

Superhydrophilic Nanoporous Oxide Surface on Zr Alloy for CRUD Mitigation

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1. Introduction

Nuclear fuel cladding is continuously exposed to high-temperature and high-pressure primary coolant, where metallic species released by corrosion and wear of structural components are transported through the coolant and deposited as Chalk River Unidentified Deposits (CRUD). CRUD accumulation can alter local heat transfer, coolant chemistry, and axial power distribution, thereby affecting fuel performance and reactor operating margins. In pressurized water reactors (PWRs), subcooled nucleate boiling is particularly important because repeated bubble growth and departure locally concentrates dissolved and particulate species near the cladding surface and accelerates deposition [1-3]. Consequently, the interfacial properties of the cladding surface, including surface chemistry, morphology, roughness, and wettability, can strongly influence the initial stages of CRUD formation.

Several approaches have been investigated to mitigate CRUD deposition, including primary-water chemistry control, Zn injection, surface polishing or etching, and protective ceramic coatings [4,5]. Although these methods can reduce corrosion-product deposition, coolant-chemistry approaches require continuous chemistry management, while externally deposited coatings may introduce concerns related to interfacial adhesion and long-term integrity. Surface engineering of the cladding itself therefore provides an alternative route for modifying the cladding-coolant interface without introducing a separate coating/substrate boundary. In such point of view, electrochemical anodization is particularly attractive because the oxide layer develops directly from the metallic substrate and its nano-structured morphology can be controlled by the applied electrochemical conditions [6].

In this study, anodization was applied to commercial Zr alloy to form a nanoporous ZrO₂ layer with enhanced wettability. The applied voltage was varied from 30 to 90 V to systematically control pore morphology and oxide growth. The resulting surfaces were evaluated in terms of pore size, oxide thickness, roughness, crystallographic structure, surface hydroxylation, and water contact angle. Particular emphasis was placed on clarifying how surface chemistry and nanoporous geometry jointly produce superhydrophilicity. The present work is intended as a fundamental surface-engineering study preceding reactor-relevant validation; potential effects on boiling behavior and CRUD deposition are therefore

discussed as prospective interfacial benefits rather than directly demonstrated performance.

2. Methodology

2.1 Materials and Surface Treatment

Zr alloy sheets (10 × 20 × 0.4 mm, chemical composition: Zr balanced, 0.93 of Sn, 0.11 of Fe, 0.12 of O, and 0.93 of Nb) were used as substrates. Prior to anodization, specimens were ultrasonically cleaned in acetone and distilled water. Anodization was conducted in a two-electrode cell using Zr alloy sheet as the working electrode and Pt foil as the counter electrode with a 25 mm spacing. The electrolyte consisted of ethylene glycol containing 0.3 wt.% NH₄F and 1 wt.% deionized water. Constant voltages of 30, 60, and 90 V were applied for 2 min at approximately 20 °C. After anodization, the specimens were ultrasonically cleaned in ethanol and heat-treated at 500 °C for 2 h (2 °C/min). A thermally oxidized specimen (HT; 500 °C for 5 h) was prepared as a reference.

2.2 Characterization

Surface and cross-sectional morphologies were examined using FE-SEM and FIB with EDS analysis. Pore diameters were measured from SEM images, and surface roughness was quantified using a stylus roughness instrument. Crystalline phases were identified by XRD. Surface hydroxylation was investigated by ATR-FTIR and XPS O 1s analysis. Static water contact angles were measured immediately after droplet deposition to evaluate wettability..

3. Results and Discussion

3.1 Morphology and Structural Characteristics

Anodization transformed the relatively smooth Zr alloy surface into a clearly developed nanoporous oxide morphology (Fig. 1). The average pore diameter increased systematically with applied voltage, from 9.60 nm at 30 V to 26.92 nm at 60 V and 36.71 nm at 90 V. The 30 V surface exhibited the finest and relatively less ordered pore structure, whereas higher voltages produced progressively enlarged pores. This voltage dependence is consistent with the competition between field-assisted oxide formation and fluoride-assisted

dissolution: increasing the applied electric field accelerates dissolution at the oxide/electrolyte interface promoting pore widening [7].

Cross-sectional FIB analysis further showed that the anodic oxide was several micrometers thick, with measured thicknesses of 6.25 ± 1.03 , 6.96 ± 0.79 , and 10.27 ± 1.00 μm for 30, 60, and 90 V, respectively. Cross-sectional EDS line profiles confirmed a Zr- and O-rich layer with a distinguishable oxide/substrate interface. Fluorine, which can remain in anodic oxides produced in NH_4F -containing electrolytes, was not detected after the post-anodization heat treatment, indicating effective removal of residual etchant species.

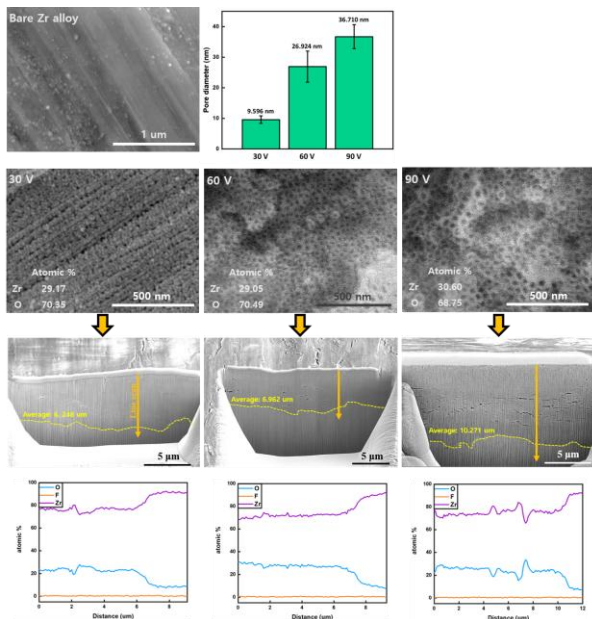


Fig. 1. Surface SEM morphology and pore-size distribution (top), and cross-sectional FIB/EDS analyses (bottom) of anodized Zr alloy prepared at 30, 60, and 90 V.

Surface roughness also increased following anodization. The R_a values were 151.4 nm for bare sample and 205.5 nm for the thermally oxidized HT specimen, whereas the anodized specimens exhibited R_a values of 309.5, 357.5, and 587.4 nm at 30, 60, and 90 V, respectively (Table 1). The corresponding R_q values showed the same tendency. This progressive roughening reflects the development of the porous oxide structures and provides an additional physical mechanism for modifying wettability.

Table 1. Surface roughness parameters of each specimens

	Bare	HT	30 V	60 V	90 V
R_a	151.438 nm	205.510 nm	309.524 nm	357.535 nm	587.360 nm
R_q	193.946 nm	260.537 nm	399.412 nm	453.336 nm	755.290 nm

XRD patterns (Fig. 2) showed predominantly Zr substrate peaks for bare sample and the as-anodized

condition, indicating that the initially formed anodic oxide was nearly amorphous. After heat treatment at 500 $^{\circ}\text{C}$, additional diffraction peaks corresponding to monoclinic ZrO_2 were observed for the HT and all anodized specimens. The relative intensity of the Zr substrate peaks decreased with increasing anodization voltage: the 30 V specimen retained clear Zr contributions, whereas the substrate peaks were strongly suppressed for the thicker 90 V oxide. This tendency agrees with the FIB thickness measurements and independently supports the voltage-dependent growth of the anodic layer. The post-heat-treatment therefore serves two purposes in the present process: removal of residual fluorine-containing species and crystallization of the anodic oxide into monoclinic ZrO_2 .

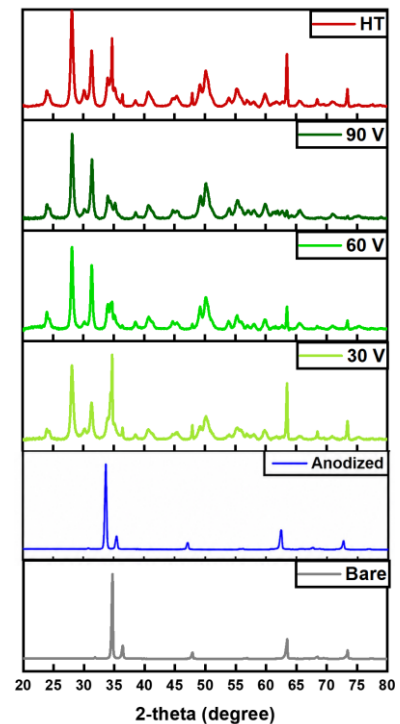


Fig. 2. XRD patterns of bare, as-anodized, heat-treated, and 30-90 V anodized/heat-treated Zr alloy specimens.

3.2 Surface Chemistry and Wettability

FT-IR and XPS analyses demonstrated that the wetting transition was accompanied by substantial changes in surface hydroxylation (Fig. 3). In the OH-stretching region of the FT-IR spectra, the anodized specimens exhibited more pronounced hydroxyl-related absorption than the HT control, with the 30 V condition showing the strongest feature. XPS O 1s analysis likewise identified an appreciable OH-related component on the anodized surfaces. Although the HT specimen also showed a surface OH contribution in XPS, its relatively weak FT-IR response suggests that this signal is dominated by hydroxyl species and adsorbed

moisture confined to the outermost surface. The stronger hydroxylation of the anodized layers is attributed to the aqueous component of the anodization electrolyte. During electrochemical oxide growth, water-derived oxygen and hydroxyl species participate directly in oxide formation, whereas hydroxylation of the thermally formed ZrO_2 surface mainly develops through subsequent interaction with atmospheric moisture. The particularly strong OH response of the 30 V specimen is also consistent with its fine nanoporous structure, which provides a large accessible surface area for hydroxyl-containing species. Surface hydroxyl groups increase affinity toward water through hydrogen-bonding interactions and therefore establish the intrinsic chemical basis for the improved hydrophilicity of ZrO_2 -bearing surfaces.

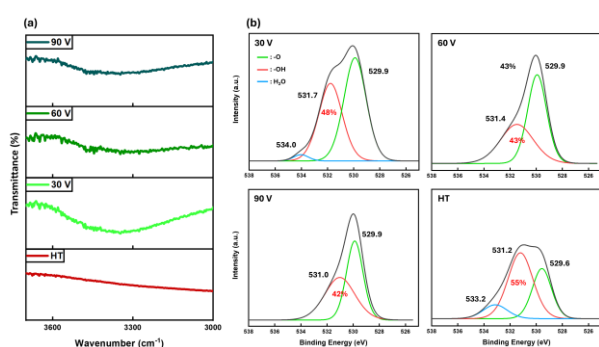


Fig. 3. Spectroscopic analysis: (a) FT-IR spectra in the OH-stretching region and (b) XPS O 1s spectra of HT and anodized Zr alloy specimens.

Contact-angle measurements clearly distinguished the wetting behavior of the different surfaces (Fig. 4). Bare Zr alloy exhibited an initial water contact angle of approximately 79° , corresponding to only moderate hydrophilicity. Formation of thermally oxidized ZrO_2 decreased the angle to approximately 34° , demonstrating that oxide formation and hydroxylation alone substantially increase water affinity. A much stronger transition occurred after anodization: all nanoporous ZrO_2 surfaces exhibited contact angles approximately below 10° . The 30 V specimen showed the lowest value ($\sim 7.5^\circ$).

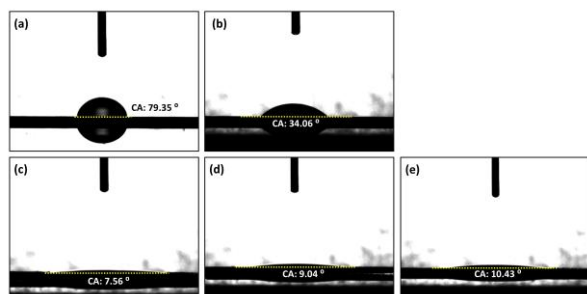


Fig. 4. Static water contact angles of (a) bare Zr alloy, (b) HT, and anodized specimens prepared at (c) 30 V, (d) 60 V, and (e) 90 V.

The marked difference between the HT specimen and the anodized specimens is particularly informative. Both contain ZrO_2 and exhibit hydroxyl-related surface species, but only the anodized surfaces possess the pronounced nanoporous architecture. Therefore, chemical modification alone cannot fully account for the superhydrophilic state. Instead, the contact-angle results support a synergistic mechanism in which surface hydroxylation establishes intrinsic hydrophilicity and the nanostructured surface further amplifies water spreading through roughness and capillary-driven infiltration. Hydroxyl groups lower the solid-liquid interfacial energy and promote hydrogen bonding with water. Surface roughness can further amplify this intrinsic hydrophilicity under a fully wetted Wenzel state [8]. In parallel, the nanoscale pores generate a capillary pressure that actively draws water into the oxide structure. Assuming ideal cylindrical pores and using the HT ZrO_2 contact angle as an approximate intrinsic pore-wall angle, theoretical capillary pressures of approximately 25.14, 8.96, and 6.57 MPa were estimated for the 30, 60, and 90 V specimens, respectively. The 30 V value is therefore approximately 2.8 and 3.8 times larger than those estimated for 60 and 90 V. This comparison provides a quantitative explanation for why the 30 V specimen exhibited the lowest contact angle despite having lower macroscopic roughness than the 90 V specimen. The smallest pores generate the strongest capillary driving force, while the same specimen also exhibited the most pronounced hydroxylation. Conversely, increasing voltage increases roughness but simultaneously enlarges the nanopores and reduces the estimated capillary pressure. The observed superhydrophilicity is therefore not controlled by a single surface parameter; rather, it emerges from the combined chemical and geometrical characteristics of the anodized oxide. Among the investigated conditions, 30 V provides the most favorable balance of fine nanopores, high hydroxylation, and sufficient roughness.

From a nuclear-interface perspective, the resulting superhydrophilic state may provide several potentially beneficial effects. Strong water affinity and capillary infiltration are expected to stabilize liquid coverage at the cladding-coolant interface and promote rapid rewetting behavior after bubble departure. A hydrated interface may also reduce direct interaction between the oxide surface and transported corrosion products. Under subcooled nucleate boiling conditions, these effects could reduce localized precipitation associated with bubble growth and departure and thereby suppress the initial stages of boiling-assisted CRUD deposition.

These implications should, however, be distinguished from experimentally demonstrated reactor performance. The present measurements were conducted as surface-engineering characterization and do not directly quantify boiling heat transfer, CRUD adhesion, corrosion resistance, hydrogen uptake, or long-term durability in high-temperature primary water. Therefore, systematic validation under realistic thermal-hydraulic and coolant-

chemistry conditions is required. Pool-boiling experiments and loop-based CRUD deposition tests are planned to evaluate whether the wetting characteristics identified here translate into improved rewetting behavior and reduced deposition under reactor-relevant conditions.

4. Conclusion

Nanoporous ZrO₂ layers were successfully formed on tested Zr alloy by short-time anodization at 30-90 V followed by heat treatment. Increasing voltage increased both pore diameter (9.60-36.71 nm) and oxide thickness (6.25-10.27 μm), while all treated layers crystallized as monoclinic ZrO₂. Anodization also increased surface roughness and promoted surface hydroxylation. Consequently, the water contact angle decreased from approximately 79° for bare specimen to approximately below 10° for all anodized specimens. The 30 V condition showed the lowest contact angle (~7.5°), despite not having the highest roughness, demonstrating the critical contribution of fine nanopores and capillary-driven infiltration. The combined effects of hydroxylation, roughness amplification, and nanoporous capillarity provide the mechanistic basis for superhydrophilicity and support further evaluation of anodized Zr-based cladding for CRUD-mitigation and boiling-interface applications.

6. Acknowledgements

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