. Many techniques have been used to create Fabry-Perot cavities, such as Bragg gratings in or on the fiber², metal coatings on the end faces of the fiber³,

and the use of air-glass interfaces at the fiber ends as the reflectors⁴. Although intrinsic Fabry-Perot sensors have been used in the past to measure several properties, extrinsic Fabry-Perot interferometers (EFPI) have shown their ability to be immune to fiber optic polarization and only sensitive to axial strain components, which gives them an advantage over other electro-mechanical and intrinsic Fabry-Perot sensors. By employing sapphire optical fibers, the sensors can potentially operate at high temperature (up to 1500°C) environment⁵. Task 3 of this program is focused on investigating single crystal sapphire based Fabry-Perot temperature sensors for use in coal gasification systems.

Absolute interferometers are much more attractive in engineering applications because they do not require initialization and/or calibration when the power is switched on. A broad spectrum LED light source is used in the system. Since the emitted light from the LED is highly multi-moded, which could cause degradation of the interference fringe visibility, the diameter of the lead-in sapphire fiber will have a significant effect on sensor performance. Fibers with larger diameter allow more modes to exist, resulting in lower fringe visibility.

By examining the interferometric output spectrum of the EFPI sensor, we can determine the absolute air gap cavity length without initialization. This is advantageous for engineering applications, where initialization and setup times can be very time-consuming, costly, and perhaps inherently hazardous. This signal processing method can be used to produce very stable and highly accurate measurements because power fluctuations caused by fiber losses and source instabilities can be compensated for.

PRINCIPLE OF OPERATION

The schematic configuration of the sapphire-fiber-based extrinsic interferometric sensor is shown in figure 1. The light from the broadband source (LED) is coupled into a silica fiber. A 3dB coupler is used in the system to inject light into the optical fiber and also direct the interference signal from the sensor head to the detector. An anti-reflection silica-to-sapphire fiber connector is used to transmit light from the silica fiber to the sapphire fiber. A sapphire air gapped EFPI sensor head is formed by inserting the lead-in single crystal sapphire fiber into the one end of the sapphire tube and inserting a short piece of sapphire fiber into the other end of the tube to act as the reflecting surface (target fiber). Both the lead-in and the target sapphire fiber ends are polished to optical quality. While one end of the target sapphire fiber is highly polished, the other end is shattered to prevent any significant reflection that would interfere with the measurements. The light propagating in the lead-in sapphire fiber is partly reflected (7%) at the first sapphire-air boundary. The transmitted light travels through the air gap and is also partially reflected (7%) at the end face of the target sapphire fiber. An interference signal is generated by these two reflected waves and the phase difference depends on the length of the air gap. The interference signal is processed in a computer-interfaced spectrometer so that the absolute cavity length can be measured.

Figure 1. Scheme of sapphire fiber based absolute interferometric sensor

The anti-reflection connection between the sapphire and silica fiber is achieved by polishing the sapphire fiber at an angle of 8° with respect to the transverse direction of the fiber. If this were not done, an unwanted reflection from this connection would be generated. By polishing the sapphire fiber with the appropriate angle, it reduces the back-reflection from the sapphire fiber endface back to the detector.

WHITE LIGHT INTERFEROMETRIC SIGNAL PROCESSING

It is assumed that the white light source has a Gaussian spectral distribution given by:

$$I_s(I) = I_0 \cdot \exp \left[-\frac{(I - I_0)^2}{(\Delta I)^2} \right] , \quad (1)$$

where I_0 is the central wavelength and $\Delta\lambda$ is the spectral width of the source. The output interference signal from the low- finesse EFPI sensor is then given by:

$$I = \frac{1}{2} I_s(I) \cdot [1 + g(L) \cos \left(\frac{4pL}{I} + j_0 \right)] , \quad (2)$$

where $\gamma(L)$ is the visibility function of the output interference fringes.

The interference phases of two different spectral components of the light source can be expressed as follows:

$$j_{1,2} = \frac{4pL}{I_{1,2}} + j_0 \quad (3)$$

So, the phase difference between these two spectral components is:

$$\Delta \mathbf{j} = \mathbf{j}_1 - \mathbf{j}_2 = \frac{4pL(I_2 - I_1)}{I_1 \cdot I_2} \quad (4)$$

The cavity length L can be calculated as:

$$L = \frac{\Delta \mathbf{j} \cdot I_1 \cdot I_2}{4p(I_2 - I_1)} \quad (5)$$

If the phase difference $\Delta \mathbf{j}$ and the corresponding wavelengths I_1 and I_2 are detected by the spectrometer or the spectral filter, the length of the F-P cavity can be calculated from equation (5). Three methods are presented to perform the required signal processing:

1. Phase difference fixed method. The phase difference of the interferometric signal is fixed to $2p$, which corresponds to the two adjacent peaks (or valleys) of the interference signal. By detecting the peak (or the valley) wavelengths of λ_1 and λ_2 the cavity length can be directly computed.
2. Wavelength fixed method. The wavelengths λ_1 and λ_2 in equation (5) are chosen to be some fixed values. By detecting the corresponding phase difference between the two wavelengths, the cavity length L can be determined.
3. Curve fitting and FFT method. Fit the interference signal as the function of the wavelength (or the optical frequency) and determine the signal frequency by FFT. From equation (2), we know that the signal frequency is determined by $2L$.

There are some limitations in the resolution and accuracy due to the finite spectral resolution of the spectrometer. These can be partially mitigated through fitting and filtering techniques, which can improve the resolution and accuracy. The demonstrated signal processing methods developed so far have been able to achieve above 10-Hertz real-time output.

Section I. Single Crystal Sapphire Sensor Development

SENSOR HEAD FABRICATION

Sensor head fabrication is one of the most challenging tasks in building reliable sapphire fiber sensors, since the bonding materials must also survive in high temperature, corrosive environments as well.

The temperature sensor design which has been used in the initial development stage is shown in Figure 2. Two sapphire fibers are bonded to a base with their polished ends facing each other to form an F-P cavity. The material of the base substrate is alumina. Since the base substrate is polycrystalline alumina, the thermal expansion coefficient will be the average thermal expansion coefficient (of the a and c crystallographic directions). The single crystal sapphire fiber is grown such that the c-axis is aligned parallel to the

optical fiber axis (along the length of the fiber). The difference between the thermal expansion coefficient of the substrate and the fiber results in a change of the air gap length between the two fiber ends when temperature changes.

Figure 2. Schematic configuration for temperature sensor head

Results of Initial Sensor Testing

A diode laser as the light source with a central frequency λ_0 of 1310 nm. An InGaAs detector was used in place of the spectrometer, and the output was viewed on an oscilloscope. An LED with a central frequency λ_0 of 850 nm and a spectral width $\Delta\lambda$ of 80nm was used in the experimentation. A silicon detector was used, with the output interference fringes shown in figure 3. We can see a decrease of the fringe visibility for the LED case, which we believe is caused by multi-modal effects of the sapphire fiber.

Figure 3. Sapphire EFPI sensor using 850nm LED, lower visibility, 0.2v/div, 0.5s/div

To demonstrate the sensor performance, we used an LED with a spectrum given in figure 4. Figure 5 shows the output interference spectrum of the sapphire EFPI sensor at a

Figure 4. Output spectrum of $\lambda_0=850\text{nm}$ LED

Figure 5. Output spectrum with $L=6.5\text{mm}$

Figure 6. Output spectrum with $L=21.8\text{mm}$

cavity length of $6.5\mu\text{m}$. Figure 6 shows the output spectrum with a cavity length of $21.8\mu\text{m}$. We see that when the cavity length is increased, the visibility decreases significantly. First we place the target sapphire fiber end on a translation stage. By moving the target fiber, we can vary the sensor air gap. Simultaneously, we use our signal processing schemes to measure the air gap length. The result is shown in figure 7. As seen in the figure, the cavity length can be measured with a very high precision, which proves that the absolute signal processing schemes work very well.

Figure 7. Sapphire EFPI sensor calibration using 1.3mm laser diode

To further investigate the multi-modal effects when using LED as the light source, we built another sensor using a lead-in fiber with a diameter of $125\mu\text{m}$. The output spectrum is shown in figure 8. As can be seen, very low fringe visibility is obtained due to the multi-modal effect.

Figure 8. Output spectrum with $L=6.5\text{mm}$, using $125\mu\text{m}$ fiber

Temperature change induced sensor air gap change

The sensor was placed into an electrical heated oven, the temperature was increased from room temperature to 950°C. The data were recorded at steps of 20°C as shown in Figure 9. The fluctuation which was seen was suspected to be the unstable heating conditions of the oven during the rapid heating.

Figure 9. Air gap change versus Temperature for Single Crystal Sapphire Sensor

In another set of experiments, the temperature was determined by measuring the amount of blackbody radiation returned to the sensor. A 100μm sapphire fiber was used with one endface polished. The fiber was placed inside the furnace and heated from 500°C to 1050°C at intervals of 50°C. An optical spectrum analyzer (OSA) was used to integrate the blackbody emission power within the spectrum range from 1100nm to 1700nm. The result is shown as follows.

Figure 10. Blackbody emission power versus temperature

The system was calibrated the emission power using first two experiment results, then conducted two other measurements. Based on the calibration curve, we converted the these two measurement results to temperature which is plotted as shown in the following figure.

Figure 11. Temperature measurement results using the calibration data obtained from first two measurements

Section II. Corrosion Testing in Coal Slag Environment

Experimental Procedure for Corrosion Testing in Coal Slag

The equipment and procedures to perform simulated testing of the corrosion resistance of the single crystal sapphire fiber optic waveguides in coal-gas environments is described below. This testing has been performed in collaboration with Dynegey, who provided the coal slag samples for testing.

An apparatus for studying the corrosion resistance of single crystal sapphire was constructed at Virginia Tech. A 1600°C tube furnace was used which was fitted with a 2.54cm O.D. high purity alumina tube. The tube was purchased in sufficient length such that the ends of the tube extended outside the ends of the furnace. The alumina tube was sealed on both ends to 0.63cm I.D. plastic tubing. The flow rate of gases in the tube was fixed at 30 ml/min. Compressed air has been used in the initial phase of the corrosion testing. Single crystal sapphire plates were purchased from commercial vendors and were cut into samples approximately 0.5cm x 0.5cm. The samples were cleaned and placed in a high purity alumina sample holder (boat). Dense, polycrystalline alumina samples were prepared and placed in the boats as a control and comparison. The alumina boats were filled with coal slag from the Wabash River Coal Gasification facility. The boats were placed in the tube furnace and heated for various periods of time up to 48hrs, at temperatures up to 1500°C.

The samples after the designed heat treatment in the coal slag were removed and cooled. The samples were removed by fracturing the coal slag (and alumina boat) and cutting with a diamond saw if necessary. Great care was taken to ensure that the coal slag region around the single crystal sapphire plate was left undisturbed. The single crystal sapphire plate with the coal slag still intact on the upper and lower surfaces was polished to expose the end view of the plate. The polished samples were examined for morphological changes across the coal slag/sapphire interface by scanning electron microscopy (SEM). The composition of the interface region was mapped by EDAX elemental analysis.

Base upon the positive results of the immersion testing of the single crystal sapphire plate results, a second apparatus was constructed. For this set of tests, two optical quality single crystal sapphire fibers were purchased from a commercial vendor along with a single crystal sapphire tube. A dense, polycrystalline boat was cut with a diamond saw to produce a thin slit approximately 500 microns on each side of the boat. The schematic layout is shown in Figure 1. The single crystal sapphire tube was cut with a diamond saw and then polished repeatedly such that the tube would “just fit” into the alumina boat. One of the single crystal sapphire fibers was inserted into the single crystal sapphire tube and then inserted into the slits in the alumina boat. The second single crystal sapphire fiber was inserted directly into the slits in the alumina boat without a single crystal sapphire tube. The slits in the alumina boats were sealed with high purity alumina cement to prevent the loss of coal slag from the boat during heat treatment. The boat with the single crystal sapphire fibers was inserted into the 1700°C box furnace. The box furnace had been drilled with appropriate size holes to allow the passage of the fibers

through the walls of the furnace. A white light source was used, which was connected to the sapphire fibers through two couplers (please refer to Fig.1.). A reference silica fiber was connected to one of the couplers to serve as a reference channel to detect possible changes in the source power. The other ends of the sapphire fibers were connected to silica fibers which were in turn connectorized. An Optical Spectrum Analyzer was used to monitor the attenuation of the white light signal in the range from 400 to 1700nm, as well as the total output power. The alumina boat was filled with slag from the Wabash River Facility. The system was heated to 1500° C and the optical attenuation as a function of wavelength was monitored.

Results of Coal Slag Corrosion Testing

The goal of this research program is to develop single crystal sapphire fiber sensors and sensor instrumentation for accurate and reliable measurement of temperature in entrained flow slagging gasifiers. The technical objectives required for this reporting period according to the technical task work schedule for this project are listed below along with the major progress achieved in each area.

1. Specify Technical Requirements – for the temperature measurement to establish a baseline for sensor performance, which will provide guidance in the sensor design and fabrication efforts. This task will be performed in conjunction with Dynegy, Inc. which is a partner in the Wabash River Coal Gasification Re-powering Project Joint Venture.

Progress:

This project began on October 1, 1999. A kickoff meeting was scheduled (by the DOE program manager) at the DOE FETC facility for all of the Phase I grantees to review their approaches. On Nov. 22, 1999, Dr. Russ May and Dr. Gary Pickrell traveled to the DOE FETC facility for a program review meeting for this project. Dr. May presented the theory underlying the single crystal sapphire sensor approach as well as the anticipated technical requirements for the overall project. During this kickoff meeting Tom Leininger of Texaco presented an overview of the Texaco gasifier plant in CA. The Texaco gasifier is an entrained flow slagging gasifier, differing from the Wabash River plant (our industrial partner) in that the syngas and the slag both travel downwards (in the Wabash plant, syngas goes up while the slag goes down). The temperatures are about 2200 - 2800° F and pressures are less than 1300 psi. Feedstocks for this system include natural gas, petroleum coke, and coal. Overall, the meeting was very beneficial.

Dynegy which operates the Wabash River Coal Gasification Repowering Project (which is the largest single train gasification facility and the cleanest coal fired power plant in the world) was selected as the industrial partner for this effort. Dynegy has agreed to host the field testing of the single crystal sapphire sensors at the Wabash facility.

The Wabash facility gasifier is a dual stage system with the first stage acting to partially combust the coal and the entrained flow second stage pyrolyzing the feedstock from the

first stage. The first stage consists of a horizontal, refractory lined vessel in which coal and oxygen are combined in partial combustion quantities with temperatures reaching approximately 1480°C and pressures up to 400psig. Dynegy provided approximately 50 lbs of coal slag for corrosion testing. Dynegy has also provided Virginia Tech. with typical analysis of the test conditions and typical coal slag chemistries that should be used in the corrosion testing section of this project to simulate the actual gasifier environment.

Dr. May and Dr. Pickrell will conduct an onsite meeting with representatives from Dynegy at the Wabash River facility in early May. It is anticipated that the facility will be in shutdown so that an inspection of the actual gasifier unit can be performed. Requirements for the field testing phase will be discussed during this trip.

2. Investigate the Corrosion Resistance – of various optical grade single crystal sapphire waveguides.

A special apparatus has been constructed at Virginia Tech. to conduct the corrosion studies on the single crystal sapphire fibers as described in the experimental procedures section. As a prelude, samples of single crystal sapphire plates have also been immersion tested in the coal slag as described in the experimental section.

2.1 Results for the Slag Immersion Testing of Single Crystal Sapphire Plates

The single crystal sapphire plate samples have been exposed to the coal slag as described under the experimental procedures section. The samples, after reaction at the required time/temperature schedule, were removed and polished for SEM/EDAX analysis. These samples were compared with a commercially available polycrystalline alumina material (which has been studied extensively in high temperature alkali containing environments), as a reference.

These single crystal sapphire plates were used as a prelude to slag immersion of the single crystal sapphire optical fibers. Analysis of the slag penetration/reaction rates in these tests should give a good indication of how the sapphire fibers will perform. Since the sapphire fibers are relatively expensive, and construction of appropriate monitoring system for observing the sapphire fibers while immersed in the coal slag at 1500°C is very time consuming, it was a prudent step to test the sapphire plate corrosion first to ensure all aspects have been considered.

Figure 4 shows the EDAX elemental analysis of the sapphire plate/coal slag interfacial region. As expected, the analysis shows a strong aluminum peak from the sapphire plate and also due to alumina in the coal slag. Silica is one of the major constituents in the coal slag as provided by Dynegy. This is the source of the strong silicon peak in the EDAX trace. Iron can also be seen in the EDAX. A small calcium and also a very small potassium peak appear as well. These results are in very good agreement with the chemical analysis of the coal slag provided by Dynegy.

Figure 4. EDAX (Energy Dispersive Analysis of X-rays) elemental of the coal slag/sapphire interface (shown in Figure 5).

A SEM micrograph of the interface between the coal slag and the sapphire plate is shown in Figure 5. This micrograph is taken from the edge view of the plate (on a polished cross-section). Also shown in Figure 5 is the elemental mapping that was performed for the major constituents known to exist in the coal slag as well as aluminum. The elemental map shows a very sharp clean interface between the coal slag and the sapphire plate. No penetration of the silica in the slag can be seen in the map. Some "lines" appear in the region adjacent to the coal slag/sapphire interface. These lines could be due to the polishing process. However, it is more likely that the lines are due to reaction with the coal slag. The elemental mapping used was not sensitive enough to detect any difference in the composition of these lines and that of the surrounding sapphire. According to the elemental maps obtained so far, it would appear that the lines are composed only of alumina. Figure 6. shows a second sapphire sample interface after 1500°C for 48h coal slag immersion test. Again a very similar microstructure occurs with the sharp sapphire/coal slag interface and the lines which form adjacent to the interface. As the results are not conclusive at this point, more work will be performed in the next performance period to answer the questions posed above

Figure 5. SEM micrographs of single crystal sapphire plate/coal slag interface after 1500°C for 48h coal slag immersion test. Lower picture is the EDAX elemental map corresponding to the upper micrograph.

Figure 6. SEM micrographs of another single crystal sapphire plate/coal slag interface after 1500°C for 48h coal slag immersion test. Lower picture is the EDAX elemental map corresponding to the upper micrograph.

Figure 7 shows the SEM micrograph of a single crystal sapphire plate/coal slag interface after 1400 C for 48h coal slag immersion test. Again, as would be expected from the results shown in Figure 5 and 6., the interfacial region between the coal slag/sapphire interface is very sharp. In this sample, the coal slag broke away from the sapphire surface during the polishing operation due to the hardness differences between the coal slag glass and the sapphire plate.

Figure 7. SEM micrographs of single crystal sapphire plate/coal slag interface after 1400° C for 48h coal slag immersion test.

The experiments at 1400° C were repeated and the results shown in Figure 8. The interfacial region is shown in the SEM micrograph and the corresponding EDAX trace shown below it. Again a sharp coal slag/sapphire interface is indicated. Very little silica or iron has penetrated into the sapphire as evidenced by the EDAX map.

For comparison, a commercially available dense, polycrystalline sample of alumina was immersed in the coal slag at 1500° C for 48 hrs. The SEM micrograph of this sample is shown in Figure 9. As can be seen, large regions of attack are present in this sample. These regions of attack may have originated at the grain boundaries or at residual porosity that was present in the sample. Comparison of the commercially available dense polycrystalline alumina sample to the sapphire samples shown in Figures 5 and 6 indicate the dramatic superiority in corrosion resistance of the single crystal sapphire sample after the 1500° C for 48 hr treatment.

Figure 8. SEM micrographs of single crystal sapphire plate/coal slag interface after 1400°C for 48h coal slag immersion test. Lower picture is the EDAX elemental map corresponding to the upper micrograph.

Figure 9. SEM Micrograph of Polycrystalline Alumina Disk Sample after Coal Slag Immersion Test at 1500°C for 48h.

Conclusions:

Requirements for the temperature sensors for implementation in the coal gasifiers has been established in conjunction with the industrial partner, Dynegy. Coal slag immersion tests indicate good corrosion resistance of the single crystal sapphire. However, a more sophisticated corrosion apparatus has been constructed in order to test the optical attenuation of a single crystal sapphire fiber immersed in the coal slag at high temperature. These results will be reported in the next period. The data to date for sapphire sensor development is promising. More extensive data on the sapphire fiber sensor development will be reported for the next period.

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