

Development of Technique for *In-Situ* Measurement of Oxide Film Thickness in High Pressure and High Temperature Environments

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ABSTRACT

Few *in-situ* corrosion monitoring techniques are available to use in high pressure and high temperature (HPHT) environments. This paper presents the outcome of the development of a technique based on optical ellipsometry that may be used to measure oxide film thickness growth in real time to better understand material degradation. Ellipsometry is an optical technique where the light from a laser is reflected off the specimen surface into a sensor to measure the polarization change (phase and amplitude changes). While this technique is used at ambient pressure and temperature, it is rarely used at HPHT. In this study, the laser light was radiated through a HPHT window attached on an autoclave. This technique was used to measure nanometer to micrometer changes in thickness of an oxide film in supercritical CO₂. The oxide film thickness measurements were compared to measurements of the thicknesses using scanning electron microscope imaging of the cross section and to data found in the literature.

Key words: *in-situ* techniques, supercritical CO₂, oxide film, optical ellipsometry

INTRODUCTION

High pressure and high temperature processes are present in a wide variety of industries and are often pushing the limits of common materials. As a result, these applications have required advanced materials as well as an improved understanding of the *in-situ* conditions. Furthermore, those processes have become more and more present in a wide range of industries such as upstream oil and gas (O&G) and power generation (in supercritical CO₂ or molten salt nuclear reactors). The corrosion performance of existing and emerging materials to the extreme environments present in next generation power must be well characterized to ensure material integrity and reduce the risk of catastrophic failures due to environmentally assisted cracking, homogeneous corrosion, thermal oxidation, or other mechanisms.

To respond to the ever-growing material needs, it is important to find new tools to study them. There is often a lack of data, for weight change, composition, oxide film thickness, hardness, etc., available for materials in HPHT environments because the properties of HPHT materials are usually only measured before and after exposing them to the environment of interest. This is usually done because of the technical complexity of performing measurements *in-situ*. However, the ability to measure corrosion of materials in real time in relevant environments would provide significant advantages including:

- Direct observations of corrosion or oxidation kinetics in response to transient conditions.
- Simplified understanding of corrosion processes uncompromised by changes in surface film properties resulting from analysis in lab air.
- Reduced overall exposure costs by avoiding shut-off/start-up procedures required for autoclave testing when examining samples at various time intervals.

The goal of this research project was to use ellipsometry to assess oxide film growth rates during an HPHT autoclave exposure. Ellipsometry is an optical technique where the light from a laser is reflected off the specimen surface into a sensor to measure changes in polarization. This technique can be used to measure nanometer changes in thickness of an oxide film during exposure, and while it is often used at ambient pressure and temperature, it has never been applied at HPHT.

Ellipsometry was chosen as *in-situ* technique because most of the components do not need to be redesigned for HPHT applications since they remain outside the autoclave. The ellipsometer was placed on the top of an autoclave. The only technical challenge is to safely transmit laser light in and out of the autoclave. This project focused on changes in surface films formed during exposure to environments found in a novel power generation technology (supercritical CO₂). Supercritical CO₂ (sCO₂) in power generation may reach temperatures up to 850 °C (1562 °F) and pressures up to 25.5 MPa (3698 psi).

Ellipsometry

Ellipsometry is a widely used optical technique that can be applied to measure various properties such as thickness, composition, roughness, and electrical conductivity. During this project, ellipsometry was used to measure the oxide layer thickness. Ellipsometry measures the polarization change that occurs when light is reflected from a surface, as shown in Figure 1.

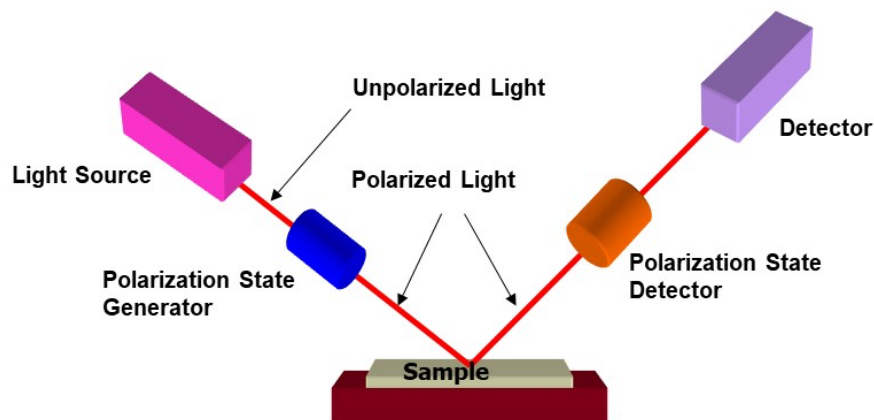


Figure 1: Simplified model of an ellipsometer.

An ellipsometer consists of a light source, a polarization state generator, a polarization state detector, and a detector. The laser light source is unpolarized and needs to pass through the polarization state generator to be polarized. The polarization state detector changes the polarization angle of the polarized light that is then captured on the detector. The optical constants of the sample, along with its thickness, change the polarization of the light when the incident light interacts with the sample surface. The changes

in polarization are measured by the amplitude component Ψ and the phase difference (Δ) through the fundamental equation of ellipsometry shown in Equation 1.

$$\rho = \frac{\tilde{r}_p}{\tilde{r}_s} = \tan \Psi e^{i\Delta} \quad (1)$$

The r_s and r_p are the amplitudes of the s and p components after reflection and normalized to their initial value. The s component oscillates perpendicular to the plane of incidence and parallel to the sample surface and the p component oscillates parallel to the plane of incidence. Ultimately, by measuring the polarization state change, it can be determined the sample thickness and optical constants.

Ellipsometry has been successfully used at high temperatures up to 790 °C (2150 °F) as early as the 1970s.^{1,2} Since then it has been widely used at high temperatures to measure the effect of variables (such as temperature, oxygen concentration, or environment flow rate) on the rate of oxide film growth.^{1,3,4} Furthermore, ellipsometry has also been used to measure the effect of exposure of supercritical carbon dioxide on the thickness of silicon film.⁵ The technique has also been used in pressurized and heated experiments in conditions up to 50 °C and 12.13 MPa (1,760 psi) or 100 °C and 100 MPa (1,450 psi).^{5,6} However, no examples of *in-situ* ellipsometry coupled with HPHT environmental exposures have been reported in the technical literature, and for many applications of technical interest, the use of this technique in HPHT environments will further the current understanding of oxide film formation and growth to better predict material performance.

Material Degradation in Supercritical CO₂.

Oxy-combustion gas turbine systems using sCO₂ have the potential to be used for the production of electricity while reducing CO₂ gas emissions. Unlike conventional gas turbines, oxy-combustion gas turbines operate at very high pressure and high temperature with sCO₂. Achieving long design life for these components will require careful material selection based on various properties such as environmental degradation, mechanical properties, or thermal conductivities. Oxidation behavior must be well understood because it can cause the initiation and growth of cracks, and, ultimately, failure.

Three types of alloys are used in high temperature sCO₂ (considered to be above 400 °C) based on the ASME Boiler & Pressure Vessel Code, Sec. VIII Div 1 and Div II:

- Martensitic/Ferritic stainless steels (up to approximately 20% chromium),
- Austenitic stainless steels (16 to 30% chromium and 2 to 20% nickel), and
- Chromium-nickel alloys.

The temperature ranges of those alloys are summarized in Table 1.⁷

Table 1
Temperature range of different types of alloys considered for use in high-temperature sCO₂.
Green means that the alloys are acceptable; red means that the alloys should not be used

Temperature (°C)→	300	350	400	450	500	550	600	650	700	750	800
Type of alloy↓											
Martensitic/Ferritic Stainless Steel											
Austenitic Stainless Steel											
NiCr alloys											

The resistance to oxidation in sCO₂ of those alloys is usually studied by measuring mass changes and establishing the composition and thickness of the oxide film, before and after exposure, using scanning electron microscopy / energy dispersive X-ray spectrometry (SEM/EDS). The oxidation behavior has been found to depend primarily on the type and composition of the material and on the temperature. Pressure has been widely assumed to have negligible effects on oxidation as long as carbon dioxide is supercritical.

Martensitic and ferritic stainless steels cannot be used in temperatures above 450 °C. Austenitic stainless steels can be used in temperatures below 650 °C. Nickel-chromium alloys are the only alloys that are useable at temperatures up to 750 °C although they may show intergranular corrosion at lower temperatures, as was observed on Inconel 718 and 738 at 700 °C and 25 MPa.⁸

In addition to oxidation, exposure to high temperature sCO₂ can also result in carburization in stainless steels. The carbon penetrates through the grain boundaries and reacts with the chromium present to form chromium carbide. Carburization underneath the oxide layers of stainless steel 316 resulted in oxide spallation at 650 °C and 20 MPa.⁹ The presence of intergranular corrosion or spallation may lead to crack growth when the material is under stress due to static and/or cyclic pressurization, potentially culminating in failure.

Furthermore, O₂ and H₂O contamination (intended or not) has long been considered to be an aggravating issue for oxidation in sCO₂. Some oxy-combustion systems will intentionally contain oxygen. However, it has only been studied at low pressures of 0.1 MPa,^{10,11} and there is a lack of information at higher pressures. The increase in contaminant water concentration likely increases the corrosivity of sCO₂,^{12,13} but it is unclear whether O₂ is beneficial or detrimental.^{14,15}

As it is often found during oxidation, the growth rates of oxide films are not linear in sCO₂. This has been widely reported in the literature using mass gain measurement (Figure 2(a)) and confirmed by using SEM measurement (Figure 2(b)).

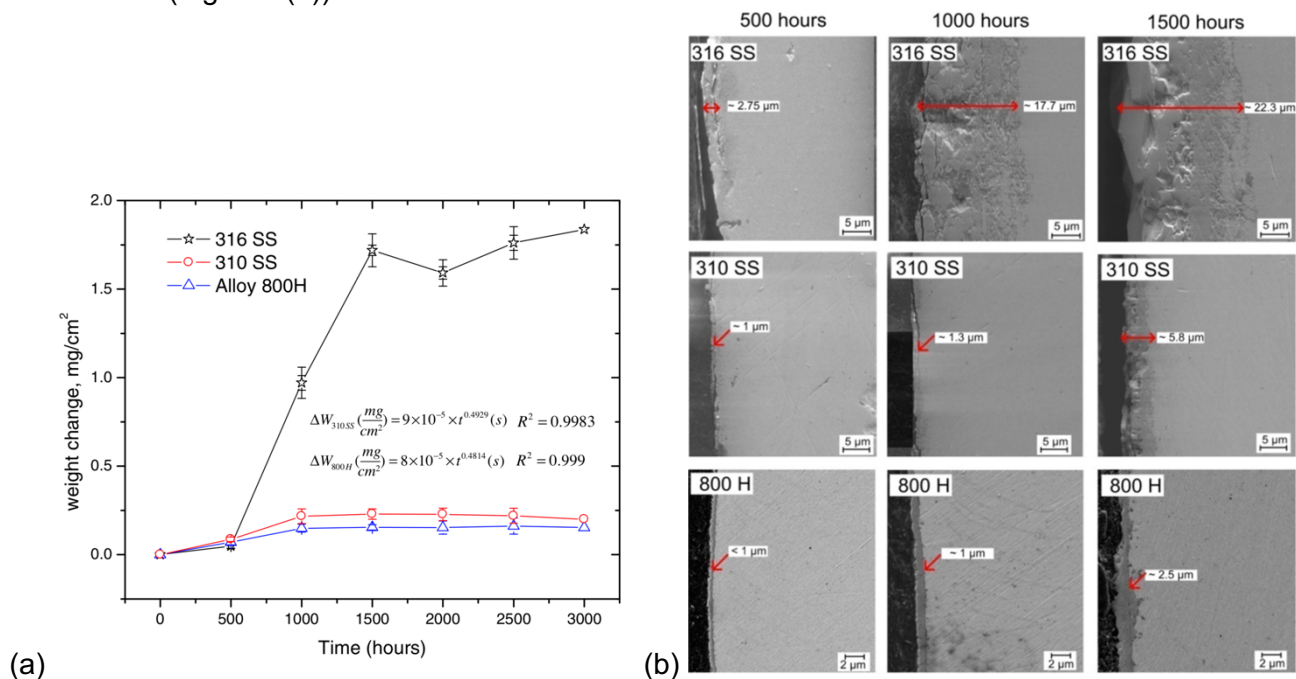


Figure 2. (a) Weight gain and (b) SEM cross sectional images of the three alloys after exposure to sCO₂ (650 °C and 20 MPa) for 500, 1000, and 1500 h, showing the oxide corrosion product layer.⁹

The understanding of the oxidation mechanism is limited by the quantity of data sets available when the technique requires the specimens to be removed from an autoclave. In this example, the stabilization of oxide film growth occurs in less than 1500 hours. This is based on only four sets of datapoints during that time frame. The ability to measure oxide film growth rates *in-situ* would provide more data, improving the understanding of the mechanism. Measuring thickness change smaller than 1 μm would also result in an improved resolution, especially relevant for alloys with small corrosion rates (such as alloy 800H in above figure).

EXPERIMENTAL PROCEDURE

There were two major technical objectives in this project:

1. Develop a single wavelength, single angle, uniaxial ellipsometer system that can be used to measure specimen thickness changes in HPHT environments.
2. Perform measurements of oxide film thickness growth rate on stainless steel and nickel alloys *in-situ* in supercritical carbon dioxide.

Ellipsometer in High Pressure and High Temperature Vessel

The assembly of the *in-situ* ellipsometer was divided into two parts: the optical ellipsometer and the high pressure and temperature test vessel.

Ellipsometer.

The ellipsometer was custom-built based on a technique called null ellipsometry. The ellipsometer consists of a light source (laser) $\Rightarrow$ polarization state generator (compensator) $\Rightarrow$ sample $\Rightarrow$ polarization state detector (linear polarizer) $\Rightarrow$ detector (camera). To perform a measurement, the orientation of the polarizer, compensator, and analyzer are adjusted to “null”, or extinguish, the light hitting the detector. Usually performed manually, this measurement technique is slow but appropriate for single wavelength measurements. Assuming quality optical elements, the null configuration is accurate and has low systematic errors.

A 10 mW, Class IIIb, 655 nm laser diode was used as the source. A Berek's compensator and rotating linear polarizer were added to control the polarization of laser light. A USB camera was used for detection. The assembled components are shown in Figure 3.

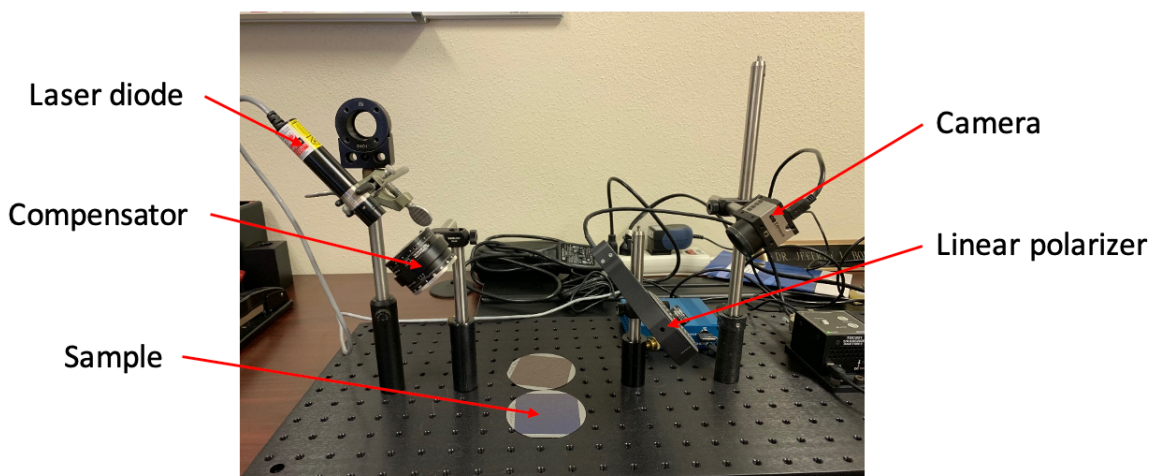


Figure 3: Assembly of the various components of the ellipsometer.