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SURFACE FILM THICKNESS DETERMINATION
BY REFLECTIVITY MEASUREMENTS*

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ABSTRACT

The thicknesses of UO_2 films from 100 to 1800 Å on uranium substrates were determined from reflectivity measurements in the visible region. The reflectivity measurements on the U- UO_2 system were analyzed by two different methods to determine film thicknesses. In the first method, film thicknesses were determined by comparing theoretical reflectivity calculations with the experimental reflectivity measurements. In the second method, film thicknesses were determined by obtaining the best match of the colorimetric properties (wavelength, excitation purity, and luminous reflectance) of the sample with the colorimetric properties of a predetermined film thickness calibration curve.

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INTRODUCTION

In manufacturing processes involving chemically reactive metals, the condition of the metal surface is often critical at certain stages of the process. For example, surface films produced by the atmospheric oxidation or contamination by lubricants or chemicals can cause difficulties in subsequent welding or brazing operation or can in themselves be unacceptable for the ultimate application of the component. Thus, a quantitative technique would be useful for certifying the condition of a metal surface.

One way of accomplishing this is by obtaining the reflectivity spectrum (fraction of incident light reflected by the surface as a function of wavelength) of the surface for the visible wavelength region. The reflectivity spectrum of a surface completely and quantitatively describes the visual appearance of the surface. The problem then is to reduce the reflectivity spectrum to a single quantity describing the surface condition of the part. The most obvious quantity is the thickness of the surface layer. This paper describes two methods of determining the surface layer thickness from the reflectivity spectrum in the visible region.

THICKNESS DETERMINATION METHODS

Method of Comparing Theoretical and Experimental Reflectivity Values

In this approach, theoretical reflectivity calculations are utilized to determine film thickness by comparison with experimental normal incidence reflectance data.

For the simplified case of normal incidence, the reflection coefficient of a single absorbing film on an absorbing substrate is given by ^{1,2}

$$\hat{r} = |r| \exp(i\delta) = \frac{\hat{r}_{12} + \hat{r}_{23} \exp(-\beta i)}{1 + \hat{r}_{12} \hat{r}_{23} \exp(-\beta i)}$$

with the reflectivity, R, given by

$$R = |r|^2 .$$

Here $\hat{r}_{12}$ and $\hat{r}_{23}$ are the Fresnel reflection coefficients for the air-film and film-substrate interfaces, respectively:

$$\hat{r}_{12} = \frac{\hat{n}_2 - n_1}{\hat{n}_2 + n_1} \quad \text{and} \quad \hat{r}_{23} = \frac{\hat{n}_3 - \hat{n}_2}{\hat{n}_3 + \hat{n}_2} .$$

The quantity β is given by

$$\beta = 4\pi\hat{n}_2 d/\lambda .$$

In these expressions:

λ = the vacuum wavelength of the light,

d = the film thickness,

n_1 = the refractive index of the surrounding medium ($n_1 = 1$),

$\hat{n}_2 = n_2 - k_2 i$; the complex refractive index of the film,

$\hat{n}_3 = n_3 - k_3 i$; the complex refractive index of the substrate, and

$i = (-1)^{\frac{1}{2}}$

The film thickness is determined by finding the film thickness, d , which minimizes the least squares expression

$$\sum_{\lambda} \left[R_{\lambda}^{\text{exp}} - R_{\lambda,d}^{\text{calc}} \right]^2$$

Here R_{λ}^{exp} is the experimental reflectivity at a specific wavelength and $R_{\lambda,d}^{\text{calc}}$ is the theoretical reflectivity at a specific wavelength and thickness. It must be noted that it is necessary to know the optical constants of the film and substrate to use this method. In this work, these were found for the material studied by ellipsometric measurements.

Color Analysis Method

Changes in color are observed with the growth of a film on a metal surface. The colors are caused by interference between light reflected at the air-film and film-metal interfaces

and have been used to observe film formation on metals.³ This phenomenon suggests that the experimental reflectivity spectra be subjected to a color analysis in order to obtain a calibration curve of color parameters versus film thickness. This calibration curve can then be used to determine thickness from the color parameters of unknown samples.

The properties selected to define the colors of the samples in this study are luminous reflectance, wavelength, and excitation purity. These properties were determined for type C illumination which represents average daylight.⁴

The method used to calculate these color properties from the reflectivity spectrum was to calculate the tristimulus values using the selected ordinate method.⁵ The tristimulus values are given by

$$X = \frac{\int_0^{\infty} \bar{x}_{\lambda} P_{\lambda} \rho_{\lambda} d\lambda}{\int_0^{\infty} \bar{y}_{\lambda} P_{\lambda} d\lambda}$$

$$Y = \frac{\int_0^{\infty} \bar{y}_{\lambda} P_{\lambda} \rho_{\lambda} d\lambda}{\int_0^{\infty} \bar{y}_{\lambda} P_{\lambda} d\lambda}$$

$$x = \frac{\int_0^\infty \bar{x}_\lambda P_\lambda \rho_\lambda d\lambda}{\int_0^\infty \bar{y}_\lambda P_\lambda d\lambda}$$

Here $\bar{x}_\lambda$, $\bar{y}_\lambda$, and $\bar{z}_\lambda$ are the tristimulus values of the spectrum adopted by the International Commission on Illumination; P_λ is the spectral distribution of the luminating light source, ρ_λ is the reflectivity, with λ representing the wavelength. The tristimulus value Y is the luminous reflectance. Chromaticity coordinates x and y are related to the tristimulus values by

$$x = \frac{X}{X + Y + Z} \text{ and}$$

$$y = \frac{Y}{X + Y + Z}$$

Thus by using the chromaticity diagram, the excitation purity (saturation) and wavelength (hue) are determined.

By calculating the color parameters for samples with known film thicknesses varying over the thickness range of interest, calibration curves are prepared. The surface film thickness of an unknown sample is then obtained from its reflectivity data by first calculating the three color properties. Then the best match to the calibration curves is determined by finding the film thickness, d, which minimizes the error

given by

$$E = \left[Y^{exp} - Y_d^{cal} \right]^2 + \left[P^{exp} - P_d^{cal} \right]^2$$

and satisfies the criterion that the wavelength region of the calibration curve at that film thickness agrees with the wavelength determined for the sample of unknown film thickness.

In this expression,

Y^{exp} = luminous reflectance determined from experimental reflectivity data,

Y_d^{cal} = luminous reflectance obtained from calibration curve at specific film thickness,

P^{exp} = excitation purity determined from experimental reflectivity data, and

P^{cal} = excitation purity obtained from calibration curve at specific film thickness.

EXPERIMENTAL METHODS

The U-UO₂ system was studied to demonstrate the thickness determination methods. Polished uranium metal coupons were slowly oxidized by heating them in air at approximately 100°C. The oxide film formed under these conditions was verified by X-ray diffraction analysis to be UO₂. As the samples oxidized, concurrent ellipsometric measurements and reflectivity measurements in the wavelength range 425 to 650 mμ were taken.

The reflectivity measurements were made with a system consisting of a bifurcated fiber optics reflectivity probe and a visible-near infrared spectrophotometer. The measurements were made relative to an evaporated aluminum front surface mirror standard.

Film thicknesses used for comparison purposes and to prepare the calibration curve were determined using ellipsometry. The wavelength of light used was 546.1 $m\mu$ and the angle of incidence was 70.00°. The ellipsometric measurements were used to calculate film thicknesses directly using the method of McCrackin and Colson.⁶ To make these calculations, the refractive indices of the film and substrate must be known. The refractive index of uranium at 546.1 $m\mu$ was previously determined⁷ to be 2.79-404i. This value is for a "clean" uranium surface in which the oxide film was removed by argon ion bombardment. The refractive index of the UO_2 film (2.2-0.44i) was determined by standard ellipsometric techniques from experimental ellipsometric measurements taken periodically as the uranium sample oxidized.⁶

RESULTS

Comparison of Theoretical and Experimental Reflectivity Values

The indices of refraction of the substrate and film determined ellipsometrically at 546.1 $m\mu$ were used over the entire wavelength region from 425 to 650 $m\mu$. Since there is little variation of the optical constants of UO_2 over this small wavelength range, the use of the optical constants at 546.1 $m\mu$ for the reflectivity calculations would have little effect on the results.

The reflectance data were analyzed over the thickness range 0 to 1800 Å in 10 Å increments. These results compared to the absolute (ellipsometric) thicknesses are shown in Figure 1.

The results are in close agreement with the absolute thicknesses except in the regions around 300 and 1300 Å. This is caused by the similar reflectance curves obtained in these film thickness regions.

Color Analysis Method

At the oxidation conditions used, uranium was found to oxidize by the following color sequence: silver, yellow, red brown, violet, blue, second order silver, second order yellow, and gray. The wavelength, excitation purity, and luminous reflectance as a function of the thickness determined ellipsometrically are shown in Figure 2. The data are for the oxidation of three samples. The chromaticity wavelengths as a function of thickness are represented by four regions. The two regions at 570-610 and 450-500 mμ are for yellow, orange and blue colors, respectively. The region indicated by a 1 in the figure includes the wavelengths rotated on the chromaticity diagram from 610 mμ through the complementary wavelengths to 450 mμ. This is the transistion zone where the color of the sample changes from the yellow, orange region to blue.

The region shown by a 2 in Figure 2 is for the wavelengths from 500 to 570 $m\mu$, and it is the transition region where the sample changes from blue to the yellow, orange range.

As stated before, the colorimetric properties as a function of thickness provide a method to determine film thickness from a sample's reflectivity measurements. Once a calibration curve of the colorimetric properties as a function of thickness is obtained, the film thickness can be determined from its reflectivity spectrum. The experimentally determined wavelength, excitation purity, and luminous reflectance of the specimen are matched with the calibration curve to determine film thickness. The reflectance data were analyzed in this manner using calibration points from 0 to 1800 $\text{\AA}$ in 10 $\text{\AA}$ increments. The results compared to the absolute (ellipsometric) thicknesses are shown in Figure 3.

The discrepancies in film thicknesses occur in the same thickness regions as the previous thickness determinations that utilized theoretical reflectivity calculations. This ambiguity arises because of the similarity of the reflectance curves of the first and second order yellow. By examining the calibration curves (Figure 2) it is noted that colorimetric data between film thicknesses of approximately 250 and 350 $\text{\AA}$ is similar to colorimetric data between film thicknesses of 1100 to 1500 $\text{\AA}$. Thus in these regions,

thickness determinations from reflectivity measurements in the wavelength range of 425 to 650 $m\mu$ are ambiguous. This ambiguity can be removed by extending the reflectivity measurements to the near infrared. Figure 4 shows the reflectivity spectrum of uranium with film thicknesses of 284 and 1274 $m\mu$. The reflectance curves are very similar between 425 and 650 $m\mu$ with a marked difference in the near infrared.

CONCLUSIONS

Spectral reflectance measurements were used to determine surface film thicknesses by two different methods. In the first method, film thicknesses are determined by comparing theoretical reflectivity calculations with experimental reflectivity measurements. The second method utilizes the phenomenon of interference colors caused by thin films on a metal surface. The reflectivity measurements are used to determine the colorimetric properties (wavelength, excitation purity, and luminous reflectance). By comparing the colorimetric measurements of a sample with a predetermined calibration curve of the colorimetric properties as a function of thickness, the thickness of the sample can be determined. In both methods, confusion can result from the similarity of the visible reflectance spectrum between first and second order colors. This ambiguity can be resolved by taking reflectivity measurements in the near infrared.

To use these methods, the type of film-metal surface system must be known. The first method requires a knowledge of the refractive indices of the metal substrate and film while in the second method it is necessary to make independent thickness measurements to prepare the colorimetric calibration curves. The second method offers the advantage that the calibration curves for the metal-film system are prepared using similar preparation and environmental conditions that the metal will experience. Thus, if the theoretical reflectivity equation for thin films fails to describe the actual metal-film system, method two will still work.

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FIGURES

Figure 1 Film thickness determined by comparison of experimental reflectivity with theoretical reflectivity calculations versus ellipsometric thickness.

Figure 2 Wavelength, excitation purity, and luminous reflectance as a function of ellipsometric thickness for U-UO₂ system. The wavelengths are represented by four regions. Region indicated by 1: dominant wavelengths 610 to 780 mμ; complementary wavelengths 493_c to 567_c mμ; and dominant wavelengths 380 to 450 mμ. Region indicated by 2 is for dominant wavelengths from 500 to 570 mμ.

Figure 3 Film thickness determined by color analysis method versus ellipsometric thickness.

Figure 4 Reflectivity spectra for UO₂ films on uranium substrates.

Fig. 1

Fig. 2

color analysis thickness (Å)

ELLIPSOMETRIC THICKNESS (Å)

Fig. 3

Fig. 4