Harsh environment sensor development for advanced energy systems

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ABSTRACT

Highly efficient, low emission power systems have extreme conditions of high temperature, high pressure, and corrosivity that require monitoring. Sensing in these harsh environments can provide key information that directly impacts process control and system reliability. To achieve the goals and demands of clean energy, the conditions under which fossil fuels are converted into heat and power are harsh compared to traditional combustion/steam cycles. Temperatures can extend as high as 1600 Celsius (°C) in certain systems and pressures can reach as high as 5000 pounds per square inch (psi)/340 atmospheres (atm). The lack of suitable measurement technology serves as a driver for the innovations in harsh environment sensor development. Two major considerations in the development of harsh environments sensors are the materials used for sensing and the design of the sensing device. This paper will highlight the U.S. Department of Energy's, Office of Fossil Energy and National Energy Technology Laboratory's Program in advanced sensing concepts that are aimed at addressing the technology needs and drivers through the development of new sensor materials and designs capable of withstanding harsh environment conditions. Recent developments with harsh environment sensors will be highlighted and future directions towards in advanced sensing will be introduced.

Keywords: Harsh environment, sensor, energy, power generation

1. INTRODUCTION

Low cost, environmentally benign power that is both ubiquitous and uninterruptable is the general expectation of developed societies. Approaches to meet these expectations include a range of energy sources and technologies to generate and deliver power. In North America, one of the most abundant and low cost sources of energy is fossil fuel. Because of the environmental concerns with traditional fossil fueled-based systems to generate power, the Department of Energy's (DOE) National Energy Technology Laboratory (NETL) has lead efforts to research, develop, and demonstrate (RD&D) new technologies that can generate power and other commodity type products under conditions where the environmental issues are minimized and controlled in an efficient manner. As part of the RD&D portfolio, advanced sensor technology is considered an enabling approach that supports the operation of advanced power plants and enables environmental performance goals to be measured and maintained.

The challenges associated with advanced sensing are the conditions under which fuel is converted to make power. Process conditions can include temperatures that extend up to 1600 Celsius (°C) in gasification systems and combustion turbines. Advanced combustion systems can efficiently generate steam at conditions near 760°C and pressures as high as 5000 pounds per square inch (psi)/340 atmospheres (atm). During advanced combustion and gasification, system conditions can support high rates of corrosion, experience varying degrees of erosion and produce a range of byproducts gases (e.g. NOx, SOx, H_2S, HCl, CO, CO_2, trace metals) that need to be measured on-line and in real time for plant operation performance within controlled within tight tolerances.

As part of NETL's RD&D effort in advanced sensing, there are multiple and concurrent efforts to develop sensors suitable for harsh environments including: fiber optic devices, micro sensors, sensor arrays, and non contact spectroscopic techniques. A significant portion of the development effort centers around materials and designs that offer the potential to provide suitable resistance to the harsh environment but to also function at an acceptable level of

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sensitivity, selectivity, and accuracy for a given measurement need. As approaches in advanced sensing evolve, the options for embedding sensors or incorporating smart sensing materials into components becomes possible and increases the overall viability of using non contact spectroscopic techniques and other wireless approaches in high temperature environments.

This paper will summarize the U.S. DOE, Office of Fossil Energy and NETL's Program in advanced sensing and highlight a portion of the RD&D work supported by DOE NETL where the development of sensor materials is a primary effort.

2. BACKGROUND

The use of domestic, abundant, and low cost energy sources is an important part of a sustainable energy portfolio. The role that advanced power generation will take, when using fossil fuels, will continue to evolve as the options advance for producing power in an environmentally benign manner. Responsible utilization of fossil fuels is projected to remain an important part of a diverse energy portfolio for the long term[1].

Integrated gasification systems, advanced oxy combustion systems, high efficiency natural gas and hydrogen turbines, fuel cells, by product gas separation and treatment, and carbon capture technologies offer a range of systems that, when integrated, can provide viable options for environmentally benign power generation (Figure 1)[2,3]. While lowering the cost of these systems is paramount, the ability to operate these systems in an integrated and continuous fashion is also a priority. Reliable and predictable operation of these integrated systems requires improvement in sensing so that the performance goals can be monitored and maintained.

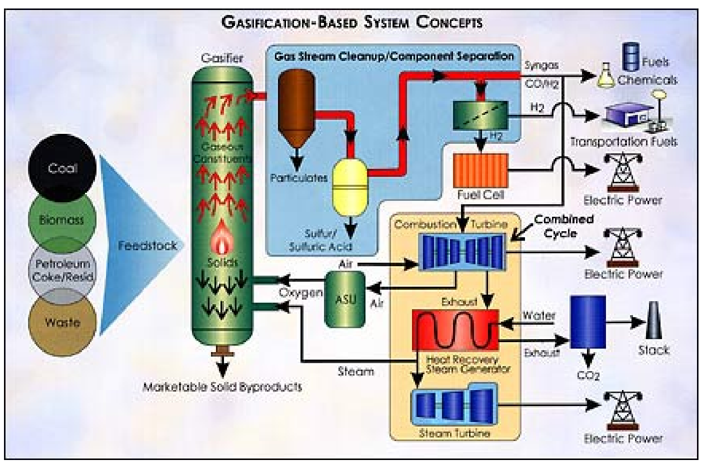

Figure 1: Advanced Concepts in Integrated Gasification Combine Cycle Power Plants

For the systems outlined above, the conditions under which fuel is converted drive the need to improve the monitoring capability of system performance in real time. The ability to sense and measure through an integrated power plant is critical for controlling the processes. Appropriate levels of sensing and actuation throughout a power plant will, when combined with process control algorithms and logic, enable targeted system performance in the presence of high system complexity and integration.

New sensing technologies will incorporate novel sensor designs and materials that address on line or in-situ measurement needs. For harsh environments, high temperature active sensing materials, novel sensor designs, virtual sensing approaches, and robust protective packaging are essential for survivability. Advances in sensing are targeting wireless, embeddable, and low cost to support an overarching strategy for heterogeneous sensor networks that enable the accurate and timely development and delivery of actionable information and minimize the use of data that causes delayed decision making.

3. OVERVIEW OF RESEARCH AND DEVELOPMENT IN HARSH ENVIRONMENT HIGH TEMPERATURE GAS SENSING

The following highlights research supported and conducted by DOE NETL. The information presented introduces approaches for sensing in high temperature and harsh environments. For a detailed account of the development efforts, please refer to appropriate references and performing organizations listed in the paper.

The application of plasmonic materials to enable non-contact gas sensing is a unique and novel approach being studied by researchers at the State University of New York at Albany in collaboration with the University of Minnesota. The objective of this research is to utilize plasmonic materials in combination with metal oxides for sensing at temperatures of 500–600°C for a range of gases including hydrogen (H_2), carbon monoxide (CO), and nitrogen dioxide (NO_2). Specific research efforts are focused on the control of ebeam patterned arrays of gold (Au) nanorods embedded in metal oxide matrices with targeted optical responses in the 600 to 1200 nm range. Preparation of the namomaterials and nanorods are key parameters in developing acceptable sensitivity to the targeted gases. The stability of the patterned materials at the high temperatures is dependent on the thermal treatments and the exposure gases used during the thermal stabilization process. In addition to the materials development effort, researchers at the University of Minnesota are identifying designs and mechanisms to integrate the plasmonic materials into a bull's-eye type sensor design that enables energy harvesting activated by the high temperatures and interrogated using a light source specific to the plasmonic materials (Figure 2). This active area of research will include efforts to understand the longer term stability of the sensor at targeted temperatures as well as selectivity for targeted gases in a mixed gas environment.[4]

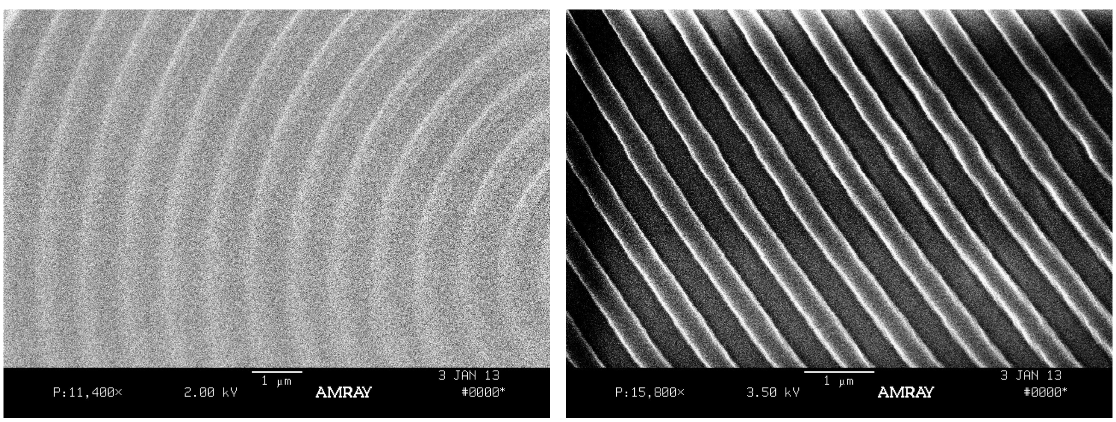

Figure 2: SEM images of a "bull's-eye" energy harvesting plasmonic device under development by the University of New York at Albany and University of Minnesota.

Researchers at the University of Cincinnati and Missouri University of Science and Technology have collaborated to successfully develop materials sets that support selective gas sensing by coating long period gratings written onto silica optical fiber. For sensing near 500°C, Dong and Xiao have demonstrated the nanocrystalline perovskite-type, proton conducting $SrCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (SCZY) for H_2 and a Cu-doped zirconia (CDZ) for CO detection are suitable for selective and repeatable sensing.[5] The nanocrystalline thin films of SCZY and CDZ were coated on long period fiber gratings (LPFG) and were overcoated with a protective nanoporous silicalite film (Figure 3). The performance of the materials and the resulting sensing device for H_2 detection was tested as in-situ sensing devices on a lab-scale coal gasifier that produced a representative synthesis gas. This was one the first demonstrations of a fiber optic gas sensor for harsh environments using a representative gas composition at temperatures and pressures representing commercial scale operational conditions. The H_2 compositions measured in-situ by the new fiber optic sensor agreed well with the values obtained by ex-situ analysis by gas chromatography.

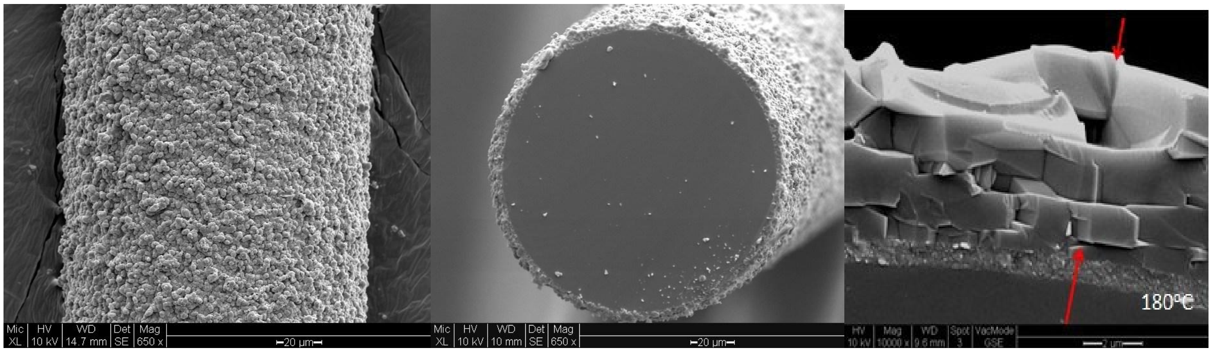

Figure 3: SEM images of the multilayer coated long period fiber grating silicalite and SCZY films for hydrogen detection at temperatures near 500°C.

Other material research by University of Cincinnati and Missouri University of Science and Technology included studies on the perovskite $SrCe_{0.95}Tb_{0.05}O_{3-\delta}$ (SCTb) nanocrystalline material as a potential sensing element for high temperature H_2S detection in coal- or natural gas-derived fuel gases. This particular materials set showed reversible detection of H_2S at high temperature of ~500°C. Additional work leading to a robust optical device for long-term, high temperature operation is underway.

Metal oxide perovskite composites are also being studied by Gao and coworkers at the University of Connecticut. The objective of this research effort is to develop multidimensional metal oxide perovskite composites and films as active sensing layers on a traditional micro sensor design. Metal oxides composites that enable a selective response to combustion gases such as O_2, CO, and NO_2 in high temperature environments (600–1000°C) are under development. Material sets under research include ZnO/La,$SrCoO_3$ and ZnO/CeO_2 composites for O_2, CO, and NO_2 response[6]. Additional work has included rapid fabrication of TiO_2 nanoporous structures assembled by the interweaving of rutile TiO_2 nanowires with uniform diameter and length. The pores of the nanoporous structure are very uniform with a size of 100nm for structures successfully formulated on sapphire substrates using the alkaline treatment of sputtered Ti film (Figure 4). The Pt decorated TiO_2 materials has a high sensitivity and a good selectivity toward CO detection at high temperatures (Figure 5).

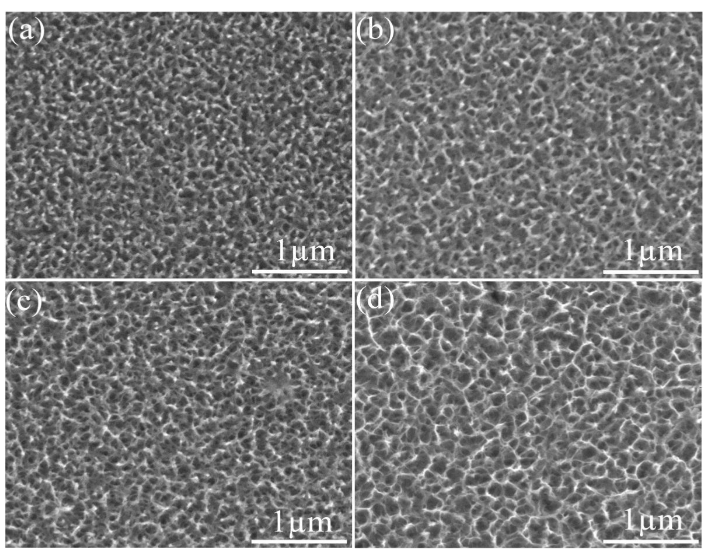

Figure 4: SEM images of the TiO_2 nanoporous films synthesized at different temperatures: (a) 80°C; (b) 120°C, (c) 160°C, and (d) 200°C, respectively.

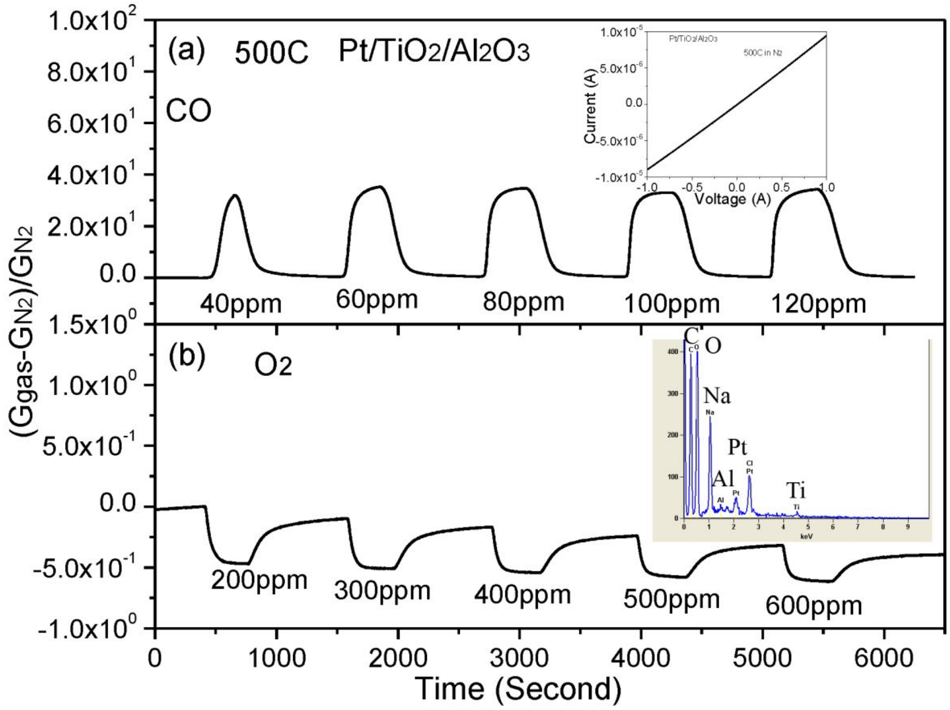

Figure 5: The sensitivity of Pt coated TiO_2 nanoporous film measured at 500°C in (a) CO and (b) O_2 with different contents. The inset of (a) shows the I-V curve at 500°C in N_2 atmosphere. The inset of (b) shows the Energy Dispersive Spectroscopy (EDS) spectrum of Pt coated TiO_2 nanoporous film.

Ohodnicki and coworkers at DOE NETL are developing thin films for optical based gas sensing. Thin nano films of SnO_2 and TiO_2 with Au doping have been identified for viable metal oxides for gas sensing at temperature ranging from 500-850°C[7,8]. Through sol gel deposition, films have been applied to silica fiber and tested for responses at various temperature and gas mixtures examining the selective response to H_2, using SnO_2, and CO using TiO_2 (Figure 6). Preliminary studies include testing up to 28 hours and suggest that these materials are viable for a controllable and reversible optical detection scheme at high temperatures.

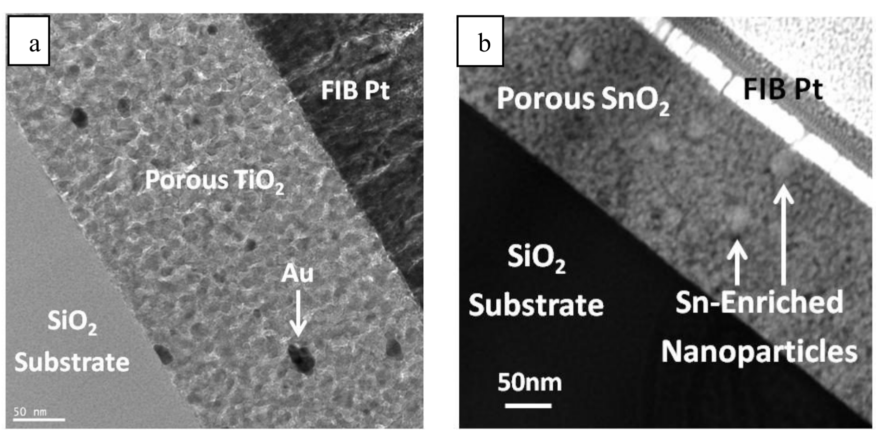

Figure 6: a) Au Incorporated TiO_2 Film Calcined at 500°C, and b) SnO_2 Thin Film After H_2 Exposure to Show Formation of Sn-Enriched Nanoparticles

Chen and co-workers at the University of Pittsburgh are examining SnO_2 nanostructures doped with catalytic materials to support rapid detection of NH_3 in air through fiber optic sensing devices (Figure 7). At present, silica fiber with fiber Bragg gratings are being coated with nanocomposites for laboratory examination of gas detection as either wavelength shift of absorption detection schemes that are functioning in temperatures up to 500°C[9].

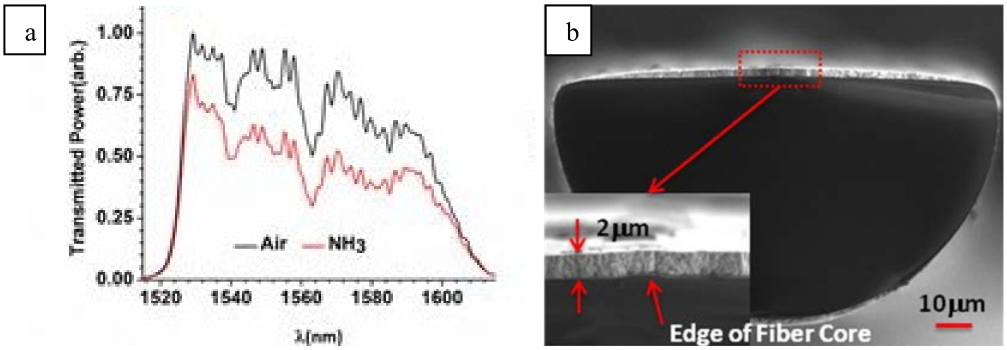

Figure 7: a) Wavelength spectra of Ammonia Detection in air using a SnO_2 doped nanocomposite, and b) SEM of coated optical fiber with metal oxide composite.

In addition to the materials highlighted above for the active sensing layers, other approaches towards sensor design and sensing techniques are under development to enable a high degree of robustness. An example of this approach is work by Pickrell and Wang at Virginia Tech's Center for Photonics Technology. In this development effort, porous nanostructured optical fibers are formed through a unique process where gaseous inclusions are created and controlled during drawing of the silica fiber[10]. Products from this process include a three dimensional interconnected porous cladding around a solid core (Figure 8). This type of fiber can be used to obtain gas species and concentration through absorption measurements. This approach has been demonstrated in the lab to have very fast response times (~ 1 second) with few issues for resolving gas species. Because the detection scheme is straight forward and the material set functions only as the delivery system, the sensing approach for high temperatures (500–850°C) is inherently robust. The process for making the porous nanostructured can also be extended to a number of other fiber based structures for sensing devices.

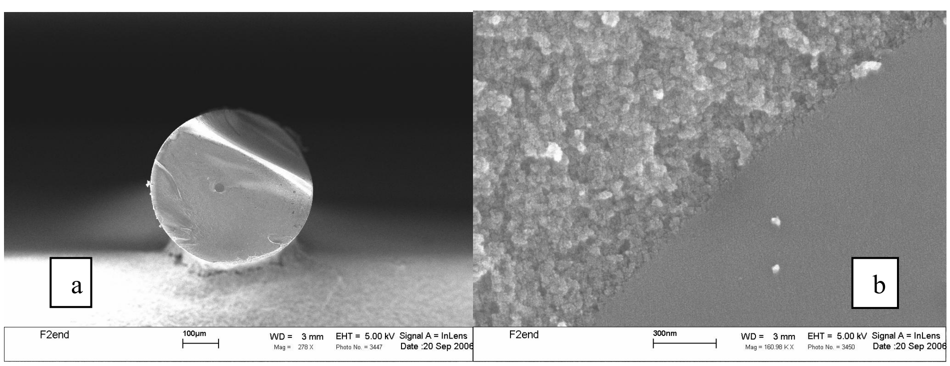

Figure 8: SEM image of porous nanostructured fiber with a) face of fiber showing porous cladding and solid core, and b) showing interface of core and porous cladding.

Other ongoing work with sensor materials and devices include the use of silicon carbide nitride (SiCN) with various dopants to enable and control conductivity and corrosion resistance. This material set and sensor designs have shown excellent performance in high temperatures harsh environments for the measurement of temperature and pressure and potentially as a wireless device. Other fields of research are focused on high temperature ceramics with tailored conductivity and novel sensor designs/concepts so that sensors can be applied (sprayed, deposited, etc) onto components for monitoring high temperature, high stress parts or components while in service[11].

As these material sets are proven in practical environments and new sensing concepts are tested, the sensing paradigm will shift to a more integrated system level approach. While traditional designs of insertion probes for extreme and harsh environments will continue, due to the need for maintenance and/or replacement of the sensors, the sensors themselves will evolve, for example, from traditional thermocouples to optical approaches that do not have EMI interference and offers designs with virtually no drift. The practical issues of measuring parameters on-line and in real time are an important part of a DOE NETL's sensor development program. However, the sensor materials and those approaches introduced in this paper offer the building blocks from which the novel concepts can transition to applied development and practical implementation for sensing in commercial scale systems such as advanced power generation.

4. CONCLUSIONS

Low cost, environmentally benign power is an overarching goal driving the development of advanced power systems that utilize low cost, domestic fuel sources. The DOE and NETL are leading efforts to conduct RD&D so that advanced power systems are commercialized at reasonable costs and designed to meet future performance expectations. Advanced sensor technology is an enabling program within DOE NETL that directly supports the operation of advanced power plants and enables environmental performance goals to be monitored and maintained. Because traditional instrumentation and sensors may not be suitable for the high temperature harsh environment of an advanced power system, new sensors, and in particular, sensor materials are under development with the targeted end use application being full-scale power generation systems.

The RD&D effort supported by NETL in advanced sensing encompasses a range of materials and sensing concepts. For high temperature materials, research in applying metal oxides, precious metals, ceramics, conductive ceramics, and nanostructured composites are potential solutions to accurate sensing in harsh conditions. Sensor designs for harsh environments range from fiber optic devices, micro sensors, sensor arrays, and non-contact spectroscopic techniques. After a successful fundamental development effort, practical issues of sensing in a commercial system should be considered, and therefore, development efforts are needed for a specific approach that provides suitable resistance to the harsh environment yet functions at an acceptable level of sensitivity, selectivity, and accuracy for a given measurement need. As advanced sensing concepts evolve and high temperature sensor material performance is well understood, the options for embedding sensors or incorporating smart sensing materials into components becomes possible and increases the overall viability of shifting the sensing paradigm to a more integrated system level approach.

5. ACKNOWLEDGEMENTS

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