

## Early Stage Oxide Films on Metallic Alloys

Jacob Norman, Jaymn Singh, Jordyn Park, Matthew Irwin and Vilupanur Ravi  
California State Polytechnic University, Pomona  
3801 W. Temple Ave  
Pomona, CA, USA, 91768

### ABSTRACT

The objective of this study was to characterize oxide films during the early stages of oxidation at high temperatures. Oxide films formed on three metallic alloys - UNS N08330, UNS G10950 and UNS R50400 - were characterized using a broad range of techniques. Test coupons were diamond polished to a 1  $\mu\text{m}$  finish prior to heating in air to different temperatures for varying time increments, between 10 to 240 minutes. The surface of the oxide film was characterized using spectral reflectometry. Data from the spectral analysis provided insights into the reflectivity in the visible light spectrum for each oxide film. The data were also analyzed to calculate the total reflectance of the oxide film. Film thicknesses were determined using ellipsometry. Additional insights into film morphology were obtained using atomic force microscopy and scanning electron microscopy.

Key words: High Temperature Oxidation, Thin Films, Test Methods, Discoloration

### INTRODUCTION

High temperature oxidation of metallic alloys is a complex phenomenon involving multiple processes such as the arrival of gaseous species at the surface of the materials, solid state diffusion, creation, and movement of defects in the material<sup>1</sup>. During the initial stages of oxidation, very thin films of oxides are formed on the surface of the metal<sup>2</sup>. This phenomenon can, in turn, be used to characterize the overall oxidation processes. By analyzing alloys common in a variety of industries, oxide films can be studied to analyze their growth in high temperature environments. UNS N08330, UNS R50400, and UNS G10950 will be the three metallic alloys of interest due to their multitude of uses. Stainless steels, which include UNS N08330, are used for a variety of applications, such as power generation units and high temperature boilers<sup>3,4</sup>. Titanium alloys, including UNS R50400, are used for a combination of their lightweight and high strength in elevated high temperature applications such as gas turbines<sup>5</sup>. In general, these alloys used for high temperature applications face complications such as oxidation susceptibility, fast oxide growth, and environmentally induced stress corrosion cracking<sup>2-6</sup>. There have been many studies on the high temperature oxidation of these materials related to the typical complications; however, the onset and initial rate of the oxide growth has yet to be fully understood. This paper examines the initial oxide films in order to further understand oxide film growth and

development using different spectral analysis techniques, primarily focusing on optical properties and their relationship to film thickness.

## EXPERIMENTAL PROCEDURE

Nominally 4 mm thick coupons of stainless steel (UNS N08330), high carbon steel (UNS G10950), and commercially pure grade two titanium (UNS R50400) were cut from rods of 0.5-inch (12.7 mm) in diameter. Coupons were ground with silicon carbide at 240, 400, 600, 800 and 1000 grit. Subsequently, the coupons were polished from 6 to 1  $\mu\text{m}$  with diamond suspended, glycol-based solution. The polished coupons were heated to different temperatures for each material, 450°C for UNS G10950, 500°C for UNS R50400, and 600°C for UNS N08330, starting at lab air conditions. Each material had the same time intervals ranging from 10 to 240 minutes: 10, 30, 60, 90, 120, and 240. The furnace temperature was increased at a rate of 25°C per minute from room temperature. The coupons were analyzed using macro photography, optical reflective analysis, ellipsometry, and atomic force microscopy. Macro and microphotographs were also taken from the normal to the oxidized surfaces of the coupons. Spectral reflectance measurements were taken using a customized optical arrangement that scanned the entire top surface of the coupon. The reflectometer was set to a baseline measurement to determine overall surface reflectance instead of analyzing for specific colors. Ellipsometry was utilized to determine the thickness measurements of the oxide films at targeted points. Atomic force microscopy was used to collect data on the surface morphology of the thin films.

## RESULTS

The UNS N08330 coupons in Figure 1 all had distinct color changes of the topmost oxide layer that corresponded to the time exposed to high temperatures. The golden oxide layer on sample 13 quickly shifted colors to a darker orange. The next scale color was blue with a purple under-tone and the oxide scales on sample 16 shifted to a purple color with an orange under-tone. Sample 17 had a silver-toned oxide layer that transformed back into purple with an orange under-tone. Samples 15 and 18 had the same color oxide scales, but the reflectance values were drastically different. This difference can be observed in the reflectance spectra in Figure 2. This spectrum revealed that the total percent reflectance increased as the oxidation time increased. Furthermore, the wave functions demonstrated a slope of higher magnitudes as the testing time increased. All the samples started between 5-30 percent reflectance values and then increased as the applied wavelength increased. Two distinct trends regarding the slope magnitude were observable when examining the increase in total percent reflectance of the N08330 samples. As shown in Figure 3, there is a higher slope magnitude for the total percent reflectance during the first 90 minutes of exposure to the high temperature environment. However, the rate of change decreased for the samples between 90 and 240 minutes. These values are consistent with the coupon pictures in Figure 1 since the coupons generally became brighter as the oxidation time increased.

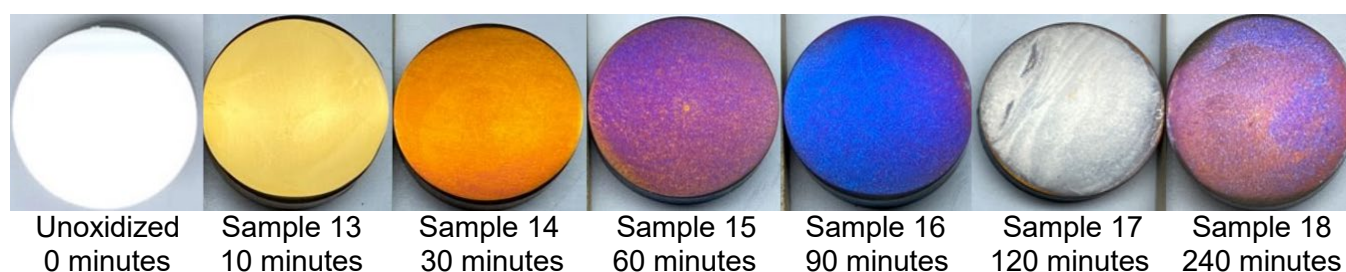


**Figure 1: The UNS N08330 Sample Palette**

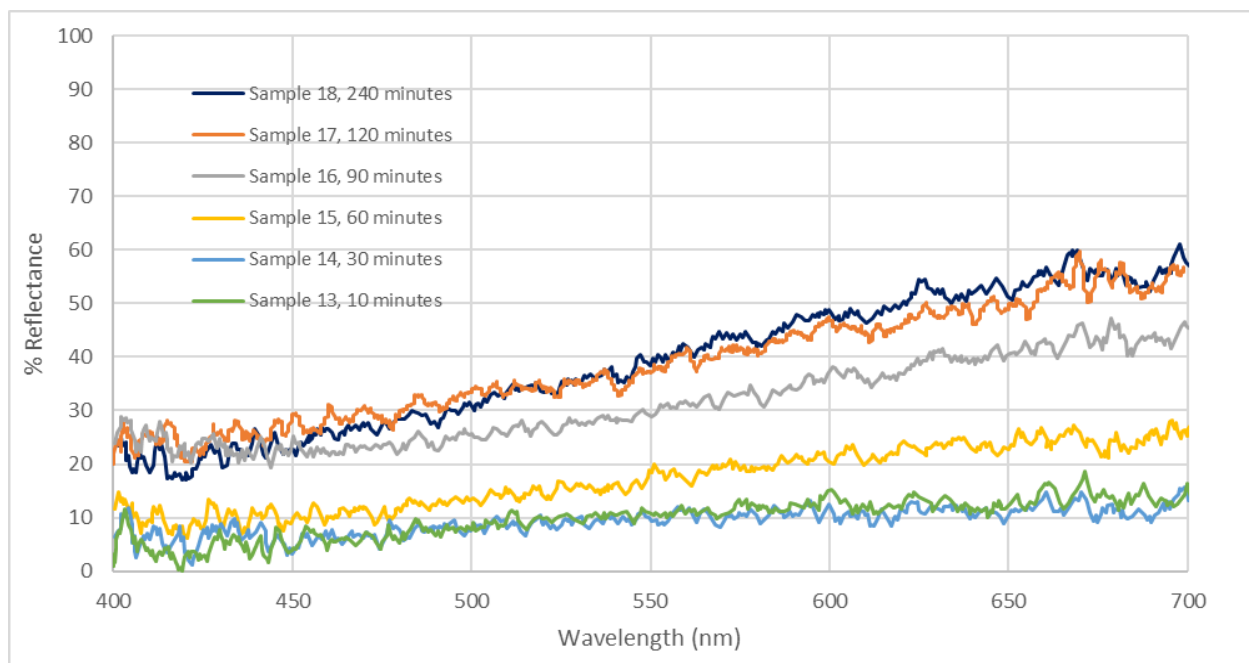


**Figure 2: The UNS N08330 Reflectance Spectra**

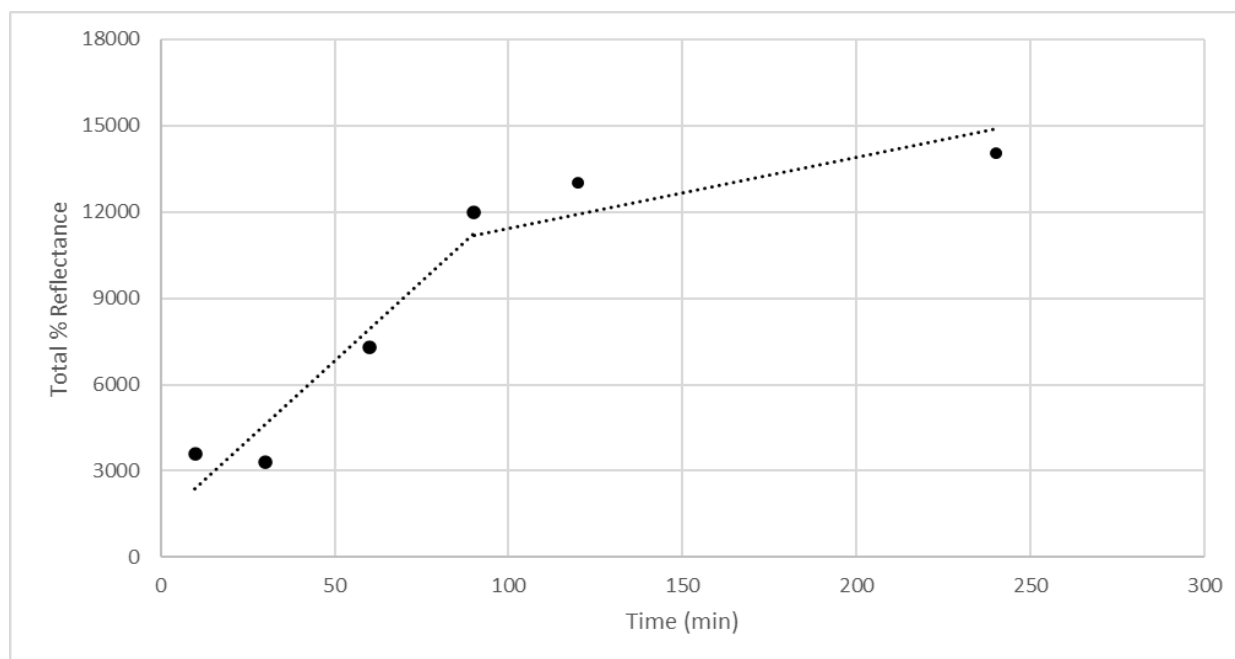


**Figure 3: The UNS N08330 comparison plot of the total percent reflectance against the oxidation time in minutes**

The UNS G10950 coupons had relatively small changes in the color of their oxide films and these coupons did not demonstrate the dynamic color changes observed in the UNS N08330 samples. The oxide scales, seen in Figure 4, started as a blue color with a grey-undertone and then transitioned into a gray scale. Sample 31 demonstrated more of a silver color while sample 32 exhibited a more intense grey hue. Sample 33 seemed to have lightened in hue before darkening again in sample 34. The transition between sample 34 to sample 35 exhibited the most drastic color change from a grey-brown

to a dark black color. Overall, the UNS G10950 coupons demonstrated a different reflectance pattern compared to the UNS N08330 coupons. Examining Figure 5, sample 30 exhibited nearly constant reflectance values relative to wavelength. Sample 31 exhibited a minimal degree of reflectance increase relative to wavelength; however, this increase in reflectance value decreased to the original value toward the end of the spectra. Sample 32 increased steadily until plateauing near the higher wavelengths. On the other hand, sample 33 displayed the most dynamic wave function in that a linear trend was observed until 550 nm of wavelength and became nearly parabolic after. Sample 34 exhibited a similar pattern to sample 33; however, sample 34 did not exhibit the distinct cut off in reflectance observed at the higher wavelengths. Sample 35 exhibited a similar pattern to sample 32 with an overall higher percent reflectance value throughout the entire domain. The G10950 coupons had two distinct trends, as seen in Figure 6, where the first trend was positive while the other showed a decrease in total percent reflectance with respect to oxidation time. The comparison between samples 30, 31, 32, and 33 suggested that samples increased in terms of overall reflectance until reaching a local maximum at 90 minutes of oxidation time. The first three samples, 30, 31, and 32, demonstrated relatively similar total percent reflectance values. Sample 33 was an outlier relative to all other UNS G10950 samples demonstrating notably high total percent reflectance values. Samples 34 and 35 had lower total reflectance values relative to sample 33, despite the increased oxidation time.

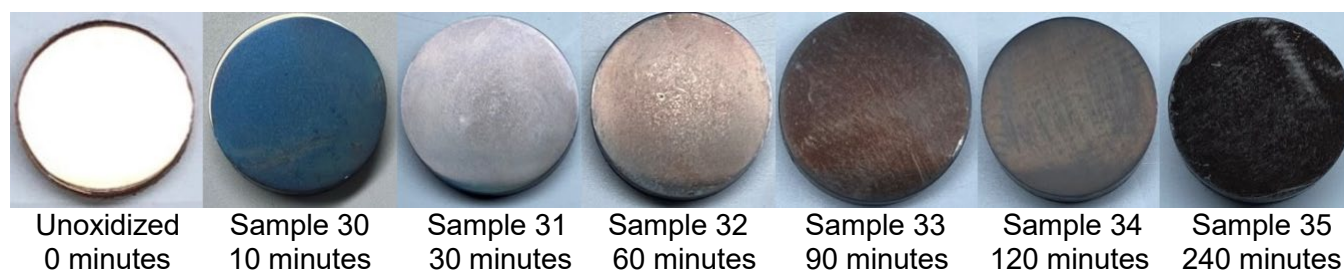


**Figure 4: The UNS G10950 Sample Palette**

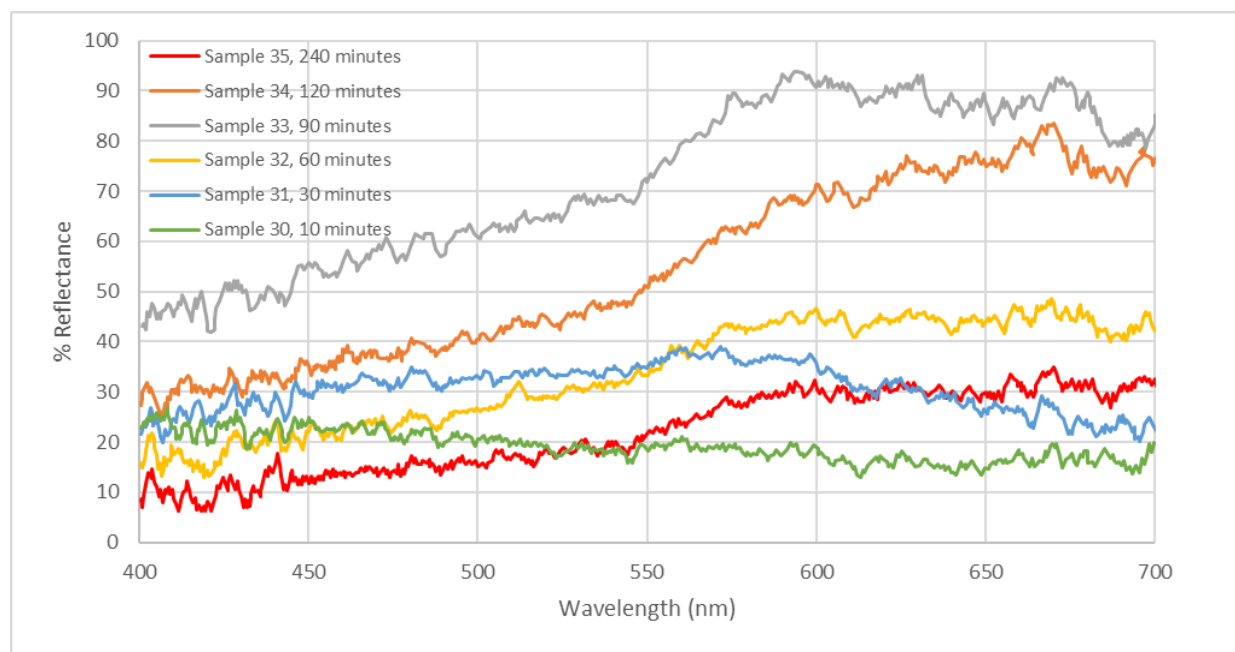


**Figure 5: The UNS G10950 Reflectance Spectra**