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In Situ Preparation and Corrosion Resistance of a ZrO₂ Film on a ZrB₂ Ceramic

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Abstract: ZrO_2 films were in situ prepared using the anodic passivation of a ZrB_2 ceramic in alkaline solutions. The composition and structure of the films were characterized using field-emission scanning electron microscopy (FE-SEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). The corrosion resistances were evaluated in 0.1 M oxalate solution using the potentiodynamic polarization method (PDP) and the electrochemical impedance spectroscopy (EIS) technique. The results show that ZrO_2 films can be prepared using anodization from -0.8 to 0.8 V standard hydrogen electrode (SHE) in 2–16 M NaOH solutions. During the anodization, the dehydration reaction of $Zr(OH)_4$ to ZrO_2 caused the volume shrinkage and tensile stress of the films. When the thickness of the films exceeded a critical value, the mud-cracking morphology occurred. The films without cracks exhibited the inhibition effect and provided effective corrosion protection in a 0.1 M H₂C₂O₄ solution, which had a positive correlation with the film thickness. The film obtained when put in an 8 M NaOH solution (near the critical thickness) was found to significantly improve its corrosion resistance when put in a 0.1 M H₂C₂O₄ solution by almost one order of magnitude compared with the bare ceramic.

Keywords: ZrO₂ film; ZrB₂; passivation; corrosion resistance; EIS

1. Introduction

Zirconia (ZrO₂), an important engineering material, has been widely applied due to its excellent comprehensive performance such as good mechanical properties, chemical inertness, good oxidation resistance and biocompatibility [1–3]. When used as a coating or film material, its applications include antireflection coatings for laser diodes [4], electrode coatings for lithium-ion batteries [5], and various anti-corrosion films [6], all of which are widely researched.

The preparation methods for ZrO_2 coatings, such as the hydrothermal treatment [6], sol-gel method [7], physical vapor deposition [8], electrodeposition [9] and spraying techniques [10] are highly developed. Among the existing methods, the in situ reaction technique is characterized by its uniform coating and the perfect bonding with the substrate. Accordingly, the coatings have important and unique applications. For example, Zhang et al. [11] prepared a Zr/ZrO_2 electrode using in situ oxidation of Zr wire in a Na₂CO₃ melt to form a thin-film on the surface. This electrode can be used as a novel Zr/ZrO_2 sensor for the in situ measurement of chemical parameters of deep-sea water. Yang et al. [12] obtained a close-packed nanoporous ZrO_2 layer formed on the surface of zirconium alloy using anodization. It dramatically improves the oxidation resistance in a high-temperature steam environment compared with a bare Zr alloy.

The application of a ZrO_2 film is primarily determined by the substrate. A Zr alloy is the leading substrate for the in situ method and thus constrains the application of in situ ZrO_2 films. However, other substrates besides Zr alloys have been the subject of limited reports in recent years. ZrB_2 , a

non-alloy, was reported as a substrate [13]. ZrB₂ powder could be coated with ZrO₂ and B₂O₃ films using high-energy ball milling. Such a coated powder promotes the densification of a ZrB₂ ceramic [13].

A ZrO_2 film has excellent corrosion resistance in aqueous solutions. Garg et al. [6] reported various nanocrystalline ZrO_2 coatings with different thicknesses grown on pre-oxidized stainless steel using a hydrothermal method in a static autoclave. These coatings significantly improve the corrosion resistance of stainless steel when put in a 0.1 M sodium sulphate solution by almost four orders of magnitude compared with the bare stainless steel. The corrosion resistances of ZrO_2 ceramic nanocoatings on superelastic NiTi alloy in Hank's simulated physiological solution were also evaluated [14]. It was found to prevent the premature failures of NiTi components and nickel release to the human body. Therefore, the ZrO_2 film in situ prepared through the anodization of a ZrB_2 ceramic is expected to enhance the corrosion resistance of the substrate ZrB_2 in aqueous solutions. In addition, the ZrO_2 coating would act as a physical barrier and thus reduce or avoid the reaction between ZrB_2 and a refractory metal at high temperature [15–17]. The refractory metal would thus be preserved and then contribute to preparing a ZrB_2 -based cermet and improving its toughness.

In this work, the anodic passivation behavior was first studied using the potentiodynamic polarization (PDP) method. Then, the composition and structure of the anodic films were characterized using the field-emission scanning electron microscopy (FE-SEM), Raman, and X-ray photoelectron spectroscopy (XPS) techniques. The corrosion resistances of the anodic films were evaluated in the $0.1 \text{ M H}_2\text{C}_2\text{O}_4$ solution, which has been reported as one of the most aggressive acids [18].

2. Experimental Procedures

2.1. Materials

The ZrB₂ ceramic was produced from commercial powder (Qinhuangdao Eno, Qinhuangdao, China; particle size range 10–15 μ m, purity 99.5%). Sintering was carried out by the plasma activated sintering technique (PAS, ED-PAS 111 equipment, Elenix, Zama Shi, Japan) at 1900 °C for 5 min using a pressure of 30 MPa. The final density of ZrB₂ ceramic was ~5.8 g·cm⁻³, corresponding to ~95.6% of its theoretical density. The obtained ceramic surfaces were ground flat by the precision surface grinding machine (Orbit 25EP, Blohm, Hamburg, Germany). It was then cut into several cylindrical specimens (Φ 5 mm × 3 mm) by a wire electrical discharge machine (Wire EDM, BM320-H, Suzhou Baoma, Suzhou, China) in preparation for the working electrodes. More details and properties have been reported in a previous paper [19].

2.2. Film Characterization

The chemical composition of the anodic films was characterized using Raman spectra (Invia, Renishaw, Wotton-under-Edge, UK) and X-ray photoelectron spectroscopy (XPS, ESCALab 250Xi, Thermo Fisher Scientific, Waltham, MA, USA). The Raman spectra was recorded in the range of 100–900 cm⁻¹. A He-Ne laser (632.8 nm) was used as the excitation source. Furthermore, the XPS measurements were performed using an Al K α (h ν = 1486.6 eV) X-ray source powered at 150 W. The high-resolution narrow spectra were recorded with electron pass energy of 30 eV and a step size of 0.05 eV. The peak-fitting of XPS data was achieved using the XPSPEAK program (version 4.1, HongKong, China).

The surface and cross-section morphology were analyzed using FE-SEM (Quanta 250, FEI, Hillsboro, OR, USA) operating at 20 kV. A platinum coating (sputter coater, Q150RES, Quorum Technologies Ltd, Lewes, UK) was performed at 20 mA for 60 s to facilitate high-resolution FE-SEM images. The optical microscope (OM, DM2500M, Leica, Wetzlar, Germany) under normal light was also used to characterize the surface of the anodic film.

2.3. Electrochemical Measurements

The working electrode was prepared from the cylindrical ZrB_2 ceramic. The specimen was connected with a copper wire on one face and then embedded in epoxy resin, leaving the circular bottom (Φ 5 mm) to contact the electrolyte. Before being used, the electrodes were abraded with up to 800 grit silicon carbide paper using an automatic polishing machine (Mecatech 334, Presi, Eybens, France), rinsed with distilled water and ethanol, and then dried in air at room temperature for 24 h.

A Pt plate counterelectrode (20 mm × 20 mm × 0.2 mm) and an Hg/HgO/1 M NaOH reference electrode (standard potential of 0.108 V [20], referred to as the standard hydrogen electrode (SHE)) were used for the potentiodynamic polarization (PDP) and the potentiostatic experiments on ZrB₂. All potentials quoted in this text are given versus the SHE. All tests were conducted using a CHI604E electrochemical work station (CH Instruments, Chenhua, Shanghai, China) in 2–16 M NaOH solutions at 40 °C.

The polarization curves were recorded at a scanning potential rate of 2 mV·s⁻¹ after the open circuit potential (OCP) was stabilized within 2 mV, starting from -1.3 V versus SHE. A potentiostatic test was carried out for preparing the anodic passive film at 0 V for 10 min after the OCP was stabilized. Then, the working electrode with a passive film was rinsed with water and ethanol, and dried in air at room temperature for 24 h. The passive film was used for a corrosion test in H₂C₂O₄ solution and for surface characterization.

The corrosion test of the passive film when put in a 0.1 M H₂C₂O₄ solution was conducted with a similar three-electrode cell. The Pt plate counterelectrode and Ag/AgCl/saturated KCl reference electrode (the standard potential was 0.198 V versus SHE) were used. Similar polarization curves were recorded at a scanning potential rate of 2 mV·s⁻¹, starting from –0.8 V to 1.4 V versuss SHE. Furthermore, the electrochemical impedance spectroscopy (EIS) experiments were performed at the OCP, within the frequency region of 10^{-2} – 10^{5} Hz and with an amplitude 5 mV. The Zsimedemo 3.30 d (Ann Arbor, MI, USA) software was used for fitting the Nyquist plots.

3. Results and Discussion

3.1. PDP of ZrB₂ in NaOH Solutions

Figure 1 exhibits the PDP curves of ZrB_2 ceramic in 2–16 M NaOH solutions. It can be seen that the ZrB_2 ceramic exhibited active–passive polarization behavior. The divisions between typical regions, such as the active region (I, below –0.95 V), transition region (II, –0.95 to –0.8 V), passive region (III, –0.8 to 0.8 V), and oxygen evolution region (IV, above 0.8 V), are shown [21,22].



Figure 1. PDP curves for the ZrB₂ ceramic in 2–16 M NaOH solutions at 40 °C.

The passive potential region was slightly affected by NaOH concentration. Furthermore, the passive current density i_p (10⁻⁵–10⁻³ A·cm⁻²) increased with the NaOH concentration. Such a high

 i_p (10⁻⁴–10⁻³ A·cm⁻², far above 10⁻⁵ A·cm⁻², >6 M NaOH) might have resulted from the persisting contact with the electrolyte through the cracks or pores of the film [23]; that is to say, the higher the i_p , the more defects the film would have.

3.2. Morphology of the Anodic Film

Some representative anodic films were prepared using potentiostatic anodization at 0 V for 10 min in different NaOH solutions. Their surfaces and cross-section morphologies are shown in Figure 2. As seen in the cross-section morphologies, there were no cracks in the joint between the film and the substrate, which shows their good combination. The film thickness (50–1200 nm) increased with the increased NaOH concentration, which reflects the same tendency of the film formation rate.



Figure 2. Surface and cross-section morphology of the films obtained using potentiostatic anodization at 0 V for 10 min in (**a**,**f**) 6 M, (**b**,**g**) 8 M, (**c**,**h**) 10 M, (**d**,**i**) 12 M, and (**e**,**j**) 14 M NaOH solution.

All the specimens were flat in accordance with the polished surface of the matrix. It indicates that the film was transformed due to the ZrB_2 surface, i.e., in situ fabricated. However, a noticeable mud-cracking behavior showed a large amount of cracks evenly distributed throughout the surface occurring in the 10 M NaOH solution (Figure 2c). The cracks broadened in 10–14 M NaOH solutions (Figure 2d,f). Such results are consistent with the above analysis of the passive current densities i_p . Generally, a temperature gradient or volume shrinkage of the film caused by the dehydration generates tensile stress is responsible for the mud-cracking [24–26]. By eliminating the temperature gradient,

the latter is the case. When the film thickness exceeds a critical value, the tensile stress is beyond the tensile strength of the films and crack initiation and propagation occurs. The critical thickness of these films was in the region 150–360 nm.

Furthermore, the film in the 6 M NaOH solution exhibited many blocks with different roughnesses, which is similar to the corroded surface under free corrosion [19]. These blocks might result from the free corrosion during the OCP test process, which was conducted before the potentiostatic anodization step in order to test the system stabilization. The anodization process without the OCP process was conducted and the corresponding surface is shown in Figure 3. It is shown that the different blocks disappeared, indicating the blocks were derived from the OCP step.



Figure 3. Surface morphology of the anodic film obtained using potentiostatic anodization at 0 V for 10 min without the OCP test process when put in a 6 M NaOH solution.

3.3. Composition of the Anodic Films

Figure 4 shows the Raman spectra of the anodic films obtained when put in a 10 M NaOH solution at 40 °C. It shows two broad peaks at 145 and 550 cm⁻¹, which is characteristic of amorphous ZrO_2 [27]. The characteristic peaks of B-containing products [28] are not found in the Raman spectra. In our previous work [19], the polyborate ions, which have highest oxidation state (oxidation number is +3) are produced at the corrosion potential and dissolved in the alkaline solution. At the higher potential, the B-containing products also have the same oxidation state and dissolve in the alkaline solution.



Figure 4. Raman spectra of the anodic film obtained using potentiostatic anodization when put in a 10 M NaOH solution at 0 V for 10 min.

Figure 5 shows the B 1*s* and Zr 3*d* XPS spectra of the above film. No peaks were found in the range of 187–194 eV that belong to the B 1*s* spectra [18]. This indicates that the element boron was completely removed from the film, which is consistent with the Raman analysis. The Zr 3*d* spectra showed that the zirconium hydroxide (Zr(OH)₄, 183.6 eV, Zr $3d_{5/2}$) [29] also existed, as well as the ZrO₂

(182.2 eV, Zr $3d_{5/2}$) [30]. It had a low molar content of Zr(OH)₄ compared with ZrO₂. Zr(OH)₄ tends to dehydrate (Zr(OH)₄ \rightarrow ZrO₂ + H₂O) and thus causes volume shrinkage. It should be noted that the loss of the adsorbed water may also lead to the volume shrinkage. Further observation of the anodic film obtained using potentiostatic anodization at 0 V for 10 min in 14 M NaOH solution without the drying process is shown in Figure 6. As can be seen, the cracks can be observed before the loss of the adsorbed water. Such results indicate that the dehydration reaction of Zr(OH)₄ was responsible for the mud-cracking morphologies.



Figure 5. B 1*s* and Zr 3*d* XPS spectra for the anodic film obtained using potentiostatic anodization at 0 V for 10 min in 10 M NaOH solution.



Figure 6. Optical image of the anodic film obtained using potentiostatic anodization when put in a 14 M NaOH solution at 0 V for 10 min without a drying process.

3.4. Corrosion Resistance of the Anodic Film When Put in a 0.1 M H₂C₂O₄ Solution

Here, the corrosion protection of the anodic film without cracks gained attention because the cracks were generally regarded as considerable defects. Figure 7 shows the PDP curves of the above anodic films recorded when put in a 0.1 M H₂C₂O₄ solution at 40 °C, where the ZrB₂ ceramic substrate is listed for comparison. All the samples show similar active–passive behaviors and the passive potentials were above 0 V versus SHE. The similar curves show that the H₂C₂O₄ solution could penetrate into the film and the curve basically reflected the interaction between the ceramic substrate and the solution.



Figure 7. PDP curves of the anodic films in 0.1 M $H_2C_2O_4$ solution at 40 °C where the substrate (bare sample) is listed for comparison. The films were prepared using potentiostatic anodization in different NaOH solutions at 0 V for 10 min.

Figure 8 shows the corrosion densities (i_{corr}) and corrosion potentials (E_{corr}) of the films calculated using the Tafel extrapolation method. As can be seen, the E_{corr} had increased, in contrast with the bare ZrB₂ ceramic (-0.3 V). The i_{corr} of the substrate ($3.5 \times 10^{-5} \text{ A} \cdot \text{cm}^{-2}$) is similar with the literature [18]. Apparently, the i_{corr} of the films was lower than the substrate and decreased with the film thickness. It should be noted that the cathodic curve of the film obtained in the 8 M NaOH solution shows the feature of oxygen diffusion, which shows the main cathodic reaction had changed from the hydrogen evolution reaction (HER) to the oxygen reduction reaction (ORR), and did not contain the Tafel line region. Thus, its i_{corr} could not be calculated using the Tafel method and is not given in Figure 8. However, it is surely lower than the result ($7.6 \times 10^{-6} \text{ A} \cdot \text{cm}^{-2}$) of the film obtained in the 6 M NaOH solution.



Figure 8. The i_{corr} and E_{corr} of the anodic films put in a 0.1 M H₂C₂O₄ solution at 40 °C calculated using the Tafel extrapolation method based on Figure 7.

Figure 9 displays the EIS results of the films without cracks put in a 0.1 M H₂C₂O₄ solution at 40 °C where the ZrB₂ substrate is listed for comparison. From the Nyquist plots (Figure 9a), the ZrB₂ substrate had a capacitive arc at high frequency and an inductive loop at low frequency. It shows one time constant (Figure 9b,c). The capacitive arc results from the double-layer capacitance and the charge transfer resistance [31]. Furthermore, the inductive loop was related to the adsorbed intermediate product [32] on the corroded surface. The corresponding equivalent circuit is shown in Figure 9d, where R_s is the solution resistance, R_t is the charge transfer resistance, Q_{dl} is a constant phase element parallel to R_t , and L is the inductance element with corresponding inductance resistance R_L .

The film displays one capacitive arc at high frequency and one inductive loop at low frequency. However, this capacitive arc should include the information of the film's resistance besides the charge transfer resistance. Furthermore, the typical equivalent circuit [33] for the films (Figure 9e) was used, where R_f is the film resistance and Q_f is a constant phase element parallel to R_f . The fitted results are shown in Figure 9f and Table 1. As can be seen, all the R_f were smaller than the R_t , which leads to the similar EIS results for the substrate. Both of the resistances increased with the film thickness, which was consistent with the analysis of the polarization curves.



Figure 9. EIS results of the anodic films of ZrB_2 ceramic when put in a 0.1 M H₂C₂O₄ solution (40 °C) at OCP: (**a**) Nyquist plots, (**b**) Bode impedance magnitude plots, (**c**) Bode phase angle plots, (**d**,**e**) equivalent circuit for the substrate and the anodic films, and (**f**) the R_t of the substrate and the films.

Table 1. Fitted results for the anodic films obtained from EIS spectra fitting where n_1 and n_2 are the indexes of Q_f and Q_{dl} , respectively.

Sample	$R_{\rm s}$ ($\Omega \cdot {\rm cm}^2$)	$\frac{R_{\rm t}}{(\Omega \cdot \rm cm^2)}$	$R_{\rm f}$ ($\Omega \cdot {\rm cm}^2$)	$R_{\rm L}$ ($\Omega \cdot {\rm cm}^2$)	$Q_{\rm f}$ (S·sec ⁿ¹ ·cm ⁻²)	<i>n</i> ₁	Q_{dl} (S·sec ⁿ² ·cm ⁻²)	<i>n</i> ₂	<i>L</i> (H·cm ^{−2})
Substrate	12.9	349.3	-	4481.0	_	-	2.2×10^{-5}	0.79	3532.5
2 M	14.9	592.9	58.9	2959.2	5.5×10^{-6}	0.96	1.2×10^{-5}	0.70	6169.3
4 M	13.6	1327.1	107.9	5974.8	4.0×10^{-6}	0.87	3.6×10^{-7}	0.98	1373.7
6 M	14.7	2551.2	431.7	7386.5	4.3×10^{-6}	0.87	2.2×10^{-7}	0.96	1570.0
8 M	17.4	3787.6	510.2	13320.5	2.9×10^{-6}	0.91	1.7×10^{-7}	0.94	4710

Usually, the R_f is used to evaluate the shielding capability of the film or coating. It is directly related to the film properties such as electrical conductivity, porosity, and thickness; furthermore, the R_t is the charge transfer resistance on the surface of the substrate, which could reflect the corrosion inhibition of the film. By comparing R_f and R_t , the contribution of the shielding ability and corrosion inhibition of the film can be clearly distinguished. Therefore, it can be seen that the corrosion inhibition of the film in this paper played a major role ($R_t > R_f$) and can be enhanced by the film thickness.

Although many studies [34–36] have reported such corrosion behaviors of films or coatings dominated by the corrosion inhibition, the research about the effects of the film thickness is not sufficient and clear [37,38]. The corrosion inhibition might result from the corrosion product, which acts as an inhibitor absorbed on the active sites [19,39]. When the film thickness increases, the diffusion of the product would decrease and the absorbed product might augment. Thus, the corrosion inhibition from the corrosion product might be enhanced. In short, the anodic film (without cracks) of ZrB₂ could provide effective corrosion protection when put in a $H_2C_2O_4$ solution, which had a positive correlation with the film thickness. The film obtained when put in a 8 M NaOH solution had the best protection effect, almost one order of magnitude greater compared with the substrate.

4. Conclusions

The ZrO_2 films were prepared in situ using the anodization of a ZrB_2 ceramic in 2–16 M NaOH solutions and characterized using the FE-SEM, Raman, and XPS techniques. Their corrosion resistances when put in a 0.1 M H₂C₂O₄ solution were evaluated using the PDP and EIS techniques. The following conclusions can be drawn:

- The anodic films could be prepared from −0.8 to 0.8 V (SHE). Furthermore, the passive current densities (10⁻⁵−10⁻³ A·cm⁻²) represented the film formation rate increase with the NaOH concentration.
- The amorphous ZrO₂ was the major component of the films. During the anodization, the dehydration reaction of Zr(OH)₄ to ZrO₂ caused the volume shrinkage and tensile stress of the films. When the thickness exceeded a critical value, the mud-cracking morphology occurred. The critical thickness was found in the region of 150–360 nm.
- The films without cracks exhibited the inhibition effect and provided effective corrosion protection when put in a 0.1 M H₂C₂O₄ solution, which had a positive correlation with the film thickness. The film obtained when put in a 8 M NaOH solution (~150 nm, near the critical thickness) performed best, almost one order of magnitude greater compared with the substrate.

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