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AN ELLIPSOMETRIC STUDY OF THE CORROSION
OF URANIUM AND URANIUM-7.5 WEIGHT
PERCENT NIOBIUM-2.5 WEIGHT
PERCENT ZIRCONIUM ALLOY

R. E. Sladky

UNION CARBIDE CORPORATION
NUCLEAR DIVISION
OAK RIDGE Y-12 PLANT

operated for the **ATOMIC ENERGY COMMISSION** *under* **U. S. GOVERNMENT Contract W-7405 eng 26**

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ABSTRACT

The ellipsometric method was used to study the sputter cleaning and oxidation of uranium and uranium alloy coupons. A calculation was made of the refractive indexes of the metals and their oxides. Corrosion curves were drawn for several different temperatures for film thicknesses up to 4500 Å, and the equations of the curves were determined. A study was made of the effect of tensile stress on the ellipsometric data.

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SUMMARY

The ellipsometric method was used to study the sputter cleaning and oxidation of coupons of uranium and the uranium-7.5 weight percent niobium-2.5 weight percent zirconium alloy (Mulberry). The refractive index of the clean surface of both of these metals and of their oxides was measured.

Corrosion films as thick as 1500 Å on uranium and 4500 Å on Mulberry were obtained by accelerating the corrosion rates at elevated temperatures. As the thickness of the oxide films increased beyond 750 Å, the refractive indexes changed and the films seemed to become multilayered. Five refractive indexes were used to cover the total film thickness of 4500 Å on the basis of a multilayered film; seven refractive indexes were used when the "average" characteristics of the entire film were considered to change. A single gradient of refractive index could not be used to cover the entire range of film thickness. The effect of stress in the film on the ellipsometer reading was shown to be too small to account for the observed change in the refractive index.

Corrosion curves (film thickness plotted against a function of time) were obtained at several temperatures. The curves were straight lines when plotted as log-log or $\sqrt[3]{\text{time}}$ functions. The equations of the curves were also obtained.

INTRODUCTION

Metal corrosion is costly to industry not only because of the deterioration of manufactured goods but also because of the difficulties created in some fabrication processes. In the field of metal bonding, poor adhesion is frequently due to a film of oxide or other foreign material at the interface. Often, oxide films form so rapidly that a surface is never free of contamination except in an ultra-high vacuum. As industrial processes have become more sophisticated, the importance of corrosion films has also grown. Diffusion bonding, the welding of two surfaces using only pressure, for instance, can only be achieved if there is no oxide on the surfaces.

The presence of a corrosion film, usually an oxide, can be studied or detected with the electron microscope, electron diffraction and X-ray diffraction instruments, electron and proton microprobes, spark source mass spectrometer, interferometer, and ellipsometer. With the exception of the interferometer and ellipsometer, all of these instruments are restricted to small samples and the procedure is destructive. The interferometer can only measure film thickness, and then only if there is a step between the film and substrate. The sample size is no problem with the ellipsometer, as long as it is reasonably flat and specularly reflecting. The measurement is nondestructive in the sense that a sample coupon can be measured periodically for years. Samples can be sealed in containers filled with various atmospheres and measured through windows. Solutions can also be used if bubbles and discoloration can be avoided.

The ellipsometer has been used to study corrosion films on silicon, iron, nickel, aluminum, and a few other metals. This report reviews the information that has been obtained on uranium and the uranium-7.5 weight percent niobium-2.5 weight percent zirconium alloy (Mulberry). Experimental results only are reported; a discussion of the theories of corrosion is beyond the scope of this report.

CORROSION STUDIES USING THE ELLIPSOMETER

LABORATORY EQUIPMENT AND TECHNIQUES

The Ellipsometer

The ellipsometer is an optical instrument which has the capability of polarizing light and measuring the change in the state of polarization caused by reflection from or transmission through a specimen. The changes in the state of polarized light are functions of the refractive index of the substrate, the refractive index and thickness of all the films on the surface of the substrate, and the refractive index of the immersion medium. Under ideal conditions, ellipsometry can measure differences in film thickness of less than one angstrom.

Figure 1 presents a view of an ellipsometer. Light from a mercury vapor lamp is filtered to pass the green spectral line ($\lambda = 5461 \text{ \AA}$). The light is then collimated, polarized, and passed through the quarter-wave plate or compensator. The compensator's fast axis is always set to

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Figure 1. THE ELLIPSOMETER.

+ or - 45 degrees to the plane of incidence. In this way, light passing through the polarizer and compensator is elliptically polarized. The rotation of the polarizer must be such that the characteristics of this elliptically polarized light, which is incident upon the specimen, are opposite to the effect that the specimen will have upon the light. After reflection from the specimen, the light will again be linearly polarized and can be extinguished by the analyzing prism. The analyzer, like the polarizer, is mounted in a rotatable circle graduated to 0.01 degree. However, the entire analyzer arm can rotate about a central axis so that the angle of incidence of the light on the specimen can be varied. A photomultiplier monitors the analyzer output, and the extinction point is determined by finding the point of minimum current. At this point the angles of the polarizer and analyzer are read and recorded. These are the only data obtained.

Ellipsometer alignment was made following the procedure suggested by McCrackin.⁽¹⁾ The ellipsometer was used at an angle of incidence of 60 or 70 degrees for all the data in this report. The chosen angle is specified where necessary. By convention, all polarizer and analyzer angles are considered positive when measured in a counterclockwise direction from

the plane of incidence when looking toward the light source. The scales of this ellipsometer were calibrated to read positive angles in a clockwise direction from the plane of incidence when used in the manner of McCrackin; that is, with the compensator mounted before the specimen.

The constants of an ellipsometric study are: the angle of incidence, usually 60 or 70 degrees; the wavelength of the incident light, 5461 Å; and the position of the quarter-wave plate. The data obtained from the instrument are: the angle of the polarizer and the angle of the analyzer, which are read when the beam of light is at the null point; ie, when the intensity of the reflected light is at a minimum. The angle of the polarizer is related to Δ , which is the phase difference between the light reflected from the specimen and the light incident upon it, while the angle of the analyzer is related to ψ , the arctangent of the factor by which the amplitudes of the polarized beams are reduced by the reflection.

The equations of ellipsometry, which relate the measured polarizer and analyzer angles, the other parameters, and the refractive indexes of the substrate and film to the thickness of the film, have been published and discussed many times in the literature,⁽¹⁻⁹⁾ often with reference to some specific problem.⁽¹⁰⁻¹⁴⁾ These equations consist of complex numbers and several computer programs have been written for the solution.⁽¹⁵⁻¹⁷⁾

The compensator, or quarter-wave plate, previously mentioned, is constructed of mica. Mica has the unique property of possessing a refractive index different for two paths at right angles through it. The thickness of the plate is such that, for a wavelength of 5461 Å, polarized light passing through the mica on one axis is retarded in phase by 90 degrees or 1/4 wave with respect to light passing through it on the perpendicular axis. From this phenomenon arises the terms "fast" and "slow" axes. It has been shown^(4, 5, 9) that the exact retardation should be used in computations and that the ratio of the transmission along the fast axis to the transmission along the slow axis of the wave plate must also be considered. This latter ratio was measured and calculated to be 1.0128, using one of the computer programs.⁽¹⁶⁾ The retardation of the compensator was also computed by two methods and found to be 92.8⁽¹⁶⁾ and 92.2 degrees,⁽⁸⁾ respectively. These results are sufficiently close to the required values of 1.00 and 90.0 degrees that no special corrections were necessary for the quarter-wave plate in the present work. However, the averaging technique⁽¹⁾ was used routinely; which, for small compensator errors, is essentially the same as using a more elaborate calculation.⁽¹⁸⁾ This approach leads to the simplification that $\Delta = 90^\circ + 2p$, and $\psi = a$, where p and a are the averages of the polarizer and analyzer readings taken in the four zones.⁽¹⁾ Then it is possible to plot the working curves of the polarizer angle versus analyzer angle, marking off the film thickness on the curve, and to convert quickly from ellipsometer readings to film thicknesses without using the computer program.

Terminology Used to Describe the Complex Refractive Index

The terminology used in this report to describe refractive indexes conforms to the Muller-Nebraska convention.⁽⁷⁾ Schematic drawings of two specimens are presented in Figures 2 and 3. The first of these shows a single film on a substrate; the second shows five individual films upon a substrate. The specimen consists of the substrate, which may be either a metal or a dielectric, upon which there are one or more films. These films may also

Figure 2. REFLECTION FROM A FILM-COVERED METAL SURFACE.

be metals, for example aluminum on glass or some other metal, or they may be dielectrics such as some metal oxides (some of which are semiconductors). Specimens are in some medium (generally air), although they may be in vacuum (eg, in the sputtering chamber), or they may be a liquid when electrochemical studies are being made. The thickness of any or all films may be zero.

The complex refractive index of any of these is defined as:

$$n_c = n - ik,$$

where "n" and "k" can simply be referred to as the real and imaginary parts of the refractive index and "i" as the square root of -1. The ratio of the speed of light in vacuum to the speed of light in some other material is denoted by "n". If a substance is not completely transparent, the electromagnetic wave is attenuated in traveling through it. The term "k" is called the extinction coefficient and is related to the intensity absorption coefficient and the penetration depth. Metals and the oxides of some metals like iron, uranium, and Mulberry, absorb strongly and "k" does not equal zero.

To distinguish between the refractive indexes of the medium, film, and substrate, numerical subscripts are used, and "N" is used to denote the complex refractive index. For example:

$$\text{Refractive Index of the Medium: } N_1 = n_1 - ik_1,$$

$$\text{Refractive Index of the Film: } N_2 = n_2 - ik_2, \text{ and}$$

$$\text{Refractive Index of the Substrate: } N_3 = n_3 - ik_3.$$

Figure 3. FIVE FILMS ON A SUBSTRATE. (Refractive Indexes of Films are n_2 to n_6 , Thicknesses of Films are d_2 to d_6 , Angle of Incidence is ϕ , and Refractive Indexes of the Surrounding Medium and Substrate are n_1 and n_7 ; from McCrackin and Colson(15))

If there is more than one film on the substrate, other subscripts may be used, as noted in Figure 3.

Sputter-Cleaning Unit

The surface of the specimen must be flat, highly polished, and ultraclean to measure the refractive index of the substrate, but moisture and the oxide film are impossible to remove completely from most materials. If any of these films are present when ellipsometric measurements are taken, the "bare metal" refractive index will be in error.

Surfaces can be cleaned in a high vacuum by bombarding them with argon or other ions.(19-22) Normally, this technique is used to coat a surface placed on the anode of the sputtering unit. The coating consists of material stripped away from the substrate (cathode); and, if the process is continued long enough and no active gases are present in the chamber, an ultraclean cathode is obtained. To adapt this procedure to the cleaning of samples, a sputtering chamber was mounted in a vertical plane (Figure 4). A new vacuum chamber was built and fitted with

windows for ellipsometric observation of the cathode upon which the sample was mounted. The windows were equipped with shutters to prevent sputtered materials from depositing on them.

Sample Preparation

The specimens were usually coupons (1" x 1" x 1/8") that were milled flat with about a 40-microinch surface finish. They were then metallographically polished by grinding on 320, 400, and 600-grit silicon carbide paper with oil. Final polishing was done with six, three, and one-micrometer diamond on nylon with ethyl alcohol, and with Linde B on Gamal cloth for one minute. A few samples were degreased and studied ellipsometrically without further polishing. The data were similar to that obtained from polished specimens, but the measurement precision was considerably worse.

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Figure 4. SPUTTERING CHAMBER FOR USE WITH THE ELLIPSOMETER. (The Ellipsometer Table is Mounted on Casters so that it can be Rolled to the Sputtering Chamber; the Two Units are Aligned by Means of Screws and a Pad Attached to the Table)

EXPERIMENTAL MEASUREMENTS AND RESULTS

Determination of the Refractive Index of the Substrate

Thirteen uranium coupons were mechanically polished and sputter cleaned to determine the refractive index. Ten of these coupons were sputter cleaned soon after polishing; the other three had acquired a heavy oxide coating and were cleaned to see how the results would compare with the other coupons. The results are presented in Table 1. In this table the complex refractive index before and after sputtering and the length of the sputtering period are given. Ellipsometer readings were taken periodically during the sputtering process until no further increase in the ellipsometer readings was obtained.

As a clean metal surface corrodes and the film thickness increases, the angle of the polarizer decreases. Conversely, the more nearly clean the surface, the higher the angle of the polarizer. Consequently, the refractive index that was adopted for clean uranium is that for Specimen 1: $N_3 = 3.28 - 4.68i$, because when the angle of incidence is 60 degrees, the polarizer angle is 32.60 degrees, and the analyzer angle is 37.00 degrees. These two angles

Table 1

POLARIZER AND ANALYZER ANGLES AND REFRACTIVE INDEXES FOR URANIUM COUPONS
BEFORE AND AFTER SPUTTER CLEANING

Coupon Number	Before Sputter Cleaning				After Sputter Cleaning					Shortly After Return to Atmosphere	
	Polarizer Angle, (1) p	Analyzer Angle, (1) a	Substrate Refractive Index		Sputter Times Minutes	In Vacuum Chamber				p(1)	a(1)
			Real, n ₃	Imaginary, k ₃		n ₃	k ₃	p(1)	a(1)		
1	22.11	34.80	1.56	- 2.81	40	3.28	4.65	32.60	37.00	26.20	36.25
2	107.30(2)	11.11	Heavy Oxide		95	2.15	3.36	26.80	35.00	24.28	35.33
3	52.04(2)	23.56	Heavy Oxide		88	2.98	4.43	31.50	36.75	26.56	36.21
4	24.83	35.87	1.76	- 3.26	60	2.15	3.34	26.75	34.90	24.96	35.26
5	24.94	36.14	1.73	- 3.29	89	3.10	4.64	32.10	37.10	26.94	36.24
6	15.64	33.94	1.15	- 1.16	29	3.10	4.55	32.00	36.80	-	-
7	21.86	34.91	1.53	- 2.80	31	2.95	4.54	31.60	37.00	-	-
8	24.70	35.90	1.73	- 3.24	90	2.36	3.89	28.85	36.30	27.69	36.33
9	25.39	35.82	1.84	- 3.31	90	3.21	4.56	32.30	36.80	26.92	36.07
10	21.87	35.23	1.50	- 2.83	58	2.36	3.77	28.60	35.95	24.14	35.41
11	- 31.71(2)	18.31	Heavy Oxide		66	2.17	3.07	26.00	33.80	22.30	33.42
12	16.48	33.93	1.21	- 2.22	61	2.51	3.21	28.00	33.70	24.00	34.90
13	14.85	34.15	1.10	- 2.11	-	2.25	3.40	27.30	34.90	23.74	34.30

(1) The angle of incidence is 60 degrees.

(2) This reading was due to the heavy oxide film on the surface.

are the starting point of the polarizer angle-analyzer angle graphs which serve as the working curves for converting ellipsometer data to film-thickness data. As such, these angles signify zero film thickness. Table 2 provides a comparison of this work with that of other reports.

Table 2
LITERATURE VALUES FOR THE REFRACTIVE
INDEX OF URANIUM

Refractive Index	Notes
1.50 - 1.87i	By ellipsometry; Stebbins and Shreir ⁽¹⁹⁾ 1961.
1.93	By interferometry; Stebbins and Shreir ⁽¹⁹⁾ 1961.
2.11 - 3.40i	Hayfield and White ⁽²⁵⁾ 1963.
3.10 - 3.06i	Sputter cleaned; by ellipsometry; Larson and Taylor. ⁽²⁰⁾
2.79 - 4.04i	Sputter cleaned; alpha phase; Larson. ⁽²¹⁾
3.28 - 4.68i	This study; sputter cleaned; by ellipsometry.

It is well known that an oxide film forms immediately on a freshly cleaned surface. It is impossible to remove an oxide film by mechanically polishing in air; uranium is even reported to oxidize in a vacuum of 10^{-6} torr.⁽²³⁾ Some sputter-cleaned coupons were retained in the vacuum chamber at 10^{-6} torr overnight, and a small decrease in the polarizer angle was noted. However, when the chamber was refilled with air prior to removing the coupon, the change in polarizer and analyzer angles was dramatic. These data are listed in the last two columns of Table 1. Coupon 4, for example, returned to very nearly the same angles that were read before cleaning. This reaction was probably a combination of oxide forming on the surface and water vapor and other gases adsorbing on the surface. This rapid reaction occurred only when the specimen had been sputter cleaned. Mere evacuating and backfilling had little effect on the ellipsometer readings.

Mulberry coupons were sputter cleaned in the manner just described for uranium. The results are given in Table 3. These results are the same as those for uranium; and, therefore, the same value of N_3 was used in subsequent calculations.

Several values for the refractive index of uranium from the literature are listed in Table 2. Variations in the literature values of the refractive index are due to variations in metal, sample preparation, and testing environment. The sample of Stebbins and Shreir⁽¹⁹⁾ was electropolished and analyzed in air. Larson and Taylor^(20, 21, 24) gave their samples a final cleaning by sputtering in an argon atmosphere, then took data ellipsometrically, repeating the procedure until there was no change in ellipsometer data produced by additional sputtering. They considered their ellipsometer data and refractive index to be representative of clean uranium. Hayfield and White⁽²⁵⁾ do not mention sample preparation specifically.

For comparison with the literature values in Table 2, the refractive index of a number of mechanically polished, but not sputter-cleaned, coupons is also given in Table 3.

Determination of the Refractive Index of Films

In many studies of thin films, the films are applied by some coating process and the number, thickness, and composition of the films are under precise control (as in applying

Table 3

POLARIZER AND ANALYZER ANGLES AND REFRACTIVE INDEXES FOR MULBERRY COUPONS
BEFORE AND AFTER SPUTTER CLEANING

Coupon Number	Before Sputter Cleaning				After Sputter Cleaning						
	Polarizer Angle, p	Analyzer Angle, a	Refractive Index		Sputter Times Minutes	In Vacuum Chamber				Shortly After Return to Atmosphere	
			Real, n ₃	Imaginary, k ₃		n ₃	k ₃	p	a	p	a
1	23.85	35.22	1.72	3.05	70	3.13	4.45	31.95	36.65	25.34	35.80
2	24.72	35.63	1.77	3.20	55	3.48	4.57	32.90	36.50	25.70	36.01
3	23.91	35.28	1.70	3.06							
4	23.98	35.26	1.72	3.07							
5	22.86	34.50	1.68	2.85							
6	22.93	34.46	1.68	2.85							
7	26.51	35.60	2.03	3.42							
8	26.56	35.84	2.02	3.47							
9	26.25	35.78	1.95	3.42							

antireflection coatings to glass surfaces). In corrosion studies, the film is the reaction product of some agent with the substrate material. In some cases it is single layered, homogeneous, and isotropic; in other cases there may be differences in density, variations in composition and thickness, and metallurgical phase differences. The ellipsometer readings are the average of all these conditions.

If the refractive index of the substrate is known and the oxide film is transparent, the two ellipsometer angles can be used to measure the real part of the refractive index of the film and the film thickness simultaneously. If the film is not transparent, the imaginary part of the refractive index cannot be obtained from one ellipsometer measurement. Sometimes it is possible to measure the film thickness or refractive index by some independent method; then the remaining data can be obtained from the ellipsometric equations. When this is not possible, the film thickness is introduced as an independent variable and it becomes necessary to take a series of readings as the film thickness increases.^(1, 2, 8, 26) The polarizer angle (p) is then plotted against the analyzer angle (a) for each film thickness. An estimate is made of the possible range of the complex refractive index of the film. This information and the known refractive index of the substrate are used in a computer calculation.^(15 - 17) This program calculates the theoretical values of Angles " p " and " a " for a range of film thicknesses—for example from 0 to 2000 angstroms in steps of 50 Å. These theoretical data are also plotted and the shape of the graph compared with that for the experimental data. If the two graphs do not coincide, a different set of refractive indexes is chosen for the theoretical curve and the process repeated until a good match is obtained.

Figure 5 is a graph of three values of the real part of the refractive index plotted using one value for the imaginary part. Note that although the shapes of the curves are similar, they cross in the lower part of the figure. At this intersection the approximate values of the polarizer and analyzer angles are $p = 80$ degrees and $a = 28$ degrees. The film thickness at this point is 700, 750, or 800 angstroms, depending upon the choice of n_2 . This characteristic makes this type of graph difficult and confusing to use when trying to establish the refractive index of the film. However, the location of the crossover point (there is another one at lower values of p) is typical of the value of the imaginary part of the refractive index. In Figure 5 it is $0.24i$. In Figure 6 the crossover point is shown for $0.38i$ and is located at $p = 93$ to 98 degrees and $a = 20$ to 20.7 degrees. The significance of the crossover point is that the experimental data passing through such a point determine the imaginary part of the refractive index in that region. The shapes of the experimental data curve and the theoretical curves then show the value of the real part of the refractive index.

Figure 7 illustrates the shape of the theoretical curves when the real part of the refractive index is constant and several values are used for the imaginary part. The curves do not cross, even when extended to several thousand angstroms. In many regions of the curve for a given film thickness, the value of the polarizer angle is the same for a large range of values of the imaginary part of the refractive index. Thus, if the real part of the refractive index is known, it is not necessary to know the imaginary part accurately in order to obtain film thickness data. If a rapid change in film thickness is being studied, it is only necessary to set the extinction point by the polarizer in order to obtain thickness data. Figure 7 also illustrates the sensitivity of the ellipsometer. In the region of a film thickness of 500 Å, the ellipsometer is capable of detecting a difference in film thickness of $1/2$ angstrom. However,

Figure 5. POLARIZER ANGLE AS A FUNCTION OF THE ANALYZER ANGLE FOR THREE DIFFERENT VALUES OF THE REFRACTIVE INDEX OF THE OXIDE FILM ON URANIUM AND MULBERRY. (Numbers Along the Curve are Film Thicknesses in Angstroms)

unless the exact value of the refractive index is known, there can be an uncertainty of 100 Å in the absolute value of the film thickness.

Some values for the refractive index of the oxide film that forms on uranium have been reported in the literature (Table 4). Eventually, the range of n_2 from 1.0 to 2.85 and k_2 from 0.00 to 0.70 was explored. It became apparent as the film thickness increased that the refractive index chosen for a thin film could not be used for a thicker film. The mathematical model of the film assumed a homogeneous, isotropic structure with only one index of refraction; and, evidently, this picture did not fit. Three other models were investigated.

A second model was based on the idea that the film could consist of several separate layers, or individual films with different refractive indexes. For example, the outer

layer of the film being in contact with the atmosphere could develop different properties of such factors as stoichiometry, strain, lattice spacing, and gas content, which would be different from conditions near the substrate since the transportation of reacting materials through the film could affect the properties in the film. A theoretical curve was then constructed on the basis of the first layer having a thickness of 1100 Å and a refractive index of 2.30 - 2.41i, and the second layer having a refractive index of 2.60 - 0.29i. Eventually it became necessary to assume five different layers to construct a curve which fit

Figure 6. CROSSOVER POINT FOR $k_2 = 0.38i$.

the experimental data to a film thickness of 4400 Å. Layer thicknesses and refractive indexes for three Mulberry coupons are given in Table 5. A fit of the theoretical curve to the experimental data is indicated in Figure 8 for two coupons of Mulberry. One advantage of this model is the smooth transition of film thickness at the points where the refractive index of the film is changed. A disadvantage is that the theoretical curve will not follow the experimental data precisely at the transition points, because the effect of the refractive index of the lower layer is very strong when the new film is thin.

Table 4

LITERATURE VALUES FOR THE REFRACTIVE INDEX OF URANIUM DIOXIDE

Refractive Index	Notes
1.88 - 0.278i	From Stebbins and Shreir(19)
2.2 - (various)i's	From Hayfield and White(25)
2.1 - 0.5i	From Larson and Taylor(20)
2.5 - 0.5i	From Larson and Taylor(24)
2.1 - 0.6i	From Larson(21)
2.48 - 0.545i	Film sublimed from solid UO ₂ Ackerman, Thorn, and Winslow(46)

Figure 7. POLARIZER ANGLE AS A FUNCTION OF THE ANALYZER ANGLE FOR A SINGLE VALUE OF THE REAL PART OF THE REFRACTIVE INDEX AND A RANGE OF VALUES FOR THE IMAGINARY PART OF THE REFRACTIVE INDEX. (Angle of Incidence = 60 Degrees, Refractive Index of the Substrate = $3.28 - 4.68i$; the Numbers Adjacent to the Points are the Film Thicknesses in Hundreds of Angstroms; the Imaginary Part of the Refractive Index is Marked Along Each Curve)

Table 5

REFRACTIVE INDEXES AND FILM THICKNESSES OF THE CORROSION FILMS
ON THREE MULBERRY COUPONS WHICH OXIDIZED AT 150° C

Medium: Air	$N_1 = 1.0 - 0.0i$	$N_1 = 1.0 - 0.0i$	$N_1 = 1.0 - 0.0i$
	700 Å	750 Å	950 Å
	$N_2 = 2.50 - 0.20i$	$N_2 = 2.50 - 0.22i$	$N_2 = 2.54 - 0.22i$
	400 Å	400 Å	350 Å
	$N_3 = 2.50 - 0.12i$	$N_3 = 2.45 - 0.16i$	$N_3 = 2.45 - 0.16i$
	900 Å	850 Å	850 Å
Films	$N_4 = 2.45 - 0.26i$	$N_4 = 2.45 - 0.28i$	$N_4 = 2.45 - 0.28i$
	1350 Å	1350 Å	1350 Å
	$N_5 = 2.60 - 0.29i$	$N_5 = 2.60 - 0.29i$	$N_5 = 2.60 - 0.29i$
	1100 Å	1100 Å	1100 Å
	$N_6 = 2.30 - 0.24i$	$N_6 = 2.30 - 0.24i$	$N_6 = 2.30 - 0.24i$
Metal Substrates	$N_7 = 3.28 - 4.68i$ M - 21	$N_7 = 3.28 - 4.68i$ M - 22	$N_7 = 3.28 - 4.68i$ M - 23

The third model was designed to do away with the seeming artificiality of five separate films by using a gradient of refractive index from the surface of the film down to the substrate. Agreement with experimental data is not as good as for the previous model. It is necessary to use several different gradients of the refractive index to match the entire curve of the experimental data. Excellent agreement could be obtained to a film thickness of about 1700 Å; beyond that the gradient seemed to be smaller. The use of the same gradient leads

Figure 8. POLARIZER ANGLE AS A FUNCTION OF THE ANALYZER ANGLE FOR MULBERRY COUPONS M-22 AND M-23. (This Curve Illustrates the Use of Five Different Refractive Indexes to Obtain a Composite Curve that will Match the Experimental Data; Numbers Along the Curve are Film Thicknesses in Angstroms)

eventually to a refractive index of the film which seems unreasonably high. Hence, it is necessary to return to assuming more than one film with different refractive indexes, or to assuming more than one gradient.

The fourth model assumes that the refractive index is uniform throughout the film and that when it changes, the change is through the whole film, with a small transition region between the refractive indexes. This "uniform refractive index through the film" is probably the average of any variations in the refractive index through the film, which is, after all, what the ellipsometer measures. The composite curve for this model was constructed with no concern for the particular refractive index that was used (see Table 6). The only requirement was that the theoretical curve fit the experimental data for a reasonable extent of film thickness, and that in the vicinity of 800 Å thickness the imaginary and real parts of the refractive index have the values indicated by the crossover points discussed earlier. The resulting curve can be seen in Figure 9 for a coupon of Mulberry. Ellipsometer data on this coupon were taken at angles of incidence of 60 and 70 degrees, and the data in the figure are that from the 70-degree angle. At this angle of incidence, data can be obtained for thicker films before a spiral is formed.

Table 6
REFRACTIVE INDEXES FOR THEORETICAL POLARIZER
ANGLE-ANALYZER ANGLE COMBINATIONS FOR
OXIDE FILM ON MULBERRY COUPON M-122
(See Figure 9)

Refractive Index	Film Thickness (Å)
2.45 - 0.23i	750
2.25 - 0.24i	1150
2.45 - 0.38i	1600
2.55 - 0.33i	2300
2.45 - 0.26i	2750
2.35 - 0.28i	3500
2.40 - 0.30i	4500

A variation of the first model is based on the assumption that the real part of the refractive index is constant, and the variation is due entirely to changes in the imaginary part of the refractive index. The magnitude of the variation in the imaginary part depends on the choice of the real part. This relationship is shown graphically in Figure 10 for three choices of the real part of the refractive index. Table 7 lists the experimental data for one coupon of Mulberry, the refractive index, and the film thickness.

Additional Comments on the Experimental Work

The ellipsometric study of the oxidation of a large number of uranium and uranium alloy coupons leads to a diversity of data from which it is difficult to draw general conclusions. One of the problem areas is the satisfactory determination and use of the refractive indexes of the film and substrate. It is primarily a matter of judgement for the individual whether the fit of the experimental and theoretical curves is satisfactory, or worth further exploration. One example is the use of the refractive index for the substrate that was obtained by sputter cleaning— $N_3 = 3.28 - 4.68i$. This value determines the starting point of the theoretical polarizer angle-analyzer angle curves and is considered to signify a clean uranium surface. However, such a clean surface may not be the true model of a mechanically polished coupon which is allowed to oxidize in room air. The refractive index typical of a well-polished coupon of uranium is $N_3 = 1.75 - 3.25i$. If this value is used for

Figure 9. COMPOSITE POLARIZER-ANALYZER ANGLE THEORETICAL CURVE FOR MULBERRY COUPON M-122. (The Curves are Made from the Refractive Indexes that Give the Best Fit with the Experimental Data; the Experimental Data are Marked by the Upright Triangles, Δ , Throughout; Angle of Incidence = 70°)

Figure 10. EXTINCTION COEFFICIENT, k_2 , FOR A URANIUM OXIDE FILM AS A FUNCTION OF THE FILM THICKNESS FOR SUBSTRATE MULBERRY COUPON M-122. (These Curves Show how the Variation in the Extinction Coefficient with Thickness of the Film is Affected by the Choice of the Real Part of the Refractive Index of the Film, n_2)

the starting point of the polarizer-analyzer curve, a theoretical curve can be found which will fit the experimental data as well as the curves obtained using the sputter-cleaned refractive index. The difference lies in the magnitude of the film thickness assigned to each point. It is about 100 Å greater if the sputter-cleaned value is used. The sputter-cleaned refractive index was used for all the data in this report to avoid the possibility of finding a polished sample with a starting film thickness less than zero. However, when the film is less than 500 Å thick, the lower refractive index may provide a better fitting curve. Since it would be very difficult to prove that the difference was statistically significant, only the sputter-cleaned refractive index was used.

Uranium corrodes very rapidly until the oxide film has become about 700 angstroms thick. The experimental data obtained from a large number of coupons showed a wide variation in the refractive index of the oxide film. In general, the real part of the refractive index varied from 2.2 to 2.5 and the imaginary part varied from 0.30i to 0.60i. For most uranium coupons the refractive index, $N_2 = 2.2 - 0.35i$, could be applied for film thicknesses up to 800 Å.

When the study of Mulberry corrosion was started it was found that the room-temperature corrosion rate was almost negligible compared with that for uranium; so the corrosion rate was accelerated by placing several coupons in an air oven. Eventually, this treatment was used at three different temperatures: 100, 110, and 150°C.

The shape of the polarizer angle-analyzer angle curve was similar for all the Mulberry coupons that were studied up to a film thickness of about 1650 Å. Small variations in the refractive index of the film had considerable influence upon the shape of the curve of each sample beyond this point. For the greatest accuracy in film thickness measurement, a theoretical curve should be determined for each coupon. Corrosion of uranium can be

Table 7

EXPERIMENTAL DATA FOR MULBERRY COUPON
M-122 OXIDIZED AT 150°C
(Abbreviated Table, See Figure 9)

Time (days)	p(1) (degrees)	a(2) (degrees)	Extinction Coefficient(3)	Thickness(4) (Å)
	0.79	32.89	~ 0.30	190
0.1	- 30.00	46.48	0.23	438
0.17	- 40.36	48.71	0.23	475
0.24	126.99	46.47	0.23	515
0.33	116.70	40.64	0.23	562
0.51	104.78	30.53	0.245	645
0.78	93.18	23.58	0.255	738
1.37	72.11	16.73	0.28	880
1.69	59.12	14.69	0.296	950
2.65	32.95	13.26	0.34	1090
3.60	15.12	14.19	0.38	1210
5.00	- 3.66	16.26	0.38	1385
6.25	- 14.66	16.65	0.378	1495
8.21	- 30.83	15.77	0.355	1645
10.08	- 44.16	13.29	0.34	1755
12.91	118.36	8.78	0.323	1893
16	91.36	4.15	0.317	2045
18	62.95	3.26	0.309	2120
20	41.53	4.42	0.286	2192
24.3	16.93	7.73	0.281	2349
36	- 14.00	12.70	0.26	2658
57	- 44.40	7.94	0.28	3012
69	132.65	3.29	0.296	3200
99	- 7.97	4.47	~ 0.34	3450
137	- 26.82	6.15	~ 0.34	4070
158	- 32.89	4.38	0.29	4300
183	- 26.90	3.18	0.28	4450

(1) p is the polarizer angle average for four zones.

(2) a is the analyzer angle average for four zones.

(3) The extinction coefficient varied to fit the data; the real part of the refractive index was held constant at 2.45.

(4) This coupon (2" x 2" x 1/4") was mechanically polished. Angle of incidence = 70 degrees.

followed at most to a film thickness of about 1500 Å, at which thickness the film becomes a dull black and no further changes can be detected ellipsometrically. On the other hand, the surface of Mulberry remains shiny up to and beyond a film thickness of 5000 Å. However, ellipsometric changes become very small and interpretation of the data is difficult for film thicknesses greater than 4500 Å. The refractive index which fits most Mulberry coupons depends upon the thickness of the film, but is in the range from $n_2 = 2.25$ to 2.55 and $k_2 = 0.22$ to 0.38.

A discussion of the mechanism of corrosion of uranium is beyond the scope of this report, but it will be helpful to review what is known in order to understand the changes in refractive index. Uranium reacts with water to form uranium dioxide; uranium hydride (UH_3) is probably an intermediate step,^(27, 28) and hydrogen is generated by the reaction. The volume of the oxide produced is larger than the volume of the metal from which it came; hence, considerable compressive stress exists in the oxide layer. The reaction continues to take place at the metal/oxide interface,⁽²⁹⁾ probably by diffusion of the hydroxide ion⁽²⁸⁾ through the pores of the oxide.⁽³⁰⁾ After some (unknown) thickness of the oxide has been reached, the oxide film ruptures which allows an easier access of moisture to the inner oxide layers. The rate-determining step may be the diffusion of water through the oxide layers.⁽²⁸⁾ Mulberry, a uranium-7.5 weight percent niobium-2.5 weight percent zirconium alloy, appears to provide a good balance of strength, stability, and corrosion resistance in the gamma phase at room temperature.⁽³¹⁾ Corrosion products can be formed epitaxially with gamma uranium, which means that the corrosion film is adherent and, being under compression, can be protective in an oxidizing environment.⁽³²⁾ Although the corrosion rate for Mulberry is much slower than that for uranium, it seems likely that the corrosion theory just described can also be applied to Mulberry. It is probable that, until the film is about 700 Å thick, very little stress will have developed and diffusion of water through the film is easy. The chemical reactions may not be complete during the early stages of corrosion; uranium hydride⁽³³⁾ may be incorporated in the film. As the hydroxide ion diffuses through the film, the reactions go to completion and the refractive index changes. The refractive index of a mixture can be calculated if the fractional volumes of the components are known.⁽³⁴⁾ It is possible, then, that the film consists of an outer layer in which the reactions are complete and an inner layer in which the reactions are occurring (composed of UO_2 , UH_3 , U, U^{+} ions, OH^- , H^+ , electrons, and possibly other species); and, as oxidation continues, the entire film becomes more compact due to compressive stress.

Since compressive stress is known to have a role in the corrosion of uranium, a separate study was undertaken to find out if stress would affect the refractive index to the extent noted in the corrosion studies. Tension was applied to unoxidized and oxidized flat tensile-test specimens⁽³⁵⁾ and the fixture mounted on the ellipsometer. Data were taken at various increments of tension to determine directly if stress could affect the refractive index. All the specimens were mechanically polished and had very little new oxide on the surface, except for one aged Mulberry specimen which had a film about 1250 Å thick. The ellipsometric measurements are summarized in Table 8. The data for iron shows the range of polarizer angle values to be 0.07 degree and the range of analyzer angle values to be 0.09 degree for tension up to 42.5 ksi; for unaged Mulberry, the range of the analyzer angle is the same but the range of the polarizer is greater, although still within the realm of experimental variation up to a tension of 107 ksi. For both samples of aged Mulberry, the variation in analyzer angle is irregular but very small. The polarizer angle in the data set for the

Table 8

POLARIZER AND ANALYZER ANGLES FOR PURE IRON AND AGED AND
UNAGED MULBERRY WHEN SUBJECT TO STRESS

Unaged Mulberry			Pure Iron			Aged Mulberry ⁽³⁾					
Tension	p ⁽¹⁾	a ⁽²⁾	Tension	p	a	Oxide Covered			Repolished		
(ksi)	(degrees)	(degrees)	(ksi)	(degrees)	(degrees)	Tension	p	a	Tension	p	a
						(ksi)	(degrees)	(degrees)	(ksi)	(degrees)	(degrees)
0	20.88	35.21	0	27.98	34.31	0	31.53	20.47	0	21.60	34.90
30.0	21.00	35.26	9.9	27.99	34.32	27.5	31.50	20.68	30.0	21.49	35.03
56.7	20.90	35.24	18.9	28.00	34.31	59.0	31.73	20.64	60.3	21.34	35.00
63.5	20.83	35.15	26.9	27.94	34.31	86.5	32.11	20.90	88.8	21.31	34.95
107.3	20.72	35.15	31.1	27.99	34.26	116.8	32.78	21.04	118.5	21.22	34.97
0	20.82	35.21	36.8	28.01	34.32	141.6	32.10	20.65	137.6	21.06	34.97
			42.5	27.98	34.35	0	31.39	20.35	0	21.12	35.06
			0	28.00	34.33						

(1) p is the polarizer angle average for four zones.

(2) a is the analyzer angle average for four zones; Angle of Incidence = 60 degrees.

(3) Aged for 100 hours at 150° C.

repolished coupon dropped about one-half degree when the tension was increased to near 140 ksi. For the oxide-coated set, the polarizer angle increased 1.2 degrees. If the change in the repolished specimen represents a change in the refractive index of the substrate due to stress, and the change in the oxide-covered specimen represents the combined effect of film and substrate, it may be that the change in the polarizer angle of the film itself is 1.7 degrees. These changes caused by tension in the film and substrate are entirely too small to be the factor responsible for the changes in the refractive index that have been observed.

Several other investigators report multifilms, changes in refractive index, and abrupt changes in film thickness. Dell'oca and Young⁽³⁶⁾ report that anodic oxide films on tantalum consist of two distinct layers. Hayfield and White,⁽³⁷⁾ who studied oxide films up to 2200 Å in thickness on polycrystalline uranium, believe that there is a true increase in oxide film absorptivity. Bockris⁽¹¹⁾ has shown that, during the passivation of nickel, the real part of the refractive index changed from 1.8 to 4.0, the extinction coefficient changed from 1.9 to 0.0 and back to 0.4, and the film thickness grew rapidly from near zero to 60 Å.

The theory of the optics of metals and films shows that the complex refractive index is related to the dielectric constant and the conductivity of the material. Studies of the electrical properties of uranium dioxide⁽³⁸⁾ show that large variations in conductivity are caused by small changes in the oxygen/uranium ratio. In general, the electrical properties of uranium dioxide are affected by quite a few factors, but particularly the amount of oxygen in the lattice. These studies⁽³⁸⁾ have been done on prepared specimens of solid uranium dioxide which, in general, have been sintered at high temperatures. It would be very difficult to make the same measurements on a thin film of oxide covering a metal substrate. However, it seems that the electrical properties might be more subject to wide variation in the metal-film case due to the incompleteness of the reactions.

The surface of two Mulberry coupons was examined in the scanning electron microscope.⁽³⁹⁾ Several typical photographs are presented in Figure 11. The oxide film on these coupons, which had been in the oven at 150° C, was about 4500 Å thick. In every area there are ridges where the oxide film appears pushed up and folded over, possibly at a grain boundary. In some places the oxide spills over on the adjacent surface; and, in many places, there are crater-like holes with sloping sides. Since the ellipsometer covers a surface area about 2 mm by 7 mm, changes in the surface features may be partly responsible for changes in the refractive index.

A metallurgical study was also made of the repolished surface of Mulberry Coupon M-22, which had been at 150° C for 370 days, and another coupon of the same material which was not aged.⁽⁴⁰⁾ The DPH values of the two pieces agree well with the values reported by Dean;⁽⁴¹⁾ namely, a DPH_{300g} value of 200 for the unaged material compared with a DPH value of 220 for Dean's gamma, solution-treated material with one percent plastic deformation. After the year of aging Coupon M-22, the DPH value had increased to 400 as the structure transformed. Dean reports a value of over 600 when the material has completely transformed. Changes in the microstructure can be seen in Figures 12 and 13. A section was removed from Coupon M-22 and the edge of the section polished. A microphotograph of the edge of the coupon showing the film of oxide indicated a film thickness of about 6000 Å.

(a) Ruptures A and B at 700X

(b) Ruptures A and B at 2,100X

(c) Rupture A at 7,000X

(d) Rupture B at 7,000X

(e) Rupture C at 700X

(f) Rupture C at 2,100X

Figure 11. SURFACE OF A MULBERRY COUPON WITH A 4500-ANGSTROM OXIDE FILM. (Photos Made by a Scanning Electron Microscope at Several Magnifications; Oxide Film Ridges are Seen at the Grain Boundaries as well as Several Ruptures of the Film)

G403e

Figure 12. MICROSTRUCTURE OF MULBERRY COUPON M-22 USED IN CORROSION STUDIES. (250X; Bright Field Illumination; Etchant - 5% Oxalic Acid Solution)

G385-1g

Figure 13. MICROSTRUCTURE OF MULBERRY COUPON M-22 USED IN CORROSION STUDY AFTER AGING FOR 370 DAYS AT 150° C. (Note Widmanstatten Structure; 250X; Bright Field Illumination; Etchant - 5% Oxalic Acid Solution)

Equations of the Corrosion Curves

Corrosion curves consist of some measure of the buildup of the film, generally thickness, plotted against time. The shape of the corrosion curve is indicative of the type of oxide, and many corrosion curves have been explained in terms of the physical chemistry of the corrosion process.^(42, 43) Computer programs were available to test fit the data to eight different equations.⁽⁴⁵⁾ Table 9 lists the equations that were used and a sample of the data from one corrosion specimen. The lowest value of the "mean square" indicates the equation of the curve that best fits the data.

The corrosion of uranium has been shown to follow the equation:^(42, 44)

$$A = c_n D^{1/n},$$

where A is a direct measure of film growth (such as the thickness in angstroms, weight gain, or weight loss of some reactant) and D is a measure of time in hours or days. When $n = 2$, the equation is that of a parabola; but, most of the time in this work, $n = 3$, or the best fit was obtained with the log-log form. These equations are presented in Tables 10 and 11 with a more detailed discussion in the subsection that follows. It is often apparent that the shapes of the curves are similar and only by means of statistics can the best fit be found. Even then, there may be no statistical differences between the first and second choices. These corrosion equations should not be used to predict film thicknesses for a longer period of time than has been measured experimentally, or extrapolated to different temperatures.

Measurement of the Corrosion Film Thickness on Uranium and Mulberry

The procedure for obtaining the polarizer angle-analyzer angle curves has been described in the preceding subsections. To recapitulate for the sake of clarity, the following procedure was used to obtain corrosion film thickness on uranium and Mulberry: Experimental data were obtained until the film was at least 1000 Å thick. Estimated values of the refractive index of the corrosion film were used with a computer program to obtain data for a theoretical polarizer-analyzer curve for a range of film thicknesses. The estimated value of the refractive index of the film was altered until the theoretical curve matched the experimental curve. In some cases, more than one refractive index was used to obtain the best match for various sections of data. The theoretical curve then became the working curve. Film thickness was obtained by interpolating between points on this curve.

Table 9

EQUATIONS USED IN CURVE FITTING AND AN EXAMPLE

Sample	Number of Data Points	Equations Used to Estimate Fit ⁽¹⁾	Mean Square
M-4 at 110° C	33	$A = a + bD$ ⁽²⁾	10,951 ⁽³⁾
		$A = c + d\sqrt{D}$	1,151
		$A = e + f\sqrt[3]{D}$	359
		$A = g + h \log D$	27,855
		$A = \text{antilog}(i + j \log D)$	13,832
		$A = k + lD + mD^2$	3,469
		$A = n + oD + pD^2 + qD^3$	1,374
		$A = (r^3 + 3sD)^{1/3}$	-

(1) From Sherrill.⁽⁴⁵⁾

(2) A represents the film thickness in angstroms and D the time in days. The other letters are constants.

(3) The equation with the smallest mean square is the best estimate of the curve which describes the data.

Table 10

EQUATIONS OF CORROSION CURVES FOR URANIUM COUPONS

Coupon Number	Study Conditions			Calculated Equations	Limit of Error of Fit, A	Comments
	Temperature (° C)	Length of Study (days)	Film Thickness at End (angstroms)			
3	23	689	1010	$A = 11 + 115 \sqrt[3]{D}$	± 55.8	Mechanically polished and sputter cleaned.
5	23	654	840	$A = \text{antilog} (2.196 + 0.265 \log D)$	± 50.6	Mechanically polished and sputter cleaned.
				Next best estimate of fit: $A = 69.9 + 96.9 \sqrt[3]{D}$	± 61.9	
C-906-2	23	722	913	$A = \text{antilog} (2.451 + 0.168 \log D)$	± 37.1	Mechanically polished.
C-906-2	23	1245	1200	$A = 246.2 + 83.9 \sqrt[3]{D}$	± 69.0	Mechanically polished. $N_2 = 2.2$ - (various) i's
				Next best estimate of fit: $A = \text{antilog} (2.474 + 0.175 \log D)$	± 83.8	
Slide 11	23	322	790	$A = 130.9 + 101.7 \sqrt[3]{D}$	± 46.5	Uranium sputter coated onto microscope slide.
				Next best estimate of fit: $A = \text{antilog} (2.389 + 0.189 \log D)$	± 49.8	$N_2 = 2.2$ - (various) i's
U-30	23	664	1208	$A = \text{antilog} (2.617 + 0.164 \log D)$	± 21.7	Mechanically polished. $N_2 = 2.2$ - (various) i's
				Next best estimate of fit: $A = 381.4 + 101.6 \sqrt[3]{D}$	± 60.3	
U-30	23	664	1108	$A = \text{antilog} (2.570 + 0.165 \log D)$	± 21.8	$N_2 = 2.35$ - (various) i's
				Next best estimate of fit: $A = 317.7 + 97.1 \sqrt[3]{D}$	± 87.2	
U-31	23	690	1115	$A = \text{antilog} (2.547 + 0.171 \log D)$	± 24.0	Mechanically polished. $N_2 = 2.20$ - (various) i's
				Next best estimate of fit: $A = 295.5 + 99.4 \sqrt[3]{D}$	± 79.1	
U-31	23	690	1010	$A = \text{antilog} (2.510 + 0.166 \log D)$	± 34.0	$N_2 = 2.35$ - (various) i's
				Next best estimate of fit: $A = 265.6 + 89.1 \sqrt[3]{D}$	± 64.2	
U-32	23	622	1170	$A = \text{antilog} (2.648 + 0.138 \log D)$	± 69.8	Mechanically polished. $N_2 = 2.2$ - (various) i's
				Next best estimate of fit: $A = 349.8 + 101.7 \sqrt[3]{D}$	± 90.9	
U-33	23	622	1225	$A = \text{antilog} (2.613 + 0.160 \log D)$	± 48.9	Mechanically polished. $N_2 = 2.2$ - (various) i's
				Next best estimate of fit: $A = 325.9 + 108.7 \sqrt[3]{D}$	± 80.8	
U-50	50	54	1287	$A = \text{antilog} (2.754 + 0.176 \log D)$	± 50.6	Mechanically polished. $N_2 = 2.2$ - (various) i's
				Next best estimate of fit: $A = 273.7 + 262.1 \sqrt[3]{D}$	± 61.2	
U-93	93	2	1465	$A = 79.3 + 1105.9 \sqrt[3]{D}$	± 21.5	Mechanically polished. $N_2 = 2.2$ - (various) i's
				Next best estimate of fit: $A = (1.703 \times 10^7 + 1.680 \times 10^9 \times D)^{1/3}$	± 33.3	

Table 11
EQUATIONS OF CORROSION CURVES FOR MULBERRY COUPONS

Coupon Number	Study Conditions		Film Thickness at End (angstroms)	Calculated Equations	Limit of Error of Fit, A	Comments
	Temperature (° C)	Length of Study (days)				
MJC-1	23	21	164	$A = 104 + 23 \sqrt[3]{D}$	± 5.9	Center of electron-beam heated spot.
MJC-2	100	24	878	$A = 92 + 237 \sqrt[3]{D}$	± 15.0	Center of electron-beam heated spot.
MJA-1	23	21	181	$A = 100 + 29 \sqrt[3]{D}$	± 5.5	Edge of electron-beam heated coupon.
MJA-2	100	24	770	$A = \text{antilog } (2.539 + 0.213 \log D)$	± 17.3	Edge of electron-beam heated coupon.
Next best estimate of fit:				$A = 157 + 186 \sqrt[3]{D}$	± 34	
M-2	23	942	288	$A = 122.6 + 5.1 \sqrt[3]{D}$	± 12.1	Mechanically polished.
Next best estimate of fit:				$A = 101.3 + 16.7 \sqrt[3]{D}$	± 12.7	
M-4	23	309	239	$A = 127 + 17 \sqrt[3]{D}$	± 8.3	Mechanically polished.
M-4	110	95	1154	$A = 148 + 221 \sqrt[3]{D}$	± 38.6	Placed in oven after 309 days in air.
M-5	23	389	312	$A = 135 + 26 \sqrt[3]{D}$	± 16.1	In vessel at 70% RH in air.
Data fit with separate curves for early and late data.						
M-21	150	26		$A = \text{antilog } (2.950 + 0.327 \log D)$		Early data; five film model; mechanically polished.
M-21	150	132		$A = \text{antilog } (2.970 + 0.310 \log D)$		Later data.
Pooled limit of error.					± 26.8	
Next best estimate of fit:				$A = 34.7 + 859.3 \sqrt[3]{D}$		Early data.
				$A = 245.7 + 785.4 \sqrt[3]{D}$		Later data.
Pooled limit of error.					± 27.4	
Data fit with one curve.						
M-21	150	158	4520	$A = \text{antilog } (2.951 + 0.321 \log D)$	± 49.9	Mechanically polished; five film model.
Next best estimate of fit:				$A = 95.6 + 822.7 \sqrt[3]{D}$	± 59.1	
M-21R	150	36	3470	$A = -155.6 + 1100 \sqrt[3]{D}$	± 90.3	{ Repolished; $\phi = 70$ deg; $N_2 = 2.45$ - (various) i's. Single film model.
Next best estimate of fit:				$A = \text{antilog } (2.974 + 0.363 \log D)$	± 94.6	
M-22	150	165	4460	$A = \text{antilog } (2.939 + 0.321 \log D)$	± 57.5	{ Mechanically polished; five film model.
Next best estimate of fit:				$A = 89.0 + 799.5 \sqrt[3]{D}$	± 65.3	
M-23	150	186	4610	$A = \text{antilog } (2.963 + 0.306 \log D)$	± 48.1	{ Mechanically polished; five film model.
Next best estimate of fit:				$A = 156.3 + 781.3 \sqrt[3]{D}$	± 58.5	
Different film model.				$A = \text{antilog } (2.937 + 0.319 \log D)$	± 78.6	{ $N_2 = 2.45$ - (various) i's. Single film model.
Next best estimate of fit:				$A = 28.7 + 818.9 \sqrt[3]{D}$	± 111.2	
M-23R(1)	150	30	3280	$A = -105 + 1088.9 \sqrt[3]{D}$	± 72.9	{ Repolished; $\phi = 60$ deg; $N_2 = 2.45$ - (various) i's.
Next best estimate of fit:				$A = \text{antilog } (2.992 + 0.344 \log D)$	± 132	
Different angle of incidence.				$A = -117.5 + 1095 \sqrt[3]{D}$	± 72.0	$\phi = 70$ degrees; $N_2 = 2.45$ - (various) i's.
Next best estimate of fit:				$A = \text{antilog } (2.987 + 0.360 \log D)$	± 76.7	
M-122	150	183	4450	$A = \text{antilog } (2.916 + 0.324 \log D)$	± 57.8	Mechanically polished; $\phi = 70$ deg; 2" x 2" x 1/4".
Next best estimate of fit:				$A = 45.5 + 781.9 \sqrt[3]{D}$	± 61.6	$N_2 = 2.45$ - (various) i's.

(1) All data on this coupon are based on the single film model.

Uranium coupons were oxidized at room temperature, at 50, and at 93° C. These coupons were first mechanically polished. Ellipsometric measurements were made as soon as possible after polishing and while the film thickness was 150 - 200 Å thick. (The limiting film thickness that can be measured on uranium before the film loses its specular reflecting characteristics is 1200 to 1500 Å. This thickness was achieved after 1,245 days for one coupon at room temperature.) The corrosion rate varies considerably for coupons studied at different times. This inconsistency may be due to differences in material, the polishing process, temperature, and humidity conditions.

If film thickness is plotted as a function of time on log-log paper, a straight line is obtained, as indicated in Figure 14. These data were obtained from two uranium samples that were studied at room temperature, and from one each at elevated temperatures. The latter two were measured in air for one or two and one-half hours, as indicated before being put in the oven, because at the start the change is so rapid that it could not be followed. The samples were removed from the oven and allowed to cool in air before data were taken. The equations of these corrosion curves are listed in Table 10. The refractive index used for most of the films was 2.2 - (various) i 's (various values of the imaginary part of the refractive index). The range of values was 0.26*i* to 0.40*i*, except for the early data where higher values were needed.

The corrosion-resistant properties of Mulberry were observed with the first specimen studied ellipsometrically. The film thickness was 320 Å after 1,452 days at room temperature. These data are shown graphically in Figure 15 with that from one of the uranium coupons for comparison. The corrosion of Mulberry was also studied at accelerated rates. Coupon M-4, after corroding in air at room temperature for 309 days, was placed in an air oven at 110° C. Coupons M-21, M-22, and M-23 were mechanically polished and placed in an oven at 150° C. The data from these coupons are given graphically in Figure 16 where the film thickness is plotted against the cube root of time.

After the film thickness on Mulberry had reached 4500 Å, the spiral formed by the polarizer angle-analyzer angle curve was very difficult to fit to a theoretical curve and no satisfactory results have been obtained. The surface of the specimen reflects specularly, but the angle of the polarizer cannot be set with sensitivity. Since it seemed useless at the time to obtain additional data, Coupons M-21 and M-23 were repolished and studied again to see if the same type of data would be obtained. These coupons had been aged at 150° C for 5,689 hours. It was thought that a rerun might show some difference in the ellipsometric data due to the aging of the Mulberry. These reruns are designated as Coupons M-21R and M-23R. There was little significant difference in the data, as seen from the polarizer angle-analyzer angle curves, except that possibly the film had a slightly higher extinction coefficient. The corrosion rate seemed considerably faster, but statistical analysis did not show the rates to be significantly different (see Figure 17).

The film-thickness data for Coupon M-23 had been obtained from a working curve using the principle of five films with distinct refractive indexes. Since the refractive indexes of Coupon M-23R were slightly different, the experimental data did not fit this curve very well. To compare data from the two runs it was necessary to either construct a new five-film curve for Coupon M-23R, or to redo the data from Coupon M-23 using 2.45 for the real part of the refractive index and various values for the imaginary part as necessary to fit the data.

Figure 14. FILM THICKNESS AS A FUNCTION OF TIME. (Coupons C-906-2 and UM-1 are at Room Temperature; the Other Two Coupons are at 50 and 90° C)

Figure 15. CORROSION FILM THICKNESS OF URANIUM AND MULBERRY COUPONS IN AIR AT ROOM TEMPERATURE. (Uranium Coupon - C-906-2; Mulberry Coupon - M-2)

Figure 16. FILM THICKNESS IN ANGSTROMS AS A FUNCTION OF THE CUBE ROOT OF TIME IN DAYS FOR FIVE MULBERRY COUPONS. (Mulberry Coupon M-4 was at Room Temperature for 309 Days and then Placed in an Air Oven at 110° C; the Other Three Coupons were in an Air Oven at 150° C for 158 Days)

The latter course was decided upon because of the time and labor involved in constructing a five-film composite. The resulting data are presented in Table 12. This table lists the complete polarizer angle, analyzer angle, and time that the sample was in the oven, then it

Figure 17. FILM THICKNESS AS A FUNCTION OF TIME FOR MULBERRY COUPON M-23. (Run 1 at 150° C for 370 Days; the Sample was then Repolished and Rerun)

Table 12

ELLIPOSOMETER DATA AND FILM THICKNESS FOR THE CORROSION OF MULBERRY AT 150° C
(Angle of Incidence - 60°)

p	a	Five-Film Model			Single-Film Model		Time (hours)
		n ₂	k ₂	t (Å)	n ₂ = 2.45 k ₂	t (Å)	
Coupon M-23							
24.93	35.66	2.3		95		95	0
45.58	53.39	2.3	0.24i	535	0.22	485	3.75
103.79	41.47			610	0.22	555	6.25
79.24	28.08	1st film		755	0.24	680	13.50
61.85	26.67			910	0.25	825	23.25
43.04	26.58	2.6	0.29i	1135	0.30	1045	49
21.96	21.28			1450	0.36	1352	101.0
9.38	14.52			1595	0.35	1530	139.5
7.13	2.59			1725	0.33	1690	185.5
67.78	0.10			1758	0.32	1712	193.0
72.60	2.15	2nd film		1775	0.32	1747	200.3
74.55	2.89			1780	0.32	1755	207.3
61.92	12.86			1920	0.30	1907	261
43.00	19.81			2225	0.28i	2205	453
31.90	19.12			2450	0.28i	2415	623
20.33	10.84			2770	0.28i	2725	902
26.48	6.75	3rd film		2885	0.28i	2840	1018
49.85	9.40			3090	0.28i	3045	1238
41.85	15.19	2.45	0.16i	3420	0.30	3335	1683
38.51	15.12	4th film		3520	0.32i	3410	1880
34.83	13.49	2.54	0.22i	3700	?	3700	2233
37.88	11.38			3935	0.28i	4150	2761
42.16	12.54	5th film		4155	0.28i	4360	3385
41.12	13.78			4380	?	4470	3745
38.46	14.51			4610	?	?	4561
Coupon M-23R							
24.40	36.25				?	100	-
2.41	37.14				0.26i	368	1.0
44.84	50.51				0.24	480	3.5
101.73	37.36				0.23	570	6.0
83.55	27.92				0.25	655	9.0
70.80	25.73				0.27	744	12.7
51.16	25.29				0.32	945	23.8
41.48	24.66				0.37	1050	33.5
30.61	22.31				0.44	1215	48.5
14.59	15.21				0.40	1500	74
3.23	7.90				0.35	1630	91
2.14	2.12				0.33	1698	102
8.43	0.38				0.32	1722	105
75.63	1.46				0.32	1739	108.5
77.60	2.22				0.32	1745	111
69.46	8.88				0.30	1830	129
58.14	15.86				0.28	1975	159
49.11	19.08				0.275	2103	198
40.98	20.11				0.28	2245	243
29.30	17.19				0.32i	2480	336
24.28	10.76				0.32i	2750	432
35.91	8.39				0.32i	2915	506
44.23	11.11				0.32i	3095	602
42.01	13.63				?	3250	700
38.57	14.53				?	3380	796
34.45	13.81				?	?	934

lists the refractive indexes and film thicknesses determined for Coupon M-23 by both the five-film working curve and the curve using $n_2 = 2.45 - (\text{various})i$'s. Finally, data are given for Coupon M-23R using $n_2 = 2.45 - (\text{various})i$'s. For the first run the difference in film thickness obtained from the two curves varies from nothing to about 200 Å, but the variations are irregular. Even where the refractive index is the same— $2.45 - 0.28i$ (two films in the first case, one film in the second case), there still is a difference of 50 Å in the two sets of data. Also notice that for both Coupon M-23 and Coupon M-23R it is not possible, using a fixed value (2.45) for the real part of the refractive index, to obtain a film thickness for the thickest films, whereas a fit can still be obtained using the five-layer scheme. As mentioned earlier, more data can be obtained, but there is no easy way to evaluate them.

Data were taken more frequently during the rerun of Coupon M-23 to obtain a better shape for the polarizer angle-analyzer angle curve. Since the specimen corroded more rapidly, shorter heating periods were used. Comparison of the data for Coupons M-23 and M-23R shows that the imaginary part of the refractive index started out slightly higher for Coupon M-23R. At a film thickness of 1400 Å it had increased to 0.36 for Coupon M-23, but had gone up to 0.46 for Coupon M-23R. At greater thicknesses it decreased to about 0.28 and then went back up to 0.32 for both films.

Possibly the best way to grasp the significance of the work on Coupons M-23 and M-23R is to study the data statistically. The results are given in Table 11. First, for Coupon M-23, the best fitting equation for both the five-film and one-film models are of the log-log form; however, the slopes of the two equations are significantly different. Also, the limit of error of the fit of the five-film equation is significantly smaller than that of the one-film equation. For Coupon M-23R, at angles of incidence of both 60 and 70 degrees, the best-fitting curve used the cube root of time, but for each a negative intercept was obtained. This possibly means that two separate curves with different slopes should be drawn through the data points. The second-best fit was the log-log curve. Comparing Coupon M-23R with Coupon M-23, using one-film models with a 60-degree angle of incidence, the slope of the curve for Coupon M-23R is significantly greater and the limit of error of the fit is also significantly larger.

Coupons M-21 and M-21R were not studied as exhaustively as the "23" pair. However, it may be pointed out that the data from the first run of Coupon M-21 (five-film model) could be divided into early-data sets (first 26 days) and later-data sets (next 132 days) to provide significantly better fits than by the use of a single curve. This approach could not be taken with Coupons M-22 and M-23.

Data have been obtained from many Mulberry coupons which are summarized in Table 11. The limit of error of fit is very good for the coupons which were studied at room temperature because data points taken months apart did not represent a large change in the film thickness. The problems of changes in the refractive index affect the films thicker than about 500 Å; and, as a result, the limit of error of fit of the curves increased from about ± 20 to ± 100 Å.

The four sets of data labeled "MJ" in Table 11 were taken from a large piece of Mulberry which had been heated at the center by an electron beam. The center bubble was ground off and the sample repolished. Because material had been lost from the center, it was thought

that this area was in tension. Data were taken at the center and at the edges to see if there were any differences. Room-temperature data did not reveal anything because of the slow corrosion rate, so the temperature was raised to 100° C. After 24 days the corrosion film at the sides was about 100 Å, 14 percent thicker than it was at the center.

Coupon M-2 in Table 11 was studied at room temperature. The first equation calculated for the data was a function of the cube root of time. When additional data were obtained, a new calculation showed that a better fit was obtained using the square root of time. Coupon M-5 was sealed in a jar in which the relative humidity was maintained at 70 percent by a saturated salt solution.

CONCLUSIONS AND RECOMMENDATIONS

The ellipsometer is an instrument which can detect surface changes in polished materials with great sensitivity. In order to relate these changes to the oxide film thickness it is necessary to know the refractive index of the material; and, often, this can be determined simultaneously. The ellipsometer data taken from Mulberry coupons corroding for a long period at an elevated temperature showed that the refractive index was not uniform throughout the layer of oxide, or that it changed as some function of thickness. Several different models for the possible construction of the oxide were tested, but no single refractive index was found to explain the experimental data. The stress developed in a growing oxide film is very important in determining the corrosion-resistance characteristics of the film and the corrosion rate. However, tensile stress did not affect the refractive index of the film significantly.

There are variations of the refractive index which seem to be related to the metallurgical history and to cleaning and polishing techniques, and these should be studied more closely. Electrical properties (dielectric constant, conductivity, and magnetic permeability) are also related to the refractive index. Although present experimental data are too divergent for calculating electrical properties, elimination of the metallurgical history as an uncontrolled variable could produce valuable results in relating the optical and electrical properties.

The curve that fit the data the best for most uranium and Mulberry coupons was a log-log curve; in a few cases a better fit was obtained using the cube root of time. The statistical study also showed a precision in the fit of the curve of ± 12 Å for the data from a sample with a thin oxide film taken over a three-year period. For a thick film using the five-layer model, the precision was about ± 50 Å; and, using the one-layer model, the precision was about ± 100 Å. The accuracy depends upon the proper choice of the refractive index of the oxide film.

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