Report Title: Novel Corrosion Sensor for Vision 21 Systems

Report Type: Technical Progress Report (Annual)

Reporting Period Start Date: August 1, 2004

Reporting Period End Date: July 31, 2005

Principal Author: Heng Ban (Associate Professor)

Date Report was Issued: December 2005

DOE Award Number: DE-FC26-03NT41807

Name and Address of Submitting Organization:

University of Alabama at Birmingham
Department of Mechanical Engineering
1150 10th Avenue South
Birmingham, AL 35294-4461

DISCLAIMER

ABSTRACT

Advanced sensor technology is identified as a key component for advanced power systems for future energy plants that would have virtually no environmental impact. This project intends to develop a novel high temperature corrosion sensor and subsequent measurement system for advanced power systems. Fireside corrosion is the metal loss caused by chemical reactions on surfaces exposed to the combustion environment. Such corrosion is the leading mechanism for boiler tube failures and has emerged to be a significant concern for current and future energy plants due to the introduction of technologies targeting emissions reduction, efficiency improvement, or fuel/oxidant flexibility. Corrosion damage can lead to catastrophic equipment failure, explosions, and forced outages. Proper management of corrosion requires real-time indication of corrosion rate. However, short-term, on-line corrosion monitoring systems for fireside corrosion remain a technical challenge to date due to the extremely harsh combustion environment.

The overall objective of this project is to develop a technology for on-line corrosion monitoring based on a new concept. This objective is to be achieved by a laboratory development of the sensor and instrumentation, testing of the measurement system in a laboratory muffle furnace, and eventually testing the system in a coal-fired furnace. The initial plan for testing at the coal-fired pilot-scale furnace was replaced by testing in a power plant, because the operation condition at the power plant is continuous and more stable. The first two-year effort was completed with the successful development sensor and measurement system, and successful testing in a muffle furnace. Because of the potential high cost in sensor fabrication, a different type of sensor was used and tested in a power plant burning eastern bituminous coals. This report summarize the experiences and results of the first two years of the three-year project, which include laboratory development and testing, and experiences and results of power plant testing.

TABLE OF CONTENTS

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Figure **Page**

INTRODUCTION

Background and Significance

Revolutionary sensor technology is a key component for DOE's approach for developing next generation energy plants that would have virtually no environmental impact. Relying on fossil fuels for a major share of our energy needs well into the 21st century and a diverse mix of energy resources, Vision 21 is the culmination of power and fuels research and development directed at resolving energy and environmental issues. The focus is to develop the critical technologies that underlie the components and subsystems ("modules") that are the building blocks of future energy plants. The key elements of the approach include: focusing on key technologies, stressing innovation and revolutionary improvements, producing early benefits, and emphasizing flexibility to meet market needs. One of the identified crosscutting technologies that are expected to be important, regardless of the actual configurations of future energy plants is the development of advanced sensors for highly integrated advanced energy systems.

Fireside corrosion is the external tube metal loss (wastage) caused by chemical reactions on water tubes exposed to the combustion environment in a furnace [1]. Corrosion is the leading mechanism for boiler tube failures [2, 3]. The direct economic cost of corrosion, through parts and labor to replace corroded equipment are often minor compared to the loss of production while the plant is under repair. For example, the cost of replaced power from the shutdown of a needed power plant can run into millions of dollars per day. Fireside corrosion typically occurs in high temperature, harsh combustion environment found in boilers and chemical recovery systems. The corrosion of boiler tubes can lead to the thinning of the tube reached more than 80% of the original thickness. Such excessive corrosion can lead to tube leakage or rupture, which can then lead to significant equipment damage and possible injuries to personnel, and in Kraft recovery boilers, smelt-water explosions.

Proper management and control of high temperature corrosion requires real-time information of corrosion rate [4]. Future trends in energy plant development tend to increase fireside corrosion due to introduction of technologies targeting emissions reduction, efficiency improvement, or fuel/oxidant flexibility. The availability of an on-line instrument capable of quantifying fireside corrosion rates would be a valuable new tool for plant operators who must meet environmental targets while minimizing the deterioration of valuable heat exchanger surfaces. Additionally, knowledge of localized corrosion rates provides critical information so that informed decisions can be made for maintenance and ongoing life extension of the plant [5-7].

This project attempts to develop a novel high temperature corrosion sensor and associated measurement system for advanced power systems. The focus is the short-term determination of fireside corrosion in a combustion environment. A novel sensor concept was conceived and examined in the Phase I study, and the intent of this project was to develop a complete measurement system and evaluate its feasibility at the laboratory and pilot scale. The investigation includes laboratory development of sensors, the probe and the measurement system, followed by the evaluation and improvement of the system in the laboratory, and the eventual testing of the complete system at a pulverized coal (PC) combustion furnace. The challenge of the proposed work is the design, fabrication and testing of the system that can function in a high temperature harsh combustion environment. The overall goal of the proposed research is to develop and prove the feasibility of the technology.

Current Knowledge and Technology

Current methods for corrosion measurement or monitoring fall into three main groups: downtime inspection, metal loss types, and electrochemical types [8-37]. The result of downtime inspection is of limited value for pro-active corrosion management because it provides only historical data. The simplest metal loss type is the weight-loss coupon, which is the most commonly used technique in corrosion research. A sample of the material of interest, of known weight, is exposed to the process for a known period. When it is removed, carefully cleaned and weighed, the change in weight is used to calculate the metal loss that may then be expressed as an annualized rate of loss (mils or millimeters per year). The coupon requires a relatively long exposure, for instance, 3 to 6 months, to the combustion process to yield accurate results. The constraints imposed by the time of exposure naturally limit the number of data points that can be obtained from a location, and ultimately do not detect process changes quickly.

Electrochemical techniques measure the corrosivity of an environment independent of actual material loss. Linear Polarization Resistance (LPR) is the most widely used technique of this type. It measures the DC current through the metal/fluid interface when the electrodes are polarized by a small electrical potential. As this current is related to the corrosion current, that in turn is directly proportional to corrosion rate, the method provides an instantaneous measurement of corrosion rate. This has advantages over metal loss methods, but is limited in the scope of its application by the requirement that the fluid be conductive, which in practice usually limits it to aqueous solutions. Other electrochemical techniques include Potentiostatic, Galvanostatic, Potentiodynamic, Galvanodynamic and AC Impedance Spectroscopy. None of these approaches have been successfully developed for field use as continuous monitors due to a variety of technical difficulties.

Electrochemical Noise (ECN) is a passive electrochemical technique that requires no polarizing current, but measures the naturally occurring electrochemical potential and current disturbances that result from corrosion. Electrical current noise is based on current variations between two nominally similar working electrodes, whereas potential noise is based on alterations between a working electrode and a stable, reference electrode. ECN is capable of giving accurate indications of general corrosion, pitting, and stress cracking when it is properly applied, but requires both expertise and complex data processing to be effective. Because ECN requires monitoring of very small signal fluctuations, this approach to corrosion monitoring is also affected by extraneous sources of signal noise in the plant. ECN is a relatively new technique and has applied the technology in coal combustion application by REI recently.

Metal loss type sensors can be combined with electrical measurements to determine the loss of metal and to provide an on-line monitoring capability. The most commonly used low-temperature corrosion probe is based on electrical resistance measurement. Because the electrical resistance of a current path increases as its cross sectional area is reduced, metal loss due to corrosion of the sample can be detected by an electrical resistance-measuring instrument. An Electrical Resistance (ER) sensor is often comprised of a sensing element that is basically a wire, strip or tube made of the alloy of concern, which is used to conduct the electric signal. When exposed to a corrosive environment, the cross-sectional area of the element is reduced. This increases the resistance of the sensing element, which can be measured and recorded as a function of time. Unlike electrochemical methods, ER sensors continue to function in the presence of non-conductive scales and are valuable tools for detecting under-deposit corrosion. As a simple and relatively inexpensive technique, ER is often the mainstay of a monitoring program in low-temperature applications, especially in the petroleum industry. In high-temperature combustion applications, however, ER sensors are significantly affected by instrumental and thermoelectric noise. The challenge is to minimize the persistent noise, whether due to thermal or electrical interference, in the power plant and combustion environment.

In summary, different corrosion monitoring technologies available for low-temperature applications are being adapted for on-line fireside corrosion monitoring. However, these technologies are either in development stage or create significant concerns for uncertainties or interferences inherent in the harsh combustion environment, which include high temperature, temperature fluctuations and ash deposition. It is necessary to development a fireside corrosion monitoring system with demonstrated power plant operation and verifiable measurement result.

The New Concept

A new sensor concept was developed and examined in the Phase I study. The concept is based on a new measurement principle that has not been previously applied for corrosion measurement. The technique uses a metal-loss type approach, which involves exposing a sensing element to a corrosive environment and measure the thickness decrease of the element as a function of exposure time. As all online approaches to corrosion measurement, the challenge is to measure a thickness change of the order of 1 micrometer or so without destroying or removing the element from the corroding environment. The new concept converts the thickness measurement to area measurement. The technique employs thin-film coating of the material to be corroded on a substrate. The thickness of the coating varies continuously, for instance, from 0 to 40 micrometers over a length of 4 cm. When the sensor element is exposed to the corrosive environment and corrodes away a layer of a certain thickness, the decrease in thickness will be proportional to the coating area recession or decrease. Thus, the design converts the depth (thickness) change of 1 micrometer to an equivalent length change of 1 mm, which is much easier to determine.

The change in size or area of the metal coating can be measured on-line by electrical capacitance. A thin ceramic plate substrate with metal coatings on both sides constitutes an electrical capacitor. The capacitance is a function of the overlapping area of the metal coatings, and the thickness and dielectric properties of the ceramic. The change of capacitance is directly proportional to the change in the overlapping area of the metal coatings. The sensor design can include a front side coating area with linear thickness variation exposed to combustion environment, and a uniform-thickness backside coating not exposed to combustion environment. The decrease of coating area on the front side due to corrosion will be reflected proportionally by a decrease in capacitance.

This innovative concept represents a significant departure from existing approaches to metal loss type of corrosion monitoring technology. It can potentially result in a significant advancement in corrosion sensing technology. The ER method is currently under development for combustion environments. ECN or other electrochemical techniques may present problems in interpreting the data when there is ash or slag deposition on the sensor element. The new concept may be better suited for the combustion environment where ash deposition and temperature fluctuation are common and almost unavoidable.

Earlier studies indicated that the new concept worked in principle and required further development. We investigated fabrication materials and methods, coated the sensor elements using vacuum sputtering technology, tried the supporting electronic system for capacitance measurement and data acquisition, and measured the sensor response to oxidation in a muffle furnace. The Phase I examination of this innovative concept indicated that the concept could be further developed to quantify corrosion rate in a power plant.

Technical Issues and Challenges

Although the concept has shown promise, clear technical challenges remain. The obvious challenge, beyond the preliminary study, is to develop a system and prove its feasibility in laboratory, pilot combustor, and power plant testing. The technology has to be proven at a full-scale boiler before it can be developed into a commercial product. For corrosion monitoring in a combustion environment, proof-of-concept testing at coal-fired furnace is a necessary step. Therefore, the following technical issues must be addressed to further develop the concepts and the technology.

(1) Options for Sensor Design and Fabrication.

We need to have answers to questions such as: what is the best design to achieve high sensitivity and low cost, or what is the best initial element thickness (or slope). For example, the element needs to be thick enough to have a long service life, yet also thin enough to provide a high signal-to-noise ratio. These answers will have to come from research and development at the laboratory scale. The sensor designs need to take into account fabrication options. A compromise may have to be reached between an ideal design and practical requirements for fabrication. The designs will also have to be tested in coal-fired furnaces to see if they can survive and achieve the sensing objective.

(2) Complete Monitoring System Development and Improvement

The proof-of-concept step requires building of a complete system and demonstrating its feasibility at a full-scale furnace. There are many questions to be answered in designing and building the complete system, which needs to match the appropriate sensor designs from laboratory tests with robust probe design. A rugged, portable electronic measurement and control system that can function in the industrial environment need to be built. The measurement system also needs to automatically acquire and store data, and upload the data through (preferably) wireless communication.

(3) System Evaluation and Testing in a Coal Combustion Furnace

The corrosion monitoring system needs to be tested at a full-scale furnace to reveal areas that require improvement or modification. In addition, the probe and ancillary instrumentation need to be tested for long-term performance to determine the service life of the sensor. Such tests will provide information on the stability and long-term performance of the new technology for fireside corrosion monitoring.

Although in theory the change in sensor capacitance is proportional to its change in thickness, the degree of deviation from the linear correlation has to be experimentally determined. Such an evaluation and the data resulting from this evaluation may provide a more accurate estimation of error range and confidence level of the corrosion rate determined by the ER method.

(4) Calibration of Results with Metrology Analysis

The corrosion rate determined from the novel sensor needs to be compared to true metal-loss measurement, either on the same element or on a separate weight-loss coupon. Industry accepts the amount of metal loss measured by coupon exposure as an absolute and correct measure of corrosion averaged over a period of time. Calibration of the corrosion rate measured by the new method provides confidence in the quantitative result from the sensor. Such comparisons will ultimately verify the result of the new sensor for fireside corrosion measurement and promote the acceptance of the technology in industry.

Anticipated Benefits

The sensor and supporting measurement system developed by this project can be used in multiple end-use sectors to increase the overall efficiency of current and future energy plants. Having the availability of a real-time fireside corrosion monitor can help to bring about one or more of the following: (1) quick diagnosis of corrosion problems; (2) monitoring the effect of operating condition changes on corrosion; (3) providing advance warning of system upsets that could lead to corrosion damage; (4) determining the need to invoke process controls; (5) establishing a realistic inspection or maintenance schedule; and (6) an accurate estimation of the useful service life of equipment. Because fireside corrosion has a significant negative economic impact on energy plant availability, corrosion management can reduce such effects and increase the overall efficiency of the plant. The loss of electricity production due to plant downtime for repairing corroded waterwall tubes can run into millions of dollars per day. If the corrosion monitoring technology developed by this project leads to the reduction of downtime for an average of one day each year for each boiler that is monitored, the overall efficiency increase for that boiler is a fraction of one percent. However, the total amount of saving could be in hundreds of millions per year due to the large number of units in the U.S. that would benefit from the application of this technology. In addition to economics, the effects of corrosion can also lead catastrophic explosions that endanger life and safety, which is an especially serious concern for Kraft recovery boilers in the pulp and paper industry. This research can help to reduce such risks by providing a timely assessment of corrosion rates and can help operators determine the most efficient modes of operation. The increase in plant efficiency from corrosion management can directly reduce the emissions per unit of production. Since corrosion is an inherent process for metals exposed to a chemically reactive environment, corrosion management and control is an important way to reduce its negative impact on plant availability for current and future energy systems.

Research Objectives and Scope

The overall goal is to develop an on-line fireside corrosion technology based on an innovative concept. This project is to design and build a system and prove its feasibility at a coal combustor. The specific objectives are to:

(1) Develop the sensor and electronic measurement system;
(2) Evaluate and improve the system in a laboratory muffle furnace;
(3) Evaluate and improve the system through tests conducted in a coal combustor.

The scope of work includes a comprehensive experimental program to be carried out in the laboratory and at a coal combustor. A corrosion monitoring system will be designed, tested, and improved in the laboratory and tested at coal combustor. The experimental effort focuses on designing and building a compete system including the sensor, temperature controlled probe, and electronic measurement and data acquisition. The system will be tested and improved through evaluations using a laboratory muffle furnace. A coal-fired combustor will be used to evaluate the technology in a coal combustion environment. Such evaluation is crucial because many technologies fail during this stage of development due to rapidly varying combustion conditions, the aggressive industrial environment, and high levels of ambient electrical noise. The technology will be evaluated to ensure that (1) it works in a combustion environment, (2) the result can be confirmed by metal-loss measurements, and (3) the system is rugged enough for the plant environment.

EXECUTIVE SUMMARY

Advanced sensor technology is identified as a key component for advanced power systems for future energy plants that would have virtually no environmental impact. This project intends to develop a novel high temperature corrosion sensor and associated measurement system for advanced power systems. Fireside corrosion should be properly managed with real-time corrosion rate information because it could lead to catastrophic equipment failure, explosions, and forced outages. However, short-term, on-line corrosion monitoring systems for fireside corrosion remain a technical challenge to date due to the extremely harsh combustion environment. The overall objective of this project is to develop a technology for short-term, on-line corrosion monitoring based on laboratory development and experiment, and coal-fired furnace testing. This report describes the progress in the first two years of the three-year project.

The specific objectives of the project are to: (1) develop the sensor and electronic measurement system, (2) evaluate and improve the system in a laboratory muffle furnace, (3) evaluate and improve the system through tests conducted in a coal combustor. The scope of work includes a experimental program to be carried out in the laboratory and at a coal combustor. The on-line corrosion monitoring system to be developed includes the sensor, temperature-controlled probe, and electronic measurement and data acquisition. The system will be tested and improved through evaluations using a laboratory muffle furnace. A coal combustor will be used to evaluate and further improve the technology in a coal combustion environment. There are three main tasks in the project. The first task is to design and build a complete system during the first year. Task 2 is to evaluate and improve the system performance in a laboratory muffle furnace. Task 3 evaluates and improves the system in a coal combustor. The corrosion rates measured by the sensor will be compared with direct metal loss measurements of the sensor.

The tasks for the first two year are successfully completed, mainly, the development of the probe and the measurement system in the laboratory, and testing of the system in a muffle furnace. The completed work included the preparation and design of a corrosion probe, on which the corrosion sensor can be mounted. The first probe, which is slightly smaller in diameter, was redesigned with improvements to accommodate ceramic connectors for electrical connection. The probe temperature measurement and control was developed based on our experience, in addition to a probe temperature control system that was already available. They are portable and rugged, suitable for operation at ambient temperatures in a power plant environment. The probe temperature, or the temperature of the sensing element, is controlled with compressed air cooling. The electronic measurement with computer data acquisition was also developed in the laboratory. The data acquisition software was developed to allow the user to select data logging rate, the temperature for the sensor, and options for various measurement sequences. It was successfully tested to automatically log and save the data for days or weeks without the need for operator intervention. The probe temperature control was also tested in laboratory muffle furnace to control the air cooling parameters and fluctuation range of the probe temperature. The project progressed according

the original plan and schedule. The next phase of the project is to test the system in coal-fired furnace.

In addition to the capacitance sensor system, a development effort on the resistance sensor system is also pursued due the potential high cost of the capacitance sensor fabrication. The resistance based system was previously tested under industrial support and had difficulty in data processing due to persistent noise. Further investigation of the resistance sensor design led us believe that the noise issue could be solved by a new design of the resistance sensor. The advantage of this new design of resistance sensor is its significantly lower cost in comparison to the capacitance sensors. The cost of the capacitance sensor can be 100 times more without mass production facility. Recent loss of the sputtering facility in the department made the fabrication of the capacitance sensor very difficult, which is one of the reasons that led us to the resistance sensor development. We can fabricate resistance sensor in the laboratory easily, whereas the capacitance sensors requires custom modification of the commercial sputtering facility, a job that many sputtering service companies would not do. Therefore, using the same temperature control, data acquisition, and high temperature probe, we focused our testing effort on the testing of the new type of resistance sensor.

We have gained significant experience at a coal-fired power plant through the interaction with plant people and preliminary testing of the resistance probe. Based on our experience in the pilot-scale furnace and power plants, it was concluded that it is easier to directly conduct testing at a power plant instead of the pilot-scale furnace because the plant is in operation all the time, and have less changes in operation condition. We decided to focus on power plant trials in the final phase of the project instead of pilot-scale furnace testing. Power plant testing of the system can also accelerate the pace to bring the technology to practical application by demonstrating the measurement system at full-scale. We have conducted preliminary tests of the complete system in a power plant, and we are in the process of setting up tests at base-load power plant for long-term testing of the system and verification of the result by metrology measurement. The project is expected to last longer, but no more than six months at no additional cost, than the original plan.

EXPERIMENTAL

Sensor Principle

The principle of the novel sensor is based on the electrical capacitance technique, which has never been used for corrosion measurement. The sensor consists of a ceramic substrate with metal coatings on both sides, which forms a classical electrical capacitor, as shown in Figure 1. The capacitance of the sensor is a function of the overlapping area of the metal coatings, the thickness of the ceramic substrate and the dielectric constant of the ceramic. The front side coating exposed for corrosion has a linearly varying thickness, or wedge-shaped. When the sensor element is exposed to the corrosive environment and corrodes away a layer of a certain thickness in wedge-shaped coating, this thickness decrease will be reflected on and proportional to the coating area reduction. This design converts very small change in the depth (or thickness) to substantial change in length, which is much easier to measure. Therefore, any loss of the metal by corrosion will result in a reduction of the coating area. The change in the area of the metal coating can be measured by electrical capacitance, which is directly proportional to the change of the overlapping area of the metal coatings. The thickness reduction due to corrosion is therefore quantified by the capacitance change. The corrosion rate can be determined based on the decrease in electrical capacitance over the time. The capacitance is measured using a four-wire method, applying 100 kHz AC current and measuring the AC voltage drop across the capacitor to determine the impedance, which can be used to calculate the capacitance.

Another technique tested, the electrical resistance method also uses a sacrificial metal coupon exposed to the corrosive environment. The relative change of the coupon thickness is determined based on the measurement of the coupon DC electrical resistance change. Because the electrical resistance of a current path increases when the cross sectional area of the conductor is reduced, the metal loss due to corrosion can be detected by an electrical resistance-measuring instrument. The sensing coupon is made of a circular disk of the alloy of concern with four electrical connections. A DC constant current is applied through the two opposite electric connections and the voltage between the other two electric connections is measured, as shown in Figure 2, which is also a four-wire measurement similar to the capacitance measurement.

The corrosion of coupon material will reduce the thickness of the coupon, and lead to an increase of measured resistance or impedance. Since the electric current is maintained at constant, the voltage between the test poles 1 & 2 will increase as the thickness decreases. Figure 3 shows the theoretical relationship between the measured DC voltage and the coupon thickness in relative percentages for the resistance technique. Figure 3 was calculated using a commercial finite element package to model the geometry effect of a specific coupon size and the location of the four electric connections. The curve for partial corrosion was calculated to account for the fact that there is little corrosion on the rim of the coupon due to sealing o-ring. Figure 3 shows an approximate linear relationship when the change of resistance is not significant.

Sensor Design

Substrate Material Selection

The physical and chemical properties of the sensor substrate materials are important factors affecting the sensor design and performance. Since the sensor developed in this research will be used for corrosion monitoring in high temperatures and corrosive combustion environments, the substrate material needs to have properties of high thermal conductivity, low thermal expansion, good electrical insulation, corrosion-resistance and stability at high temperature environments.

The substrate of the sensor is a ceramic plate with high thermal conductivity and low thermal expansion coefficients. There are a few commonly used ceramic materials available for the sensor substrate. These materials include Beryllium Oxide (BeO), Aluminum Nitride (AlN) and Alumina (Al_2O_3). The comparisons of main properties of these materials are provided in Table 1 and Figure 4. Because of the presence of water vapor in combustion, AlN is not considered in this case.

Beryllium Oxide (BeO) is a ceramic material that combines excellent electrical insulating properties with high thermal conductivity. It is also corrosion resistant. Although beryllium oxide powders are toxic when inhaled or ingested, and the cost of machining is high, there are many applications that exploit its singular properties. BeO is a unique material for electrical and mechanical applications, which require dielectric property, mechanical strength and high thermal conductivity. It is particularly well suited for a heat sink and heat dissipation medium in integrated circuitry.

Therefore, BeO is distinguished by thermal conductivity comparable to that of electrical conductors, while retaining dielectric constant, loss factor and dielectric strength in the range of the most efficient electrical insulators. This unique combination of properties in conjunction with good mechanical strength and thermal shock resistance enable BeO to be the best substrate material of the sensor in this research.

Aluminum Oxide (Al_2O_3) or Alumina is the second choice for the sensor substrate although its thermal conductivity is not as high as BeO. The high volume resistivity, chemical stability at aggressive and high temperature environments, high dielectric constant coupled with low dielectric loss and excellent electrical insulation lead to its wide applications in electronics as substrates. More importantly, Alumina costs much less than BeO.

Table 1 Properties for BeO and Alumina (99.6 % Al2O3) .

Property	BeO	99.6% Al_2O_3
Electrical		
Dielectric constant @1 MHz	6.7	9.8

Dielectric loss @1 MHz	0.0002	0.0001
Dielectric Strength (KV/mm)	>9.5	35
Electrical resistivity (Ohm-cm)	$>10^{14}$	$>10^{14}$
Mechanical		
Density (g/cm^3)	2.88	3.75
Youngs Modulus (GPa)	340	390
Thermal Properties		
CTE($\times10^{-6}$/°C) (25~400°C)	6.7	6.9
Thermal Conductivity (W/Mk)	290	30

Because the dielectric constant of the sensor substrate is the usually a function of temperature and there are temperature fluctuations during the measurement. It is important to determine the relationship between the dielectric constant and temperature because the measured capacitance becomes temperature-dependent through the dielectric constant of the ceramic substrate. A change in sensor capacitance could be caused by two reasons, corrosion of the front coating or sensor temperature change. To eliminate the capacitance change from the sensor temperature variations and obtain the corrosion rate, a temperature compensation technique is used to process test data based on measured sensor temperature and the relationship between the temperature and dielectric constant. The compensation can remove the influence of temperature variations on capacitance measurement.

For the resistance sensor, a specially designed holder was used as a sandwich structure for the sacrificial plate of low carbon steel 1010. This is a common carbon steel used for boiler tubes in small boilers and its chemical composition of which is shown in Table 2. High temperature ceramic adhesive was used to glue the sandwich structure together. Electrodes are spot welded on the metal plate, as well as the thermocouple for temperature control and measurement. Ceramic connectors were used to easy sensor replacement during the plant testing.

Table 2 Chemical composition of the low carbon steel for coupon (%).

Carbon, max	.25
Manganese, max	.90
Phosphorous, max	.025
Sulfur, max	.025
Nickel, max	.20
Chromium, max	.15
Molybdenum, max	.06

Sensor Fabrication

Sputtering Deposition Technology for Sensor Fabrication

The key for sensor fabrication is the forming a wedge-shaped front side coating to be exposed to combustion, with linear thickness variation. The sensor element design is shown in Figure 5. The backside coating not exposed to combustion has a uniform thickness and is relatively easy to make. The coating materials are different for the two coating deposition. Since backside coating should have no corrosion, it is better to select a material that does not corrode in air environment.

Sputtering deposition is a technique by which atoms and ions of Argon or other gases from the plasma bombard a target, thereby knocking atoms off of the target. These material atoms travel to a substrate where they are deposited and form a thin film. It is necessary to provide a uniform and abundant supply of ions over the surface of the target. This is achieved by maintaining a charge differential facilitating the movement of the sputtered atoms across the gap between the target and the substrate.

DC magnetron sputtering deposition technology was used for one type of the sensor coating deposition. The fabrication included the design and machining of accessory parts for substrate installation during the coating, target material preparation and the coating fabrication. A Denton DVI-SJ-24 multi-cathode DC/RF magnetron sputtering deposition system in the department, as shown in Figure 6, was utilized to deposit the iron coating on corrosion side and titanium coating on other side of the substrate. The DVI-SJ-24 is based on a “box coater” that provides easy access to substrates, sources, and instrumentation while maintaining excellent pumping characteristics. This system is designed to simplify the geometries necessary for the coordination of multiple source depositions. The system’s inherent flexibility allows for the operation of three sputter sources and the ability to heat, RF bias, and rotate the substrate. In a confocal cathode arrangement, the cathodes are focused on a central area of the substrate table. Table rotation during sputtering permits co-deposition, provides continuous substrate exposure to the cathodes, and results in excellent coating uniformity. With this arrangement, the cathodes can be smaller than the substrate and still provides uniformity of the coating.

We used a slow moving shutter for the specific purpose of depositing the linearly increasing thickness on the front side for corrosion. A special substrate holder with mask was designed and machined to support the sensor substrate during the sputtering. The substrate holder was adjustable in x, y, z directions to keep the mask and substrate in the appropriate position. Since the coatings on the two side of the sensor consisted of different target materials, the deposition rate and sputtering time were different for the coating on two sides. To achieve the required coating slope, experimental coatings were conducted to provide information on deposition rates. The needed exposure time of the substrate in plasma and shutter moving speed were calculated before the sputtering operation. The wedge-shaped coating was deposited by gradually moving the shutter over the coating area of the substrate during the sputtering. The area with longest exposure time had maximum coating thickness. The deposited coating had a gradual linearly changing thickness.

Low carbon steel 1010 was used as target materials to create wedge-shaped coatings. It took 7.5 hours for this deposition to complete, with total 45 steps along total length of 15 mm at 10-minute interval for each step. The maximum coating thickness measured by the profilometer was about 1.7 μm, because deposition rate for this material is very low. The whole process was extremely labor intensive because of the slow moving shutter, at the speed of about 1 inch per 7.5 hours, was manually operated moving stage with controls through the high vacuum chamber. Later, as the sputtering system was not available in the department due to the departure of a faculty member, the fabrication was done at a NASA facility through a technical collaborator. No commercial sputtering service company is able to fabricate our design for a limited number of pieces with reasonable cost.

For the backside coating, all unmasked area of the substrate had the same exposure time and the sensor holder rotated continuously during the sputtering. Since Titanium has a relatively higher deposition rate than low carbon steel 1010, the backside coating thickness achieved 2 μm during 1.5 hours of the deposition.

Plasma Spray Technology for Sensor Fabrication

Plasma spray process is basically the spraying of molten or heat softened material onto a surface to form a coating. Material in the form of powder is injected into a very high temperature plasma flame, where it is rapidly heated and accelerated to a high velocity. The hot material impacts on the substrate surface and rapidly cools down forming a coating. Such a plasma spray process carried out correctly is called a "cold process" (relative to the substrate material being coated) as the substrate temperature can be kept low during processing avoiding damage, metallurgical changes and distortion to the substrate material.

A plasma spray system in Plasma Process Inc., in Huntsville, Alabama was tested to fabricate the front and back side coatings. The front side wedge-shaped coating thickness varies from the thinnest to the thickest of 50 μm over a total length of 61mm. The backside coating has a uniform coating thickness of 100 μm. The target material was a low carbon steel “Atomet 95”. In addition, a layer of Titanium coating was sprayed around the holes for electrical connection of the sensor. The purpose of Titanium was to prevent the coating oxidation (or corrosion) at electrical connection areas.

The linear thickness change is not guaranteed because it is a manual spray gun operation. Our sample is too small and it is almost impossible to produce a linear slope of thickness change. For our sensor, such non-linear thickness variation is detrimental to the metal loss measurement because the measured capacitance is not proportional to the corrosion anymore. Qualitatively, manual plasma spray can generate a coating thick on one side and thinner on the opposite side. The deviation from the linear thickness change can only be determined by the measurement of each sensor. We did not pursue further on the plasma spray technique for the fabrication of the capacitance sensor.

Probe Design

The probe for the application in coal-fired furnace was re-designed to accommodate the ceramic connectors for the sensor element. The requirement for the probe includes mounting of the sensor element at the end, the temperature control of the sensor element with compressed air cooling, and the flange mount for insertion to the combustor. The existing probe is shorter and slightly smaller in diameter. The new probe is longer, which can be used to access superheater section of the boiler. The new design incorporated features for more ruggedness and future applications in power plants.

Probe Temperature Control and Data Acquisition

The temperature control system and the data acquisition systems were developed. We previously used this temperature control system in pilot furnace experiments and had good experience with it. It was proved to be rugged and precise for the similar furnace probe applications. Our original temperature control system can control the probe temperature precisely. However the size of the control cabinet is large and not as convenient. Both systems would be evaluated in our experiments.

The computer data acquisition with a LCZ meter was developed. The 4-wire measurement technique was applied to measure capacitance, similar to the resistance measurement. One pair of leads supplied test current to the sensor and a separate pair of leads made the voltage measurement. The method can prevent the voltage drop in current carrying wires from affecting the voltage measurement. The 4-wire method were also arranged to eliminate the impedance from the electrical leads as source of error, and thus improved the measurement accuracy. The data can be converted to corrosion rate information on a continuous online basis. An OMEGA thermometer/controller connected to a thermocouple transfers the temperature of the sensor element to the computer. Data acquisition software was developed to perform automatic data collection by the computer to obtain the test data from the SR175LCR meter and thermometer respectively. The rate of data acquisition could be adjusted by program. The data acquisition computer could acquire and display the measured capacitance and temperature of the sensor on real time basis, and the measurement results were programmed to be automatically saved every four hours for further data processing and analysis. The data acquisition software can run continuously until it receives the stop command.

For the resistance method, a constant DC current source was used with a high precision digital voltmeter. A measurement of the resistance takes several steps. First the voltage is measured without applying the current. The reading is the background noise to be subtracted from the voltage signal with current on. Then the current is turned on and the voltage is measured. The same procedure is then applied to a standard resistor. The sensor resistance is comparative obtained from the known standard resistor. Such a procedure can remove significant noise, including the thermocouple effect from the wiring.

RESULTS AND DISCUSSION

The tasks for the first two years are to design and build a corrosion sensor, probe and measurement system, and testing in a muffle furnace in the laboratory. These goals have been achieved. The completed work also included the preparation and design of a second corrosion probe for more flexible plant test. The schematic diagram for the laboratory experiment setup is shown in Figure 7. The assembly drawing of the second probe is shown in Figure 8. The wedge-shaped coating of the sensor element is shown in Figure 9.

The probe temperature measurement and control components were developed based on our experience in pilot and plant furnaces, shown in Figure 10. The existing probe temperature control system that was already developed has a cabinet. These two control systems are rugged and suitable for operation in a power plant environment. The probe temperature, or the temperature of the sensing element, is controlled with compressed air cooling. These temperature control units have been tested in a muffle furnace in the laboratory and in a coal-fired furnace. Both functioned well as designed. Both can control the sensor temperature for extended period without the need for intervention, and the temperature data are automatically logged into the computer.

The electronic measurement with computer data acquisition was also developed and tested successfully in the laboratory. For capacitance, the laboratory setup for the probe, temperature and measurement system is shown in Figure 11. A muffle furnace is used and the sensor end of the probe is inserted into the muffle furnace. The compressed air cooling, and temperature control system is connected. A desktop computer or a laptop computer can be used for data acquisition and control. The data acquisition software was developed to allow the user to select data logging rate, the set temperature for the sensor, and options for various measurement sequences. In the muffle furnace test, the system automatically logged and saved data for days or weeks without the need for operator intervention.

While the complete system has been performed well in the muffle furnace, however, the fabrication of the capacitance sensor turned out to be very difficult and costly. Initially, we used the sputtering system available in the department. We modified the system to enable a graduate student to operate manually the slow moving shutter in 8 hours of sputtering time for one side of the sensor substrate. The procedure is labor intensive and requires special modification of the sputtering system. Later, the sputtering system was not available in the department anymore, and the sensor fabrication was done in a similar system at NASA through a collaborator. When the NASA system is down, we looked for commercial sputtering companies to fabricate the sensor. But no commercial sputtering service company is able to fabricate our design at a reasonable cost. Furthermore, the sputtering deposition of iron is very slow, less than 2 μm per 8 hours. Ideally, the sensor should have a coating of a linear thickness variation of a 0-40 μm slope on the front side. This design minimizes the effect of initial higher corrosion period of a fresh metal surface. The corresponding sputtering time, however, would be 176 hours for one side of the substrate, making the fabrication process extremely costly.

At the time when the fabrication of the capacitance sensor turned out to be difficult, a further investigation on the resistance sensor system was pursued. The resistance based system was previously tested under industrial support and had difficulty in data processing due to persistent noise. Our further investigation of the resistance sensor design led us believe that problems could be solved by a new design of the sensor element. Another advantage of the new design of resistance sensor is its significantly lower cost in comparison to the capacitance sensors. The cost of the capacitance sensor can be 100 times more than the resistance sensor without mass production facility. We can fabricate resistance sensors in the laboratory easily, whereas making the capacitance sensors requires custom modification of the commercial sputtering facility, a job that many sputtering service companies would not do. Therefore, using the same temperature control, data acquisition, and high temperature probe, we shifted our focus to the new type of resistance sensor.

We have gained significant experience at a coal-fired power plant through the interaction with plant operators and preliminary testing of the resistance sensor and measurement system. The experience led to design modifications for the practical constraints in a plant environment. Based on our experience in the pilot-scale furnace and the power plant, it was concluded that it is easier to directly conduct power plant test because the plant operates all the time, and have less changes in operation condition. We decided to focus on power plant trials in the final phase of the project, instead of pilot-scale furnace testing. Power plant testing of the system can also accelerate the pace of bringing the technology to practical application by demonstrating the measurement system at full-scale. Therefore, we focused effort on the testing of the resistance-based system at a coal-fired power plant.

We have tested the system in a power plant. Figure 12 shows the probe and sensor elements. The probe was assembled and ready to be inserted into the furnace. Figure 13 shows the probe inserted into the waterwall with the instrumentation cabinet on the side. Figure 14 is a close-up picture of the probe inserted through the manhole door at superheater location. Preliminary tests were conducted to examine whether the system can function and whether the sensor can provide meaningful corrosion data.

The result of preliminary tests indicated that the system could determine metal corrosion rate in a relatively short period. We are in the process of setting up tests at a base-load power plant for more stable operation of the measurement system because the plant we conducted the preliminary tests varied its load during the day and night. The main task of the next phase is to conduct plant measurements and verify the result with metrology measurement. Longer term experiments with constant condition are necessary to obtain the metrology data. The project is expected to last longer than the original plan, but no more than six months at no additional cost.

CONLUSIONS

The corrosion monitoring system was designed and built in the laboratory, and successfully tested in a muffle furnace. While tasks for the first two years in original plan were completed, the difficulty and high cost of sensor fabrication led us to focus our effort in a new design of resistance sensors. It was also determined that the focus of the testing will be completed at full-scale power plants instead of the pilot-scale furnace. Preliminary tests in the muffle furnace and in a power plant waterwall and superheat indicated that the system can determine the corrosion rate for waterwall and superheat tubes. The next phase of the project is to perform long-term experiments at a base-load power plant to verify the probe result with metrology data.

REFERENCES

[1] Harb, J. N. and Smith, E. E., 1990, "Fireside Corrosion in PC-fired Boilers," Progress in Energy and Combustion Science, **16**, No. 3, pp.169-190.

[2] Dooley, B. and Chang, P., 2000, "The Current State of Boiler Tube Failures in Fossil Plants," Power Plant Chemistry 2000, **2**, No. 4.

[3] Cultler, A. J. B., Flatley, T. and Hay, K. A., 1980, "Fireside Corrosion in Power-station Boilers," Combustion, **12**, pp. 17-25.

[4] Kane, R. D., 2002, "Corrosion Monitoring for Industrial and Process Applications," Corrosioneering, Newsletter, InterCorr International, Inc., Houston, Texas USA.

[5] Natesan, K., Purohit, A. and Rink, D. L., 2001,"Fireside Corrosion of Alloys for Combustion Power Plants," Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439.

[6] Natesan, K., 2001, "Fireside Corrosion of Alloys for Combustion Power Plants," Advanced Research Materials Program, Work Breakdown Structure Element ANL-4, Under Contract w-31-109-Eng-38.

[7] Natesan, K. and Kraus, C., 2000, "Corrosion Performance of Structure Alloys and Coatings in Presence of Deposits," *Proc. 15th Ann. Conf. on Fossil Energy Materials*, Knoxville, TN, USA.

[8] Viswanathan, R. and Bakker, W. T., 2000, "Materials for Boilers in Ultra Supercritical Power Plants," *Proceeding of 2000 International Joint Power Generation Conference*, Miami Beach, Florida.

[9] Farrell, D. M. and Robbins, B. J., 2000, "Online Corrosion and Thermal Mapping of Industrial Plants by Non-intrusive Means," Rowan Technologies Ltd, UK, Corrosion 2000.

[10] Jaske, C. E., Beavers, J. A. and Thompson, N. G., 1995, "Improving Plant Reliability Through Corrosion Monitoring," *Fourth International Conference on Process Plant Reliability,* Houston, Texas, USA.

[11] ASTM Standard: G96-90 (2001) e1 Standard Guide for On-line Monitoring of Corrosion in Plant Equipment (Electrical and Electrochemical Methods), 2002 ASTM International, West Conshohocken, PA.

[12] ASTM Standard: G1-90 (1999) e1 Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens, 2002 ASTM International, West Conshohocken, PA.

[13] Blough, J. L. and Seitz, W. W., 1996, "Fireside Corrosion Testing of Candidate Superheater Tube Alloy and Cladding Phase II Field Testing," Technical Report, Livingston, NJ: Foster Wheel Development Corporation, ORNL/SUB/93-SM401/01.

[14] Weele, S. V. and Blough, J. L., 1990, "Literature Search Update • Fireside Corrosion Testing of Candidate Superheater Tube Alloys, Coating and Cladding," NJ: Foster Wheel Development Corporation. FWC/FWDC/TR-90-11.

[15] Weele, S. Van and Blough, J. L., 1991, "Literature Search Update•Fireside Corrosion Testing of Candidate Superheater Tube Alloys, Coating and Cladding," NJ: Foster Wheel Development Corporation. ORNL/SUB/89-SA187/02.

[16] Hurley, J. P. and Weber, G. F. et al, 2000, "Engineering Development of Coal-fired High-Performance Power Generation Systems Phase II and Phase III," Corrosion Testing to Support the Development of Advanced, High-performance Coal-fired Power Systems, Combustion 2000.

[17] Davis, K. A., Green, G. C., Linjewile, T. and Harding, S., 2001, "Evaluation of an On-line Technique for Corrosion Characterization in Furnaces," *Joint International Combustion Symposium*, AFRC/JFRC/IEA, Kauai, HI.

[18] Farell, D. M. and Robins, B. J., 1998, "Online Monitoring of Furnace Wall and Superheater Corrosion in Power Generation Boilers," VTER Technical Paper, CSS 98, 39th corrosion Science Symposium, 8th Sept. 98, University of Northumbria at Newcastle, U.K.

[19] Jaske, C. E. and Shannon, B. E., 2002, "Inspection and Remaining Life Evaluation of Process Plant Equipment," *Proceedings of the Process & Power Plant Reliability Conference*.

[20] Farrel, D. M. and Robins, B. J., 2002, "On-line Corrosion Mapping Using Advanced Electrical Resistance Techniques," UK NDT 2002 Conference.

[21] Seth, V. K., and Sagues, A. A., 1983, "Use of a Continuously Monitoring Corrosion Probe in a Fluidized Bed Combustor," Paper 38, Corrosion 83, NACE, Houston.

[22] McKenzie, M. and Vassie, P. R., 1985, "Use of a Weight Loss Coupons and Electrical Resistance Probes in Atmosphere Corrosion Tests," British Corrosion Journal, **20**, No. 3, pp. 117-124.

[23] Haynes G. S. and Baboian R., 1983, "Laboratory Corrosion Test and Standards," ASTM Special Technical Publication 866, Texas Instruments, Incorporated, Philadelphia.

[24] Gareau, F. S, 1988, "Remote Corrosion Monitoring Using an Interactive Data Acquisition and Transfer System," Paper 107, Corrosion 88, NACE, Houston.

[25] Bergstrom, D. R., 1981, "Case Histories- Electrical Resistance Probes Control Corrosion in Chemical System," Materials Performance, **20**, No. 9, pp.17-21.

[26] Davis, C. J., James, P. J. and Pinder, L. W., 1997, "Combustion Rig Studies of Fireside Corrosion in Coal-fired Boilers," Corrosion 97, New Orleans, Louisiana, USA.

[26] Nelson, W. and Cain, C., Jr., 1960, "Corrosion of Superheaters and Reheaters of Pulverized Coal-fired Boilers and Gas Turbines," Transactions of the ASME, Journal of Engineering for Power, **7**, pp. 194-204.

[28] Hladky, K. and Dawson, J. L., 1982, "The Measurement of Corrosion Using Electrochemical Noise," Corrosion Science, **22**, No. 3, pp. 231-237.

[29] Eden, D. A., Hladky, K., John, D. G. and Dawson, J. L., 1986, "Electrochemical Noise-Simultaneous Monitoring of Potential and Current Noise Signals from Corroding Electrodes," Paper 274, Corrosion 86, NACE, Houston.

[30] Magaino, S., 1988, "Corrosion System Noise Analysis," Corrosion Engineering, **37**, No. 11, pp. 629-635.

[31] Roberge, P. R., Beauudon, R. and Sastri, V. S., 1989, "Electrochemical Noise Measurement for Field Applications," Corrosion Science, **29**, No. 10, pp. 1231-1233.

[32] Farrel, D. M., 1989, "Electrochemical Noise Processes," *Proceeding from UK Corrosion 89*, Vol. 3, Blackpool, pp. 93-107.

[33] Butcher, D. W., 1983, *On-Line Monitoring of Continuous Process Plants*, Ellis Horwood, Ltd., UK. and John Wiley & Sons, Inc., USA.

[34] Eden, D. A., Rothwell, A. N. and Dawson, J. L., 1991, "Electrochemical Noise for Detection of Susceptibility to Stress Corrosion Cracking," Paper 444, Corrosion 91, NACE, Houston, USA.

[35] Hlladky, K. and Dawson, J. L., 1981, "The Measurement of Localized Corrosion Using Electrochemical Noise," Corrosion Science, **21**, No.4, pp. 317-322.

[36] Eden, D. A. et al., 1985, "Electrochemical Noise Measurement and Their Applications to Coated Systems," Division. of PMSE, Papers 1985, Vol. 53, ACS, pp. 388-390.

[37] Farrel, D. M., Scott, F. H., Rocchini, G. and Golombo, A., 1992, "Influence of Electrochemical Processes on High Temperature Corrosion Reactions in Combustion System," Materials at High Temperature, **10,** No. 1, pp. 11-19.

FIGURES

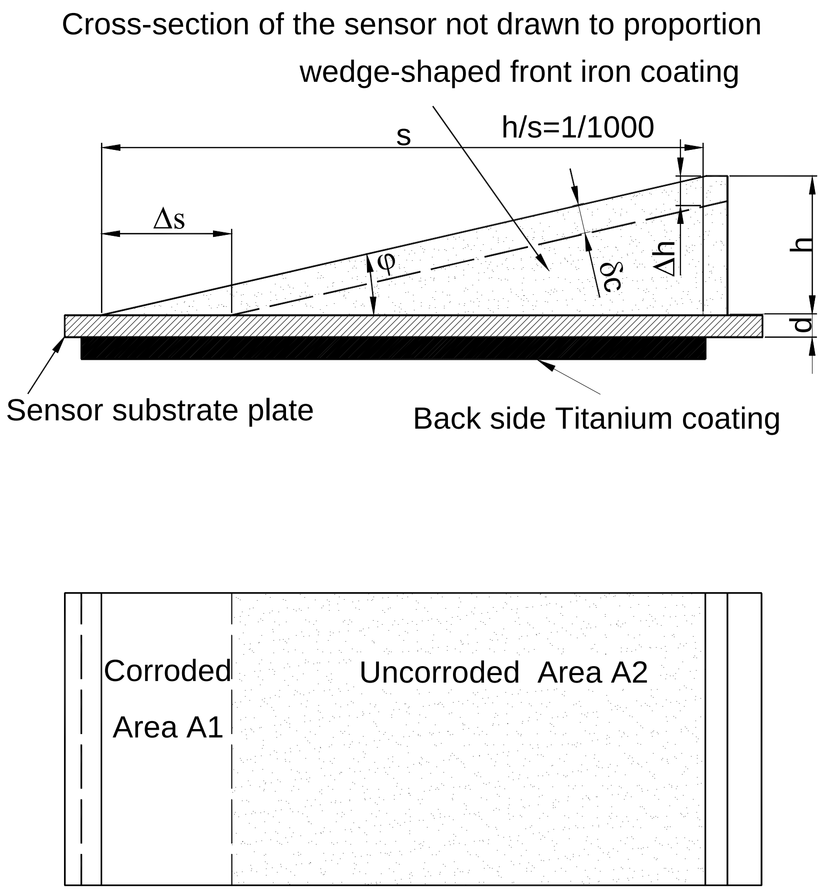

Figure 1 A schematic diagram of capacitance sensor principle.

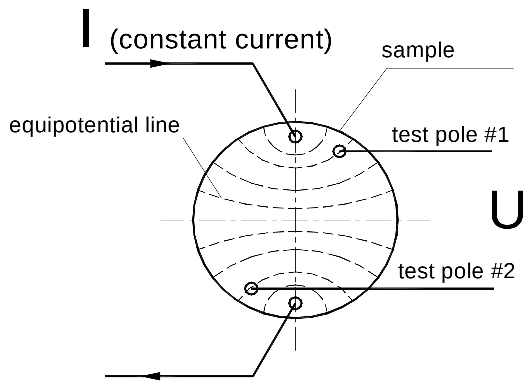

Figure 2 A schematic diagram of equal potential lines for resistance sensor.

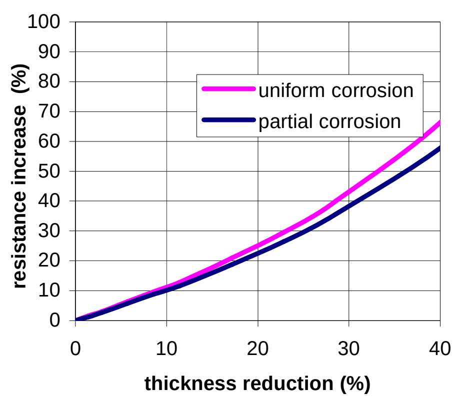

Figure 3 Resistance change with metal thickness reduction

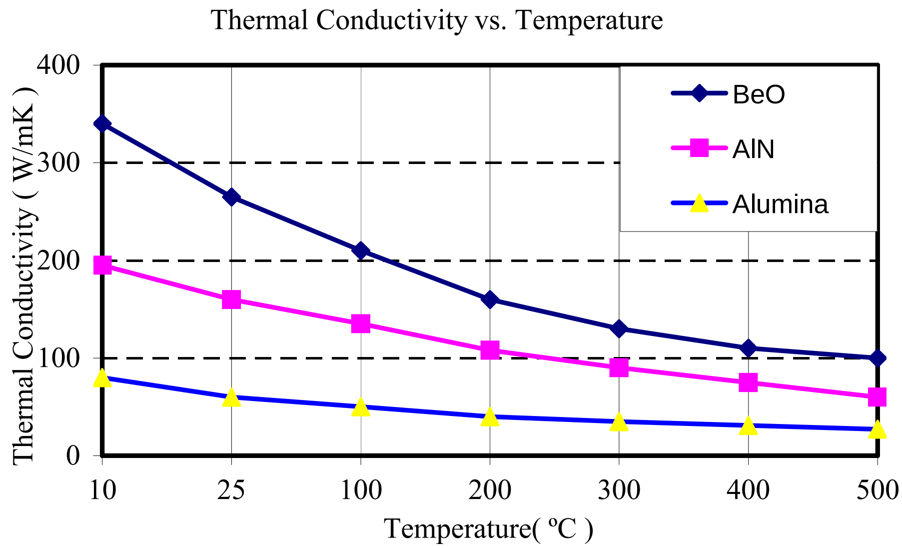

Figure 4 Thermal conductivity of BeO, Alumina (99.6%Al_2O_3) and AlN.

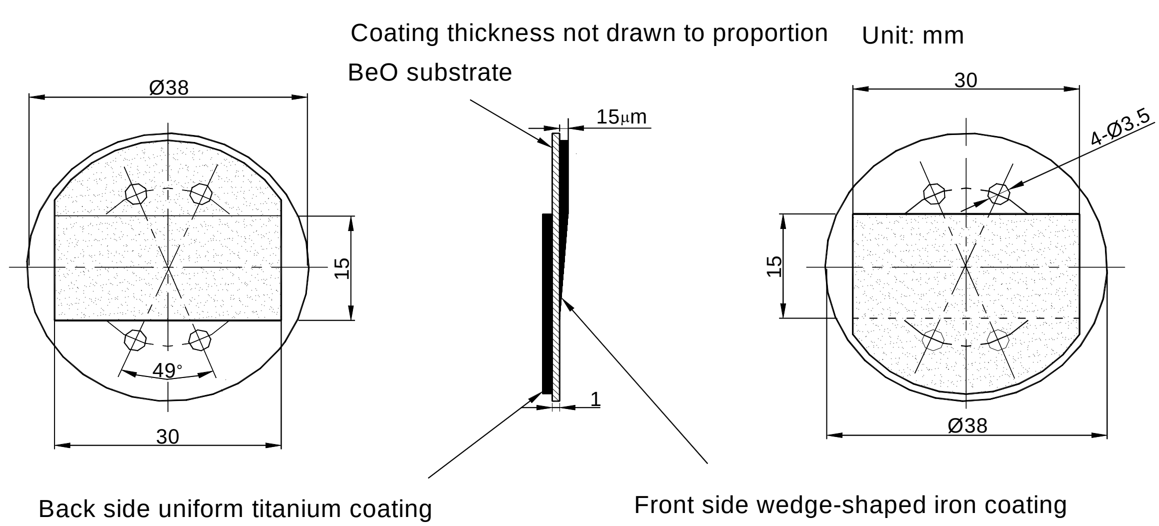

Figure 5 Design drawings of the the capacitance sensor.

Figure 6 A picture of the DC magnetron sputtering deposition system.

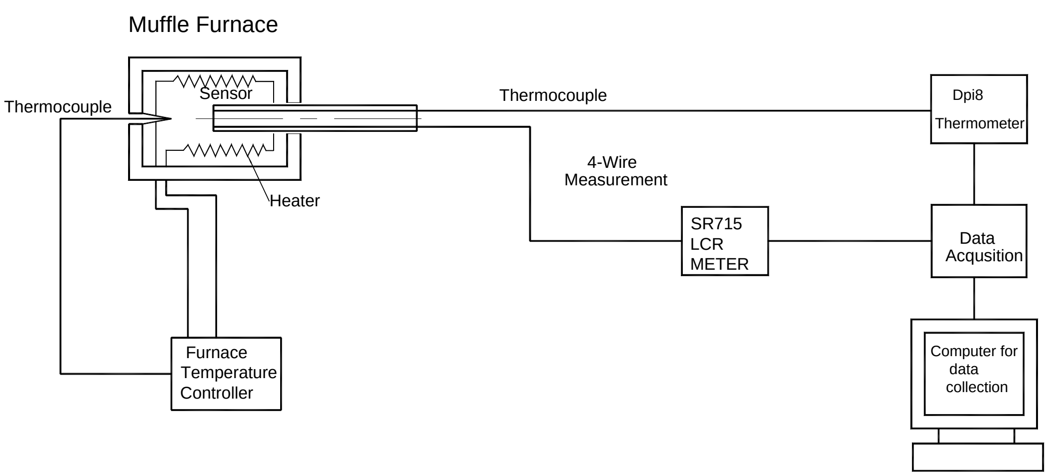

Figure 7 A schematic diagram for the laboratory experimental setup.

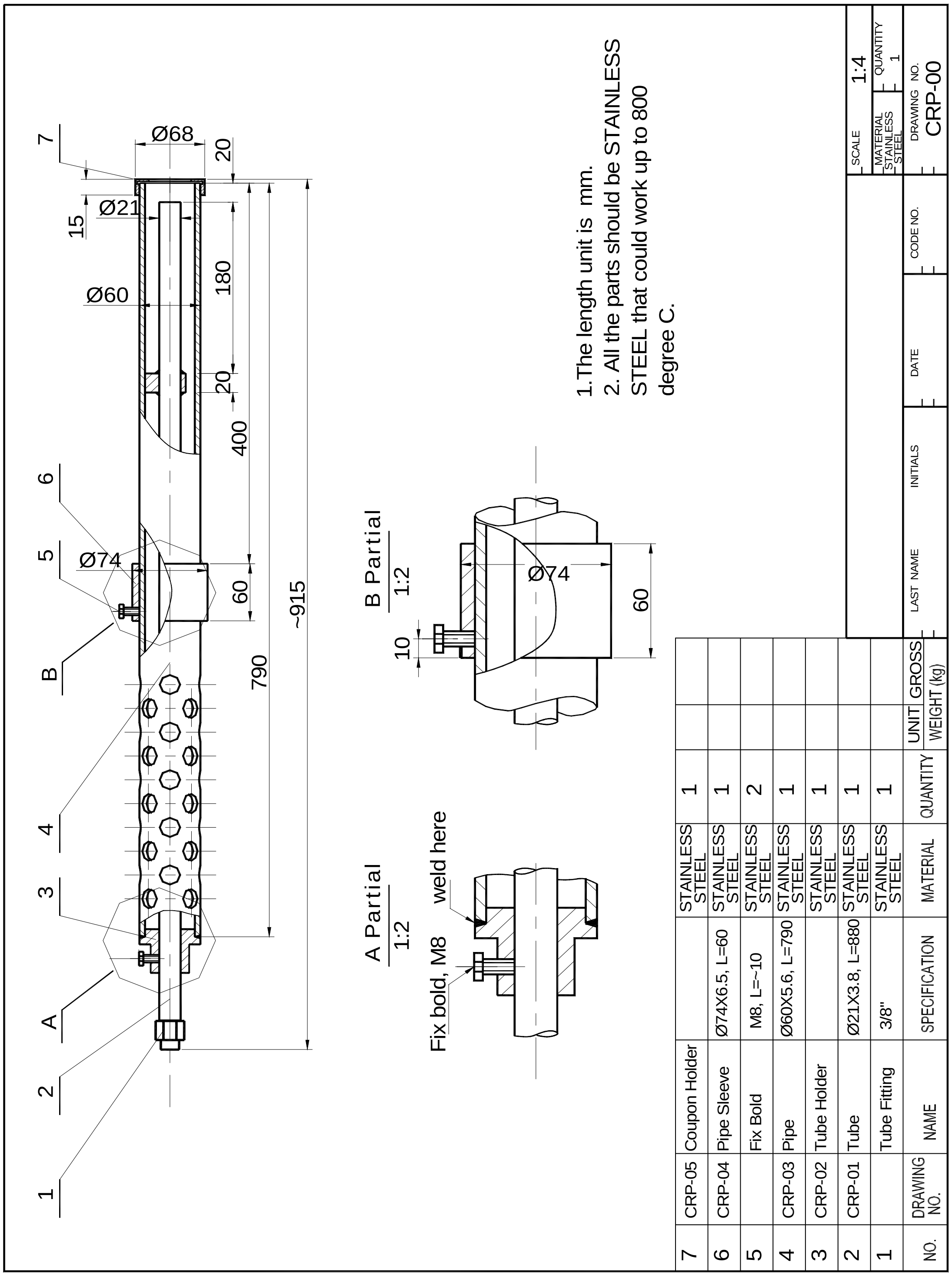

Figure 8 Assembly drawing of the probe.

Figure 9 A pictures of sloped iron coating on the capacitance sensor.

Figure 10 Temperature control system for the probe.

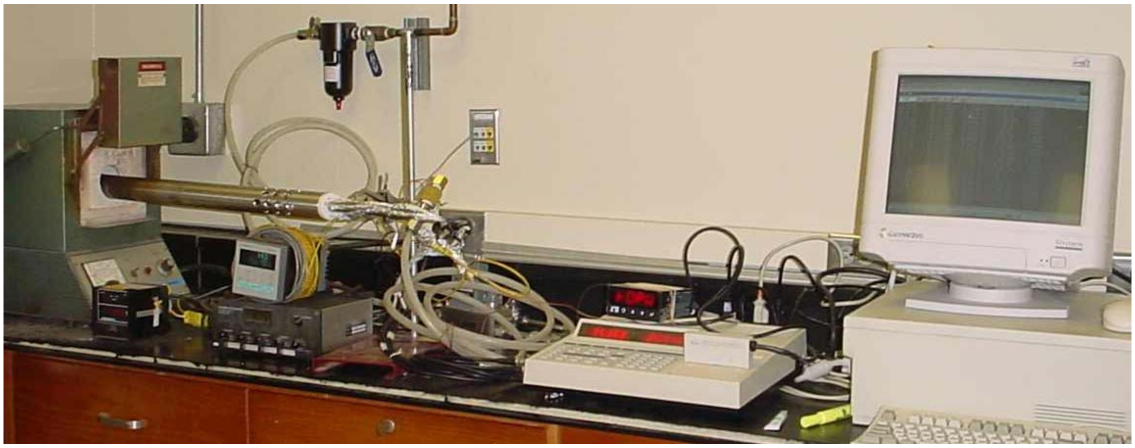

Figure 11 Complete measurement system layout in the laboratory.

Figure 12 Corrosion probe (left) and the sensor assembly (right)

Figure 13 Power plant waterwall measurement.

Figure 14 Corrosion probe inserted through the manhole at superheaters.