Anodic Dissolution Behavior of Zirconium in n-Butanol Solutions Containing Buⁿ₄NBr

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ABSTRACT

Anodic dissolution of zirconium in Buⁿ₄NBr-containing n-butanol solutions was investigated using cyclic voltammetry, linear sweep voltammetry and potentiostatic current–time transient and scanning electron microscopy (SEM). Zirconium did not exhibit active dissolution due to passivation in the potential region of 0.2 to 1.2 V vs. SCE. The zirconium dissolution in passive state was under mass transfer control. Pitting corrosion took place as a result of passivity breakdown by Br[−] anions and the typical steady-state pitting potential was between 1.55–1.60 V vs. SCE in n-butanol solutions containing 0.08 M Buⁿ₄NBr. SEM images confirmed the occurrence and the intensification of pits with an increase of potential. Increasing Buⁿ₄NBr concentration accelerated the pit nucleation and growth. The reaction order leading to pit nucleation process was 1.0 with respect to bromide anions. The dissolution of zirconium in n-butanol solution produced Zr(OC₄H₉)₄.

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Keywords : Zirconium, Pitting Corrosion, n-Butanol, Bromide Ion

1. Introduction

Zirconium oxide has received considerable attention as a storage capacitor in dynamic random access memories, a gate oxide in field effect transistors, an antireflection layer for solar cells and photo-protective agent for wood due to its high dielectric constant, high refractivity and stable photochemical properties.^{1–3} It is usually prepared by chemical vapor deposition of zirconium alkoxide, an important precursor for zirconium oxide.^{4,5} The most commonly used, technically simple and economically viable preparation of zirconium alkoxide generally proceeds from zirconium tetrachloride with ethyl formate and dry ammonia.⁶ However, this method consumes large amount of organic solvents and liberates harmful NH₃ gas. In addition, the yield is low.⁷ Electrochemical dissolution of metals in absolute alcohols containing a supporting electrolyte has proved to be a promising synthesis method of metal alkoxides.⁸ Many researchers synthesized niobium, zirconium and hafnium alkoxides using electrochemical method.^{9,10} High purity tantalum ethoxide is prepared by a combination of electrochemical synthesis and vacuum distillation.¹¹ In Russia, this technique has been successfully employed for the commercial production of alkoxides of Y, Ti, Zr, Nb, Ta, Mo, W, Cu, Ge and Sn.¹²

To synthesize zirconium alkoxide, it is essential to understand the electrochemical dissolution behavior of zirconium in alcohols. Zirconium is known to be a passive metal due to formation of a protective oxide film on the surface.¹³ However, the passive film would break down under the attack of certain anions like chloride and bromide, consequently inducing pitting corrosion.^{14,15} The corrosion behaviors of zirconium in aqueous solutions have been widely investigated.^{16,17} But few publications have been found describing the pitting corrosion in non-aqueous solutions.¹⁸ The corrosion behaviors of titanium in non-aqueous solutions like methanol, ethanol and propanol solutions were investigated with respect to the effect of water and aggressive ions.^{19,20} The passive film properties of titanium are dependent of water content and carbon number in alcohol. Aggressive ions can break the passive film and induce pitting corrosion. Zirconium and titanium are regarded as sister metals with similar physical and chemical properties. However, they show much difference in corrosion

properties. For example, zirconium does not exhibit the active region as titanium and most other passive metals do in acidic chloride solutions. Zirconium is more suitable than titanium for handling reducing acids and strong alkalis.²¹ Thus, the corrosion behavior of zirconium in non-aqueous solutions would be different from titanium and deserve detailed investigation.

Zirconium n-butanoxide is an important precursor for zirconium oxide. It is found that Buⁿ₄NBr is a good supporting electrolyte due to high conductivity and solubility in n-butanol.²² In this work, the electrochemical behaviors of zirconium were investigated in n-butanol solutions containing Buⁿ₄NBr, using cyclic voltammetry, linear sweep voltammetry and potentiostatic current–time transient techniques. The effects of applied potential, scan rate and Buⁿ₄NBr concentration on the anodic dissolution of zirconium were discussed, which would be helpful to understand the reaction mechanism and disclose the relationship between anodic dissolution rate and the concentration of bromide ions.

2. Experimental

2.1 Materials and electrolyte solution

The electrolyte solution was prepared using n-butanol (99.5%, Tianjing Damao), tetrabutylammonium bromide (99.0% Buⁿ₄NBr, Shanghai Aladdin) and acetonitrile (99.0%, Sinopharm chemical Reagent, China). All chemicals were analytical grade and used without further purification. The water content is less than 0.2 wt% and 0.3 wt% for AR grade n-butanol and acetonitrile, respectively. The standard solution employed was 0.08 M Buⁿ₄NBr, 90% n-butanol and 10% acetonitrile by volume as solvent. The addition of acetonitrile was to increase the conductivity of the solution from 276 to 535 μS/cm. No further drying of the solvent was carried out. The water content in the solution is about 0.23 wt%.

Electrochemical experiments were carried out in a conventional three-electrode glass electrochemical cell. A zirconium rod as working electrode (5.0 mm diameter, 20 cm long) was supplied by Zhuzhou Cemented Carbide Group Corporation, with a chemical composition (wt%): O 0.02, C 0.005, N 0.003, Fe 0.005, Si 0.0013, Mo 0.005, Ni 0.005, Cr 0.0009, Hf 0.0096 and Zr balance. The electrode was mounted in epoxy resin with an apparent exposed area

of 0.19 cm². The counter electrode was a platinum foil (about 2 cm²). All potentials were measured and reported relative to a saturated calomel electrode (SCE). An electrolyte filled bridge with a Luggin capillary was used to minimize the IR drop.

2.2 Electrochemical measurement and characterization

Electrochemical measurements were performed using CHI 660C electrochemical workstation (CH Instruments Inc, Shanghai) connected with a personal computer. Cyclic voltammetry measurements (CV) were carried out by sweeping the potential from −1.0 V vs. SCE in the positive direction at a given scan rate up to the desired potential and then reversing with the same scan rate to the starting potential. Linear sweep voltammetry (LSV) experiments were conducted by automatically changing the potential from the open circuit potential to 3.7 V vs. SCE at a scan rate of 10 mV/s. The chronoamperometry (anodic current transients) at a constant anodic potential were recorded for 60 s. All measurements were carried out at a temperature of 20 ± 0.5°C. The electrode surface was examined by a JSM-6360 LV scanning electron microscope after anodic polarization at various potentials for 10 min in the mixed solvent containing 0.08 M Bu₄NBr. The conductivity of electrolyte was measured using DDS-11C conductivity meter (INESA Instrument, Shanghai).

Prior to each experiment, the electrolyte solution was deaerated using ultra-pure nitrogen and then maintained under a nitrogen atmosphere throughout the whole process. The working electrode was successively abraded with a series of emery papers, from a coarse grade 400 to a fine grade 3600. After that, the electrode was rinsed with acetone, ethanol, dried and finally dipped in the electrolytic solution. Before each experiment, the electrode was allowed to corrode freely for a period of 1.0 h to obtain a steady state open circuit potential.

3. Results and Discussion

3.1 Effect of applied potential on zirconium dissolution

Figure 1 shows the cyclic voltammogram curve for Zr in the mixed solvent containing 0.08 M Bu₄NBr at a scan rate of 50 mV/s. On the forward scan, the inserted curve shows a corrosion potential (E_{corr}) of −0.52 V vs. SCE below which the current is cathodic. The cathodic current probably corresponds to hydrogen evolution.^{6,19} The anodic current density increases from E_{corr} to 0.2 V vs. SCE and then attains a plateau value about 115–135 μA/cm² until 1.2 V vs. SCE. The low limiting current density indicates that zirconium does not exhibit active dissolution in the potential region of 0.2 to 1.2 V vs. SCE. The lack of active dissolution can be attributed to

passivation due to the presence of a passive film on the zirconium surface. Zirconium has a remarkable capability to form zirconium oxide in an oxygen-containing environment, such as O₂, H₂O and CO₂.¹⁸ This capability is less conditional than that of most other passive metals. The passive film could be formed through contact with traces of water in the mixed solvent according to the following reaction (1) or spontaneous passivation on exposure to atmosphere due to highly active nature indicated by the standard potential for $\text{Zr} \rightarrow \text{Zr}^{4+} + 4\text{e}^-$ to be −1.539 V versus SHE or due to alcohol decomposition which produces water and then causes zirconium butanoxide hydrolysis as the following reaction (2) to reaction (4).^{23,24} The reaction (4) continues until oxide film is formed. However, this passive film is not stable enough and can be broken, which makes the dissolution go on. Thus, with the potential further moving towards the noble direction, the anodic current density gradually increases, which results from the attack of the passive film by Br[−] anions according to reaction (5).^{15,23}

When the anodic potential exceeds a certain critical value E_b , the current density rises more quickly than ever before, without any sign of oxygen evolution, suggesting the breakdown of the passive film, initiation and propagation of pitting corrosion. When the potential is reversely scanned, the current density shows a continuous and small increase, typical of an autocatalytic character of pitting corrosion. Afterward, the current density begins to decrease and forms a positive hysteresis loop. The initial linear decrease of current density suggests that an ohmic-controlled process is taking place.¹⁴ It is reported that during the growing processes of an occluded pit, the concentration of metallic cations increases gradually due to the active dissolution within pits. Once the saturated concentration is reached, a salt film (corrosion product) will be formed at the bottom of the pit. The dissolved metallic cations move outward through the salt film. The stronger the field is, the faster the metallic cations move through the film. In this stage, the growth of the pits is controlled by the ohmic potential drop across the salt film.²⁵ The later nonlinear decrease of current density with potential may result from the existing pits to be smaller and shallower and/or partial repassivation.^{26,27} Finally, the reverse scan intersects the forward scan at the repassivation potential (E_{rp}) with a value about −0.021 V vs. SCE. E_{rp} corresponds to the potential value below which no pitting occurs and above which pit nucleation begins.²⁶ The existence of a positive hysteresis loop in a cyclic voltammogram curve indicates a delay in repassivation of an existing pit. The larger the hysteresis loop, the more difficult it becomes to repassivate the pit.²⁵ The results obtained here are in good agreement with those reported previously regarding Ta.¹⁵ The locations of E_{rp} and E_b are defined in Fig. 1.

To get a steady state E_b , the current–time transients for Zr in n-butanol solutions at various anodic potentials are shown in Fig. 2. When the potential is larger than 1.6 V vs. SCE, the current density initially decreases with time and reaches a minimum at a certain incubation time (t_i). The decrease in the current density is due to passive film growth on the anode surface. The reciprocal of the incubation time (t_i^{-1}) is taken as the rate of pit nucleation.¹⁵ After t_i , the current density begins to rise and then reaches a steady state. The increase in current density is attributed to the breakdown of passivity caused by the aggressive attack of Br[−] anions and subsequent formation and growth of pits. The steady-state current means an

Figure 1. (Color online) Cyclic voltammogram for Zr in n-butanol solutions with 0.08 M Bu₄NBr. Scan rate, 50 mV/s.

Figure 2. (Color online) Current–time transients for Zr in n-butanol solutions with 0.08 M Bu₄NBr at different anodic potentials.

Figure 3. SEM images for Zr in n-butanol solutions anodizing at different anodic potentials for 10 min (a) 0.8 V, (b) 1.8 V, (c) 3.0 V.

equilibrium process going on in the pits, indicating that the metal dissolution rate is equal to the oxide film formation rate. As for potential 1.55 and 1.50 V vs. SCE, the current density decays gradually to a stable value with the presence of oscillation. This response is interpreted as when the potential is just below the stable pit nucleation potential, unstable pitting exists as a result of repetitive new pit formation and repassivation in the early stage, which leads to the oscillation in steady-state current density.^{14,28} The results indicate that the steady-state pitting potential E_b (i.e., the minimum potential required for stable pit initiation and growth) is between 1.55–1.60 V vs. SCE.

Figure 3 shows the SEM images of the electrode surface anodized for 10 min at various potentials. It is very clear that the ratio of pitted area to total surface area and the depth of pits vary with the applied potential. No pitting occurs when zirconium was held at 0.8 V vs. SCE (Fig. 3a). Anodizing at 1.8 V vs. SCE induces obvious pits on the specimen (Fig. 3b). Further increasing potential to 3.0 V vs. SCE yields a rough etched surface with deep localized pits. The radial growth of large pits seems to begin by the coalescence of small pits. The increase in pitting susceptibility with an increase in potential could be explained on the basis that an increase in the applied potential may increase the electric field across the passive film and therefore enhances the adsorption of the aggressive Br[−] anions on the passive electrode surface. Similar results were also reported by Yang et al.⁶ and Ono and Habazaki.²⁹

Figure 4. (Color online) Cyclic voltammetry for different scan rates for Zr in n-butanol solutions with 0.08 M Bu₄NBr.

Figure 5. Relationship between limiting current density and $\nu^{1/2}$ for Zr in n-butanol solutions with 0.08 M Bu₄NBr.

3.2 Effect of scan rate on zirconium dissolution

Figure 4 presents the effects of scan rate (ν) on the cyclic voltammetry curves of Zr in n-butanol with 0.08 M Bu₄NBr. All curves show a potential region from 0.2 to 1.2 V vs. SCE where zirconium surface is passive at a low limiting current density (less than 450 $\mu\text{A}/\text{cm}^2$). The limiting current density increases linearly with an increase of $\nu^{1/2}$ shown in Fig. 5. The linear relationship indicates that the current is attributed to the transport throughout the oxide film of metallic ions derived from the anodic dissolution at the metal/oxide interface.^{23,24,26} The pitting potential E_b shows little difference when the scan rate increases from 10 to 50 mV/s. While further increasing the scan rate to 200 mV/s leads to a positive shift of E_b about 250 mV. The initiation of the pitting attack can be attributed to the adsorption of Br[−] anions on the passive film.^{15,30} The adsorbed anions can penetrate through the passive film, especially at its defect points and flaws, with the assistance of a high electric field to reach the base zirconium surface and form a soluble complex. Following this, an incubation time and a certain amount of bromide anions are needed to perforate the passive film. When the scan rate is too high, which corresponds to a sufficiently short time to reach the same potential, bromide ions have little time to form a soluble complex. Consequently, pitting initiation occurs only at a more positive potential.

3.3 Effect of Bu₄NBr concentration on zirconium dissolution

The effect of Bu₄NBr concentration on the linear sweep voltammetry of zirconium is given in Fig. 6. It is observed that an increase of concentration of Bu₄NBr increases the anodic current density. The acceleration effect of Bu₄NBr is due to the adsorption of Br[−] on the zirconium surface and subsequent participation in the active dissolution to form a soluble complex. Furthermore, the conductivity of electrolyte increases with increasing Bu₄NBr

Figure 6. (Color online) Effect of Bu_4NBr concentration on linear sweep voltammetry for Zr in n-butanol solutions, Scan rate, 10 mV/s.

Figure 7. (Color online) Current–time transients for Zr in n-butanol with various Bu_4NBr concentrations at a constant anodic potential of 3.0 V.

concentration, which correspondingly accelerates the zirconium dissolution. For all the cases, the conductivity was measured in the range of 340 to 928 $\mu\text{S}/\text{cm}$. For a current density of 3 mA/cm^2 , it is estimated that the ohmic potential drop is between 59.8 to 163.3 mV,¹⁹ which becomes significant only at high currents. Thus, the data are presented and uncorrected for IR drop. It is observed that the breakdown potential E_b shifts negatively with increasing Bu_4NBr concentration. This response is interpreted that bromide anions attack the passive film and subsequently form pits. The increase of the amount of bromide ions may make passive film breakdown easier. As a result, the initiation of pitting occurs at a more negative potential.

The current-time transients for Zr in n-butanol with various Bu_4NBr concentrations at a constant anodic potential of 3.0 V vs. SCE are shown in Fig. 7. With increasing Bu_4NBr concentrations, the incubation time t_i slightly decreases while the plateau current density increases. It is interpreted that a higher Br^- concentration increases the probability of initiating pit formation and accelerates pit growth. Similar results were previously reported in the study of pitting corrosion of stainless steel and tin in several media containing aggressive anions.^{31,32}

The reciprocal of the incubation time (t_i^{-1}) was taken as the rate of pit nucleation. The pit nucleation rate as a function of bromide anion concentration was observed to follow the relationship

$$1/t_i = kC_{\text{Br}^-}^n \quad (6)$$

Where n is the reaction order, k is a constant, C_{Br^-} is the concentration of bromide ions, M. The value of n obtained from the slope of $\log t_i^{-1}$ vs. $\log [C_{\text{Br}^-}]$ plot is shown in Fig. 8. It can be seen that the slope n is 0.90 which indicates a first-order reaction with respect to bromide anion. The reaction order is interpreted that only

Figure 8. Dependence of pit nucleation rate t_i^{-1} on bromide ion concentration for Zr in n-butanol solutions at an applied potential of 3.0 V.

Figure 9. (Color online) Dependence of pit growth current density on $t^{1/2}$ for Zr in n-butanol solutions with various Bu_4NBr concentrations.

Table 1. Pit growth rate at different Bu_4NBr concentrations.

C/M	0.04	0.08	0.12	0.16	0.20
A ($\text{mA}/\text{cm}^2 \text{s}^{1/2}$)	0.70	0.98	1.77	2.10	3.37

one bromide anion per zirconium atom participating in the pitting nucleation process.

To better understand the role of Br^- anions on the pit growth, the current density in the rising part at various concentrations of Bu_4NBr was analyzed and shown in Fig. 9. A linear relationship between current density and $t^{1/2}$ is found and can be expressed as follows.

$$i = At^{1/2} \quad (7)$$

Where A is slope, i is current density, mA/cm^2 , t is time, s. It is suggested that the pit growth is an instantaneous three dimensional nucleation followed by diffusion-controlled growth.²⁴ The slope A , indexed as the rate of pit growth, is obtained by fitting the data and shown in Table 1. The rate of pit growth increases with an increase of Bu_4NBr concentrations but not a linear relationship indicating a change in pit growth mechanism with an increase of bromide ion concentration.

3.4 Mechanism of zirconium dissolution in n-butanol solutions

Once zirconium is exposed to the n-butanol solutions, a passive film can form on the surface, which may consist of oxide and hydroxide of zirconium. Its exact composition and structure

deserve further study. However, bromide anions can adsorb on the specimens and destroy the passive film and induce pitting corrosion, which means the start of the dissolution reaction.

Combining all the experiments results and the corrosion behaviors of other metals,^{15,22} the dissolution mechanism for Zr in n-butanol solutions containing Buⁿ₄NBr may be written as follows.

The anodic reaction is initially zirconium dissolution and forms Zr(OC₄H₉)₄ according to reaction (3). Then Zr(OC₄H₉)₄ combines with Br[−] and forms Zr(OC₄H₉)₃Br. The cathodic reactions are hydrogen reduction and transformation of Zr(OC₄H₉)₃Br to Zr(OC₄H₉)₄ and bromide anions. The bromide anions can combine with tetrabutylammonium cations to form Buⁿ₄NBr, which again behaves as supporting electrolyte. In addition, Zr(OC₄H₉)₄ may hydrolyze and produce zirconium oxide as follows.

If reaction (11) continues, reaction (8) will not take place, and the exposed surface will be passivated again. If a small amount of water is present, hydrolysis is to occur within the diffusion layer, the effective local activity of water will be reduced and the rate of oxide film growth therefore also reduced, thus, dissolution of zirconium should retard the repassivation rate and the repassivation of zirconium retards the dissolution rate. The processes of dissolution and repassivation are thereby interdependent. Finally, the dissolution rate is equal to the oxide film formation rate, which leads to a constant current density as shown in current-time transients.

4. Conclusions

Zirconium does not exhibit active dissolution due to the presence of passive film on the zirconium surface in the potential region of 0.2 to 1.2 V vs. SCE in n-butanol solutions containing Buⁿ₄NBr. Under the aggressive attack of bromide anions, zirconium suffers from pitting corrosion. The typical steady-state pit potential is between 1.55–1.60 V vs. SCE when Buⁿ₄NBr concentration is 0.08 M, but decreases with an increase of Buⁿ₄NBr concentration. SEM images confirm the existence of pits on the zirconium surface in n-butanol solutions containing 0.08 M Buⁿ₄NBr. The depth and breadth of pits are intensified when the potential increases from 1.8 to 3.0 V vs. SCE.

The potentiostatic current–time transient reveals that the incubation time for pitting corrosion decreases with increasing anodic potential and Buⁿ₄NBr concentration. The reaction order leading to the pit nucleation process is 1.0 with respect to bromide anion. The electrochemical dissolution mechanism is put forward.

Acknowledgments

This work was supported by National Nature Science Foundation of China (Grant No 51374254) and Teacher Research Foundation of Central South University in China (Grant No 2013JSJJ026). The authors thank Jun Guo and Yongqiang Huang for English help.

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