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Ellipsometric study of anodic oxide films formed on niobium surfaces

Abstract Anodic oxide films formed potentiostatically on niobium surfaces, from open circuit potential (OCP) to 10 V, were studied by performing in situ and ex situ ellipsometric measurements. The kinetics of the film thickness growth in 1 M H_2SO_4 and complex indices of refraction of these films were determined. A strong influence of the surface preparation conditions on the complex refractive indices of the metal substrate and anodic oxide films was shown. By steady-state measurements at OCP, a small thickening of the natural air-formed oxide film with chemical composition Nb_2O_5 in 1 M H_2SO_4 solution was detected. With cathodic pretreatment, only partial reduction and small thinning of the natural air-formed oxide film was possible. The thicknesses of the natural air-formed oxide films on fine mechanically polished and electropolished Nb surfaces were determined. The build up of the natural air-formed oxide film, at ex situ conditions, on the already formed anodic oxide films was confirmed. It was shown that electropolishing gives more similar optical surface properties to the bare metal than the fine mechanical polishing.

Keywords Niobium surfaces · Electropolishing · Anodic oxidation · Ellipsometry · Optical constants

Introduction

Over the last 50 years, oxide films on niobium have been studied extensively in order to increase the use of this metal and its alloys in various branches of the chemical, mechanical and electronic industries. Most of the work is concentrated on thermal oxidation because this metal exhibits unusual oxidation features. At each temperature and pressure the oxidation rate has been found to follow a complex series of kinetic laws [1, 2, 3]. A smaller number of studies were devoted to the anodic oxidation and electrochemical, optical and structural properties of anodic oxide films [4, 5]. According to Huang et al. [6], in the passive region the anodic oxide film is composed of amorphous NbO_2 and Nb_2O_5. At higher potentials the thick anodic film primarily consists of well-crystallized Nb_2O_5. In most of the studies the purpose of the anodic oxidation was to improve the resistance to surface corrosion of Nb [7], to develop new materials suitable for production of display devices based on electrochromic effects [8], and also to develop new electrode materials for electrolytic capacitors [9].

The electrochemical formation of anodic films on Nb surfaces in moderately acidic and alkaline solutions yields an oxide of compact thickness of several hundred nanometers, as in the case of the valve metals: Ti [10], Zr [11] and Ta [12]. According to the literature data, the properties of the films and the film thickness growth could be modified either by controlling the electrolyte composition or the electrochemical perturbation during the film formation [13, 14]. However, so far, not much attention has been paid to the anodization behavior of various kinds of surface preparation conditions of Nb electrodes.

The aim of this work was to study the influence of the surface preparation conditions on the optical properties and film thickness growth of anodic oxide films on Nb electrodes.

Experimental

Electrodes

Cylindrical Nb discs, 12.7 mm in diameter and 10 mm thick, with 99.8% purity (Alfa Aesar Johnson Matthey) were covered in epoxy resin (Struers), leaving one base of the cylinder to be in contact with the solution in the electrolytic cell. The working surfaces of the Nb electrodes were mechanically polished using metallurgical papers of grade 600, than ultrasonically cleaned and

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degreased with methanol. In the next step, two kinds of surface preparations were performed: fine mechanical polishing and electropolishing. During the fine mechanical polishing the electrode surfaces were ground with a set of emery papers from grade 600 up to 5000 and than mirror polished with diamond sprays from 6 to 0.1 μm. During the electrochemical polishing, the previously roughly polished Nb surfaces with metallurgical paper 600 were electropolished in a bath consisting of 170 mL concentrated $HNO_3 + 50$ mL 49% HF + 150 mL $CH_3OH + 5$ g citric acid, using a voltage of 15.2 V and vigorously stirring for 1 min, at a bath temperature of –5 °C.

A Pt grid was used as a counter electrode and saturated $Hg/Hg_2SO_4/K_2SO_4$ as a reference electrode. All potentials in this work are referred to the normal hydrogen electrode (NHE).

Optical-electrolytic cell

The anodic oxidation and ellipsometric measurements were performed in a specially adopted optical-electrolytic cell with two optical quartz windows, fixed at an angle of incidence of 70° and similar in design to those described elsewhere [15].

Solutions

Aqueous H_2SO_4 solutions (Acros Organics), with a concentration of 1 M were prepared in redistilled and deionized water. After each measurement the electrolyte in the cell was exchanged in order to avoid eventual build-up of soluble Nb species.

Apparatus

The anodic oxidation from open circuit potential (OCP) to 10 V was performed potentiostatically using a Heka model 488 potentiostat/galvanostat interfaced with a personal computer. The potential was successively increased in increments of 0.5 V and polarization studies were done in the range between 0 and 10 V.

The ellipsometric measurements were performed with a Rudolph Research type 436003-200 Thin Film Ellipsometer at a wavelength of 546.1 nm and an incident angle of 70°.

Experimental procedure

Under open circuit conditions the freshly prepared electrode surfaces were immersed in the optical-electrolytic cell and their position was adjusted until the maximum photomultiplier response of the reflected ellipsometric light was obtained. The electrode was then anodized at various potentials for a 30 s period of time. In order to prevent the evolution of oxygen bubbles during the ellipsometric measurements, especially for potentials higher than 2 V, the following precautions were taken: when the working electrode was anodized at potentials higher than 2 V (NHE), after 30 s the potential was rapidly decreased and was kept at a constant value of 2 V (small anodic current flowing during the measurements). In this manner the ellipsometric measurements were performed under potentiostatic control.

Results and discussion

After mechanical or electrochemical polishing the Nb samples were immediately immersed in the cell with aqueous 1 M H_2SO_4 solution and the OCP was recorded (Fig. 1). The measurements had a satisfactory reproducibility and the recorded curves showed a regular OCP increase in an anodic direction, suggesting small changes in the surface properties.
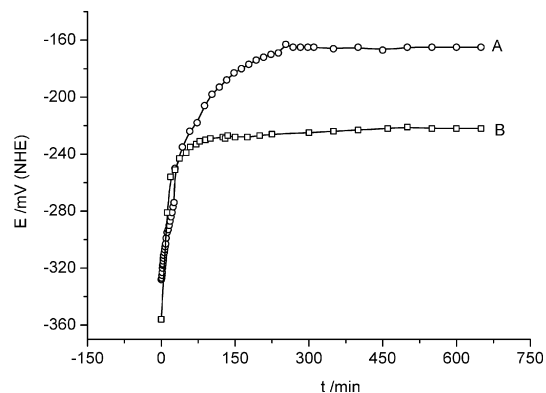

Fig. 1 Variation of OCP versus time of Nb electrode in 1 M H_2SO_4 for various kinds of surface preparation: *A* fine mechanical polishing; *B* electropolishing

In order to make a more accurate verification of the existence of some surface reactions, with OCP we performed simultaneous ellipsometric measurements. The very small variations of the ellipsometric parameters Δ and Ψ confirmed that the surface reactions were not correlated with any noticeable chemical reactions or changes in surface properties. The only possible surface reaction seems to be the negligible thickening of the previously natural air-formed oxide film. From Fig. 1 it is evident that the electropolished Nb surface (curve B) reached stabilization of the OCP for a shorter period of time than the fine mechanically polished surface (curve A) and showed a more regular shape, without any oscillation of the potential values. Therefore the smaller changes of OCP of the electropolished Nb surface during the whole measurement time proved that the electropolishing to be the better and more reproducible manner of surface preparation, with a more resistant surface than fine mechanical polishing.

In the ellipsometric measurements, for a three-component system (medium, oxide film, metal substrate), the experimentally measured Δ and Ψ were related as a complex function with the following parameters:

$$\tan \Psi \exp(i\Delta) = f(\hat{n}_1, \hat{n}_2, \hat{n}_3, d, \lambda, \varphi) \qquad (1)$$

where $\hat{n}_1 = \hat{n}_1(1 - k_1 i)$, $\hat{n}_2 = n_2(1 - k_2 i)$ and $\hat{n}_3 = (1 - k_3 i)$, the complex refractive indices of the medium, oxide films and metal substrate, respectively; d = film thickness, λ = wavelength of incidence light; and φ = angle of incidence.

Refractive indices of the medium

A simple way of determining the refractive indices of the medium is by using an Abbé refractometer. For a 1 M H_2SO_4 solution at a temperature of 20 °C the measured value of n_1 was 1.3442. This value is in good agreement with the literature data [16]. The complex index of refraction for air surrounding a medium is $n_1 = 1$. In both

cases the medium is a transparent and an imaginary part of refractive index $k_1 = 0$.

Refractive indices of metal substrate

In determining the complex refractive indices of the metal substrate, the principal difficulty was how to obtain a bare metal substrate without the presence of any surface oxide films or attached impurities during the handling of the electrode surface. One possibility is cathodic reduction. For each kind of sample preparation we made a cathodic reduction at cathodic potentials that varied from –0.5 V (NHE) to –1.1 V (NHE). At the same time, we followed the change of ellipsometric parameters Δ and Ψ for electrodes in the as-polished states. Only the change from one to the other oxide state of the natural air-formed oxide film and its small thinning is possible. For cathodic potentials more negative than –1.1 V (NHE), intensive gas evolution on electrode surfaces occurred and ellipsometric measurements started to lose sensitivity.

The other possibility is evaporating the metal in vacuum and performing the measurements under high vacuum conditions. In this manner, during the measurements the risks of surface contamination or oxidation would be prevented. However, the validity of using the refractive indices of evaporated films, instead of the bulk metal, is sometimes questionable. The structure of both metal substrates is not the same. In the literature data a big discrepancy exists in the values of the refractive indices of Nb, mainly due to the different procedures utilized in the surface preparation [4, 16, 17].

As shown in our previous work, an incorrect determination of the refractive indices of bare metal substrates is one of the essential errors in ellipsomtric measurements [18, 19, 20]. The other source of error, not pointed out sufficiently enough in the literature, is always determining the thickness-voltage relationship for high-voltage oxides. Thus, the thickness-voltage relationship cannot be valid for lower voltage oxides, unless the existence of the natural air-formed oxide film and its possible transformation is not taken into consideration as supplemental surface phenomena. Owing to these reasons, our ellipsometric measurements were performed up to potential values of 10 V. In addition, various methods for determination of metal substrate indices of refraction were also proposed.

One method is direct ellipsometric measurements of freshly prepared electrode surfaces. For this method, in order to minimize the influence of the air-formed natural oxide film on the values of the metal substrate, after each kind of surface preparation the electrode was immediately immersed in an electrolytic cell and the ellipsometric measurements were performed. The obtained values of the refractive indices represent some hypothetical average values of a metal substrate with a small participation of the natural air-formed oxide film. In this manner the determined hypothetical values of the metal substrate for fine mechanical polishing and electropolishing were $\hat{n}_3 = 2.85(1 - 0.901i)$ and $\hat{n}_3 = 2.9(1 - 1.175i)$, respectively. A comparison of the literature data and the refractive indices values we determined by using direct ellipsometric measurements is given in Table 1. Taking into account that electropolished Nb surfaces have higher reflectivity than fine mechanically polished surfaces, we also performed direct ellipsometric measurements of Nb surfaces in ex situ conditions, immediately after electropolishing in air ambient conditions and before immersing the electrode in the electrolytic solution.

As can be seen in Table 1, only for fine mechanical polishing are our hypothetical values of the refractive indices close to the literature data [4]. The real part is the same, but the small difference in the imaginary part suggests that our samples should have a little lower quality of surface preparation, or a little thicker natural air-formed oxide film. For electropolished Nb surfaces the proposed values of the refractive indices in the literature were not directly measured, but calculated [14]. This is the main reason why there is a big difference between our values and the ones found in the literature.

Refractive indices of anodic oxide films and metal substrate

The other method of determining $\hat{n}_3$ is utilizing a fitting procedure of experimentally measured Δ-Ψ values for anodic oxide films with the theoretical Δ-Ψ plot calculated from Fresnell's equation for a three-component system (medium, oxide film, metal substrate) [19]. Using this method, with $\hat{n}_3$ we have simultaneously determined also the indices of refraction and the coefficient of film thickness grown for anodic oxide films.

In Fig. 2 the experimentally measured Δ-Ψ parameters for the anodic oxide films formed on fine mechanically polished Nb surfaces in 1 M H_2SO_4 are shown. Between the experimental points is fitted the theoretical

Table 1 Refractive indices of hypothetical ellipsometric measured values and literature proposed values of Nb substrates

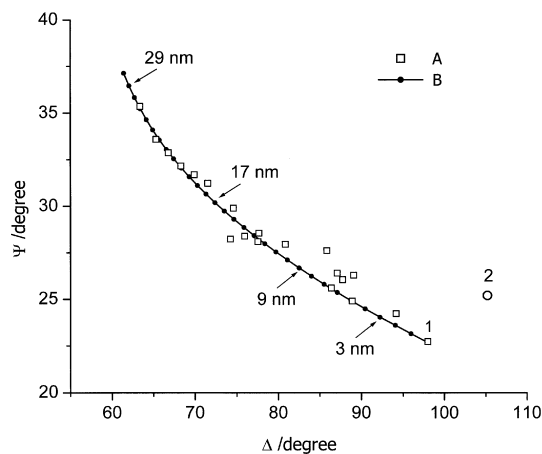| Surface preparation	Measurement conditions	$\hat{n}_3 = n_3(1 - k_3i)$		Ref
		This work	Literature	
Fine mechanical polishing	In situ	2.85(1–0.901i)	2.85(1–1.050i)	[4]
Electropolishing	In situ	2.90(1–1.175i)	3.60(1–1.000i)	[14]
Electropolishing	Ex situ	2.72(1–1.231i)	3.17(1–1.132i)	[17]

Fig. 2 Graphical plot of the ellipsometric Δ and Ψ parameters during anodic oxidation of fine mechanically polished Nb in 1 M H_2SO_4: *A* experimentally measured data; *B* theoretical fitted curve; *1* our measurements for the metal substrate; *2* literature data for the metal substrate [4]. On the computed curve, some values of the film thickness are shown

Fig. 3 Graphical presentation of the film thickness growth on Nb surfaces versus applied potential in 1 M H_2SO_4: *A* fine mechanical polishing; *B* electropolishing. The intersections at –0.225 V and –0.165 V correspond to the film thickness at the OCP. The *inset* represents the extrapolation of linear plot *B* and the determination of the thickness of the natural air-formed film under ex situ (–0.355 V) and in situ (–0.225 V) conditions

plot, which is derived from hypothetical values of the metal substrate, $\hat{n}_3 = 2.85(1 - 0.901i)$, the film refractive indices of $\hat{n}_3 = 2.27(1 - 0.009i)$ for film thickness grown in 1 M H_2SO_4. The fitting procedure was performed by a specially prepared computer program in which $\hat{n}_2$ was searched for prior given values of the thickness in increments of 1 nm, in an increasing direction [20]. The number of theoretical Δ-Ψ points on the theoretical fitted curve depends on the thickness increment given by us during the computation. The relatively large dispersion of experimental points from the theoretically fitted curve indicates low reproducibility of the fine mechanically polished Nb surfaces before the anodization. It should be noted that, during the fine mechanical polishing, smooth surfaces with mirror brightness were obtained. However, mechanical polishing leaves numerous micro-surface scratches and defects with random distributions which cause areas of differing electrical potentials due to surface stress.

The first experimental point, marked with number 1 on Fig. 2, corresponds to Δ and Ψ values of the metal substrate we measured. This point lies on the theoretical fitted curve. Point 2 corresponds to values of Δ and Ψ from the literature-proposed refractive indices of the metal substrate, $\hat{n}_3 = 2.85(1 - 1.105i)$ [4], which were not directly measured, but calculated.

The large discrepancy of this point, compared to other experimental points and the theoretical fitted curve, did not give us the possibility to calculate $\hat{n}_3$ simultaneously with $\hat{n}_2$. Thus, for calculation of the theoretical fitted curve, our experimental values for the metal substrate were taken. From the experimentally measured Δ and Ψ and the theoretical fitted curve it is possible to determine the thickness of the anodic oxide films for various values of applied potentials (Fig. 3). As can be seen from the figure, a linear kinetic law of the film thickness growth exists in the potential range
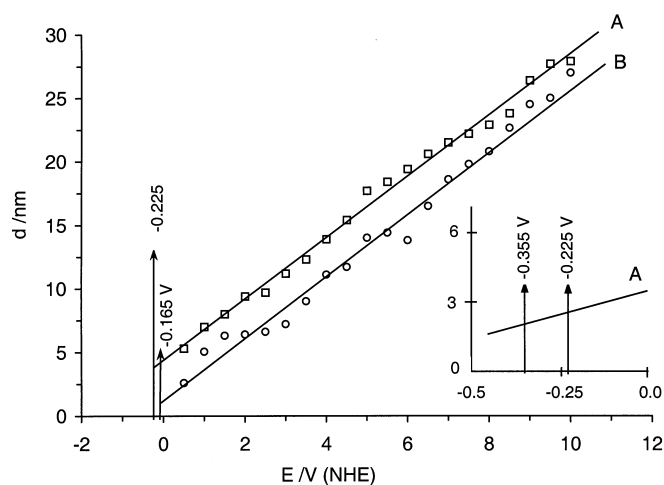
between 0 and 10 V (NHE). With extrapolation of the linear plot A on Fig. 3 to the value of –0.165 V (NHE), a thickening of about 1 nm of the air-formed natural oxide film in electrolytic solution for the fine mechanically polished Nb surface was determined. The value of –0.165 V (HNE) corresponds to the stabilization of the OCP, determined from curve A on Fig. 1. From the slope of the linear plot A on Fig. 3, the coefficient of the film thickness grown was also determined: $\alpha = 2.52$ nm/V.

On Fig. 4 are shown the experimentally measured Δ-Ψ parameters under in situ conditions for anodic oxide films formed on electropolished Nb surfaces in 1 M H_2SO_4. The theoretical plot (similarly calculated as in the case of fine mechanical polishing, Fig. 2) was derived from hypothetical values of the refractive indices of the metal substrate, $\hat{n}_3 = 2.90(1 - 1.175i)$, under in situ conditions. From this theoretical plot, the film refractive indices of $\hat{n}_2 = 2.4(1 - 0.0005i)$ for film thickness growth in 1 M H_2SO_4 solution were fitted. The imaginary part of the refractive index, $k_2 = 0.0005$, has a smaller value than in the case of the fine mechanical polishing. This suggests that on the electropolished Nb surfaces the formed anodic films gave more transparent and homogeneous films than on the fine mechanically polished ones.

The experimentally measured points on Fig. 4 deviated very little from the theoretical fitted curve, indicating a high reproducibility of electropolished Nb surfaces before anodization. We measured the first experimental point, marked with number 1, corresponding to Δ and Ψ values of the metal substrate (consisting of small parts of the natural oxide film). This point is superposed well on the theoretical fitted curve. Li and Young [17], for a film grown in 1 M KCl and H_3PO_4,
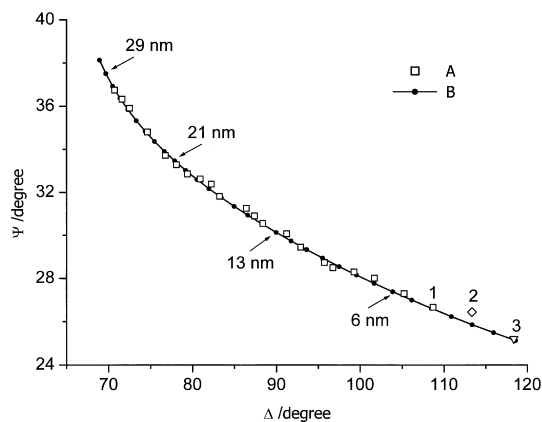
Fig. 4 Graphical plot of the ellipsometric Δ and Ψ parameters during anodic oxidation of electropolished Nb in 1 M H_2SO_4: *A* experimentally measured data; *B* theoretical fitted curve; *1* our measurements for the metal substrate; *2* literature data for the metal substrate [14]; *3* literature data for the metal substrate [17]. On the computed curve, some values of the film thickness are shown

gave a value of $\hat{n}_3 = 3.17(1 - 1.132i)$ for the electropolished Nb substrate. Later, for a film grown in 0.1 M H_2SO_4, Young and Zobel [14] also gave a value for an electropolished Nb substrate of $\hat{n}_3 = 3.6(1 - 1i)$. The point marked with number 2 on Fig. 4 corresponds to the values of Δ and Ψ calculated from $\hat{n}_3 = 3.17(1 - 1.132i)$, while the point marked with number 3, for Δ and Ψ calculated from $\hat{n}_3 = 3.6(1 - 1i)$. It is evident that the value of Δ and Ψ calculated from $\hat{n}_3 = 3.6(1 - 1i)$ better fits the theoretical curve than the values of Δ and Ψ calculated from $\hat{n}_3 = 3.17(1 - 1.132i)$. Thus, near the point of Δ and Ψ which corresponds to $\hat{n}_3 = 3.6(1 - 1i)$, from the theoretical fitted curve we determined very precisely the values of $\Delta = 118.58$ and $\Psi = 25.12$, which are located just on the theoretical fitted curve. From these two values of Δ and Ψ we determined the complex refractive indices of the metal substrate, $\hat{n}_3 = 3.62(1 - 0.993i)$, which was used in all our further fitting procedures with experimental data and calculations of theoretically fitted curves.

From experimentally measured values of Δ and Ψ and the theoretically fitted curve, similar to the case of fine mechanical polishing, it is possible for electropolishing to determine the dependence of the thickness of anodic oxide films on the applied potentials. A linear kinetic law of film thickness growth in the potential range between 0 and 10 V exists (Fig. 3B). With extrapolation to the potential of –0.225 V (NHE), stabilization of the OCP (see Fig. 1 curve B), and from the slope of the linear plot, the thickness of 2.6 nm for the air-formed oxide film and the coefficient $\alpha = 2.52$ nm/V for film thickness growth are determined. The thickness of 2.6 nm in reality represents the sum of the film thickness of the natural air-formed oxide film before immersing the electrode in electrolytic solution (2.1 nm) and the thickening of this film in electrolytic solution up to 2.6 nm. The thickness of

2.1 nm was determined by extrapolation of linear plot B (insert on Fig. 3) to the value of –0.355 V (NHE), which corresponds to the first experimental point of the OCP, measured immediately after immersion of the electrode surface in the electrolytic solution (curve B on Fig. 1). This is not a case for fine mechanical polishing, because our calculations began from the first experimental point, with a hypothetical value for the metal substrate.

For testing the possible build-up of natural air-formed oxide film on the already formed anodic oxide films, after anodization and ellipsometric in situ measurements, each sample was measured under ex situ conditions from the OCP to the potential of 10 V (NHE). The electrodes were taken out of electrolytic cell, washed with distilled water and methanol and dried in stream of pressurized air. Then, the ellipsometric measurements were continued in an air ambient condition where $n_1 = 1$. The same procedure for calculating the values of $\hat{n}_2$ and α was performed as in the previous two cases for the fine mechanical polishing and electropolishing under in situ conditions. For electropolished Nb surfaces in ex situ conditions, the following values were determined: $\hat{n}_2 = 2.34(1 - 0.0005i)$ and $\alpha = 2.64$ nm/V.

In Table 2, a comparison of the values of $\hat{n}_2$ and α for mechanically polished and electropolished Nb surfaces are given. From Table 2 one can conclude that the coefficient of the film thickness growth does not depend on the preparation mode of the metal substrate, but it depends on the measurement conditions. For fine mechanical and electropolished Nb surfaces, measured under in situ conditions, the same values for α are obtained. However, under ex situ conditions the films were thicker as a result of build-up of a natural air-formed film on the previously formed anodic oxide films. On the other hand, the surface preparation conditions strongly affected the film refractive indices. The higher value of the real part and the lower value of the imaginary part indicated that on the electropolished Nb surfaces the anodic oxide films are more homogeneous and more transparent than on the fine mechanically polished surfaces. However, the values of the imaginary part do not change during the measurements under in situ and ex situ conditions because the build-up of a very thin natural oxide on the anodic oxides, under ex situ conditions, cannot perturb the homogeneity and transparency of the previously formed anodic oxide films.

Table 2 Refractive indices and coefficient of anodic film thickness grown on Nb surfaces

Surface preparation	Measurement conditions	α (nm/V)	$\hat{n}_2 = n_2 (1 - k_2 i)$
Fine mechanical polishing	In situ	2.52	2.27(1–0.009i)
Electropolishing	In situ	2.52	2.40(1–0.0005i)
Electropolishing	Ex situ	2.64	2.34(1–0.0005i)

Conclusions

From ellipsometric measurements of anodic oxide films formed on Nb surfaces in 1 M H_2SO_4 for a potential range from the OCP to 10 V, the following conclusions were drawn:

1. The Nb surface was well resistant in 1 M H_2SO_4 and only small surface reactions, including thickening of the natural air-formed oxide film at the OCP, were possible.
2. The anodic oxidation was well established as a procedure in the case of Nb and the thickness of the anodic oxide films increased linearly with the applied potential, independent of the surface preparation conditions of the metal substrate. The thickness of the natural oxide film formed on the electropolished surface was about 2.1 nm, while the thickness of the natural oxide films formed on the anodic oxide films was 1.2 nm, for a period of time of about 5 min after anodization.
3. By extrapolation of the theoretical plot with the experimental Δ-Ψ loci to the Δ-Ψ literature data, the refractive index of the electropolished Nb surface, $\hat{n}_3 = 3.62(1 - 0.993i)$, which corresponds to a bare metal substrate, was determined. The values of the refractive indices show that the anodic oxide films formed on electropolished Nb surfaces under in situ conditions, $\hat{n}_2 = 2.4(1 - 0.0005i)$, and under ex situ conditions, $\hat{n}_2 = 2.34(1 - 0.0005i)$, are more homogeneous and more transparent than the anodic oxide films, with refractive indices of $\hat{n}_2 = 2.27(1 - 0.009i)$ formed on fine mechanically polished surfaces.
4. At temperature of 20 °C, the coefficient of the film thickness growth determined ellipsometrically on electropolished Nb surfaces was $\alpha = 2.52$ nm/V. The reciprocal value of this coefficient, $1/\alpha = 3.97 \times 10^6$ V/cm,

indicated a very strong electrical field crossing the anodic oxide films. Theoretically, anodic oxide films should be insulators, but practically, with the existence of some surface defects, they have semiconducting properties.

References

1. Sheasby JS, Wallwork GR, Smeltzer WW (1966) J Electrochem Soc 113:1255
2. Sheasby JS (1968) J Electrochem Soc 115:695
3. Gomes MA, de S Bulhoes LO, de Castro SC, Damiao AJ (1990) J Electrochem Soc 137:3067
4. Dyer CK, Leach JSL (1978) J Electrochem Soc 125:23
5. Badawy WA, Feske A, Plieth WJ (1989) Electrochim Acta 34:1711
6. Huang BX, Wang K, Church JS, Li YS (1999) Electrochim Acta 44:2571
7. Uebara I, Sakai T, Ishikawa H, Takenaka H (1989) Corrosion 45:548
8. Faria RC, de S Bulhoes LO (1994) J Electrochem Soc 141:L29
9. Bairachnyi BI, Gomozov VP, Lyashok LV, Skatkov LI (1989) Elektrokhimiya 25:994
10. Arsov Lj (1982) Electrochim Acta 27:663
11. Patritio EM, Macagno VA (1994) J Electroanal Chem 371:59
12. Ord JL, Hopper MA, Wang WP (1972) J Electrochem Soc 119:439
13. Alkaine CVD, de Souza LMM, Nart FC (1993) Corros Sci 34:109
14. Young L, Zobel FGR (1966) J Electrochem Soc 113:277
15. Arsov Lj (1985) Electrochim Acta 30:1645
16. Weast RC (1975) Handbook of chemistry and physics, 56th edn. CRC Press, Boca Raton, Fla
17. Li YM, Young L (2000) J Electrochem Soc 147:1344
18. Efremova A, Arsov Lj (1992) Electrochim Acta 37:2099
19. Hristova E, Arsov Lj, White R, Popov B (1997) J Electrochem Soc 144:2319
20. Efremova A, Arsov Lj (1992) J Phys France II 1353