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Scientific paper
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Reflectivity from electrochemically protected Nb surfaces

Corrosion resistance of fine mechanically polished and electro-polished Nb surfaces were tested by elliposmetric measurements the reflectivity at various angle of incidence. The same measurements were also repeated on electro-polished Nb surface anodically oxidized in 1M H_2SO_4 during 30 s in the potential/voltage range from 0 to 100 V. From the minimum value of measured reflectivity parallel to plane of incidence, the Brewster angle for each investigated sample was determined. The simultaneous measurements of corrosion parameters Brewster angle have shown that the values of Brewster's angle should be used for fast testing the quality of protected metal surfaces.

Keywords: *niobium, anodic oxide films, ellipsometry, Brewster's angle.*

1. INTRODUCTION

The valve metal niobium generally is very stable in various corrosive media, as a result of existence the natural oxide films which in atmospheric conditions are spontaneously building on its surfaces [1]. But the corrosion stability of this metal could be considerably approved by electrochemical way using electrochemical polishing or anodic oxidation [2-4]. The protective properties of electro-polished or anodically oxidized metal surfaces with various film thicknesses can estimate by the values of reflectivity at Brewster's angles. One of the most precise methods for determination the reflectivity at Brewster's angles is ellipso-metry. By measuring the ellipsometric parametrs Δ and Ψ at various angles of incidence, the reflec-tivity of each angle can calculate and then the Brewster angle can determined. For exact deter-mination of Brewster's angle of bare metal surface it is necessary to prepare and measure very clean metal surface without existence of any impurities and natural oxide film. In literature can find the data for reflectivity of various bare metal surfaces prepared by evaporation in high vacuum and deposited in microscope quartz glass [5,6]. In this way, the authors believed that examined metals get completely pure and well defined homogeneous surfaces. Over the last forty years we can also find the data for reflectivity at pseudo Brewster's angle of electro-polished metal surfaces with cathodic pre-treatment and measured at in-situ conditions during the cathodic polarization [7,8]. Many previous results confirmed that with electro-polishing the most of surface impurities are dissolved in solution of electro-polishing baths and with cathodic polarization the thickness of natural oxide film is minimized [2,9]. But still is arguable possible inclusion of anions from electro-polishing bath in the crystals of metal surfaces.

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So far a number of authors have discussed the application of ellipsometry to the determinations of complex refractive indices, film thicknesses, reflectivity's and the source of errors occurred during the measurements of ellipsometric para-meters Δ and Ψ [10,11]. But no one has proposed the relation between measurements the reflecti-vity's at Brewster's angle and corrosion resistance of metal surfaces. The aim of this paper is to show possibility how through the ellipsometric measurements at Brewster's angle of electro-polished Nb surfaces can estimate the relative corrosion resistance without existence and with existence of anodically formed oxide films.

2. MATERIAL AND METHODS

Electrodes: Commercially pure 99.8 % (Alfa Aesar Johnson Matthey) Nb discs with diameter 12.7 mm have been wrapped in araldite resin and mechanically polished with emery paper grade 600. From this grade the next step was two kinds of surface preparation: (i) Mechanical stepwise polishing with lower grades of emery papers, from 600 to 5000. Then, fine mechanical polishing was continue, also by stepwise change the grades of diamond sprays from 6 to 0.1 μm. Finally the plane fine mechanical polished Nb surfaces with mirror brightness were obtained., (ii) Electro-polishing of the roughly mechanical polished Nb surfaces with emery paper 600, in the bath containing: 170 ml HNO_3 + 50 ml HF + 510 ml CH_3OH + 5 g citric acid. The best electro-polishing was obtained for voltage of 21 V on temperature of -5 ^{O}C and vigorous stirring of bath electrolyte during 1 min. [12]. Finally, in both cases of polishing the electrodes were carefully rinsed with distilled water and ultrasonically degreased in acetone and ethanol. In this way were obtained mirror bright electro-polished surfaces with mean square micro- geometry denivelation of the grains inside less than 5 nm. The quality of electro polishing was controlled interferometrically on metallography's microscope using Nomarski's method [13] and ellipsometrically measurements of reflectivity at fixed angle of incidence.

A Pt grid with a large surface area and a saturated calomel electrode were used as the counter and reference electrode, respectively.

Solutions. Aqueous solution of sulfuric acid with concentration of 1M was prepared by diluting concentrated 96 % H_2SO_4 (Merck, extra pure) with triply distilled water. The electrolyte in the electrochemical cell was exchanged after each experiment, in order to avoid eventual buildup of soluble Nb species

Apparatus. Anodic oxidation was performed potentiostatically in 1M H2SO4 during 30 s from OCP to 10 V using HEKA 488 potentiostat/ galvanostat interfaced with PC. For higher voltage than 10 V, the high stabilized electrical system (Drusch 5140) was used.

The ellipsometric measurements were carried out with “Thin Film Ellipsometer” type 43603-200 Rudolph Research. The polarizer and compensator were placed before examined reflecting surface, while the analyzer and detector were placed after this surface. The wavelength of measurements was fixed at 546.1 nm using Hg lamp and an interferential optical filter.

3. RESULTS AND DISCUSSIONS

The magnitude of ellipsometric parameters Δ and Ψ vary as a function of the angle of incidence, as well as physico-chemical and structural properties of the investigated metal surface.

Reflectivity from electropolished Nb surface. In fig 1 the dependence of Δ and Ψ from angle of incidence for electro-polished Nb surface is presented.

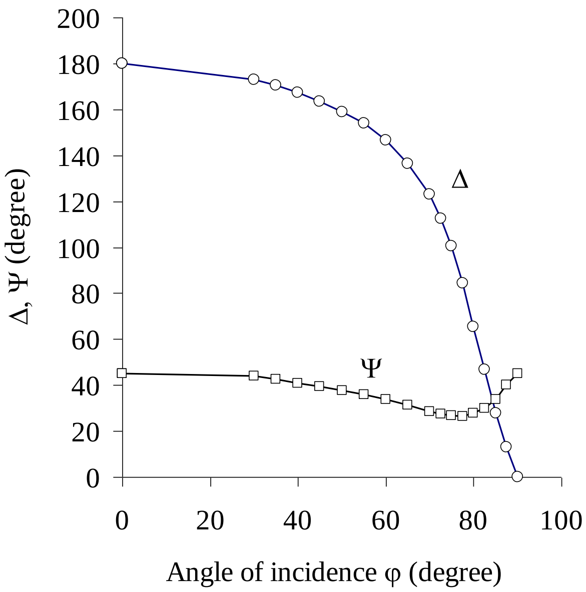

Figure 1 - Dependence of ellipsometric parameters Δ and Ψ on angle of incidence

The measurements were performed in the limits of incidence angles from 30 to 87.5 degree. Techni-cally it was not possible to perform the measure-ments for lower values of incidence angle than 30 degree. Technically it was not also possible to perform the measurements for incidence angle of 90 degree because the incidence beam will be in the same plane as metal surface and there should not be reflection. The values of Δ and Ψ for $\varphi = 0$ degree are extrapolated to their theoretical values of Δ = 180 and Ψ = 45, whereas for φ = 90 they are extrapolated also to their theoretical values of Δ = 0 and Ψ = 45. For ellipsometric measurements always should be choose the angle of incidence where for small change of this angle would have the biggest change of Δ and Ψ. In this case the measurements will be most sensitive.

Observing figure 1 it can conclude that the point of inflection on the curve for Δ corresponds to minimum value of Ψ. Theoretically the point of inflection should be located on Δ = 90 degree and the biggest change of values for Δ should be for angles of incidence near the inflection point. The angle of incidence which correspond to Δ = 90 degree is called principle angle. For majority of metals the values of principle angle move from 55 to 80 degree. But oppositely near the principle angle the curve for Ψ forms one minimum and in this region the change of values for Ψ with angle of incidence are the smallest. Taking into account that the change of values for Δ with angle of incidence are 5 to 10 times bigger than for values of Ψ, it has been suggested that the most sensitive ellipsometric measurements would be obtained for angle of incidence some degrees lower than principle angle. As it can see from fig.1, for angle of incidence some degree lower than principle angle begins to increase the change of values for Ψ and the values for Δ are still highly changeable with angle of incidence.

From the measured values of Δ and Ψ in fig.1, the reflectivity for different incidence angle were calculated using following equations:

$$R_S = \frac{(p - n_o \,\text{g}\cos\psi)^2 + q^2}{(p - n_o \,\text{g}\cos\psi)^2 + q^2} \qquad (1)$$

$$Rp = Rs \,\text{g}\tan^2\psi \qquad (2)$$

where

$$p = n_o \,\text{g}\tan\varphi \,\text{g}\sin\varphi \frac{\cos 2\psi}{1 + \sin 2\psi \,\text{g}\cos\Delta} \qquad (3)$$

$$q = n_o \,\text{g}\tan\varphi \,\text{g}\sin\varphi \frac{\sin 2\psi \,\text{g}\sin\Delta}{1 + \sin 2\psi \,\text{g}\cos\Delta} \qquad (4)$$

$$R = \frac{Rs + Rp}{2} \qquad (5)$$

In figure 2 the calculated values of Rs and Rp are presented. The center curve is arithmetic average between Rs and Rp.

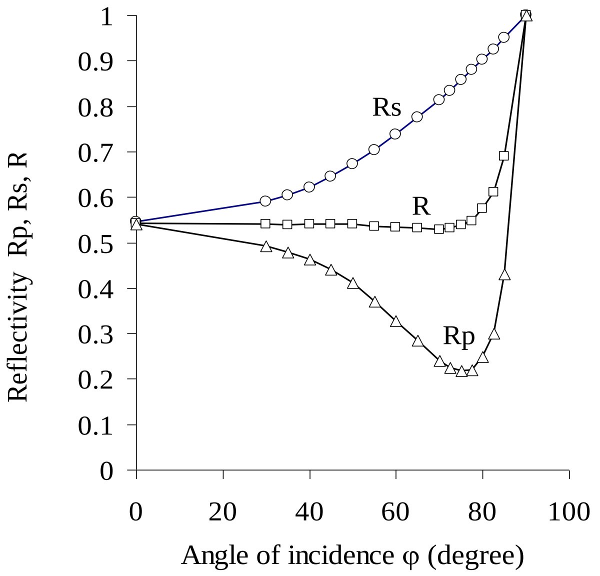

Figure 2 - The dependence of reflectivity on incidence angle

As can see from figure 2, Rs increase monotonically from its minimum value at φ = 0 to unity when incidence angle reach the value φ = 90, whereas *Rp* exhibits the minimum at the pseudo-Brewster angle of about 76.1 degree. This angle depends from the refraction indices and each metal or metal oxide has specific refraction indices, i.e. specific Brewster's angle.

Reflectivity from anodically oxidized Nb surface. For checking if the anodically formed oxide films on Nb surface have higher corrosion stability than electropolished Nb surfaces the anodic oxidation was performed each 5 V from 0 to 100 V. In this voltage region the film thickness increase linear and coefficient of film thickness growth is α = 2.35 nm/V [13]. Firstly the electro-polished Nb surfaces were anodized at constants potentials/volltages and the kinetic law of film thickness growth for each applied potentials/voltages has been determined. For example in fig 3 is shown the film thickness growth at potential of 5 V (a) and corresponding kinetic law (b). The faster film growth is in the first 20 s and then it progressively dimi-nished with time of polarization. The kinetic law was determined for all applied potentials/ voltages and it was observed that over the 100 V the formed films begin in big measure to losses their homogeneity. The loss of film homogeneity is developed also at lower voltages during the longer time polarization than 30 sec. But breakdown of the anodic oxide films begin for much lower voltages than 100 V that was confirmed by oscillo-scopic measurements for various applied voltages during the polarization [14].

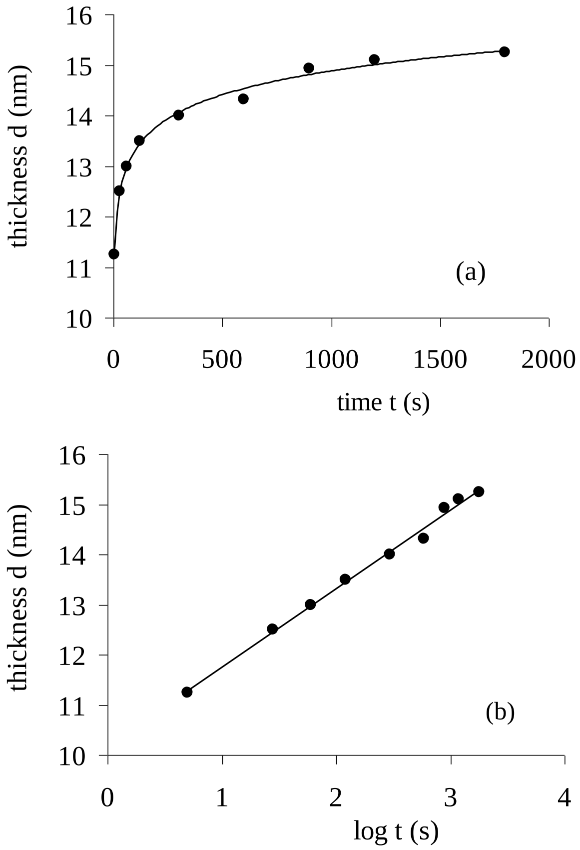

Figure 3 - Film thickness growth of anodically formed films on electro-polished Nb surface in 1M H_2SO_4 at potential of 5 V (sce). (a) in function of time, (b) logarithmic kinetic law

The anodic oxide films on Nb are already transparent with very small coefficient of absorption, about 0.0012 which represent the imaginary part of the complex indices of refraction [12]. Theoretically the anodic oxide films formed on Nb surfaces should be isolators with zero coefficient of absorption. Practically they are semiconductors. The semi-conducting properties of the films were provoked from non-stoichiometric participation of niobium and oxygen in the chemical composition of the film. During the polarization, especially at higher voltages, structural defects and possible inclusions of the anions from H_2SO_4 in the films can also increase conductivity of the insolating film. The deficit of oxygen results in formation of n-type semiconductor. By metallographic micro-scope it was confirmed that the structural defects in the film increases with augmentation the voltage of anodization, whereas by ellipsometric measure-ments it was confirmed that with augmentation the voltage of anodization increase the coefficient of absorption.

From the ellipsometrically measured parameters Δ and Ψ, as in previous case for electropolished Nb surface at various angle of incidence, the reflec-tivity parallel and perpendicular to the plan of incidence, as well as for ordinary non polarized light, for all investigated anodic oxide films for-med from 0 to 100 V were calculated, figure 4.

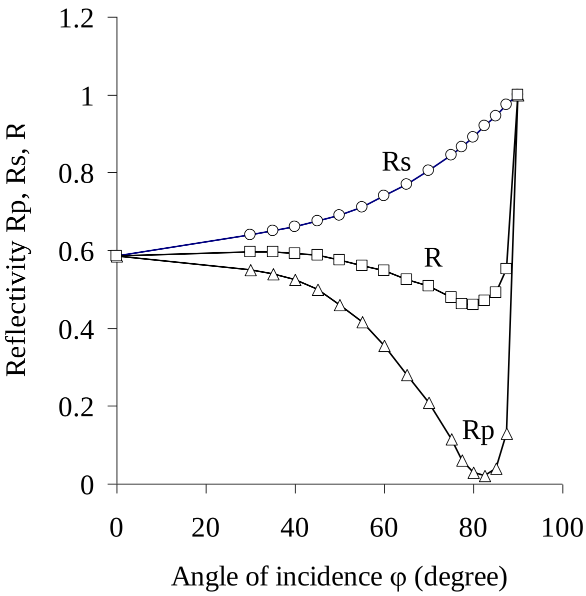

Figure 4 - Dependence of reflectivity on angle of incidence for electro-polished and anodically oxidized Nb surface in 1M H_2SO_4 during 30 s at 40 V

As it can see from fig.4 the minimum for Rp, which correspond to Brewster angle reach the value near the zero reflectivity. Theoretically Brewster angle represent some characteristic inci-dence angle when un-polarized light fall to tran-sparent surface and the reflected ray will be completely linearly polarized because the reflec-tion coefficient parallel to the plane of incidence is zero. The maximum polarization of reflected ray occurs when the reflected ray is perpendicular to the refracted ray. For ideally transparent substrates the value of Rp at Brewster angle should be zero. But for any real transparent substrate this value is a little bit higher than zero.

For fine mechanical polished and electro-polished Nb surfaces the metal substrate has not been transparent and the calculated minimum for Rp was higher than 0.2. This is the reason why for these minimums we have used terminology “pseudo Brewster angle” and for anodic oxide films where the minimum of Rp is near to zero we used simply Brewster angle. For fine mechanically polished Nb surface the Brewster’s angle was 75.8 degree and Rp = 0.24.

In Table 1 the film thicknesses of anodic oxide films formed at various potentials/voltages and corresponding Brewster’s angles determined from minimum of Rp curves are presented.

Table 1 - Determined values of Brewster’s angles at minimum reflectivity of Rp for anodic oxide films formed on electro-polished Nb in 1M H_2SO_4

Potential/ voltage (V)	Film thickness (nm)	Brewster’s angle degree	Rp
0	/	76.1	0.21
5	11.75	77.1	0.17
10	23.5	78.2	0.13
15	35.25	80.0	0.1
20	47	80.4	0.07
25	58.75	80.9	0.05
30	70.5	81.3	0.04
35	82.25	81.7	0.03
40	94	82.1	0.02
45	105.75	81.6	0.03
50	117.5	80.2	0.05
60	141	78.5	0.07
80	188	75.9	0.11
100	235	71.4	0.15

For each anodic oxide film presented in Table 1 the corrosion resistance in 1M H_2SO_4 was also investigated. The polarization measurements were performed within the range of -300 to 300 mV from the corrosion potential whereas the corrosion currents were determined from Tafel plots. For fine mechanically polished Nb surface the corrosion current was 1.45 $\mu A/cm^2$ and corrosion rate 10.2 μm/year. For electro-polished Nb surface corrosion current was 1.16 $\mu A/cm^2$ and corrosion rate 8.29 μm/year. The obtained corrosion parameters for all anodic oxide films fitted well with values of Brewster’s angles. With increasing the film thickness up to 94 nm, which correspond to anodic oxidation of 40 V, increase the corrosion resistance and the Brewster’s angles move to higher values up to 82.1 degree. At higher voltages than 40 V begins the breakdown process in the film and the surface defects increase together with film inhomogeneity. The values of Brewster’s angle begin to decrease whereas in the same time reflectivity at Brewster’s angle slightly increases. More detailed studies about the corrosion resistance of Nb with anodic oxide films in various concentrations of mineral acids and alkaline solution of will be presented in one of our next publications.

4. CONCLUSIONS

From ellipsometric measurements the reflectivity of mechanically polished and electro-polished Nb surfaces as well as electro polished Nb surfaces with formation of anodic oxide films the following conclusions could be drawn:

- The corrosion resistance of fine mechanically polished Nb surface is lower than electro-polished

- With increasing the film thickness of anodic oxide films formed on electro-polished Nb surface, increase the corrosion stability of these surfaces and Brewster's angles move towards higher values.
- For anodic voltages over the 40 V in the oxide films breakdown process begins to occur with development of film inhomogeneity and for anodic oxide film formed at 100 V Brewster's angles move to lower values until 71.4 degree With development of surface defects increased the conductivity of semi-conductive films and quality of surface protection is diminished.
- Finally it can concluded that the simple and fast measurements of Brewster's angles of metal surfaces and metal surfaces protected with anodic oxide films should serve as indicator for quality of protected metal surfaced against corrosion

NOMENCLATURE

Δ – relative phase change of the light polarized parallel and perpendicular for the plane of incidence

Ψ - relative amplitude attenuation of the light polarized parallel and perpendicular to the plane of incidence

Rp - reflectivity parallel to plane of incidence

Rs - reflectivity perpendicular to plane of incidence

no – index of refraction of medium

φ – angle of incidence

d – film thickness

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IZVOD

REFLEKTIVNOST ELEKTROHEMIJSKI ZAŠTIĆENIH Nb POVRŠINA

Koroziona otpornost fino mehanički poliranih i elektropoliranih Nb površina testirana je pomoću elipsometriskih merenja reflektivnosti kod različitih upadnih uglova incidentnog zraka. Ista merenja bila su ponovljena i kod elektropoliranih Nb površina anodno oksidiranih u 1 M H_2SO_4 u vremenu od 30 s za potencijalno/naponsko područje od 0 do 100 V. Od minimalne vrednosti merene reflektivnosti, koja je paralelna upadnoj ravni, odredjivan je Brewsterov ugao za svaki ispitivani primerak. Simultana merenja korozionih parametara i Brewsterovog ugla pokazala su da vrednosti Brewsterovih ugla mogu da se koriste za brzo testiranje kvaliteta zatićenih metalnih površina.

Ključne reči: *niobijum, film anodnog oksida, elipsometrija, Brewsterov ugao.*

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