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Active/Passive Transition of Niobium in Strong Acid and Alkaline Solutions

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Abstract

By cyclic voltammetry the active/passive transition of Nb electrode has been investigated in concentration range from 0.1 M to 10 M aqueous solutions of H_2SO_4 and KOH. Results indicate the strong influence of the concentration and electrolyte nature to the active/passive transitions and stability of passive films.

Depending on electrolyte concentrations, at potential of 1 V the calculated thickness of passive films varied from 2.2 nm to 3.2 nm. For the same concentrations of H_2SO_4 and KOH the formed passive films in KOH are thicker than in H_2SO_4.

By multiple cycle sequences in which the final anodic potential is gradually enlarged, the barrier properties of passive films on Nb electrode were confirmed.

In the first positive scan after the active/passive transition, no cathodic or reactivation peaks for both 1 M H_2SO_4 and KOH were observed. Only for higher concentrations of KOH (> 2 M) the small reactivation process was recorded. In concentration of 5 M and 10 M KOH, if after the passive film formation the Nb electrodes were maintained for 15 min at cathodic potential of -1.55 (SHE), the cyclic voltammograms indicated the complete dissolution of passive films. The voltammetric data have confirmed that the Nb electrode is more resistant in concentrated H_2SO_4 than in concentrated KOH solutions.

Keywords: niobium, passivity, cyclic voltammetry, reactivation.

Introduction

Research on the electrochemical behaviors and passivity of valve metals is still of big interest and covers a wide range of topics such as: anodic films growth,

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chemical composition of the film, breakdown processes, dielectric properties, electron transfer, optical properties and, finally, stability and corrodibility [1-4]. Valve metals in general are known to form stable oxide films in aqueous media [5,6]. Niobium is one of these metals and has been subjected to extensive studies. Most of these studies were generally concerned with the kinetics of the film thickness growth on its surface.

Electrochemical passivity of niobium has been mainly studied using galvanostatic, potentiostatic, potentiodynamic and EIS techniques in weak acid and alkaline solutions, as well as neutral and puffer solutions [7-9]. The special problem in the study of passivity of niobium is its very high tendency to be previously oxidized in air forming a very stable film that cannot be totally reduced by cathodic polarization. The presence of pre-film on active metal dissolution has been ignored by most authors and only a few studies have been directed towards the stability of passive films in aggressive media [10-12]. Although the studies of metals passivity exist for almost 200 years, so far in literature data it is not possible to find the electrochemical parameters for active/passive transition and reactivation of Nb in higher concentrations of strong mineral acid and alkaline solutions. A few electrochemical information on this subject could be only found in our recent papers accepted for publications [13,14].

The purpose of the present investigation is to study the active/passive transition of Nb electrode depending on electrolyte concentration (acidity and alkalinity over the measurable range of pH values). Special attention is concentrated on the reactivation and re-passivation processes in high concentration of H_2SO_4 and KOH solutions. The comparative studies of the formation of passive films under potentiodynamic conditions, as well as reactivation processes at low over-potentials are presented.

Experimental

Electrodes

Massive cylindrical niobium rod 6.35 mm in diameter (Alfa Aesar a Johnson Matthey company with purity of 99.8 %) was used as a working electrode. The Nb disc prepared from the cylindrical rod was embedded in epoxy holders (Struers) to offer a Nb exposed geometric surface area of 0.316 cm^2. A stout copper wire was employed as the electrical contact. The electrode surfaces were mechanically polished on emery SiC paper No 600, then rinsed with distilled water, and ultrasonically degreased in acetone and ethyl alcohol. Finally they were dried in hot air just prior to be transferred into the electrochemical cell. After each experiment the electrode surfaces were mechanically re-polished in order to avoid any traces of film formation and surface perturbation during the experiment.

As a counter electrode a Pt grid with large surface area, as a reference a saturated calomel electrode (SCE) for H_2SO_4 electrolytes, a Hg/HgO/1 M KOH for KOH electrolytes were used. All the measured potentials are referred to the standard hydrogen electrode (SHE).

Electrochemical cell

The pyrex glass vessel equipped with three cylindrical compartments, Luggin capillary and an inlet and outlet for bubbling inert gas was used as electrochemical cell. When the electrodes were dipped in the electrochemical cell, the solution in the cell was de-aerated by flowing argon gas through fritted bubbler for at least 30 min prior the run.

Solutions

Aqueous solutions of sulfuric acid and potassium hydroxide with concentrations of 0.1, 1, 2, 5 and 10 M were freshly prepared from concentrated p.a. H_2SO_4 and KOH crystals (Across Organic) and triply distilled water.

Apparatus

The electrochemical measurements were performed using HEKA Model 488 potentiostat/galvanostat interfaced with a PC.

Results and discussion

The potentiodynamic measurements were performed 30 min after immersion of Nb electrode in the electrolytic cell at open circuit potential (OCP). During this period the steady-state condition of the Nb electrode was established and only small variations of (OCP) were observed [14].

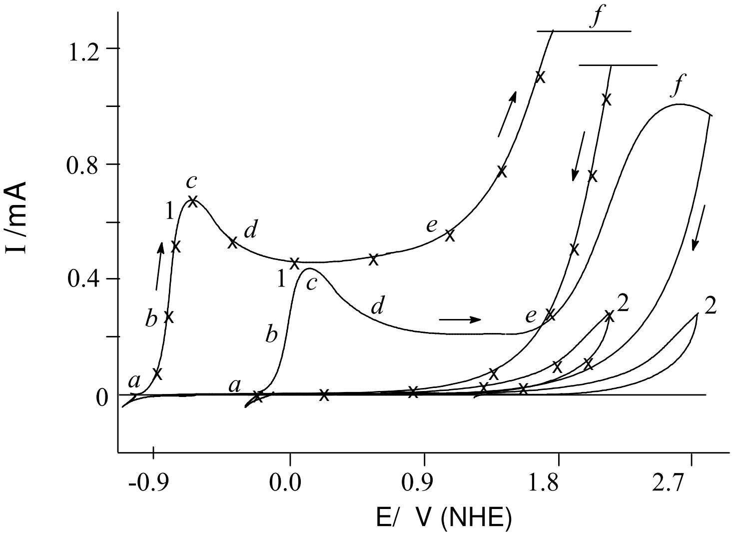

Figure 1. Cyclic voltammograms of Nb electrode in: --- 1 M H_2SO_4, --x-- 1 M KOH, 1 – first cycle, 2 – second cycle (v = 50 mV/s).

In Fig. 1. potentiodynamic I-E profiles for 1st and 2nd cycles of Nb electrode registered in 1 M H_2SO_4 and 1 M KOH are shown. The potential sweeps were initiated from OCP and finished nearly from OCP (-0.25 V for 1 M H_2SO_4 and – 0.92 V for 1 M KOH), so that the starting currents approached zero values.

In the first positive scan four distinct regions for both potentiodynamic curves were observed.

- The first region could be defined as an active dissolution region between points *a* – *b*, where the anodic current increases exponentially with a scanning potential, up to point *c* where the anodic current peak is formed. In this region the metal dissolution takes place following the reaction

$$Nb \rightarrow Nb^{5+} + 5e^{-} \qquad (1)$$

- In the second region *c* – *d* the anodic current decreases towards a low value, corresponding to the beginning of the passivation of the electrode following the reaction

$$2\mathrm{Nb} + 5\mathrm{H_2O} \rightarrow \mathrm{Nb_2O_5} + 10\mathrm{H^+} + 10\mathrm{e^-} \qquad (2)$$

- In the third region, *d* – *e*, the anodic current is almost constant independent of the applied potential, and surface layers of stable oxides are formed. The thickness of the passive films grows by reaction (2) and the metal dissolution is increasingly hindered. The shape of the curves in the regions *c* - *d* and *d* - *e*, as well as ageing of passive films and progress of reaction (2), strongly depends on the concentration of H_2SO_4 and KOH, surface pre-treatments of the electrodes and initial electrochemical conditions [13,14].

The ageing of passive films involves various transformations such as: stoichiometric changes, swelling or dehydration, corrosion further growth, recrystallization, or depletion of defects.

The thickness *d* of passive films ranges from monomolecular to the micrometer range and can be determined by chemical, electrochemical and spectroscopic techniques. The interpretation of coulometric data according to Faraday's law gives a first information

$$d = \frac{q \times M}{z \times F \times \rho} \qquad (3)$$

where *d* is the film thickness (cm/V), *M* is the molecular weight of the passive film, (in our case for Nb_2O_5 M = 265.8 g/mol), *q* is the charge crossed the film (C), *z* is the number of electron exchanged (according to reaction 2 for Nb_2O_5 z = 10), ρ is the density of a presumed homogeneous oxide (for Nb_2O_5 $\rho = 4.47$ g/cm^3) and *F* is the Faraday constant (=96500 C/mol)

According to reaction (3) the calculated thickness of the passive films varied from 2.2 nm to 3.2 nm at potential of 1 V and the film formed in KOH is a little bit thicker than in H_2SO_4. But the assumption of a constant thickness, stoichiometry and density of a crystalline film is a first range approximation only. The density of amorphous passive films is less than of crystalline modification. Moreover, gradients of stoichiometry limit the accuracy of thickness determinations that often only refer to parts of the passive film. More precise values of film thickness can be determined by in-situ ellipsometric measurements, which will be the subject of our further investigations.

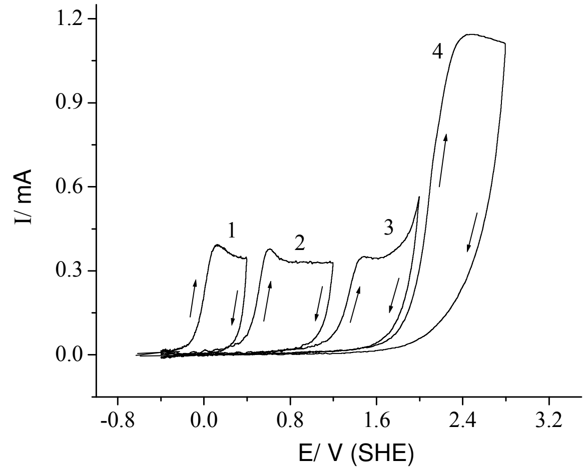

Figure 2. Multiple cycles at increasing final anodic potential starting from bare Nb electrode in 1 M H_2SO_4 (v = 50 mV/s). 1, 2, 3, 4 – represent number of cycles.

Real oxide films usually are non-stoichiometric due to an excess of metal ions or a deficiency of oxygen ions. Foreign ions like protons or impurities can contribute to the donors, acceptors or traps in the band gap. Defect concentrations of passive films are usually in the range from 10^{19} to 10^{21} cm^{-3}.

- The forth region *e – f* is trans-passivity region where anodic breakdown and evaluation of oxygen take place. The passive films on valve metals are of the barrier type, i.e., they show low ionic and electronic conductivity and low and medium field strengths (E < 1 MV/cm). Under some special conditions (applied potential, pH of electrolyte, presence of active anions, etc.), with increasing of local conductivity, passivity breakdown is observed. The breakdown of passive films means a spontaneous local increase of conductivity, sometimes by many decades. The process of local breakdown represents metal dissolution whose intensity depends on the electrical and chemical energy stored in the system. In that case the passive films can be simulated as dielectric medium of a capacitor, which is short-circuited by the local breakdown.

In the first reverse scans, up to potential of –0.25 V for 1 M H_2SO_4 and up to –0.92 V for 1 M KOH, Fig. 1, no cathodic peaks or reactivation anodic peaks were observed. In the second cycles constant currents close to zero for both forward and reverse scans were recorded. The voltammograms in the subsequent cycles were almost identical to the second ones. It is evident that after the 1st forward cycle the Nb electrode in 1 M H_2SO_4 and 1 M KOH remained passive in the whole investigated potential range and the formed passive films blocked all possible redox reactions Nb/passive film/electrolyte at the interface.

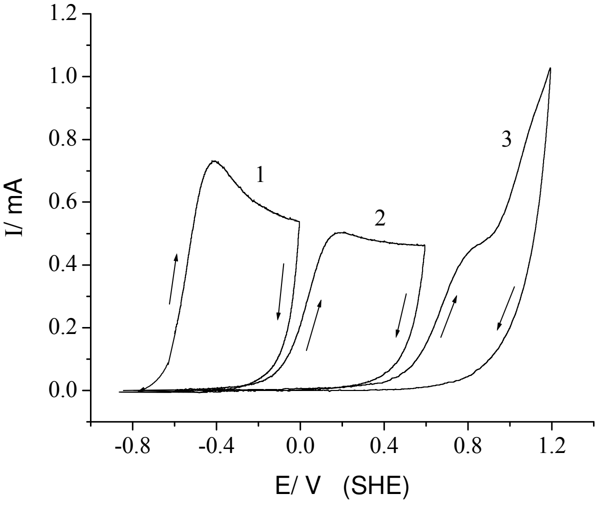

Figure 3. Multiple cycles at increasing final anodic potential starting from bare Nb electrode in 1 M KOH, (v = 50 mV/s). 1, 2, 3 – represent number of cycles.

The barrier properties of anodically formed passive films can most easily interrelated by performing of sequences of cyclic voltammetry measurements where the final anodic potential is gradually enlarged in each next cycle, Fig. 2 and 3. As shown on Fig. 2 and 3, the progress of film thickness with anodic oxidation may take place only if the actual potential exceeds the maximum value attained in the previous cycle. The shapes of the sequences recorded on Fig. 2 and 3 represent just the copy segments of the corresponding voltammograms recorded in Fig. 1. It is evident that by gradually increasing the final anodic potentials the passive films grow by additional building of the new films on the already existing.

In higher concentrations of H_2SO_4 and KOH the active region and metal dissolution on potentiodynamic I-E curves are more pronounced. The critical current in KOH is much higher than in H_2SO_4. For example, the critical current in 10 M KOH is about 15 times more intense than in 10 M H_2SO_4. In 10 M H_2SO_4 the potentiodynamic I-E profile has similar shape as for 1 M H_2SO_4 in Fig. 1. For all concentrations of H_2SO_4 in the reverse scans no reactivation peaks were monitored and the currents have almost constant anodic values near to zero.

Moreover, for concentrations of KOH higher than 2 M, in the reverse scans the reactivation processes appear, Fig. 4. The formed passive films in the first positive scan are chemically attacked from KOH and become porous with many surface defects. From the potentiodynamic window on Fig. 4 it is not possible to speak about reductive electrochemical dissolution or differential reduction to lower oxides of passive film. In principle, the reductive dissolution of passive films occurs only for cathodic potentials when the cathodic current flows through the electrochemical cell. Reduction to lower oxides takes place if electron transfer through the passive film is possible, and if the reduction potential of the oxide exceeds the potential of the hydrogen evolution. In our case the reactivation process on Fig. 4 could be attributed to the dissolution of metal substrate, following reaction (1), through the pores and defects of the passive films. In the whole investigated potential range no redox peaks, cathodic current or hydrogen evolutions were recorded.

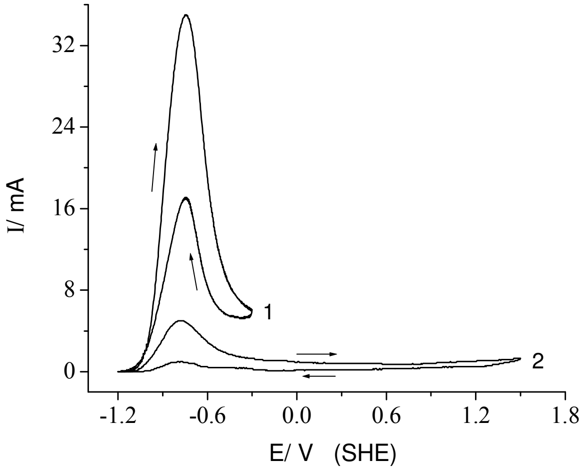

Figure 4. Cyclic voltammograms of Nb electrode in 10 M KOH; 1 – first cycle, 2 – second cycle (v = 100 mV/s).

In order to verify the possibility of the cathodic reduction of whole electrochemically formed passive film, after the continuous multi-cycle scans we have maintained the Nb electrodes for some period of time on cathodic potential of −1.55 V.

Fig. 5 shows voltammograms recorded on Nb electrode in 10 M KOH. In the first positive scan the well-distinguished active peak (*a*) appears. In the first reverse scan the small reactivation peak *b* is observed. In the second positive scan the small active peak with similar intensity as peak *b* again appears. In the second reverse scan very small hardly visible reactivation peak *c* is present. If after these two continuous cycles the scan is interrupted, and if the Nb electrode is maintained for 15 min at initial cathodic potential of –1.55 V, the next two scans will show already the same shape as the first two.

From Fig. 5 it is evident that with cathodic pretreatment the formed passive film is completely dissolved. The cathodic reduction of passive film is only possible by assistance of chemical dissolution of more concentrated KOH solutions. According to Badawy *et al.* [12], in aggressive alkaline solutions with concentration > 2 M the most probable dissolution reaction is

$$3\mathrm{Nb_2O_5} + 6\mathrm{OH^-} \rightarrow 6\mathrm{NbO_3^-} + 3\mathrm{H_2O} \qquad (4)$$

The participation of chemical dissolution and cathodic reduction in the process of the electrode reactivation depending on the concentration of KOH will be the subject of our further in-situ ellipsometric studies.

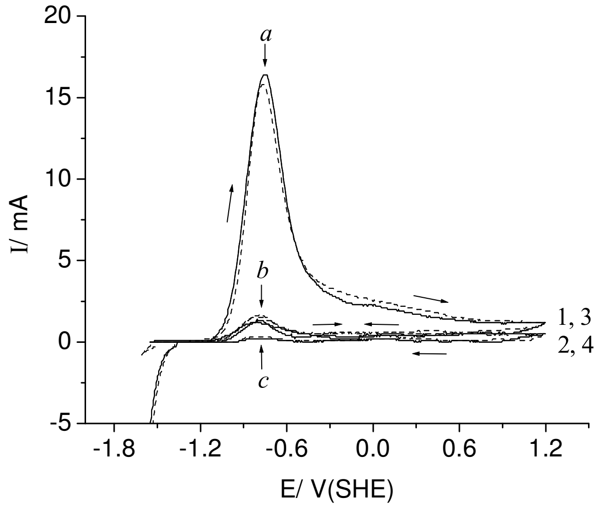

Figure 5. Cyclic voltammograms on Nb electrode recorded in 10 M KON; 1 and 2 – first and second cycles, 3 and 4 – third and fourth cycles recorded on the same electrode after cathodic pre-treatment for 15 min at potential of -1.55 V (v = 50 mV/s).

Conclusions

- The active passive transition of Nb electrodes shows the shifts of primary passivation potential towards more positive potentials with increasing the concentrations of H_2SO_4, and shifts to more negative potentials with increasing the concentrations of KOH. The critical current for all investigated concentrations is much higher in KOH than in H_2SO_4.

- The oxide films formed in H_2SO_4 and KOH solutions are of the barrier type where the film thickness depends on the formation potential. The film thickness subsequently grows with subsequently increasing the final anodic potential confirming barrier properties of formed passive films.

- In all investigated concentration of H_2SO_4 the formed passive films are stable and do not undergo any reduction or dissolution process, even with cathodic pre-treatment of electrode surface.

- In concentration of KOH over the 2 M ($C_{KOH} > 2$ M) the potentiodynamically formed oxide films are porous and they are subject to continuous dissolution, so the dissolution rate being dependent on the alkali concentration. That was confirmed in the reverse scans when the apparition of reactivation peaks results from dissolution of metal substrate through the pores of the passive films. With cathodic pre-treatment of electrode surface the passive film was completely reduced.

- The Nb passive films are more resistant against corrosion in H_2SO_4 than in KOH.

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References

1. I. Arsova, A. Prusi and Lj. Arsov, *J. Solid State Electrochem*. 7 (2003) 217-222.
2. T. Hurlen, H. Bentzen, S. Hornkjo, *Electrochim. Acta* 32 (1987) 1613-1617.
3. K. Hensler, M. Schulze, *Electrochim. Acta* 20 (1975) 237-244.
4 I. Uehera, T. Sakai, H. Ishikawa, H. Takenaka, *Corrosion* 45(7) (1989) 548-553.
5. A. Prusi and Lj. Arsov, *Corrosion Sci*. 3(1) (1991) 153-164.
6. A. Prusi, Lj. Arsov, B. Popov, B. Haran, *J. Electrochem. Soc*. 149 (11) (2001) B491-B498.
7. F. Di Quarto, S. Piazza, C. Sunseri, *Electrochim. Acta* 35(1) (1990) 99-107.
8. G.E. Cavigliasso, M.J. Esplandiu, V.A. Macagno, *J. Appl. Electrochem*. 28 (1998) 1213-1219.
9. M. Edilberg, D. Sandulor, *Electrokhimiya* 23(4) (1985) 533-535.
10. K. Sugimoto, G. Belanger, D. Piron, *J. Electrochem. Soc*. 126(4) (1979), 535-541.
11. A.G. Gad Allah, *J. Appl. Electrochem*. 21 (1991) 346-351.
12. W.A. Badawy, A. Gad-Allah, H. Rehan, *J. Appl. Electrochem*. 17 (1987) 559-566.
13. I. Arsova, A. Prusi, T. Grcev, Lj. Arsov, *J. Serb. Chem. Soc*. 2 (2006) (in-press).
14. I. Mickova, A. Prusi, T. Grcev, Lj. Arsov, *Croat. Chim. Acta* (accepted).