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## Influence of the cathodic polarization on the stability of Ti surface in concentrated KOH solutions

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**Abstract** The stability of spontaneous thin layers and thin layers formed upon cathodical polarization of Ti in KOH solutions have been studied by potentiostatic and ellipsometric methods. At open circuit potential (OCP) the strongly adherent films, whose thickness depends on the concentration of the KOH solution, were formed. During the cathodic polarization the transformation of these films to weakly adsorbed precipitated layers on the electrode surface was observed. Comparing the theoretically computed curves with the experimental  $\Psi$  vs  $\Delta$  loci measured ellipsometrically, the complex indices of refraction and the thickness of the generated films, from 3.6 to 60 nm in 1 M KOH and from 36 to 105 nm in 5 M KOH (adherent to the electrode surface), were determined. At OCP the rate of film growth increases with increasing the concentration of KOH solution. Cathodic polarizations change the chemical composition and retard the rate of film growth. Based on the ellipsometric and electrochemical data the chemical compositions of the formed films consisted of  $\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{TiO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{Ti}(\text{OH})_3$  and  $\text{TiOOH} \cdot n\text{H}_2\text{O}$ .

**Keywords** Ti surface films · Cathodic polarization · Ellipsometry · Refractive indices · KOH solutions

### Introduction

The research of titanium and its alloys has recently been directed towards the preparation of corrosion-resistant materials to be used as support of dimensionally stable anode for efficient oxyhalogenides production in very alkaline solutions [1]. To fully understand the corrosion behavior of Ti, it is important to know the nature (chemical and structural properties) of the oxides that form on its

surface. Armstrong et al. have studied the electrochemical behavior of titanium-passive films in 1 M  $\text{HClO}_4$  and 0.5 M  $\text{H}_2\text{SO}_4$  using X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) [2]. They have confirmed that the mixed valent oxides of  $\text{TiO}$ ,  $\text{Ti}_2\text{O}_3$  and  $\text{TiO}_2$  coexist in the chemical composition of passive films. Films formed at higher anodic potentials have greater  $\text{TiO}_2$  character.

In practice, the corrosion of Ti is inhibited by the spontaneous formation of natural oxide film on its surface in contact with air or passive thin layers in contact with aqueous media. However, the stability of this oxide film in de-aerated aqueous solutions in the pH region from neutral to the concentrated alkaline has not been systematically investigated in spite of recent importance of Ti as one of the candidate materials for overpacking of nuclear waste stored in an underground bentonite clay where no oxygen is present [3, 4]. The thickening of this film by anodic or thermal oxidation has been used to provide higher inhibition of corrosion and to prevent rapid surface dissolution in aggressive media [5, 6]. So far, many attempts have been made to produce thick films using anodization in various acidic, neutral and buffered solutions [7–12]. Literature data concerning the behavior of titanium in alkaline solutions are very limited and, as a rule, refer to dilute solutions at relatively low anodic potentials [13, 14]. The surface films formed in moderate and strong alkaline solutions have a noticeable thickness, and the most discussed point is the formation of various meta-stable and intermediate products adsorbed on Ti surface [15]. It was claimed that in alkaline solutions at OCP hydrated  $[\text{Ti}(\text{OH})_3]_{\text{ads}}$  species are formed at the initial stages of the Ti electro-oxidation process. These species are precursor for further electro-oxidation, finally leading to a compact Ti oxide film of  $\text{TiO}_2$  and  $\text{Ti}_2\text{O}_3$  [16]. Bonilla and Zinola discussed formation of golden colored film with chemical composition of  $\text{TiO}_3 \cdot 2\text{H}_2\text{O}$  at cathodic potential of  $-1.2$  V vs SCE and also growth of a blue-violet film, probably  $\text{Ti}_2\text{O}_3$  or  $\text{Ti}_3\text{O}_5$ , during the potential scan from  $-1.2$  to 3 V SCE in 0.1 M KOH solution [17]. The existence of a suboxide layer of  $\text{TiO}_3$  between the Ti metal

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and TiO<sub>2</sub> film was also evidenced [3]. Using potentiostatic and galvanostatic techniques Muller et al. [18] studied the stability of passive films on Ti electrodes in alkaline (NaOH) and acid (H<sub>2</sub>SO<sub>4</sub>) solutions. They found that in acidic medium the oxide electroformation is accompanied by different dissolution processes, one of which is a potential independent chemical dissolution.

Taking into account that Ti may be used as a support of dimensionally stable anode in very alkaline solutions and that Ti corrodes preferably at the places at which catalyst is detached [19], the electrochemical formation and reduction of Ti oxides in alkaline solutions need further researches. In alkaline solutions Ti is generally considered as a stable self-passivating metal, and some authors believed that Ti oxide forms spontaneously even at high cathodic potentials [1]. So far, a great number of papers have been published concerning electrochemical behavior of Ti in acidic media during cathodic polarization [20–24], but only a very few in alkaline solutions [1, 23].

The purpose of this work is to enlarge the initially studied domain of spontaneous self-passivated films on Ti surfaces in KOH solutions and to show the influence of cathodic polarization on the chemical composition of these films. We correlate the electrochemical and ellipsometric data with the chemical composition of the formed films.

## Experimental

**Electrodes** Ti cylinders with chemical purity 99.7% (UT 40, Ugine Kuhleman) with a diameter of 25 mm and a height of 10 mm were embedded in epoxy resin (Lam Plan), leaving one base to be in contact with the solution in the electrolytic cell. Prior to performing each series of measurements the working electrodes with constant surface area of 4.9 cm<sup>2</sup> were first mechanically polished with emery paper 600 and then ultrasonically degreased with methanol and finally electropolished according to the procedure given elsewhere [15].

A Pt grid with a large surface area was used as a counter electrode, and a saturated calomel electrode (SCE) served as the reference.

**Optical-electrolytic cell** A two-compartment optical-electrolytic cell was adopted for the electrochemical-ellipsometric in situ measurements. It was a Pyrex vessel (250 cm<sup>3</sup> in capacity) with two optical quartz windows fixed at an angle of 70° and similar in design to those described in Ref. [25]. A Luggin probe reference assembly containing an isolating stopcock to avoid contamination of chloride ions from the reference electrode was separated from the main solution. Prior to running any experiments, the solution in the cell was de-aerated by flowing pre-purified nitrogen gas through a fritted bubbler for at least 30 min. The gas flow was disconnected during the run. The cell was cleaned in a mixture of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, and rinsed through distilled water. The electrolyte in the cell was exchanged after each series of measurements to avoid build up of any soluble Ti species.

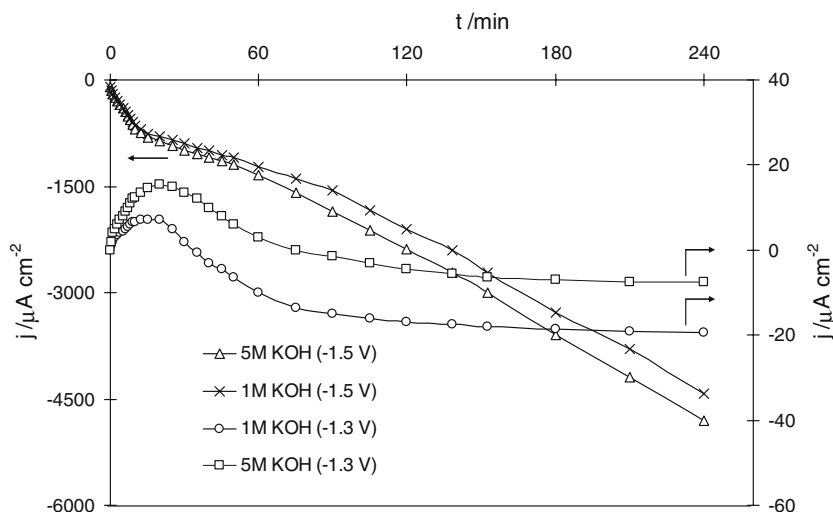
**Solutions** Aqueous solutions of 1 and 5 M KOH were prepared by dissolving reagent grade potassium hydroxide (Across Organics) with double-distilled and deionized water.

**Apparatus** The cathodic polarization was performed potentiostatically using Heka Model 488 potentiostat/galvanostat interfaced with a PC. The ellipsometric measurements were performed with a Rudolph-Research type 43603-200 thin film ellipsometer at a wavelength of 546.1 nm and an incident angle of 70°.

## Results

Figure 1 shows the potentiostatic *j*-*t* curves for two fixed cathodic potentials at -1.3 and -1.5 V vs NHE in 1 and 5 M KOH. The potential of -1.3 V was the lowest cathodic

**Fig. 1** Polarization curves for Ti in 1 M KOH and 5 M KOH Ti cathodic potentials of -1.3 and -1.5 V vs SCE



potential applied when the cathodic current begins to pass through the electrolytic cell. For higher cathodic potentials than  $-1.5$  V vs SCE the cathodic current increases rapidly, and the intensive gas evolution occurred on the electrode surface.

For cathodic potential of  $-1.3$  V the corrosion of Ti electrodes was hindered in both concentration of KOH solutions, and after the polarization time of about 70 min, they tend to reach a plateau. For  $-1.5$  V the permanent amounting of current in cathodic direction may be explained by the adsorption of H atoms in the Ti lattice, leading to the initial stages of Ti hydrates and low hydrogen evolution reaction.

Ellipsometric measurements were performed in 1 and 5 M KOH at in situ condition for OCP and for fixed potentials of  $-1.3$  and  $-1.5$  V, simultaneous during the tracing of  $j-t$  curves. Over potential of  $-1.5$  V the cathodic current increases rapidly, the visible gas evolution occurred on electrode surface and the ellipsometric measurements were lost in sensitivity.

As already pointed out in many publications [6, 10, 15, 26], for a three-component system (medium, surface film, metal substrate) the general problem is to determine five unknown parameters for each measured point, namely, the complex indices of metal substrate  $\hat{n}_S = n_S(1 - k_S \cdot i)$ , the complex indices of the surface film  $\hat{n}_f = n_f(1 - k_f \cdot i)$  and the film thickness  $d$ , with only two measured parameters  $\psi$  and  $\Delta$ . The index of refraction of the medium  $\hat{n}_m = n_m(1 - k_m \cdot i)$  can be determined by using Abbe's refractometer independently of the ellipsometric measurements. Using Abbe's refractometer it is only possible to determine the real part  $n_m$ , while for transparent electrolytes, in our case the aqueous KOH solutions, the imaginary part  $k_m=0$ . The measured values of  $n_m$  for 1 and 5 M KOH were 1.3438 and 1.3763, respectively.

The determination of the optical indices of a thin film grown on a metallic substrate using ellipsometric measurements demands a preliminary knowledge of the optical indices of the substrate. However, to determine these indices separately, the principal difficulty is that a natural air-formed oxide film is always present in this case. The optical constants determined for the Ti metal substrate were found to be dependent on the preparation of the electrode and on the pre-polarization conditions. The values ranged between  $n_s=2.4-3$  and  $k_s=3-3.3$  [27]. The wide scatter in the values of the optical constants was attributed to the difficulty in obtaining a reproducible initial surface. It seems unlikely that an oxide- or hydride-free titanium surface can be prepared under electrochemical conditions, and oxide and hydroxide phases may coexist on the surface.

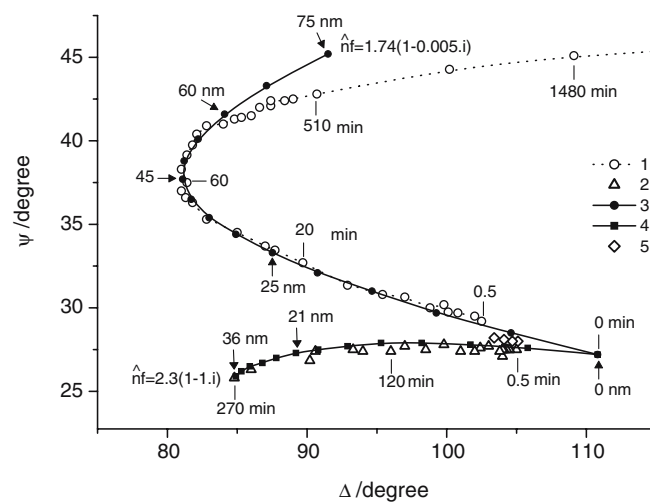
In our previous work, by cathodic polarization of an electropolished Ti surface in  $H_2SO_4$ , we have succeeded in determining very precisely the optical constants of the metal substrate of  $\hat{n}_S = 2.94(1 - 1.217 \cdot i)$  and the thickness of the initial air-formed oxide film, about 1.4 nm [25]. These two values were used in all of our further calculations. From these values the theoretically

fitted curves calculated using Fresnell's equations for a three-component system were begun [26]. The method of computation is given elsewhere [28].

*1 M KOH* Figure 2 shows the experimentally measured parameters  $\Psi$  vs  $\Delta$  plots for spontaneous film formation at OCP and during the cathodic polarization of  $-1.3$  vs SCE and  $-1.5$  V vs SCE. From the present plots, by comparing the theoretically fitted curves with the experimental data it is possible to calculate the thickness during the progress of film formation and also the optical constants of the formed films. The values of  $\psi$  and  $\Delta$  which correspond to bare metal substrate  $\hat{n}_S = 2.94(1 - 1.217 \cdot i)$  are marked with point 0.

The theoretical curve at OCP fitted well to the experimental data for the values of  $n_m=1.3438$ ,  $\hat{n}_f = 1.74(1 - 0.005 \cdot i)$  and  $\hat{n}_S = 2.94(1 - 1.217 \cdot i)$ . The starting experimental point, indicated with 0.5, represents the time (min) of the first experimental measurement after immersion of Ti specimen in KOH solution. The final measurement point was performed after 1480 min. The fairly good agreement between the experimentally and the theoretically fitted curve is only for film thickness between bare metal substrate and 60 nm. The deviations for the thicker film may be attributed to the changes in the chemical composition of the film.

For cathodic polarization of  $-1.3$  V (SCE), there was a small change in  $\Delta$  and  $\psi$  with time. The spontaneous film formation at OCP was discontinued, and in the following measurements, no significant changes in  $\Delta$  and  $\psi$  were observed. The growth of any surface film is stopped, and the experimental points did not form a large-enough distance for precise calculation and determination of  $\hat{n}_f$ .

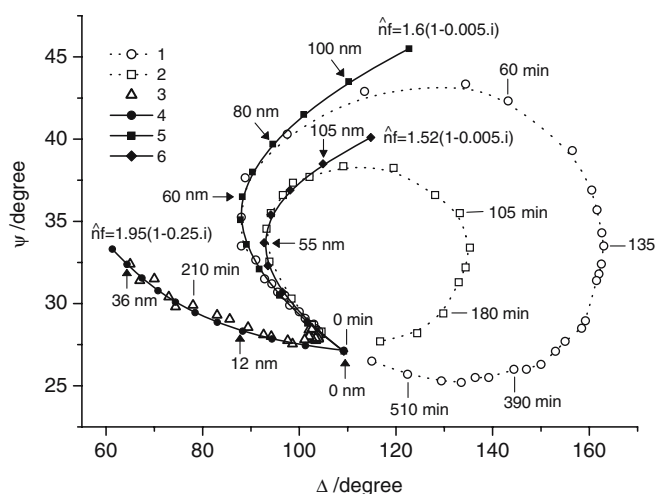


**Fig. 2** Graphical presentation of ellipsometric parameters  $\psi$  vs  $\Delta$  during the electrochemical treatment of Ti in 1 M KOH: 1, OCP; 2, ( $-1.5$  V SCE); 3 and 4, theoretical computed curves corresponding to experimental data 1 and 2, respectively; 5, ( $-1.3$  V SCE). On experimental data (dashed lines), some values of measured times (min), are shown. On theoretical computed curves (solid lines), some values of film thickness marked with arrows are also shown

For cathodic polarization of  $-1.5$  V the experimentally determined  $\psi$  and  $\Delta$  loci indicated progress in electrochemical formation of surface films. This progress was stopped after 270 min and film thickness of  $d=36$  nm. The prolonged polarization did not change the values of  $\psi$  and  $\Delta$  noticeably. The theoretically computed curve fitted well with the experimental data; overall, the measurement region and the complex index of refraction of the formed film  $\hat{n}_f = 2.3(1 - 1.00 \cdot i)$  was calculated.

**5 M KOH** To make a more accurate verification for the existence of films with various chemical compositions on the Ti surface, we repeated the previous measurements in higher concentrations of KOH, where the formation of thicker films was expected. In Fig. 3, the  $\psi$  vs  $\Delta$  loci for spontaneous film formation at OCP and cathodic polarization at  $-1.3$  and  $-1.5$  V vs SCE of Ti electrode in 5 M KOH are presented. By comparing the experimentally measured data with the theoretically fitted curves, the optical constants and thickness during the progress of film thickness growth were calculated. For the  $\psi$  vs  $\Delta$  plot at OCP the progress in film thickness growth is monitored up to a final measurement point corresponding to 600 min, when the experimental loop close the first cycle. The fairly good agreement between the computed data and the experimental results was found for  $\hat{n}_f = 1.6(1 - 0.005 \cdot i)$ . This agreement is only between bare metal substrate and film thickness of 80 nm. The deviations for the thicker film, as in a previous case, may be attributed to the changes in the chemical composition of the film.

For  $-1.3$  V (SCE) the fitted curve computed for  $\hat{n}_f = 1.52(1 - 0.005 \cdot i)$  offered a good agreement between bare metal surface and film thickness of 105 nm, as a value of



**Fig. 3** Graphical presentation of ellipsometric parameters  $\psi$  vs  $\Delta$  during the electrochemical treatment of Ti in 5 M KOH: 1, OCP; 2, ( $-1.3$  V SCE); 3, ( $-1.5$  V SCE); 4, 5 and 6, theoretical computed curves corresponding to the experimental data 3, 1 and 2, respectively. On experimental data (dashed lines), some values of measured times (min) are shown. On theoretical computed curves (solid lines), some values of film thickness marked with arrows are also shown

the best agreement with the experimental loci. The experimentally measured curve at this potential seems shorter than the OCP curve. This indicates various rates of film thickness growth depending on the formation potential.

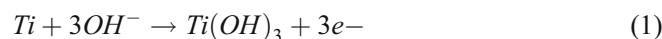
For  $-1.5$  V vs SCE the progress of film thickness growth is very slow that after 360 min (the last measurement point), the film thickness is only 36 nm. The best fit between the theoretical and experimental data in overall measured region for  $\hat{n}_f = 1.95(1 - 0.25 \cdot i)$  was found.

## Discussion

The ellipsometric measurements confirmed many different processes on the Ti surfaces depending on the applied potential and the concentration of KOH. The changes in the values of the refractive indices indicated changes in chemical composition of the formed films. Our discussion will be based on the values of the calculated refractive indices from the theoretically fitted curves superposed on the experimental measurements and on the deviation of these curves for thicker films.

In Table 1 the calculated values of refractive indices of the films formed at OCP and during the cathodic polarization are listed. Up to limit thickness, given in Table 1, there exists a good agreement between theoretical computed curves and experimental data. The time of last experimental point represents our last ellipsometric measurement or the limit time of noticeable changes of ellipsometric parameters  $\psi$  and  $\Delta$ .

**Spontaneous film formation at OCP** After immersion of Ti electrode in 1 or 5 M alkaline solution, the  $\text{OH}^-$  ions from solution had a permanent access to the metal electrode forming surface film of  $\text{Ti}(\text{OH})_3$ .



The concentration gradient of the  $\text{OH}^-$  ions between the solution and the metal surface provoked growths of film thickness. The reaction (Eq. 1) is in accordance with Pourbaix's diagrams and is approved in our previous study in Refs. [29] and [15]. The smaller values of calculated  $n_f$  for 5 than in 1 M KOH result from lower electronic polarizability of  $\text{OH}^-$  compared to  $\text{O}_2$  [10] during the oxidation of Ti surface. In general the metal hydroxide exhibits a refractive index smaller than its oxide, so that the higher concentration of  $\text{OH}^-$  ions in 5 N KOH is the origin of the lower refractive index of the formed films. The decrease in the real part of the complex refractive index from 1 to 5 M KOH may be attributed to the increase in the accumulation of  $\text{OH}^-$  ions and formation of a bigger number of  $\text{OH}^-$  species bonding with the metal surface.

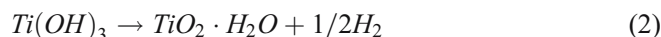
The deviation of the theoretically fitted curves from the experimental loci began for films thicker than 60 nm, i.e. for a time longer than 90 min in 1 M KOH and for films thicker than 80 nm, i.e. for a time longer than 32 min in 5 M



**Table 1** Refractive indices and some governing parameters of Ti electrode as a function of polarization potential and KOH concentration

KOH concentration (M)	Potential voltage (SCE)	$\hat{n}_f = n_f(1 - k_f \cdot i)$	Limiting thickness (nm)	Time of last experimental point (min)
1	OCP	1.74 (1-0.005·i)	60	1,480
	-1.3	/	/	510
	-1.5	2.30 (1-1.00·i)	36	270
5	OCP	1.60 (1-0.005·i)	80	600
	-1.3	1.52 (1-0.005·i)	105	240
	-1.5	1.95 (1-0.250·i)	36	360

KOH. This indicated that after 90 min in 1 M KOH and 32 min in 5 M KOH, the second phase of film formation began, which can be envisaged as a slow transformation of  $Ti(OH)_3$  into a hydrated layer by the reaction



As time passed the conversion of  $Ti(OH)_3$  to  $TiO_2 \cdot 2H_2O$  occurred, the surface film grew and a dynamic equilibrium between  $Ti(OH)_3$  and  $TiO_2 \cdot 2H_2O$  was established. This equilibrium depended only upon the physical properties of the solution (concentration and temperature). The OCP film formation in 5 M KOH was significantly faster than in 1 M KOH, and the experimental loci formed a very long loop that finished near the starting experimental loci. The superposition of the starting and final points gave very low values for the extinction index, i.e. conversion of  $Ti(OH)_3$  to  $TiO_2 \cdot 2H_2O$  occurs without a change in the number of  $O^{2-}$  ions in the chemical composition of the film. It should be noticed that Shibata and Zhu [30] showed that the anodic oxide film on Ti contains bounded water, especially in the outermost part of the electrode surface. The dissociation of water molecules may be a main cause of hydration of the passive film under the very high electric field.

After finishing the measurements, when the sample with spontaneously formed films at OCP was taken out of the solution, various colors were seen on the electrode surface: yellow, blue, brown etc. All formed films were stable in atmospheric conditions, well adherent and strongly connected to the electrode surface.

**Cathodic polarization** For a cathodic potential of -1.3 V vs SCE in 1 M KOH, the measured values of ellipsometric parameters  $\psi$  and  $\Delta$  were already unchangeable, indicating that no surface reactions occurred on the Ti electrode. It seems that the spontaneous film formation in 1 M KOH was completely blocked, or every quantity of spontaneously formed film was immediately destroyed in Ti-soluble species. When, after the 510 min of polarization, the sample was taken out of the solution, the surface had the same properties as before its immersion in the solution.

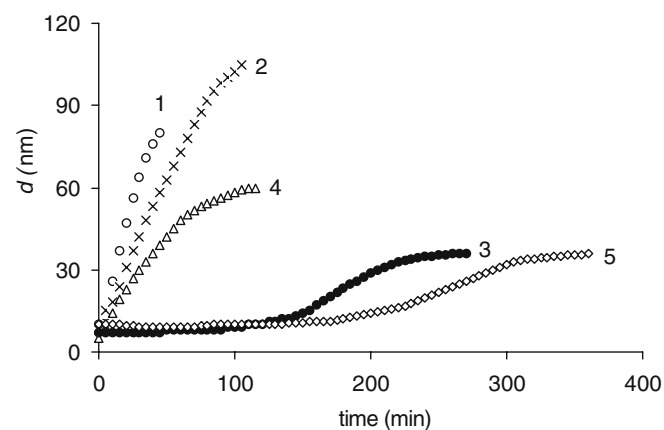
For the same concentration of KOH and cathodic potential of -1.5 V vs SCE, the drastic increase in the refractive indices, especially in the imaginary part ( $k_i=1$ ), indicated chemical change of the spontaneous formed films

in the precipitated layer by the reaction



The small changes in  $\psi$  indicated that the formed films were not well adherent to the electrode surface. The transformation of the well-adherent  $TiO_2 \cdot H_2O$  film to the precipitated layer of  $TiOOH \cdot H_2O$  is probably due to the adsorbed  $H^+$  from the solution to the electrode surface during the cathodic polarization. The increase in the refractive indices confirmed general hydration of  $TiOOH$ . Dyer and Leach [10], by cathodic polarization of the Ti electrode in acid solution, have shown a small increase in refractive indices and about 50% transformation of  $TiO_2$  into  $TiOOH$ .

In 5 M KOH, for a potential of -1.3 V vs SCE, the complex film formation with various chemical compositions can be seen most easily by variations in  $\psi$  and  $\Delta$  (Fig. 3). In contrast to results in 1 M KOH, in this case, the  $\psi$  vs  $\Delta$  plot forms a loop similar to that formed at OCP, but noticeably shorter. The fall of the real part in the refractive index of the surface film provides indirect proof of the higher level of hydration of the film than in the case of spontaneously formed films at OCP. After finishing the polarization, when the electrode was taken out of the solution, the well-adherent films with blue color were seen on the surface.



**Fig. 4** Film thickness growth vs time on Ti surface in KOH solutions: 1, 5 M KOH (OCP); 2, 5 M KOH (-1.3 V SCE); 3, 5 M KOH (-1.5 V SCE); 4, 1 M KOH (OCP); 5, 1 M KOH (-1.5 V SCE)

For a potential of  $-1.5$  V vs NHE, in 5 M KOH, as in the case of 1 M KOH, a precipitated layer, as suggested by reaction 3, was formed. The small increases in the real and imaginary parts of the refractive indices of this layer suggest that, as in the case of 1 M KOH, the  $\text{TiO}_2 \cdot \text{H}_2\text{O}$  was not completely transformed to  $\text{TiOOH} \cdot \text{H}_2\text{O}$ . When the electrode was taken out of the electrolytic solution, the brown layer, which peeled off of the electrode surface, was obtained.

According to the Pourbaix diagrams, at very negative potentials in extremely alkaline solutions,  $\text{TiO}_2$  and  $\text{Ti}_2\text{O}_3$  must be present in the film composition [29]. The increase in real part of refractive indices in 5 M KOH at  $-1.5$  V vs SCE suggests possible existence of oxides in the outer part between metal and precipitated layer, as pointed out in Ref. [30].

**Film thickness** Figure 4 shows spontaneous film thickness growth vs time on Ti surface at OCP and during the cathodic polarization in KOH solutions. The dependence of film thickness growth with time, determined ellipsometrically, was presented only in the region when theoretical plots fitted well to the experimental  $\psi$  vs  $\Delta$  loci (Figs. 1 and 2). The other experimental points which deviate from the theoretical plot correspond to the change of chemical composition of the film and are not taken into consideration.

In 1 M KOH the rate of spontaneous film formation at OCP is slower than in 5 M KOH, while the cathodic polarization at  $-1.3$  V vs SCE blocked completely the oxide film formation. No change in the surface thickness was seen in the ellipsometric data. Probably, the very small cathodic current of about  $15$  to  $20 \mu\text{A cm}^{-2}$  established an equilibrium opposite force to spontaneous formation of  $\text{Ti}(\text{OH})_3$ . For cathodic potential of  $-1.5$  V vs SCE, the precipitated layer was formed, indicating that the equilibrium between spontaneous film formation and its transformation in precipitated layer was established.

The highest rate of film thickness grown is in 5 M KOH at OCP, when the limiting thickness of 80 nm is reached in 45 min. For cathodic potential of  $-1.3$  V vs SCE the rate of film thickness growth is retarded, and the limiting thickness of 105 nm is reached after 95 min. For cathodic potential of  $-1.5$  V vs SCE the rate of film thickness growth drastically decreases, and a value of film thickness of 36 nm is obtained in 360 min.

## Conclusions

- In alkaline solutions, at OCP on the Ti surface, the film with the chemical composition  $\text{Ti}(\text{OH})_3$  and  $\text{TiO}_2 \cdot \text{H}_2\text{O}$  was formed. This is confirmed in change of film refractive indices from  $\hat{n}_f = 1.74(1 - 0.005 \cdot i)$  in 1 M KOH to  $\hat{n}_f = 1.60(1 - 0.005 \cdot i)$  in 5 M KOH. The ratio  $\text{Ti}(\text{OH})_3/\text{TiO}_2 \cdot \text{H}_2\text{O}$  strongly depends on the concentration of the solution and the film thickness.
- The transformation of well-adherent spontaneously formed film to the precipitated layers was due to the

hydrogen adsorption. The amount of adsorbed hydrogen is a function of the applied cathodic potential. The change in chemical composition of the surface films was accompanied by a large change in the optical properties of the film. This change is more pronounced for both real and imaginary part at cathodic potential of  $-1.5$  V when the complex indices of the formed films are  $\hat{n}_f = 2.30(1 - 1.00 \cdot i)$  for 1 M KOH and  $\hat{n}_f = 1.95(1 - 0.250 \cdot i)$  for 5 M KOH.

- The cathodic polarization retarded or blocked the spontaneous film formation and transformed it into a  $\text{TiOOH} \cdot n\text{H}_2\text{O}$  precipitated layer. The level of hydration depends on the cathodic potential and concentration of the alkaline solutions.

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## References

1. Pjesic J, Mentus S, Blagojevic N (2002) Mater Corros (1995) 53:44
2. Armstrong R, Quinn R (1977) Surf Sci 67:451
3. Shoosmith D, Ikeda B, Le Neveu D (1997) Corrosion (Houst, Tex) 53:820
4. Azumi K, Seo M (2001) Corros Sci 43:553
5. Armstrong R, Harrison J, Thirsk H, Whifield R (1970) J Electrochem Soc 117:1003
6. Hristova E, Arsov LJ, Popov B, White R (1997) J Electrochem Soc 144:2319
7. Blackwood D, Greef R, Peter L (1989) Electrochim Acta 34:875
8. Arsov LJ, Efremova A (1992) Electrochim Acta 37:2009
9. Ohtsuka T, Masuda M, Sato N (1985) J Electrochem Soc 132:787
10. Dyer C, Leach J (1978) J Electrochem Soc 125:23
11. Schultze J, Schweinsberg M (1998) Electrochim Acta 43:2761
12. Felske A, Badawy W, Plieth W (1990) J Electrochem Soc 137:1804
13. Sanghi I, Visvanathan S (1962) Electrochim Acta 7:567
14. McAller J, Peter M (1982) J Electrochem Soc 129:1252
15. Prusi A, Arsov LJ (1991) Corros Sci 33(1):153
16. Kelly E (1982) In: Bockris J, Conway B, White R (eds) Modern aspects in electrochemistry, vol 14. Plenum, New York, p 319
17. Bonilla S, Zinola C (1998) Electrochim Acta 43:423
18. Muller A, Popkirov G, Schindler R (1992) Ber Bunsenges Phys Chem 96:1432
19. Tomcsanyi L, De Battisty A (1996) Electrochim Acta 41:291
20. Torresi R, Camara O, De Pauli C, Giordano M (1987) Electrochim Acta 32:1291
21. Herranen M, Carlsson J (2001) Corros Sci 43:365
22. Marino C, De Oliveira E, Rocha-Filho R, Biaggio S (2001) Corros Sci 43:1465
23. Thomas N, Nobe K (1970) J Electrochem Soc 117:622
24. Suhotin A, Tungusova L (1971) Zashita Metallov 7:259
25. Arsov LJ (1985) Electrochim Acta 30(12):1645
26. Arsova I, Prusi A, Arsov LJ (2003) J Solid State Electrochem 7:217
27. Torresi R, Camara O, De Pauli C (1987) Electrochim Acta 32:1357
28. Efremova A, Arsov LJ (1992) J Phys II 2:1353
29. Pourbaix M (1963) Atlas d'equilibres electrochim. Gauthier Villars, Paris
30. Shibata T, Zhu Y (1995) Corros Sci 37:253