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Microstructural Evolution and Corrosion Behavior of W-Coated Zr-4 Alloy Deposited by DC Sputtering at Different Voltages

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ABSTRACT

Zirconium (Zr) alloys are widely used as nuclear fuel cladding materials due to their low neutron absorption, high mechanical properties, and good corrosion resistance in high temperature aqueous environments. However, their performance might degrade under severe accident conditions. Tungsten (W), a refractory metal with high thermal stability and irradiation resistance, is a promising candidate material for protective coating. Nevertheless, the tungsten oxide film is not as stable in aqueous environments as the passive ZrO₂ film. The effect of DC sputtering voltage on the microstructure, mechanical properties and corrosion behavior of W-coated Zr-4 substrates for nuclear applications was studied. To investigate the effect of deposition energy on coating characteristics, W coatings were deposited at 4, 5 and 6 kV. XRF and SEM-EDS analysis confirmed successful W deposition, with the sample at 5 kV having the most uniform coating coverage. SEM observations and cross-sectional analyses show that the coating microstructure and thickness are strongly dependent on the sputtering voltage. The coating thickness increased from ~4.8 to 7.8 µm at 4 and 5 kV and decreased to 5.2 µm at 6 kV. The coating density increased with increasing sputtering voltage, and at 6 kV the higher ion energy caused partial resputtering and, hence, a reduction in coating thickness. XRD results revealed the formation of nanocrystalline BCC (body-centered cubic) tungsten with crystallite sizes decreasing from 8.98 to 5.56 nm with increasing voltage. The hardness of Zr-4 substrate was only 187.63 ± 5.06 HV, while the coated sample reached 480-620 HV due to grain refinement and densification. The potentiodynamic polarization tests showed that the corrosion potential (E_{corr}) shifted from -3.05×10^{-1} V for the uncoated substrate to -3.12×10^{-1} V for the 5 kV-coated sample, while the corrosion current density (I_{corr}) increased from 1.44×10^{-7} A/cm² to 4.86×10^{-7} A/cm². The results show lower corrosion resistance after coating deposition under the conditions explored. Nevertheless, the 5 kV coating showed the best compromise between mechanical enhancement and corrosion performance due to its compact microstructure and high hardness, suggesting the trade-off between the hardness enhancement and corrosion behavior. The increase in the corrosion current density is likely due to coating defects and the lower stability of tungsten oxide films compared with the protective ZrO₂ layer on uncoated Zr-4.

Keywords: DC sputtering, tungsten coating, Zircaloy-4, corrosion, nuclear cladding.



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INTRODUCTION

Zirconium (Zr)-based alloys are widely used as fuel cladding materials in light water reactors (LWRs), especially in pressurized water reactors (PWRs), owing to their low thermal neutron absorption cross-section, good mechanical performance, and excellent corrosion resistance in high-temperature water environments. These properties allow Zr-based alloys to conserve neutron economy and provide sufficient structural integrity during the normal operation of reactors. Zr-based alloys are the current industrial standard for the cladding of nuclear fuels applications. Nevertheless, the Fukushima Daiichi nuclear accident in 2011 demonstrated the inherent limitations of zirconium alloys in severe accident situations, particularly in loss-of-coolant accident (LOCA) situations. Fast Zr oxidation can be initiated in a high temperature steam environment, causing considerable hydrogen generation, exothermic heat release, and progressive degradation of cladding integrity [1]. Such phenomena significantly influence the safety margins of the reactor and drive intensive investigations in the development of Accident Tolerant Fuel (ATF) systems with improved oxidation resistance, thermal stability, and overall accident tolerance during off normal and severe operating conditions [2].

Protective surface coatings have been suggested as a promising approach for ATF development in zirconium-based cladding systems. Coating technologies maintain the good neutron economy of zirconium and improve the surface performance without significantly affecting the bulk properties compared to the full replacement of conventional cladding materials [2], [3]. Various coating materials, such as chromium-based compounds and refractory metals, have been studied to enhance oxidation resistance and mechanical stability under severe operating conditions. Among the refractory candidates, tungsten (W) has received special attention because of its ultra-high melting temperature, low sputtering yield, and excellent resistance to extreme thermal and particle-loading environments, which have led to its wide application as a plasma-facing material in fusion systems such as ITER [4]. Therefore, the deposition of W coatings on Zr substrates is a strategic approach to combine the superior neutronic properties of Zr with the excellent environmental stability of W, which

has great potential to improve the safety and reliability of next-generation ATF cladding systems [3].

DC sputtering is a widely used thin-film deposition technique due to its strong adhesion, precise parameter control, and uniform film formation [5]. The applied sputtering voltage is critical in controlling the ion bombardment energy, deposition kinetics, adatom mobility, film densification, grain refinement, and defect evolution. Thus, it is of great importance to the microstructure and functional performance of the resulting coating [6]. Too low a deposition energy generally leads to porous films with incomplete surface coverage and too high ion energy may lead to re-sputtering and accumulation of internal stress, which deteriorates the stability of the coating [7]. Previous research on coated cladding systems has mainly focused on the high temperature oxidation resistance and thermal stability, but the relationship between the sputtering voltage, the evolution of microstructure, the enhancement of mechanical properties, and corrosion behavior of tungsten coated Zr-4 alloys is still not well understood. In particular, the trade-off between mechanical strengthening and corrosion degradation becomes a critical issue in the optimization of coating performance for nuclear applications [8].

In this work, the effect of DC sputtering voltage on the mechanical properties and corrosion behavior of W coated Zr-4 substrates for nuclear applications was evaluated. To examine the correlation between deposition energy, coating microstructure, hardness enhancement, and electrochemical performance, W coatings were sputtered at different sputtering voltages. The microstructural evolution and its effect on the performance of the coating were characterized by XRF, SEM-EDS, XRD, Vickers hardness and potentiodynamic polarization analysis. The study also aimed to determine the optimum sputtering condition to produce dense and homogeneous W coatings with improved mechanical strength and enhanced surface stability for Zr-based nuclear cladding materials.

METHODOLOGY

a. W coating deposition

Zirconium (Zr) alloy substrates were sputtered using DC sputtering technique (Figure 1). The substrates had a chemical

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composition of 0.22 ± 0.06 wt.% Fe, 0.10 ± 0.05 wt.% Cr, and 1.35 ± 0.15 wt.% Sn, the balance being Zr. Tungsten (W) was used as the sputtering target for coating deposition. The substrates (1.1 cm diameter, 3 mm thickness) were mechanically ground before deposition using silicon carbide (SiC) abrasive papers (grit size P500–P2400) followed by polishing for a smooth surface finish. The samples were then cleaned in distilled water and ethanol to remove surface contamination and to improve adhesion of the coating.

Before deposition, the chamber was evacuated to an initial pressure of about 2.7×10^{-2} mbar by a rotary pump and then to a higher vacuum of about 2.7×10^{-3} mbar by a diffusion pump. The evacuation process was kept for about 1.5 h to ensure a stable vacuum environment. The deposition was performed at a working pressure of 2.67×10^{-3} mbar using ultra-high purity (UHP) argon (Ar) as sputtering gas with a flow rate of 173 mL/min. The sputtering voltage varied at 4, 5 and 6 kV with constant current of 10 mA to study the effect of sputtering voltage on the coating properties. Each deposition was performed for 4 h to get enough film thickness and uniform coating formation. The samples were cooled for 30 min in the chamber after deposition to minimize thermal stress and to maintain the integrity of the coating.

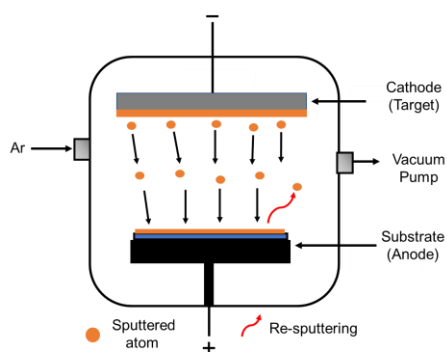


Figure 1. Schematic illustration of DC sputtering

b. Sample characterization

The surface morphology and cross section feature of the W coatings were examined by a JEOL scanning electron microscope equipped with energy-dispersive spectroscopy (SEM-EDS). The phase composition and crystallographic structure were studied by X-ray diffraction (XRD) with

Cu K α radiation. Equation 1 The crystallite size was calculated using the Scherrer equation [9].

The microhardness was measured by the Vickers indentation method with an error of 0.44% which is far below the 2% tolerance limit in ASTM E92-17 and ASTM E384-14 [10]. The microhardness (HV) was calculated by the formula in the following Equation (2). Corrosion Behavior of W Coated Zr-4 Alloy The corrosion behavior of the W coated Zr-4 alloy was evaluated by potentiodynamic polarization using a GAMRY Reference 600 system in an electrolyte of 4000 ppm H₃BO₃ and 2.5 ppm LiOH at room temperature. This method enables us to determine the corrosion potential (E_{corr}) and the corrosion current density (I_{corr}). All the experiments were carried out at the National Research and Innovation Agency (BRIN) facilities, Indonesia.

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

$$HV = 1.854 \times 10^3 \times \frac{F}{d^2} \quad (2)$$

In the Equation (1), D is the mean size of the crystallites, k is the shape factor (~ 0.9), λ is the X-ray wavelength (m), β is the full width at half maximum (FWHM) of the diffraction peak (in radians), and θ is the Bragg diffraction angle (rad). The Vickers hardness (HV) was obtained from Equation (2) where HV (kgf/mm²) is the hardness value, F (kgf) is the applied load, and d (mm) is the average diagonal length of the indentation measured from the cross-sectional surface.

RESULTS AND DISCUSSION

a. Elemental composition of Zr-4 and W-coated Zr-4

The XRF results of the Zr-4 substrate and W coatings deposited at different sputtering voltages are shown in Figure 2 and Table 1. The Zr-4 substrate without coating was mainly composed of Zr with an average content of 98.33 ± 0.17 wt.%, and trace alloying elements such as Sn (1.35 ± 0.15 wt.%), Fe (0.22 ± 0.06 wt.%), and Cr (0.10 ± 0.05 wt.%). The XRF spectra confirmed the successful formation of W coatings after W sputter deposition at the applied voltages of 4 to 6 kV as indicated by the significant increase of W content in all coated samples. The W concentration was 81.33 ± 0.21 wt.% for the 4

kV sample, increased further to 87.09 ± 0.35 wt.% at 5 kV and then decreased slightly to 84.21 ± 0.38 wt.% at 6 kV. On the other hand, the Zr concentration detected was substantially lower than the uncoated substrate and was 17.04 ± 0.19 wt.% (4 kV), 11.45 ± 0.32 wt.% (5 kV) and 14.20 ± 0.35

wt.% (6 kV), respectively. The significant attenuation of the Zr signal indicates that the deposited W layer effectively covered the substrate surface, suppressing the fluorescent contribution from the underlying Zr substrate [11].

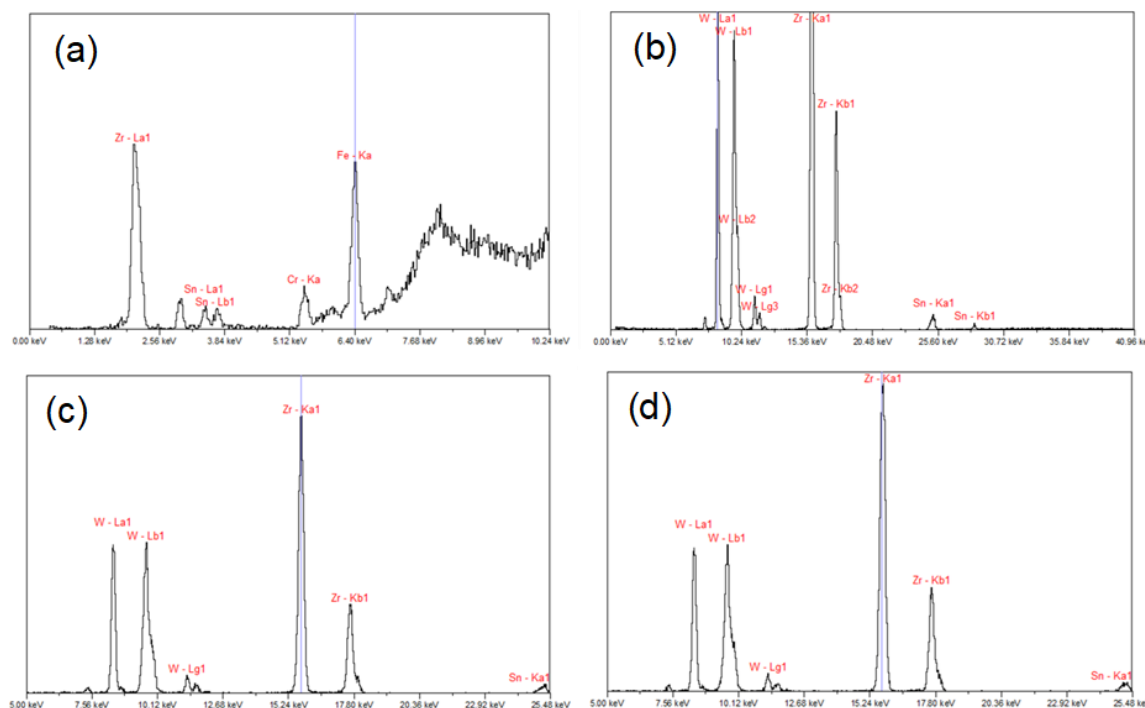


Figure 2. XRF spectra of W coatings on Zr substrates with different sputtering voltages: (a) bare Zr substrate, (b) 4 kV, (c) 5 kV, and (d) 6 kV.

Table 1. XRF elemental composition of the Zr substrate and W coatings deposited at different voltages.

Elemental composition	Elemental concentration (wt.%)			
	Zr substrate	W 4 kV	W 5 kV	W 6 kV
Fe	0.22 ± 0.06			
Zr	98.33 ± 0.17	17.04 ± 0.19	11.45 ± 0.32	14.20 ± 0.35
Sn	1.35 ± 0.15	0.78 ± 0.06	0.60 ± 0.10	0.66 ± 0.11
W	-	81.33 ± 0.21	87.09 ± 0.35	84.21 ± 0.38

The maximum concentration obtained at 5 kV shows that this deposition voltage could offer the best sputtering energy to enhance the deposition rate and the transfer efficiency of the W atoms on the substrate surface. This is confirmed by the highest W content (87.09 ± 0.35 wt.%) and lowest residual Zr signal in all coated samples, confirming a thicker and more homogeneous coating layer was formed [12]. Mechanistically, the increase of the sputtering

voltage will enhance the ion bombardment on the W target, which is beneficial to the ejection of more W atoms and the increase of their kinetic energy in the process of transportation and condensation on the substrate surface [13]. These conditions are generally linked with a higher densification and microstructural uniformity of the coating [14].

For the 6 kV-treated sample, slight reduction of W concentration was observed but with renewed increase of Zr fraction. This

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behavior suggests that too high sputtering energy may result in harmful high energy plasma effects, particularly re-sputtering of previously deposited W atoms from the surface of the growing film. Moreover, the increased bombardment at higher voltages can facilitate interfacial diffusion between the coating and the substrate, resulting in greater exposure of the underlying Zr signal in the XRF analysis [13]. A similar voltage dependent behavior has been widely reported for sputter deposited refractory metal coatings, where excessive ion energy promotes interdiffusion phenomena within the coating/substrate system.

These results show that deposition voltage is an important parameter to control the competition between deposition efficiency and plasma re-sputtering effects [15], [16]. Therefore, the 5 kV condition appears to have the best processing window for high W incorporation, effective substrate coverage and good coating homogeneity. These features are important to enhance the structural stability and protective performance of W-coated Zr systems for the advanced nuclear material applications [17].

b. Morphological and elemental characteristics of Zr-4 and W-coated Zr-4

W coatings were successfully deposited on Zr substrates by DC sputtering under different voltages. From the SEM images (Figure 3), the surface morphology is drastically changed with increasing sputtering voltage. At 4 kV the coating has a relatively non-uniform surface with localized irregularities whilst at higher voltages (5 and 6 kV) the surface becomes progressively denser and more homogeneous. This morphological evolution suggests an improvement in the quality of the coating with the increase of the deposition energy. This can be explained by the increased adatom mobility at higher ion energies which favors the surface diffusion and the formation of compact and continuous films [18]. This mechanism is in line with the established thin film growth models, that sufficient energy input leads to better coating uniformity and structural integrity.

EDS analysis shows a strong dependence of the elemental distribution on the sputtering voltage. The Zr and O signals at 4 kV indicate the presence of uncoated areas of the surface and oxidation of exposed areas

of the substrate. On the contrary, the coatings deposited at 5 and 6 kV show a strong W signal and no detectable Zr, revealing a good coverage of the substrate. This transition suggests that increased ion energy leads to improved deposition efficiency and film continuity [18]. The lack of the substrate signal at higher voltages is attributed to the higher sputtering yield and the improved film densification, which effectively screens the substrate [19]. These results are in accordance with the classical sputtering theory that sufficient bombardment results in uniform deposition and strong adhesion of the coating.

SEM images of cross-sections (Figure 4) reveal that the thickness of the coating strongly depends on the sputtering voltage. The thickness is increased from approximately 4.8 μm at 4 kV to 7.8 μm at 5 kV and then decreased to 5.2 μm at 6 kV. Maximum thickness at 5 kV indicates the optimum deposition condition. This trend suggests a trade-off between sputtering yield and deposition rate at intermediate voltage for film growth maximization [19]. Nevertheless, at higher voltage (6 kV) thickness decrease shows the beginning of re-sputtering effects, where previously deposited atoms are removed by high energy ions. This phenomenon is controlled by excess ion energy which increases surface bombardment and decreases net deposition efficiency as extensively reported in sputtering systems [13].

The compositional differences at the interface are reflected in the cross-sectional EDS results of Figure 5. The coatings are mainly W (≈ 100 wt%) at 4 and 6 kV, indicating the formation of relatively pure tungsten layers. However, at 5 kV, the composition of the interfacial region is a mixture of W (64.34 wt%), Zr (31.23 wt%), and O (4.4 wt%). This suggests the formation of an interdiffusion layer at intermediate voltages. Such a layer may be the consequence of the increased atomic mobility that favors the diffusion-controlled intermixing at the coating/substrate interface [20], [21]. This interfacial interaction is driven by ion energy and can cause the formation of complex phases or oxide compounds. Similar interdiffusion behavior has been reported in earlier studies, that moderate ion energies enhance the interfacial bonding and preserve the structural stability [21].

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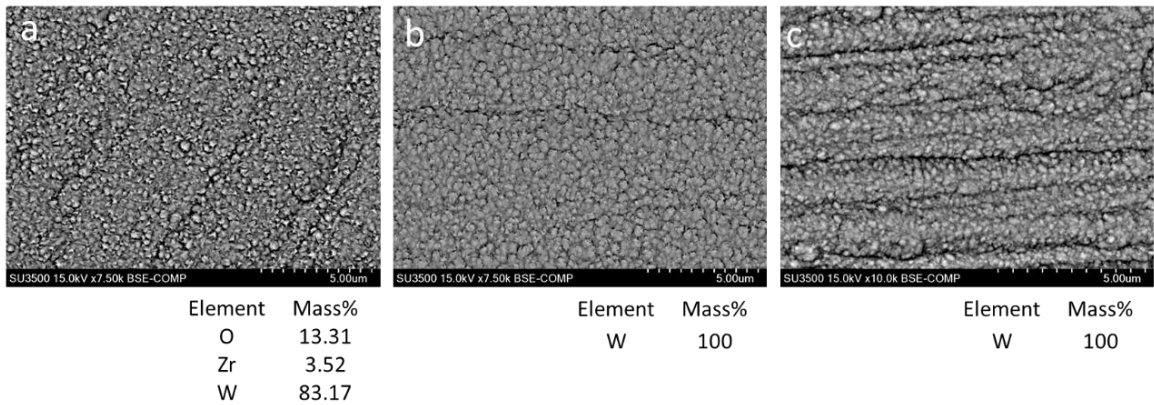


Figure 3. SEM images of surface morphology of W coatings deposited on Zr-4 substrate under different sputtering voltages: (a) 4 kV, (b) 5 kV, and (c) 6 kV.

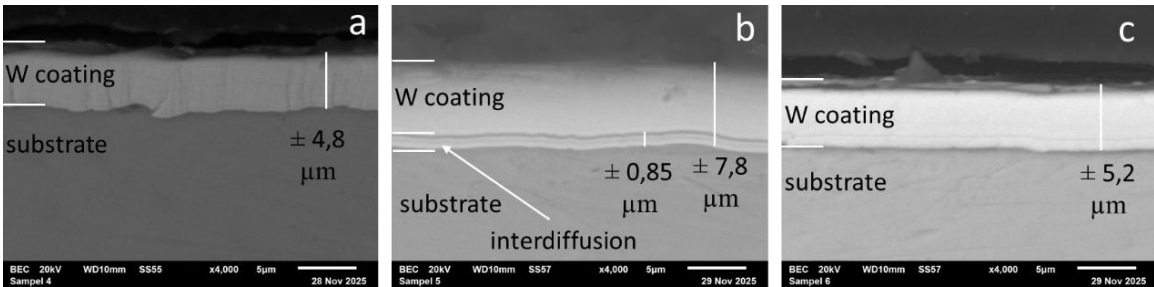


Figure 4. SEM cross-sectional images of W coatings made at different sputtering voltages: (a) 4 kV, (b) 5 kV, and (c) 6 kV.

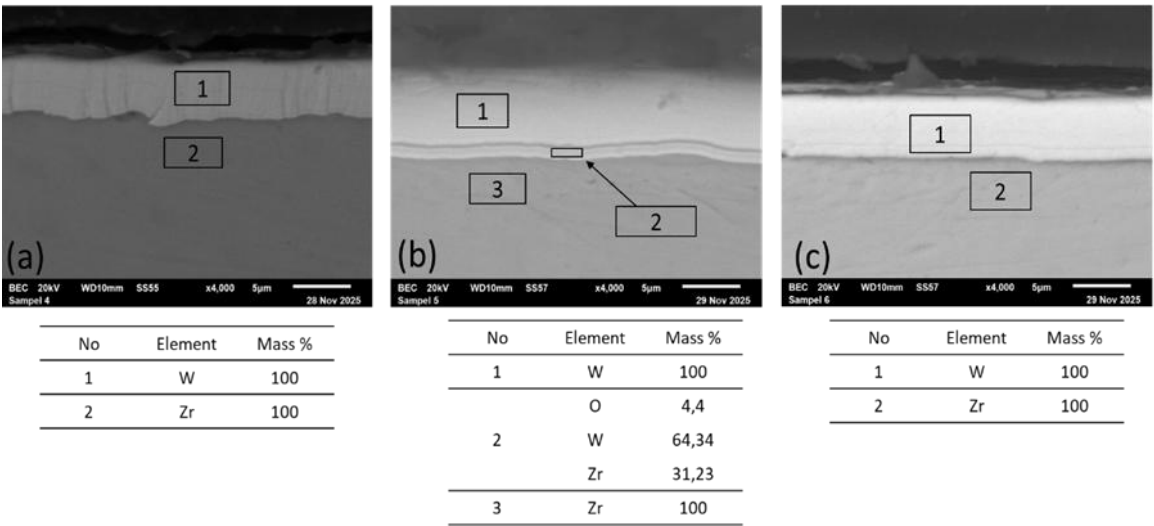


Figure 5. Typical EDS spot spectra acquired on the cross-sections of W coatings deposited at different sputtering voltages: (a) 4 kV, (b) 5 kV, and (c) 6 kV.

c. Crystalline phase profile of Zr-4 and W-coated Zr-4

The XRD pattern (Figure 6 and Table 2) shows several sharp diffraction peaks typical of Zr substrate indicating well crystallized

structure with relatively large crystallite size. The crystallite size is calculated to be ~21.54 nm based on Scherrer equation. This indicates good crystallinity of the substrate with minimum lattice distortion due to its stable

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bulk structure. Such behavior is consistent with typical metallic substrates with low defect density [22].

The crystallite size estimated from the XRD results by the Scherrer equation is summarized in Table 2. The W film deposited at 4 kV shows one dominant W (110) peak at $2\theta \approx 40^\circ$ with no detectable (200) and (211) reflections. This reflects on a strong preferred orientation and limited crystal growth at the low deposition voltage. The crystallite size is about 8.98 nm, indicating the formation of nano crystalline structure. This suggests that the energy of the deposition is not sufficient to enhance the adatom mobility to favor the atomic diffusion and the formation of a fully developed BCC structure, typical of low energy thin film growth conditions [13].

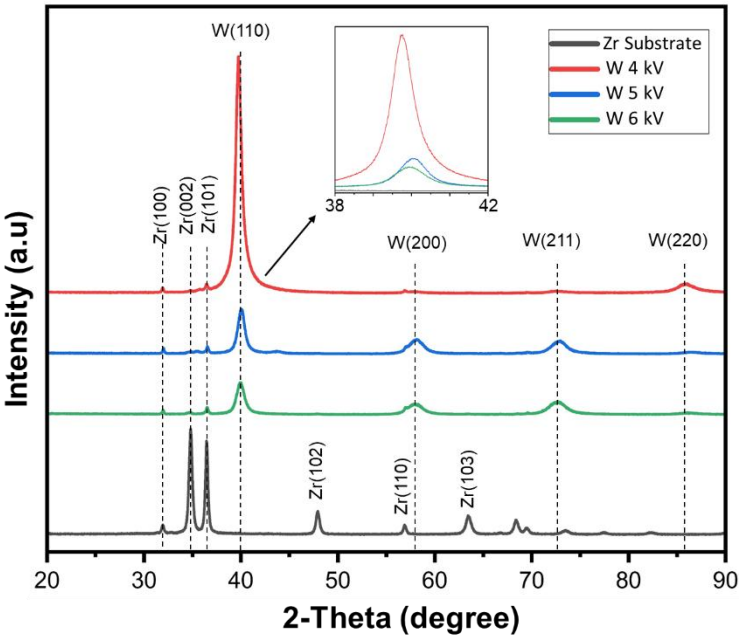


Figure 6. X-ray diffraction patterns for Zr substrate and W coatings deposited at different sputtering voltages (4, 5, and 6 kV).

Table 2. Crystallite size (D) of the Zr substrate and W coatings deposited at different sputtering voltages.

Sample	hkl	2 Theta (°)	FWHM (°)	D Scherrer (nm)	Standard deviation (nm)
Zr Substrate	100	31.93904	0.32640	21.54	3.32
	002	34.81648	0.44719		
	101	36.46754	0.35848		
	102	47.93115	0.46017		
W 4 kV	110	39.77837	0.94039	8.98	— (1 peak)
	110	40.04406	0.95001		
W 5 kV	200	58.08096	1.82686	6.34	2.22
	211	72.82756	1.91975		
	110	39.96319	1.07417		
W 6 kV	200	57.94537	1.90091	5.74	1.84
	211	72.66082	2.15113		

hkl = Miller indices, FWHM = full width at half maximum

When the deposition voltage was increased to 5 kV and 6 kV, additional peaks appeared for the W (200) and W (211) planes, indicating an increased formation of the BCC tungsten phase. However, these peaks are still significantly broadened ($\text{FWHM} > 1^\circ$) suggesting smaller crystallite size. The crystallite size decreases from about 6.14 nm (5 kV) to 5.56 nm (6 kV) showing progressive grain refinement. This means the increase of deposition voltage improves the density of nucleation and bombardment of energetic particles, which inhibits the grain growth. Similar trends have been reported extensively in sputtered metallic thin films [15].

The overall results show the transition from a partly developed strong texture structure at 4 kV to a more complete nanocrystalline BCC W structure at higher deposition voltages. This structural transformation is controlled by increased adatom mobility and nucleation dynamics. With increasing deposition energy, phase formation is favored, but at the same time, crystallite growth is restricted [23].

d. Vickers hardness

The hardness of the W-coated samples was significantly improved from 187.63 ± 5.6 HV of the Zr substrate to 479.56 ± 57.35 HV (4 kV), 592.10 ± 77.77 HV (5 kV), and 620.49 ± 112.64 HV (6 kV). This increase is correlated with a clear evolution of the surface morphology, where SEM observations show a transition from a non-uniform and partially covered surface at 4 kV to a dense and homogeneous coating at higher voltages. This means that the quality and the continuity of the coating are greatly improved by increasing the sputtering voltage. This behavior can be explained by the increase of the adatom mobility with the ion energy which improves the surface diffusion and allows the formation of a more compact and continuous film [24]. This densification is necessary for the improvement of mechanical properties, because a dense structure decreases porosity and increases the load-bearing capacity, which agrees with the previous reports on sputtered metallic thin films [25].

XRD analysis indicates that the crystallite size decreases from ~9 nm at 4 kV to ~6.14 nm at 5 kV and ~5.56 nm at 6 kV, estimated using Scherrer equation. This reduction in crystallite size is in accordance

with the progressive hardness increase observed in the coated samples. The decrease in crystallite size shows the better grain refinement with increase in sputtering voltage. This strengthening behavior can be attributed to the Hall–Petch mechanism, that smaller grain size increases the resistance to dislocation motion and increases hardness [13]. The refinement of crystallite size is attributed to the enhanced nucleation density and the increased ion energy during deposition that restricts the grain growth and facilitates the formation of nanocrystalline structure. This trend is in good agreement with thin film growth models and previous studies on sputtered coatings in general [26].

Table 3 Average Vickers hardness (HV) of uncoated Zr substrate and W coatings deposited at different sputtering voltages.

Sample	HV	Standard deviation
Zr substrate	187.63	5.06
W 4 kV	479.56	57.35
W 5 kV	592.10	77.77
W 6 kV	620.49	112.64

The hardness also keeps increasing with 6 kV, but the improvement rate is not as obvious as that of 5 kV. This fact is also confirmed by the cross-section SEM images where the coating thickness increases to a maximum (~7.8 μm) at 5 kV and decreases (~5.2 μm) at 6 kV. This implies that the deposition efficiency decreases at higher sputtering voltage, although the grain refinement continues. The decrease in thickness could be attributed to the onset of re-sputtering effects where the excess energy of the ions results in the removal of previously deposited atoms, thereby limiting the net film growth [27]. Hence, although the grain refinement still has a strengthening effect, the thinner coating thickness and less efficient deposition restrict the further increase in hardness to some extent. This suggests that for optimum mechanical performance an ideal compromise between the deposition energy, coating thickness and microstructural refinement is necessary, in line with well-known behavior in high energy sputtering processes [15].

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e. Potentiodynamic polarization

The potentiodynamic polarization (PDP) results (Figure 7 and Table 4) clearly show the significant changes in the electrochemical behavior of Zr after deposition of W. The Zr substrate without coating had an E_{corr} of -3.05×10^{-1} V and a corrosion I_{corr} of 1.440×10^{-7} A/cm². The E_{corr} values moved to less negative potentials after depositing W coatings by DC sputtering, i.e., -2.34×10^{-1} V, -3.12×10^{-1} V, and -2.46×10^{-1} V for the coatings deposited at 4, 5, and 6 kV, respectively. A change in the surface electrochemical response and the development of passive properties on the coated samples are the general tendencies observed. However, the corrosion current densities of the coated specimens were also higher than the bare substrate with values of 6.55×10^{-7} A/cm², 4.86×10^{-7} A/cm² and 3.51×10^{-7} A/cm² for the deposition voltages. The increase in I_{corr} suggests that the deposited W layers were not sufficient to protect against corrosion in the aqueous environment studied [28].

The microstructure was well correlated with the deterioration in corrosion performance of the sputtered coatings. Sputter depositions often create defects such as micropores, pinholes, and microcracks due to the accumulation of residual stress and non-uniform film growth [29]. These structural defects provide preferential ingress pathways for electrolyte and hence provide direct access of the corrosive environment to the underlying zirconium substrate [30]. When the electrolyte reaches the interface between the coating and the substrate, the local electrochemical reactions may become more intense, causing an increase in the corrosion current density. The electrochemical potential difference between W and Zr can also be responsible for localized galvanic effects that accelerate the degradation of the interface [31].

The results obtained also show the basic difference between Zr and W in their corrosion behavior in water-based media. Zr has very good corrosion resistance due to the spontaneous formation of a compact and chemically stable ZrO₂ passive film [32]. The oxide layer shows good adhesion and low oxygen diffusivity, which effectively inhibits further electrochemical reactions on the surface of the substrate. In contrast, the tungsten oxide films prepared in water are generally less stable and can be partially

dissolved in aggressive ionic environment [33], [34]. However, W shows better thermal stability and oxidation resistance at high temperature, but its passive behavior in aqueous media is relatively less protective than Zr. Thus, in the presence of coating defects, the protective ability of the W layer is significantly reduced.

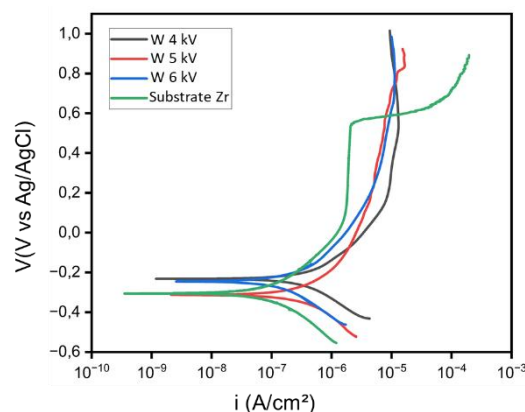


Figure 7. Potentiodynamic polarization curves of Zr-4 alloy and W coatings deposited at different voltages in 4000 ppm H₃BO₃+2.5 ppm LiOH solution at room temperature.

Table 4. Values of corrosion rate for uncoated Zr substrate and W coatings deposited at different sputtering voltages.

Sample	E_{corr} (V)	I_{corr} (A/cm ²)
Zr substrate	-3.05×10^{-1}	1.440×10^{-7}
W 4 kV	-2.34×10^{-1}	6.55×10^{-7}
W 5 kV	-3.12×10^{-1}	4.86×10^{-7}
W 6 kV	-2.46×10^{-1}	3.51×10^{-7}

The sample deposited at 6 kV has the lowest I_{corr} value among the coated specimens, according to the deposition parameters. The behavior is likely related to the higher energy of sputtered particles that increases the surface mobility of deposited atoms and thus leads to a relatively denser structure of the coating. Then the defect density decrease will limit the electrolyte infiltration and suppress localized corrosion activity [17]. However, despite the improvements, the corrosion resistance of the coated samples was still inferior to the original Zr substrate, indicating that the coating was not sufficiently dense to compensate for the

better passivation behavior naturally offered by Zr [35].

Overall, the present study indicates that the optimization of the sputtering parameters is still required to improve the corrosion performance of W-coated on Zr substrates. Parameters such as deposition pressure, coating thickness, substrate temperature, and deposition time are expected to strongly affect the coating's compactness and defect formation [3]. In addition, multilayer structures or interfacial buffer layers might be a more promising approach for reducing coating defects and improving interfacial stability [36]. Such improvements are important to make W-coated Zr cladding materials applicable in Accident Tolerant Fuel (ATF) systems.

CONCLUSIONS

The DC sputtering method was successfully used to deposit tungsten (W) coatings on Zr-4 substrates at deposition voltages of 4–6 kV, and it was found that the applied voltage had a significant effect on the coating characteristics, microstructure, mechanical properties, and corrosion behavior. XRF and SEM-EDS analysis confirmed the presence of W coatings, and the 5 kV condition generated the highest W content and the most effective substrate coverage. SEM observation of surface and cross-section shows that the coating densification and homogeneity improve with the increase of sputtering voltage. However, the excessive voltage of 6 kV leads to re-sputtering and reduction of the coating thickness. XRD results demonstrated the formation of nanocrystalline BCC tungsten structures, with crystallite size decreasing from 8.98 nm at 4 kV to 5.56 nm at 6 kV due to enhanced nucleation and grain refinement at higher ion energies. The Vickers hardness increased significantly after coating deposition and reached a maximum of 620 HV at 6 kV. This may be attributed to coating densification and crystallite refinement, which are likely associated with the Hall–Petch strengthening mechanism.

However, the potentiodynamic polarization results showed that the W-coated samples had higher corrosion current densities than the uncoated Zr substrate, indicating the corrosion resistance of the samples was poorer in the investigated aqueous environment. This degradation was associated with coating defects including

pores and microcracks, which allowed electrolyte ingress and local galvanic interactions between W and Zr. Nevertheless, the coating deposited at 6 kV showed the best corrosion performance compared to the coated samples, owing to its relatively denser microstructure. Overall, this study demonstrates that sputtering voltage plays a significant role in controlling coating growth, microstructural evolution, hardness, and corrosion behavior of W coatings deposited on Zr-4 substrates. While increasing the sputtering voltage, particularly to 5 kV, improved coating quality and mechanical performance, all coated samples exhibited lower corrosion resistance than the uncoated Zr-4 substrate under the investigated aqueous environment, indicating a trade-off between mechanical strengthening and corrosion performance. These findings provide experimental insight into the effect of sputtering voltage on W-coated Zr-4 systems and may serve as a basis for further optimization of coating microstructure and interfacial integrity. Additional studies under high-temperature and reactor-relevant conditions are required to evaluate their suitability for nuclear cladding applications.

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REFERENCES

- [1] S. J. Zinkle, K. A. Terrani, J. C. Gehin, L. J. Ott, and L. L. Snead, "Accident tolerant fuels for LWRs: A perspective," *Journal of Nuclear Materials*, vol. 448, no. 1–3, pp. 374–379, May 2014, doi: 10.1016/J.JNUCMAT.2013.12.005.
- [2] K. A. Terrani, "Accident tolerant fuel cladding development: Promise, status, and challenges," *Journal of Nuclear Materials*, vol. 501, pp. 13–30, Apr. 2018, doi: 10.1016/J.JNUCMAT.2017.12.043.
- [3] E. Kashkarov, B. Aforu, D. Sidelev, M. Krinitcyn, V. Gouws, and A. Lider, "Recent Advances in Protective Coatings for Accident Tolerant Zr-Based Fuel Claddings," *Coatings 2021, Vol. 11, Page 557*, vol. 11, no. 5, p. 557, May 2021, doi: 10.3390/COATINGS11050557.

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- [4] A. Cacheris *et al.*, "The effectiveness of D2 pellet and gas injection in reducing intra-ELM tungsten erosion and heat flux in the DIII-D small angle slot divertor," *Nuclear Materials and Energy*, Jun. 2026, doi: 10.1016/j.nme.2026.102094.
- [5] S. Gul *et al.*, "Adhesion mechanisms, evaluation techniques and modeling strategies in PVD coatings: From fundamentals to data-driven design," *Journal of Materials Research and Technology*, vol. 41, no. November 2025, pp. 3618–3649, Mar. 2026, doi: 10.1016/J.JMRT.2026.01.234.
- [6] A. Boukhoutie, S. Boumendjel, and N. E. H. Sobhi, "Effect of current density on the microstructure and morphology of the electrodeposited nickel coatings," *Turk. J. Chem.*, vol. 45, no. 5, p. 1599, 2021, doi: 10.3906/KIM-2102-46.
- [7] P. Borowski and J. Myśliwiec, "Recent Advances in Magnetron Sputtering: From Fundamentals to Industrial Applications," *Coatings 2025*, Vol. 15, Page 922, vol. 15, no. 8, p. 922, Aug. 2025, doi: 10.3390/COATINGS15080922.
- [8] S. Markelj *et al.*, "Deuterium retention in tungsten simultaneously damaged by high energy W ions and loaded by D atoms," *Nuclear Materials and Energy*, vol. 12, pp. 169–174, Aug. 2017, doi: 10.1016/J.NME.2016.11.010.
- [9] K. Koca and Y. E. Benkli, "Microstructural and elemental characterization of pumice–bauxite–clay ceramics: effects of sintering temperature and scherrer-based analysis," *Journal of the Australian Ceramic Society 2025 62:1*, vol. 62, no. 1, pp. 135–151, Jul. 2025, doi: 10.1007/S41779-025-01242-8.
- [10] K. E. Metzger, T. W. Knight, E. Roberts, and X. Huang, "Determination of mechanical behavior of U3Si2 nuclear fuel by microindentation method," *Progress in Nuclear Energy*, vol. 99, pp. 147–154, Aug. 2017, doi: 10.1016/J.PNUCENE.2017.05.007.
- [11] L. Yongli, Z. Jian, H. Cheng, and M. Hailiang, "A Thickness Determination Method Based on Energy-Dispersive X-Ray Fluorescence and Application in Zirconium Alloy Coatings," *Coatings 2026*, Vol. 16, Page 341, vol. 16, no. 3, p. 341, Mar. 2026, doi: 10.3390/COATINGS16030341.
- [12] E. Vassallo *et al.*, "Effect of Negative Substrate Bias Voltage and Pressure on the Structure and Properties of Tungsten Films Deposited by Magnetron Sputtering Technique," *Coatings 2025*, Vol. 15, Page 319, vol. 15, no. 3, p. 319, Mar. 2025, doi: 10.3390/COATINGS15030319.
- [13] G. Abadias *et al.*, "Review Article: Stress in thin films and coatings: Current status, challenges, and prospects," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 36, no. 2, Mar. 2018, doi: 10.1116/1.5011790/246484.
- [14] J. T. Gudmundsson, N. Brenning, D. Lundin, and U. Helmersson, "High power impulse magnetron sputtering discharge," *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 30, no. 3, May 2012, doi: 10.1116/1.3691832/244537.
- [15] A. Anders, "Tutorial: Reactive high power impulse magnetron sputtering (R-HiPIMS)," *J. Appl. Phys.*, vol. 121, no. 17, May 2017, doi: 10.1063/1.4978350/945026.
- [16] R. Garg *et al.*, "Sputtering thin films: Materials, applications, challenges and future directions," *Adv. Colloid Interface Sci.*, vol. 330, p. 103203, Aug. 2024, doi: 10.1016/J.CIS.2024.103203.
- [17] B. Sartowska, W. Starosta, L. Waliś, J. Smolik, and E. Pańczyk, "Multi-Elemental Coatings on Zirconium Alloy for Corrosion Resistance Improvement," *Coatings 2022*, Vol. 12, Page 1112, vol. 12, no. 8, p. 1112, Aug. 2022, doi: 10.3390/COATINGS12081112.
- [18] B. P. Sahu, A. Dutta, and R. Mitra, "Influence of substrate bias voltage on structure and properties of DC magnetron sputtered Ni–Zr alloy thin films," *J. Mater. Res.*, vol. 35, no. 12, pp. 1543–1555, Jun. 2020, doi: 10.1557/JMR.2020.89.
- [19] J. Hnilica, P. Klein, M. Učík, S. Debnárová, J. Klusoň, and P. Vašina,

- "On direct-current magnetron sputtering at industrial conditions with high ionization fraction of sputtered species," *Surf. Coat. Technol.*, vol. 487, p. 131028, Jul. 2024, doi: 10.1016/J.SURFCOAT.2024.131028.
- [20] K. Wang, X. Liu, T. Liu, C. He, and J. Liu, "Interdiffusion in Zr-Mo/W Intermetallics," *Applied Sciences* 2023, Vol. 13, Page 6375, vol. 13, no. 11, p. 6375, May 2023, doi: 10.3390/APP13116375.
- [21] S. Wei, Y. Li, R. Zhang, B. Wang, T. Liang, and W. Yin, "Microstructure and Mechanical Properties of Tungsten Zircaloy-4 Diffusion Welding Interface," *Materials* 2025, Vol. 18, Page 2823, vol. 18, no. 12, p. 2823, Jun. 2025, doi: 10.3390/MA18122823.
- [22] C. Purushottam Bhat *et al.*, "Investigations on Bi Doped Cu₂Se Prepared by Solid State Reaction Technique for Thermoelectric Applications," *Energies* 2023, Vol. 16, Page 3010, vol. 16, no. 7, p. 3010, Mar. 2023, doi: 10.3390/EN16073010.
- [23] F. T. N. Vüllers and R. Spolenak, "Alpha- vs. beta-W nanocrystalline thin films: A comprehensive study of sputter parameters and resulting materials' properties," *Thin Solid Films*, vol. 577, pp. 26–34, Feb. 2015, doi: 10.1016/J.TSF.2015.01.030.
- [24] B. jurnal, Y. Gigih Wicaksono, and A. Manaf, "The Effect of Current Density on The Surface Morphology in the Thin Coating Process of Nickel on Zr-2 Using the Electroplating Method," *Urania: Jurnal Ilmiah Daur Bahan Bakar Nuklir*, vol. 31, no. 2, pp. 83–90, Nov. 2025, doi: 10.55981/URANIA.2025.9199.
- [25] Y. G. Wicaksono, Ridwan, A. Saputra, and A. Manaf, "Effect of heat treatment on the hardness and corrosion rate of oxide-coated zirconium alloy prepared via electroplating with chromium and nickel solutions," *Phys. Scr.*, vol. 101, no. 25, p. 255908, Jun. 2026, doi: 10.1088/1402-4896/AE7B12.
- [26] Y. Liang *et al.*, "Growth Mechanisms and the Effects of Deposition Parameters on the Structure and Properties of High Entropy Film by Magnetron Sputtering," *Materials*, vol. 12, no. 18, p. 3008, Sep. 2019, doi: 10.3390/MA12183008.
- [27] F. A. Vargas *et al.*, "On-axis radio frequency magnetron sputtering of stoichiometric BaTiO₃ target: Localized re-sputtering and substrate etching during thin film growth," *Thin Solid Films*, vol. 596, pp. 77–82, Jan. 2015, doi: 10.1016/J.TSF.2015.07.065.
- [28] V. V. Dushik, Y. V. Lakhokin, V. P. Kuzmin, T. V. Rybkina, N. V. Rozhanskii, and B. A. Rychkov, "The Corrosion and Electrochemical Behavior of Tungsten-Based CVD Coatings in Alkaline Aqueous Solutions," *Protection of Metals and Physical Chemistry of Surfaces*, vol. 54, no. 7, pp. 1315–1319, Dec. 2018, doi: 10.1134/S2070205118070092.
- [29] Y. Liu *et al.*, "Controllable defect engineering to enhance the corrosion resistance of Cr/GLC multilayered coating for deep-sea applications," *Corros. Sci.*, vol. 199, p. 110175, May 2022, doi: 10.1016/J.CORSCI.2022.110175.
- [30] O. E. Hudak *et al.*, "Pitting corrosion – Preferred chloride diffusion pathways in physical vapor deposited AlCrN coatings," *Corros. Sci.*, vol. 211, p. 110901, Feb. 2023, doi: 10.1016/J.CORSCI.2022.110901.
- [31] Y. Xu, X. Qiu, S. Wang, C. Chen, F. Xing, and K. Suganuma, "Interfacial microstructures and corrosion behavior of tungsten heavy alloy/superalloy dissimilar joints: design, regulation and mechanism," *Journal of Materials Research and Technology*, vol. 25, pp. 6323–6337, Jul. 2023, doi: 10.1016/J.JMRT.2023.07.094.
- [32] Q. Liu *et al.*, "Mechanisms of water chemistry on oxide microstructures in zirconium alloy corrosion: A comparative study via PED-EELS," *Corros. Sci.*, vol. 256, p. 113189, Nov. 2025, doi: 10.1016/J.CORSCI.2025.113189.
- [33] J. Knöppel, S. Zhang, F. D. Speck, K. J. J. Mayrhofer, C. Scheu, and S. Cherevko, "Time-resolved analysis of dissolution phenomena in photoelectrochemistry – A case study of WO₃ photocorrosion," *Electrochem.*

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- commun.*, vol. 96, pp. 53–56, Nov. 2018, doi: 10.1016/J.ELECOM.2018.09.008.
- [34] J. Knöppel *et al.*, “Photocorrosion of WO₃ Photoanodes in Different Electrolytes,” *ACS Physical Chemistry Au*, vol. 1, no. 1, pp. 6–13, Nov. 2021, doi: 10.1021/ACSPHYSCHEMAU.1C00004.
- [35] U. Stoll and N. Slavinskaya, “Corrosion behavior of zirconium alloys in the aqueous environment. Phenomenological aspects. Overview,” *J. Nucl. Sci. Technol.*, vol. 60, no. 5, pp. 573–602, May 2023, doi: 10.1080/00223131.2022.2127954.
- [36] J. Ko, J. W. Kim, H. W. Min, Y. Kim, and Y. S. Yoon, “Review of manufacturing technologies for coated accident tolerant fuel cladding,” *Journal of Nuclear Materials*, vol. 561, p. 153562, Apr. 2022, doi: 10.1016/J.JNUCMAT.2022.153562.