Ellipsometric Study of Anodic Oxide Films on Alloys of the Ti–Al System

A. N. Kamkin, L. A. Fishgoit, N. G. Bukhan’ko, V. I. Portnov, and V. A. Safonov

Moscow State University, Vorob’evy gory, Moscow, 119899 Russia

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Abstract—Anodic oxide films (AOF) on neat titanium and on alloys of the Ti–Al system (Ti–10 at. % Al, Ti–24 at. % Al, Ti–50 at. % Al, Ti–75 at. % Al) formed in borate buffer solution are studied by ellipsometry. A model is proposed, which adequately describes the shape of the alloy surface with and without AOF. The model takes into account the roughness factor, allowing one to more correctly determine optical parameters of AOF and dependence of its thickness on anodic potential. It is found that the alloy surface roughness is effectively smoothed with increasing applied potential.

INTRODUCTION

An accurate and sensitive method allowing one to fix variations occurring in oxide films with increasing potential is ellipsometry. Basic regularities of elliptic polarization of reflected light were formulated by Drude as far back as at the end of the 19th century (for a modern exposition of these questions, the reader is referred to [1–3]). The Drude theory links optical parameters of a surface to variations in parameters of elliptically polarized light reflected from the surface. The state of elliptic light polarization may be characterized by a pair of physical parameters. One is the difference \( \Delta \) between phases of oscillations of components of electric vector of the light wave parallel (\( || \)) and perpendicular (\( \perp \)) to the incidence plane. The other is the ratio between amplitudes of these components, \( \tan \psi = (R_2/R_1) \).

In the general case, the basic ellipsometric equation may be represented in the form of functional dependence

\[
\tan \psi \exp (i\Delta) = f(n_1, k_1, n_2, k_2, \phi, \lambda \{ \text{surface parameters} \}),
\]

where \( n_1 \) and \( k_1 \) are index of refraction and absorption coefficient of oxide film, \( n_2 \) and \( k_2 \) are similar parameters of metal (alloy), \( \phi \) is the angle of incidence of light beam, and \( \lambda \) is the wavelength. The surface parameters, which are determined by the shape of roughness and thickness of the oxide film, will be considered below. Note that, by the physical meaning of quantities \( \psi \) and \( \Delta \), the interval of changes in \( \psi \) is 0 to 90°, and that in \( \Delta \) is 0 to 360°. However, another approach, in which both \( \psi \) and \( \Delta \) vary from 0 to 180°, is also possible [3].

Consider the case where optical parameters \( n_2 \) and \( k_2 \) of metal are known, and a homogeneous anodic oxide film (AOF) of thickness \( d \) with unknown parameters \( n_1 \) and \( k_1 \) exists on a flat surface. In this case, to solve this equation, one should find \( n_1, k_1, \) and \( d \) from known values of \( \psi \) and \( \Delta \) determined with the aid of an ellipsometer. The problem is most readily solved for nonabsorbing films \((k_1 = 0)\); then one can calculate \( n_1 \) and \( d \) accurately enough from a single measurement. The calculation error will be defined only by experimental accuracy.

For light-absorbing AOF \((k_1 \neq 0)\), one obviously cannot reliably calculate three unknown quantities \( n_1, k_1, \) and \( d \) from two parameters \( \psi \) and \( \Delta \) obtained in a single experiment. The problem becomes even more daunting if the film is multilayered, the determination of constants for neat metal is fraught with difficulties, and the surface cannot be viewed as flat. There are some approaches to the search for a solution of basic ellipsometric equation in the case of such complications, in particular, for absorbing films. The most widely used method is the construction of theoretical nomographs describing dependence of \( \Delta \) on \( \psi \) for films of different thicknesses while varying \( n_1 \) and \( k_1 \) in certain limits. Having obtained a series of nomographs, one compares theoretical plots with experimental. This method is very labor-consuming and is applied in the cases where one can follow ellipsometrically the film growth to relatively large thicknesses. In other cases, one can perform additional measurements, as in the following three examples. In the first, the film thickness is determined by coulometry or some other technique. Afterwards, the problem reduces to solving a set of two equations for \( \Delta \) and \( \psi \) with two unknowns, \( n_1, k_1 \). In the second, the film composition is known. Then, assuming that optical parameters of a bulk oxide of this particular composition and the film are identical, one determines complex refraction coefficient for the film (from literature data or by directly investigating the bulk oxide). In this manner one reduces the problem to solving basic ellipsometric equation with one unknown, \( d \). In the third approach, ellipsometric measurements are performed under different conditions; in media with different values of the index of refraction, all other conditions
being the same; at different angles of incidence; or at different wavelengths (spectroscopic ellipsometry). This technique produces additional experimental data, thus allowing one to ensure that the number of experimental parameters exceed that of parameters to be determined.

All these methods have certain drawbacks and limitations. For example, in a coulometric thickness determination, one has to invoke assumptions about composition and density of the film, which are not always sufficiently justified; in spectroscopic ellipsometry, the complicating factor is dispersion of index of refraction and adsorption coefficient of the film; substituting one medium for another can alter properties of the oxide film itself; and so on. Moreover, these methods are inapplicable to studying very thin films, which cannot be viewed as phases of definite composition with fixed optical parameters.

In view of what we stated in the foregoing, we undertook an ellipsometric study of oxide films formed in a boric-borate buffer solution on Ti–Al alloys of different composition. To obtain sufficient amount of experimental data, ellipsometric measurements were performed at three angles of incidence. The ellipsometric data and their modeling description were complemented by a comparison with earlier independent studies carried out by methods of X-ray photoelectron spectroscopy (XPS), Auger spectroscopy, and chromato-mass spectrometry.

EXPERIMENTAL

For the study, we selected samples of neat titanium and alloys Ti–10 at. % Al, Ti–24 at. % Al, Ti–50 at. % Al, and Ti–75 at. % Al, which constituted phase \( \alpha \)-Ti and intermetallic compounds Ti\(_2\)Al\(_3\)(\( \gamma_2 \)), \( \gamma \)-TiAl, and TiAl\(_3\), respectively. The procedure used for preparing alloys is described elsewhere [4]. The working surface of electrodes was stringently abraded with water-wetted emery paper. The polishing was done on a grinding wheel clad in cloth by a suspension of fine powder-like emery paper. The polishing was done on a grinding wheel clad in cloth by a suspension of fine powder-like emery paper. The polishing was done on a grinding wheel clad in cloth by a suspension of fine powder-like emery paper. The polishing was done on a grinding wheel clad in cloth by a suspension of fine powder-like emery paper. The polishing was done on a grinding wheel clad in cloth by a suspension of fine powder-like emery paper.

Anodic oxide films were formed in a potentiostatic regime in a boric-borate buffer \( (0.075 \text{ M Na}_3\text{BO}_3 + 0.15 \text{ M H}_3\text{BO}_3, \text{pH} 8.7) \) prepared from reactants of reagent grade using distilled water. For the film formation, we employed a setup comprising a P-5827M potentiostat and standard three-electrode cell. A saturated silver–silver chloride electrode was the reference electrode, and a platinum plate served as the auxiliary electrode.

Ellipsometric measurements were carried out on an ellipsometer manufactured at the Russian Federation Scientific Center “Karpov Research Institute of Physical Chemistry,” at angles of incidence of 65, 70, and 75°. The light wavelength \( \lambda \) was 602 nm. Initial measurements were taken on samples covered with an oxide film formed in air (OFFA). Then a sample would be placed into cell filled with working solution and the first (lowest) potential would be imposed. The oxide formation time at each potential was one hour. Once the potential was switched off, the sample was rinsed with distilled water, dried in air, and ellipsometric measurements were taken once more, at the same angles of incidence. Subsequently the oxide was formed at a higher potential, and the measurement cycle was repeated.

THE SURFACE MODEL

As follows from the literature, a single-layer model usually fails to adequately describe ellipsometric data. Within such a model, optical constants of an oxide film are severely dependent on its thickness, which defies physical sense.

Employing two- and multi-layer models [5, 6] offers some substantial advantages from the viewpoint of adequacy of the experimental data description. In this case an oxide film may usually be represented as a number of layers with constant optical parameters. For example, experimental data on the growth of an oxide layer on titanium were satisfactorily described with a two-layer model in [7–9], where it was found that the oxide layer closest to the metal had a higher density and semiconductor properties (higher absorption coefficient). At the same time, application of such models, where surface oxide is modeled as a set of plane-parallel layers with invariant optical constants, provokes some objections. On the one hand, this is related to the fact that introducing an additional layer makes it necessary to calculate three additional parameters (index of refraction, adsorption coefficient, layer thickness). As the amount of experimental data is usually not sufficient enough, the reliability of computed parameters could be unsatisfactory. On the other hand, in real experimental conditions, even a polished metal surface has substantial microroughness. In these circumstances, use of models of plane-parallel oxide layers for oxide layers whose thickness does not exceed the characteristic size of the roughness becomes quite problematic. It should be noted that oxide layers that form on alloys studied in this work have exactly such thicknesses.

Taking into account roughness of a metal surface, on which an oxide layer forms, when interpreting ellipsometric data is a very difficult physical task. In [10], optical parameters of the surface of reduced and oxidized iron were described by an effective-film model. The model represented a surface layer, which includes microroughness, as a plane-parallel film. The film’s optical constants were defined by metal, oxide, and solution volume fractions in the film through the Maxwell–Garnett equation. This approach, which used optical parameters of metal, oxide, and solution obtained beforehand, markedly reduced the number of parame-