

EVALUATION OF THE ANODIC OXIDE GROWTH ON ZIRCONIUM IN NaOH SOLUTIONS USING ELLIPSOMETRY

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Abstract: Ellipsometry, is one of the most convenient and accurate techniques for the measurements of film thickness and refractive indexes of thin films on solid surfaces. The characterization of a thin film grown on a metallic substrate requires a preliminary knowledge of the optical indexes of the substrate and surrounding media.

Ellipsometry measures the change in polarization state of light reflected from the surface of a sample.

The optical constants define how light interacts with a material. The complex refractive index is a representation of the optical constants of a material. It is represented by $\tilde{n}=n-ik$. The real part or index of refraction, n , defines the phase velocity of light in material. The imaginary part or extinction coefficient, k , determines how fast the amplitude of the wave decreases.

The anodic oxidation of zirconium in $0,1 \text{ mol}\cdot\text{dm}^{-3}$ NaOH was studied by ellipsometric method at in situ and ex situ conditions. The oxides were formed on mechanically polished zirconium electrode under potentiostatic conditions up to final potential of 65 V. The anodization was carried out 30 s at each investigated potential.

Ellipsometric method was employed to determine the thickness of spontaneously formed oxide on the zirconium surface and the thicknesses for the anodically formed oxide at different potentials at in situ and ex situ conditions. Thickness of the spontaneously film formed at in situ conditions was 3,74 nm, while at ex situ conditions the corresponding thickness was 4,84 nm. Anodic oxidation of zirconium in NaOH solution is characteristic with two coefficients of anodization, for in situ and for ex situ condition. The anodization coefficients at in situ investigations for the anodic oxidation at potentials 0 to 20 V was 2,43 nm/V and for potential up to 20 V the coefficient was 1,81 nm/V. The anodization coefficients determined at ex situ conditions were 2,66 nm/V for the potentials below 20 V and 2,05 nm/V at potentials 20 to 50 V.

Optical constant n and k of both, zirconium substrate and anodic oxide were determined. The complex refractive index for metal substrate was $\tilde{n}_s=2,53-i2,73$, for anodic oxide at in situ $\tilde{n}_f=2,21 - i\cdot0,209$, and for ex situ conditions $\tilde{n}_f=2,09 - i\cdot0,148$.

The electric field strength for in situ and ex situ conditions was also calculated. The electric field strength for in situ condition up to 20 V is $4,1\cdot10^6 \text{ V/cm}$ and at higher potentials increases to $5,6\cdot10^6 \text{ V/cm}$. The electric field strength for same potential ranges is lower, $3,7\cdot10^6$ and $4,9\cdot10^6 \text{ V/cm}$.

The anodic oxide film growth in NaOH solution is with accordance with high field strength mechanism.

Keywords: zirconium, anodic oxidation, ZrO_2 , ellipsometry

1. INTRODUCTION

Because of many excellent bulk properties like low thermal neutron capture cross section, favorable mechanical properties and good corrosion resistance even at high temperatures, zirconium and its alloys are widely used in nuclear reactors as fuel cladding and as reactor structural elements, chemical engineering, and lately in biomedical applications. [1,2].

The use of Zr in such wide range of applications arises due to its excellent corrosion resistance. Zr instantaneously forms a surface oxide film when exposed to the atmosphere. The excellent corrosion resistance of Zr is attributed to this spontaneous natural surface oxide film. is caused by the formation on the surface of a dense oxide film which slows further oxidation. This film can be formed in air or in electrolytes at open circuit. [3]

Zirconium oxide has a high dielectric constant ($\epsilon=20-25$) and high refractive index. It is a promising candidate for storage capacitors in dynamic random access memories, gate oxides in field effect transistors, optical waveguides, and antireflection layers for solar cells [4,5].

Zirconia (ZrO_2) thin films have potential applications in optics such as protective barriers, interference filters, anti-reflection, selective reflection coatings, photochromism, high power laser mirrors and passive and active waveguides and in functional applications such as oxygen sensors or buffer layers in micro- electronic devices. All of these applications are based on the interesting combination of mechanical, chemical, and physical properties [6].

Zirconium oxide possesses many highly desired materials qualities useful for structural and electrical applications such as fracture toughness, chemical robustness, thermal stability, and biocompatibility. It is already used as catalyst support [7], chemical sensor [8], and thermal barrier coating.

The parameters, refractive index and the thickness of the film, play an important role in optical applications. The thickness can be controlled by the deposition process and the refractive index can be tuned by the temperature treatment. There are different techniques to characterize the thickness and refractive index, such as by measuring the transmittance, by ellipsometry [9] and by the Brewster angle technique [10].

In this work in situ and ex situ measurements of ellipsometry were carried out to monitor the electrochemical growth of anodic oxide films on zirconium in NaOH solution. Growth of the anodic oxide was performed using potentiostatic method.

2. EXPERIMENTAL

Electrodes - The working electrode was a rod of polycrystalline (99.2%+Hf) zirconium (the main impurities were 0.16.% O and 0.08 Fe) purchased from Alfa, fixed in a special Teflon holder. The exposed area was 1.2 cm². Platinum grid with large surface area was used as a cathode.

Surface preparation - After abrasion with emery paper, the sample was polished on metallurgical cloths with diamond paste of 9 and 3 μm. The polishing with 3 μm diamond paste left a mirror-like surface. The polishing procedure was then continued with 0.5 μm Al₂O₃ to end with 0.05 μm Al₂O₃ for 30 min. Among the different polishing session, the electrode was subjected to ultrasonic cleaning.

Optical electrolytic cell - A three-compartment optical-electrolytic cell was adopted for electrochemical-ellipsometric in situ measurements. Experiments were done in a Pyrex vessel 250 cm³ in capacity with two optical quartz windows fixed at an angle of incidence of 70°. A Luggin probe reference electrode assembly, containing an isolating stopcock to avoid contamination from the reference electrode by the chloride solution, was employed. Prior to running any experiments, the solution in the cell was deaerated by flowing argon gas through a fritted bubbler for at least 30 min. The gas flow was discontinued during the run

Solutions - Measurements were performed in the 0,1 mol·dm⁻³ NaOH. The solutions were prepared from A.R quality chemical and twice distilled water. The electrolyte was exchanged after each measurement in order to avoid buildup of soluble Zr species that are known to enhance the stability of the surface oxides.

Apparatus - The anodic oxidation was performed potentiostatically using HEKA potentiostat/ galvanostat modified as a two electrode potentiostat so that the potential could extend up to potentials of 100 V. The measurements were performed with a Rudolph Research type 43603-200 thin-film ellipsometer at a wavelength of 632.8 nm and an incident angle of 70°.

3. RESULTS AND DISCUSSION

Ellipsometry measures the change in polarization state of light reflected from the surface of a sample. The measured values are expressed as Ψ and Δ . These values are related to the ratio of Fresnel reflection coefficients, R_p and R_s for p and s -polarized light, respectively.

$$\tan(\Psi)e^{i\Delta} = R_p/R_s \quad 1$$

The optical constants define how light interacts with a material. The complex refractive index is a representation of the optical constants of a material, it is represented by $\tilde{n}=n-ik$. The real part or index of refraction, n , defines the phase velocity of light in material $v = c/n$, where v is the speed of light in the material and c is the speed of light in vacuum.

The imaginary part or extinction coefficient, k , determines how fast the amplitude of the wave decreases. The extinction coefficient is directly related to the absorption of a material and is related to the absorption coefficient by $\alpha = 4\pi k/\lambda$, where α is absorption coefficient and λ is the wavelength of light.

3.1 Optical constants for Zr metal substrate

The main problem in the ellipsometric investigations is right determination of the optical constants of the metal substrate. Practically it is very difficult to obtain metal substrate without natural oxide film on its surface. Wrong determined optical constants for metal substrate affected to the determination of the thickness and optical constants of the anodic oxide film. To minimize the thickness of the naturally formed oxide film on the Zr surface the cathodic reduction was used in this work. The mechanically polished Zr electrode was cathodically polarized in 0,1 mol·dm⁻³ NaOH for 10 min at potential of -1 V, and after that ellipsometric investigations were made. From measured ellipsometric parameters Δ and Ψ , the complex refractive index for metal substrate and reflectivity were calculated. The complex refractive index for metal substrate was $\tilde{n}_s=2,53-i2,73$. The reflectivity of the metal surface was $R_o = 0,397$.

3.2 Optical constants and thickness of the anodic oxide film

The optical constants and thickness of the anodic oxide films formed in 0,1 mol·dm⁻³ NaOH were determined at in- situ and ex-situ conditions. The mechanically polished Zr electrode was anodically polarized at the different potentials for the potential range between 0 and 65 V. The electrode was polarized 30 sec at each

potential. The ellipsometric investigations were made in the solution at in-situ conditions and in atmosphere at ex-situ conditions.

At in-situ and ex-situ conditions the ellipsometric measurements are characterized with three complex refractive indexes: $\tilde{n}_m$ - for medium ($0,1 \text{ mol}\cdot\text{dm}^{-3}$ NaOH at in situ conditions and air at ex situ conditions), $\tilde{n}_f$ - for film with thickness d and $\tilde{n}_s$ - for Zr metal substrate.

$$\tilde{n}_m = n_m - ik_m \quad 2$$

$$\tilde{n}_f = n_f - ik_f$$

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$$\tilde{n}_s = n_s - ik_s \quad 4$$

The ellipsometric parameters Δ and Ψ are the functions of different variable parameters:

$$\tan(\Psi)e^{i\Delta} = f(\tilde{n}_m, \tilde{n}_f, \tilde{n}_s, d, \phi, \lambda) \quad 5$$

where:

$\tilde{n}_m = 1,342$ for $0,1 \text{ mol}\cdot\text{dm}^{-3}$ NaOH and 1 for the air, because the imaginary part of the refraction index of medium $k_m = 0$;

$\tilde{n}_s = 2,54 - i2,93$;

$\phi = 70^\circ$;

$\lambda = 632,8 \text{ nm}$.

From the optical data P and A in four main zones the ellipsometric parameters Δ and Ψ at in situ and ex situ conditions for all potentials were calculated.

On fig. 1 the experimentally measured Δ - Ψ parameters for anodically formed films in $0,1 \text{ mol}\cdot\text{dm}^{-3}$ NaOH at in situ conditions are fitted to the theoretically computed Δ - Ψ curve. Each experimental Δ - Ψ point on fig. 1 corresponds to exact applied potential or voltage of anodization. Experimentally measured Δ - Ψ parameters fitted to the theoretically computed Δ - Ψ curve are presented on fig.2.

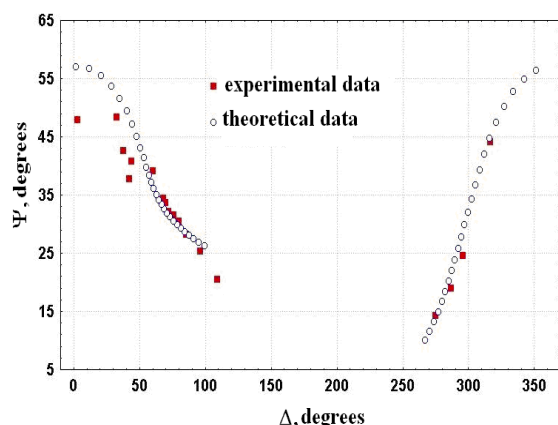


Fig.1 Variation of the ellipsometric angles during oxide growth on Zr electrode in 0,1M NaOH (in situ)

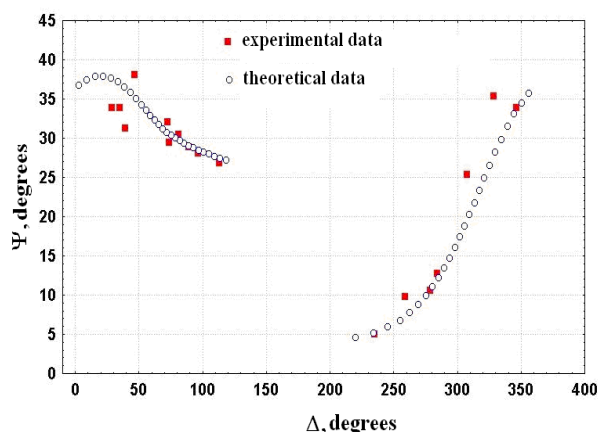


Fig.2 Variation of the ellipsometric angles during oxide growth on Zr electrode in 0,1M NaOH (ex situ)

The complex refractive index for the film $\tilde{n}_f = 2,21 - i0,209$ and the thickness of the film corresponded to the Δ - Ψ data sets at in-situ conditions were determined from the fitted curve presented in figure 1. Figure 1 presents good quality of the fit, but at the potentials above 50 V the experimental points deviate from the fitted curve. This deviation can be the result of the formation of the porous film on the surface.

The investigations at ex situ conditions were carried out at some electrode as at in situ conditions. After determination of the optical data, P and A at in-situ conditions the electrode was washed with distilled water and $\text{C}_2\text{H}_5\text{OH}$. The electrode was dried and the optical data P and A were determined in the air.

Figure 2 shows the variation of the ellipsometric angles during oxide growth on mechanically polished Zr electrode in $0,1 \text{ mol}\cdot\text{dm}^{-3}$ NaOH at ex situ conditions. The complex refractive index for the film, $\tilde{n}_f = 2,09 - i0,148$ was determined using the fitted curve.

It is well known that the anodization of zirconium and its alloys generally results in the formation of barrier films.

Incorporation of the electrolyte anions in the oxide may be the factor influencing the formation of porous oxide films [11]. Fig. 3 shows the thickness-potential curve obtained from the fits of the Δ - Ψ profile for oxide growth

in $0,1 \text{ mol}\cdot\text{dm}^{-3}$ NaOH at in situ conditions. The thickness of the oxide increases with increasing the anodic potential.

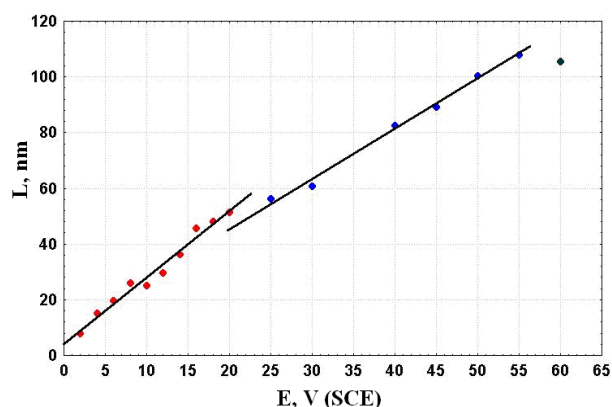


Fig.3 Variation of the oxide thickness with potential for oxide growth in $0,1 \text{ mol}\cdot\text{dm}^{-3}$ NaOH (in situ)

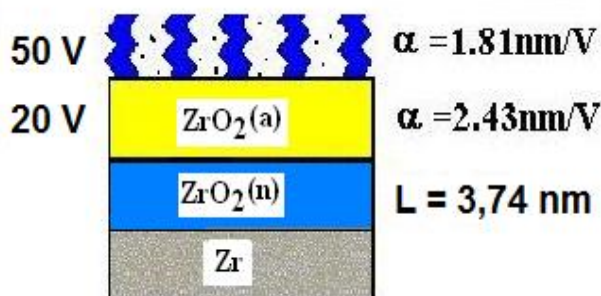


Fig.4 Idealized model for the structure of the anodic film formed on Zr electrode in $0,1 \text{ M mol}\cdot\text{dm}^{-3}$, (in situ)

Figure 3 indicate linear L-E dependence with change in slope over 20 V. The rate of oxide growth is calculated at potentials below and above 20 V with the corresponding electric field strengs. The idealized model for the structure of the anodic film formed on Zr electrode in $0,1 \text{ M NaOH}$ at in-situ conditions is presented on figure 4. The anodization coefficient below 20 V was $2,43 \text{ nm/V}$ approximately. From the intercept of the linear part of the curve with the ordinate the thickness of the naturally formed oxide film was determined, $L_n = 2,74 \text{ nm}$. As a result of the higher porosity of the formed film at the potentials above 20 V the solution can penetrate in the formed pores. The oxide growth rate is $1,81 \text{ nm/V}$. At the potentials above 50 V the porosity is much higher and the reflected beam can't produce an elliptically polarization. The electric field strength up to 20 V is $4,1 \cdot 10^6 \text{ V/cm}$ and then increases to $5,6 \cdot 10^6 \text{ V/cm}$. Such effect is due to the formation of the porous oxide and anion incorporation within the oxide.

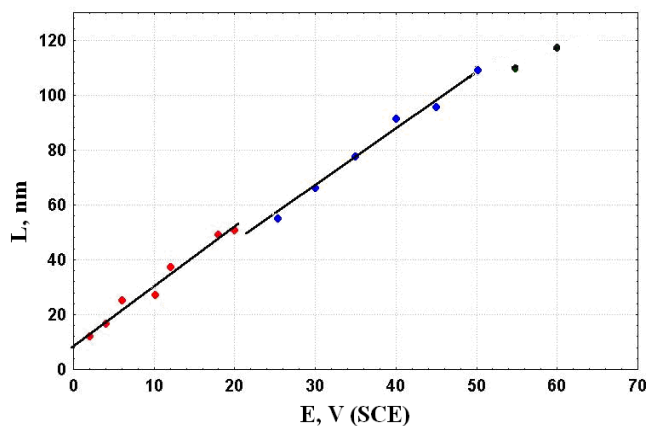


Fig.5 Variation of the oxide thickness with potential anodic for oxide growth in $0,1 \text{ M NaOH}$ (ex situ)

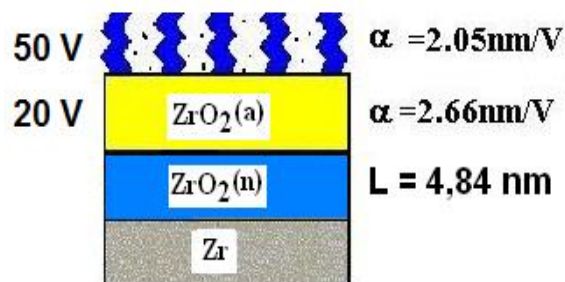


Fig.6 Idealized model for the structure of the film formed on Zr electrode in $0,1 \text{ M NaOH}$, (ex situ)

Figure 5 shows the thickness - potential curve for oxide growth in $0,1 \text{ mol}\cdot\text{dm}^{-3}$ NaOH at ex situ conditions. The idealized model for the structure of the anodic film formed at ex situ conditions is presented on figure 6. There is the change in the slope at about 20 V. Same as at in situ conditions there are two anodization coefficients, one obtained at the potentials up to 20 V, and other at the potentials above 20 V. The electric field strength up to 20 V is $3,7 \cdot 10^6 \text{ V/cm}$ and then increases to $4,9 \cdot 10^6 \text{ V/cm}$.

Because the investigations at ex-situ conditions were done in air it penetrates in the pores which were formed at the higher potentials. At ex situ conditions the thickness of the naturally formed oxide is 4,84 nm. The higher thickness of the naturally formed film at ex situ conditions is consequence of the supplementary formed oxide film on the surface during the picking out from the electrolyte and drying the electrode with hot air. As can be seen on fig.5, the thickness of the oxide at ex situ conditions compared with those obtained at in situ conditions is higher. Some as at in situ conditions there is an increasing of the electric field strength at the higher potentials.

CONCLUSIONS

The anodic oxidation of zirconium in $0,1 \text{ mol}\cdot\text{dm}^{-3}$ NaOH was studied by in situ and ex situ ellipsometry. The oxides were grown on mechanically polished zirconium under potentiostatic conditions up to final potentials of 60 V.

Thickness of the spontaneously film formed at in situ conditions was 3,74 nm, while at ex situ conditions the corresponding thickness was 4,84 nm. The higher thickness of the naturally formed film at ex situ conditions is consequence of the supplementary formed oxide film on the surface during the picking out from the electrolyte and drying the electrode with hot air.

Anodic oxidation of zirconium in NaOH solution is characteristic with two coefficients of anodization, for in situ and also for ex situ condition. The anodization coefficients at in situ investigations for the anodic oxidation at potentials 0 to 20 V was 2,43 nm/V and for potential up to 20 V the coefficient was 1,81 nm/V. The anodization coefficients at some potentials for ex situ conditions were 2,66 nm/V and 2,05 nm/V.

The complex refractive index for metal substrate was $\tilde{n}_s = 2.54 - i2.93$, for anodic oxide at in situ $\tilde{n}_f = 2,21 - i0,209$, at ex situ conditions $\tilde{n}_f = 2,09 - i0,148$. The higher index of refraction for the oxides formed at in situ conditions is a result of the penetration of the electrolyte in the oxide pores.

The electric field strength up to 20 V is $4,1 \cdot 10^6 \text{ V/cm}$ and then increases to $5,6 \cdot 10^6 \text{ V/cm}$ at in situ conditions. The electric field strength for same potentials at some potentials were $3,7 \cdot 10^6 \text{ V/cm}$ and $4,9 \cdot 10^6$ at ex situ conditions.

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