

금속 부식과 부동화에 관한 전기화학적 및 광학적 연구.
순철의 부동화 피막에 관한 전기화학적 및 광학적 연구

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An Electrochemical and Optical Study on the Corrosion and
Passivation of Metals. An Electrochemical and Optical
Study on the Passivation Film of Electrolytic Iron

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요 약. 음극 환원상태에 있는 철과 양극산화로 부동상태에 있는 철의 표면에 대하여 반사율과 광학적(ellipsometry) 측정을 하였다. 환원상태와 부동상태에 있는 표면들 사이의 광학적 파라미터들 (Δ , ϕ 및 반사율)의 차이를 측정하여 그로부터 부동상태에서 금속 표면을 덮고 있는 표면막의 두께와 광학적 상수들을 정할 수가 있었다. 포화 칼로멜전극에 대하여 -400 mV에서 부동화된 표면의 산화막은 약 11 \AA 의 두께와 $\tilde{n}=2.8-0.8i$ 의 광학상수를 갖고 있는 것으로 나타났다. 이로부터 부동상태의 표면막은 적지 않은 전자 전기전도성을 가지고 있음을 알 수 있다.

ABSTRACT. Ellipsometric and reflectance measurements were made on an iron surface in a cathodically reduced state and in an anodically passivated state. From the differences in the optical parameters (Δ , ϕ , and reflectance) between the reduced (film-free) and passivated (film-covered) states the thickness and optical constants of the surface film were determined. In the passive state at -400 mV vs. SCE in borate-boric acid buffer solution the anodic film had a thickness of about 11 \AA and optical constants of $\tilde{n}=2.8-0.8i$. This value indicates a substantial electronic conductivity of the anodic film.

INTRODUCTION

One of the fundamental problems in the science of corrosion is to find out the nature and thickness of the surface films formed on metals in the passive state.

The combined technique of ellipsometric measurement and reflectance measurement on a

metal/electrolyte interface was found to be a promising as a valuable method for investigating thin surface films with non-zero light extinction coefficients. It was first applied successfully to studying the anodic surface film formed on cobalt passivated in an electrolyte solution.^{1,2} It was also applied to anodic films on platinum³⁻⁵

and on gold⁵.

The principle of the method lies in the fact that a plane polarized light incident at an oblique angle upon a specularly reflecting planar surface becomes elliptically polarized on reflection. The components of amplitude of the optical wave parallel and perpendicular to the plane of incidence are reduced to certain degrees determined by the properties of the surface film as well as of the ambient medium and the underlying substrate metal. The ellipticity of the reflected light polarization is determined by the relative phase difference between the parallel and perpendicular components of the reflected light wave. The relative phase difference, Δ , and the amplitudes of the components of reflected light are in turn determined by the nature and thickness of the surface film. Therefore, it is possible to determine the complex optical constant $\tilde{n}=n-ik$ and the thickness τ of a surface film from only optical measurements.

In conventional ellipsometry, the measured quantities are the relative phase difference Δ and the relative amplitude deminution $\tan \phi$ defined by

$$\tan \phi = \frac{|r_p|}{|r_s|}$$

where r_p and r_s represent complex reflection coefficients of the components of light that are parallel and perpendicular to the plane of incidence, respectively. Since only two properties of light, Δ and ϕ are measured, it was not possible to determine unique values of the three properties of the film n , k and τ unless one of them can be independently measured or estimated. However, if a measurement of the total reflectance r , which is equal to $(r_p^2 + r_s^2)^{1/2}$, is made and combined with the ellipsometric Δ and ϕ , a unique numerical solution for the three values of n , k and τ is obtained.

We have attempted to apply this method to

iron. Iron has been studied by numerous workers with conventional ellipsometry and electrochemical measurements⁶⁻⁹. However, an unequivocal determination of its thickness and the optical properties of the surface film has not been possible. The values of the optical constants provide a clue to the electronic properties of the film.

EXPERIMENTAL

1. Ellipsometer. A manual ellipsometer was built in our laboratory from components including optical benches, a quarter-wave plate (Barbinet-Soloil), two polarizer prisms mounted on graduated rotating prism holders with a vernier, and a variable wavelength interference filter. A concentric arc lamp was used as the light source with a collimating assembly. A phototransistor was used as the detector. The quarter-wave plate was positioned between the polarizer and the sample cell with its fast axis at the aximuthal angle of 45° from the plane of incidence so that Δ is determined from the orientation of the polarizer with respect to the wave plate and ϕ is determined from the orientation of the analyzer.

The interference filter was positioned just in front of the detector to minimize the interference from room light. Since the monochromaticity of the light passing through the filter depends on the width of the entering light beam, the collimated light of cross-sectional diameter 8 mm after the analyzing prism was focused on the filter by a long focal length convex lens. The effect of deviation from the normal incidence upon the filter as a result of using the lens is negligible since the convex lens has a long focal length of about 25 cm. The general layout of the components in the assembled ellipsometer is presented in *Fig. 1*.

2. Electrochemical Cell. The iron specimen and a counter electrode made of platinum wire

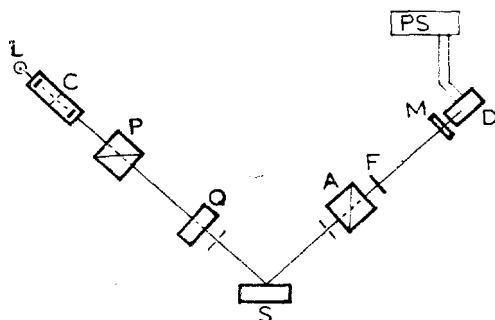


Fig. 1. Layout of components in the assembled ellipsometer.

L: concentric arc lamp; C: collimating assembly; P: polarizer; Q: 1/4-wave plate; S: sample surface; A: analyzer; F: focussing lens; M: monochromatic filter; D: photodetector; PS: power supply.

were placed in a rectangular cell with flat glass windows on two sides. A fine Luggin capillary from the reference electrode was positioned at the front edge of the specimen iron disc. The cell was made air-tight so that the solution could be deoxygenated by bubbling purified nitrogen. The potential of the iron electrode with respect to the reference electrode was controlled by a polarography unit used in the potentiostatic mode.

3. Specimen and Electrolyte Preparation.

Iron plate was made of electrolytic iron loaf of 99.95 % purity* by the cold rolling method and then punched into a cylindrical disc. The diameter of the disc was 1.9 cm. It was mechanically polished with fine sand paper for specular reflection. Powdered γ -alumina of 0.05μ was used in the final polishing. An electrical contact to the back of the iron disc was made by enamelled copper wire and sliver paint. The back surface and the wire was then coated with epoxy resin. 12.30 g of boric acid and 19.07 g of borax were dissolved in one

liter of doubly distilled water. Its pH was 8.4. This electrolyte solution was immediately deoxygenated when introduced into the cell by continuously bubbling nitrogen gas.

4. Measurement. The iron specimen was held at a cathodic potential of about -850 mV vs. saturated calomel electrode (SCE) for more than 3 hours before the optical measurements to make sure the surface is free of oxide film. The iron could be passivated by swift change of potential to above about -500 mV (SCE) and by allowing a few minutes to pass until the current density decreased to less than $1 \mu\text{a}/\text{cm}^2$. It could also be reduced quite reversibly back to the film-free state within several minutes when the potential was held at -850 mV. This conclusion was supported by the fact that the values of the optical parameters obtained from the reduced surface (denoted by Δ_0 , ψ_0 and r_0) could be reproduced within reasonable range (see Results).

All the optical measurements reported in this paper are made with wavelength off 550 nm.

The angle of incidence of the light was chosen to be 60 degrees at the metal/solution interface as a result of a preliminary calculation. This choice was made to enhance the sensitivity of the measurement of reflectance at a small sacrifice of the sensitivity in Δ measurement.^{1,2} Δ and ψ were measured for both film-free surface and the surface passivated at -400 mV (SCE) by the usual method of swinging polarizer in the vicinity of the light-extinction positions. ψ values were determined also by recording the transient light intensities $I_{//}$ and I_{\perp} passing through the analyzer oriented at 0° and at 90° . By recording the transient changes of the light intensities small variations in ψ could be determined with greater precision¹⁰. From the variations of the light intensities, the relative variations of the total reflectance on passivation and on reduction were also determined.

* Analysis of the iron sample by atomic absorption spectroscopy and carbon sulfur analyzer resulted in the following weight percentages of impurities: p 0.0016 %, Ni 0.0071, Mn 0.009, Cu 0.0015, C 0.018, S less than 0.008 %.

RESULTS AND DISCUSSIONS

The Δ and ϕ values from the cathodically reduced surface (denoted by Δ_0 and ϕ_0) were $145.24^\circ \pm 0.09$ and $31.08^\circ \pm 0.03^\circ$ respectively, both being the average of about a dozen measurements.

From these values the optical constants $\tilde{n}_m = n_m - ik_m$ of the iron were calculated to be $n_m = 3.52$ and $k_m = 3.60$. This result is close to that of Ord and DeSmet (3.50 and 3.66 respectively)⁶. However, this n_m value is slightly larger than the values reported for 545 nm by other previous authors and the k_m value is slightly smaller than their k_m values^{8,9,11~14}. The difference seems to be due partly to the differences in the crystalline states of iron used. (Table 1).

The Δ , ϕ and r values decreased as the iron was passivated at -400 mV (SCE) and returned to the initial values when iron was reduced again as is partly shown in Fig. 2. Averages were taken from the observed values of changes in

Table 1. Ellipsometric parameters determined for film-free surface of iron and the deduced optical constants of iron.

Ellipsometric parameters		Optical constants
Δ_0	ϕ_0	$\tilde{n}_m = 3.52 \sim 3.60$
145.24°	31.08°	$i = -1$
± 0.09	± 0.03	

Table 2. Changes in the ellipsometric parameters due to the surface film and the calculated properties of the film.

$\delta\Delta$, degree	$\delta\phi$, degree	$\frac{\delta r ^2}{ r_0 ^2} \times 100$	n_f	k_f	τ , Å
-1.92 ± 0.09	-0.164 ± 0.01	-1.09 ± 0.10	2.77 ± 0.16	0.8 ± 0.2	10.7 ± 0.6
Other works					
Brusic <i>et al.</i> by ellipsometry and coulometry ¹⁰			2.1~2.5	0.1	15~18
Sato and Kud, by ellipsometry ⁸			2.55	0.35	15
Ord and DeSmet by ellipsometry ⁶			2.6	0.4	

the above optical parameters obtained from repeated oxidation and reduction steps. The results are listed in Table 1.

A single film model was used to calculate the thickness τ and the optical constants n_f and k_f of the surface film the magnitudes of Δ , ϕ and r change. In this model an isotropic and uniform layer lies between the metallic iron and the electrolyte solution that are also assumed to be uniform from their respective bulks up to

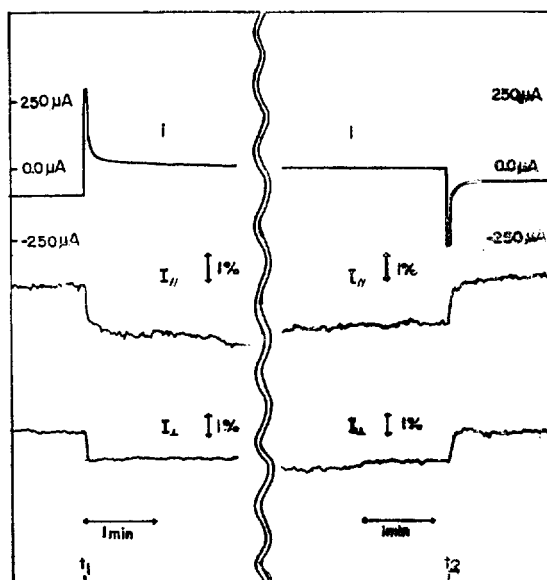


Fig. 2. Transients of current i and light intensities $I_{//}$ and I_{\perp} on passivation (from t_1) and reduction (from t_2). Variations in $(I_{//}/I_{\perp})^{1/2}$ is equivalent to changes in $\tan \phi$. Variations in $(I_{//} + I_{\perp})$ is equivalent to changes in r^2 .

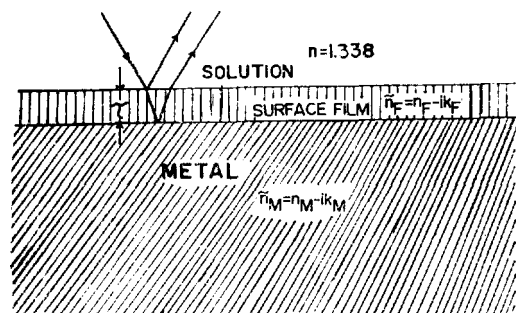


Fig. 3. Single-film model for a surface film covering metal and protecting it from the electrolyte solution.

the interfaces as is depicted in Fig. 3.

A computer program utilizing iteration processes for calculation with the model was employed in calculating n_f , k_f and τ from $\delta\Delta$, $\delta\phi$ and $\delta|r|/|r^0|$. The calculated values are 2.77 ± 0.16 , 0.8 ± 0.2 , and 10.7 ± 0.6 Å respectively (see Table 2). Results by other workers obtained under similar conditions are also shown for comparison.

The optical constants obtained in this work fall between those reported for cubic magentite (FeOFe_2O_3) and for hematite ($\alpha\text{-Fe}_2\text{O}_3$). It is therefore premature to identify the passivating film with any of the known oxides with this optical data. It seems necessary to extend the investigation into other potential regions to see if there are variations in the properties of the film with potential. One significance of the numerical value of k_f which is non-zero and is comparable in magnitude to those of semiconductor, is that it indicates an electronic conductivity. Therefore, it can be supposed that electrical field sustained in the layer of the surface film is not very strong in the state of passivation. Existence of the electrical field is a necessary condition for a field-assisted migration of ions through the layer, which in turn is one way of continued oxidation.

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