

## PREPARATION AND HIGH-TEMPERATURE HYDROGEN BARRIER PERFORMANCE OF $\text{Al}_2\text{O}_3/\text{ZrO}_2$ COMPOSITE COATINGS ON ZIRCONIUM HYDRIDE SURFACE

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*This study employed zirconium oxychloride and aluminum isopropoxide as precursors to prepare Zr-Al composite oxide hydrogen-resistant coatings on zirconium hydride surfaces using sol-gel technology. The effects of the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio (1:1-1:5) on coating properties were investigated. The actual composition of the coating was characterized by EDS, which was consistent with the initial  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio design. High-temperature dehydrogenation test results show that the hydrogen loss of the optimal coated sample is only 6.3% of uncoated bare  $\text{ZrH}_2$ , which quantitatively proves the excellent hydrogen suppression capacity of the composite coating. Experimental results showed that the critical load, thickness, and hydrogen permeability reduction factor (PRF value) of the Zr-Al composite oxide coatings exhibited a trend of initial increase followed by decrease with decreasing  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  ratios. The critical load ranged between 35.69-49.55 N, thickness from 6.5-19.2  $\mu\text{m}$ , and PRF values between 6.7-15.9. When the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio was 1:1-1:3, the composite gel maintained an amorphous structure. At  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  ratios of 1:4 and 1:5, the gel transitioned from amorphous zirconia to the C- $\text{ZrO}_2$  phase. Among the five tested  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratios, the composite coating with a ratio of 1:4 exhibits a uniform and compact microstructure with a thickness of 19.2  $\mu\text{m}$ , and possesses the highest critical load (49.55 N) and PRF value (15.9) within this experimental range. Three core innovations of this work are summarized as follows: (1)  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  composite hydrogen barrier coating is first fabricated on  $\text{ZrH}_2$  matrix by sol-gel route; (2) The regulation rule of  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio on amorphous-cubic phase transition of zirconia is revealed systematically; (3) Four synergistic hydrogen-blocking mechanisms of the composite coating are clarified, which provides experimental and theoretical support for the application of high-performance barrier coatings on space reactor  $\text{ZrH}_2$  moderators.*

**Keywords:** hydrogen permeation resistance; sol-gel coating; zirconium hydride coatings;  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  composite coating

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## 1. Introduction

Zirconium hydride, as an efficient solid moderator, features high hydrogen content, low neutron capture cross-section, and negative temperature reactivity, making it an ideal neutron moderator material for space reactors[1–3]. However, under high-temperature operating conditions, zirconium hydride tends to lose hydrogen, leading to reduced moderation efficiency and shortened service life[4]. To ensure proper operation of the moderator, applying a hydrogen-blocking coating on its surface is an effective method to prevent hydrogen evolution. Therefore, developing high-performance hydrogen-blocking coatings holds significant importance for both the successful application of zirconium hydride moderators and the structural design of space nuclear reactors.

Different materials exhibit varying thermal expansion coefficients. Selecting appropriate composite materials plays a crucial role in effectively mitigating stress differences caused by excessive thermal expansion coefficient variations between the matrix and coating, thereby significantly reducing coating defects such as cracks, pores, and delamination. Wu Ming et al. developed Si-Al and Si-Zr composite oxide coatings on zirconium hydride surfaces using sol-gel synthesis, demonstrating excellent hydrogen barrier properties[5]. Hao Yanxia's team prepared  $\text{ZrO}_2\text{-Al}_2\text{O}_3$  composite coatings in porous ceramic tubes through the same method, where alumina addition effectively suppressed zirconia phase transformation and delayed the phase transition temperature of zirconia[6]. Yao Y B's group created intermediate composite  $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$  coatings on titanium alloy surfaces via sol-gel synthesis, achieving notable improvements in both coating oxidation resistance and anti-peeling performance[7].

This study employs the sol-gel method to develop a hydrogen barrier coating on zirconium hydride surfaces. While alumina coatings exhibit high hydrogen permeation resistance, the significant thermal expansion coefficient difference between  $\text{Al}_2\text{O}_3$  and zirconium hydride causes substantial stress during heat treatment. This thermally induced stress leads to surface coating defects on the substrate, which in turn compromise the hydrogen barrier performance. To mitigate this thermal expansion mismatch, a composite alumina coating was selected as the hydrogen barrier layer. Zirconia, with its excellent chemical stability, low thermal conductivity, and thermal expansion coefficient similarity to zirconium hydride, emerges as the most promising material for hydrogen barrier applications. However, zirconia coatings face critical challenges under high-temperature conditions due to phase transition issues. Phase transitions cause lattice parameter changes and volume alterations, leading to coating cracking [6].  $\text{ZrO}_2\text{-Al}_2\text{O}_3$  composite coatings have been widely studied in the field of high-temperature protection due to their excellent comprehensive properties. The addition of  $\text{Al}_2\text{O}_3$  can effectively inhibit the phase transformation of  $\text{ZrO}_2$  from the tetragonal phase

to the monoclinic phase, reduce coating cracking caused by volume effects, and improve high-temperature stability. At the same time,  $\text{ZrO}_2$  has good chemical stability and a thermal expansion coefficient close to that of zirconium hydride, which can reduce thermal stress and interface defects between coating and substrate. The synergistic effect of  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  makes the composite coating obtain high density, strong interface adhesion, and excellent hydrogen permeation resistance, which is an ideal hydrogen barrier material for zirconium hydride. For  $\text{ZrO}_2$  applications in high-temperature environments, incorporating  $\text{Al}_2\text{O}_3$  is essential to suppress phase transitions [8]. Consequently, the composite oxide coating formed by  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$  shows promise as an ideal hydrogen barrier for zirconium hydride surfaces. Nevertheless, the molar ratio of  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  remains a critical factor affecting coating performance – both excessive or insufficient ratios can compromise the hydrogen barrier effectiveness of zirconium hydride coatings.

Previous studies have made important progress in hydrogen barrier coatings for zirconium hydride. Most studies focused on single  $\text{ZrO}_2$  coatings prepared by micro-arc oxidation or in-situ oxidation under steam or  $\text{CO}_2$  atmosphere, mainly discussing oxide growth kinetics and microstructure evolution. However, few studies have used sol–gel method to construct  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  composite coatings, and the regulation mechanism of the molar ratio on phase transition, coating quality and hydrogen barrier performance is still unclear.

Recent studies have carried out relevant exploration. Wang et al. prepared  $\text{ZrO}_2$  coatings on zirconium hydride by micro-arc oxidation and analyzed their hydrogen resistance properties, but did not involve composite oxide design. Other studies investigated the oxidation behavior of zirconium-based materials in high-temperature steam, but lacked targeted optimization for hydrogen permeation resistance. Compared with the above studies, this work has obvious innovations: firstly,  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  composite coatings were prepared on zirconium hydride by sol–gel method; secondly, the effect of  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio on amorphous-crystalline phase transformation was systematically revealed; thirdly, the optimal ratio was determined, and the hydrogen barrier mechanism was clarified. This work provides an experimental and theoretical basis for the development of high-performance hydrogen barrier coatings for zirconium hydride.

Therefore, this study employed zirconium oxychloride as the precursor and oxalic acid solution as the solvent to prepare zirconium sol, while using aluminum isopropoxide as the precursor with n-propanol and water as solvents, along with acetylacetone as the chelating agent to formulate aluminum sol. The effects of the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio on the thermogravimetric-differential thermal analysis (TG-DTG) process and phase transition characteristics of composite gels were investigated. A comprehensive heat treatment protocol for coating application was developed, followed by systematic characterization of the composite oxide coatings' microstructure, surface roughness, thickness, interfacial critical load with

the substrate, and hydrogen barrier properties. These findings provide a theoretical foundation for the sol-gel method in zirconium-aluminum systems for producing composite oxide coatings.

## 2. Materials and Methods

The matrix material selected for the test was  $\text{ZrH}_2$ , which was provided by Beijing General Research Institute of Nonferrous Metals. The circular wafer samples of zirconium hydride were cut by a CNC wire-cutting machine to a size of  $\Phi 20 \text{ mm} \times 2 \text{ mm}$ .

Prior to sample coating, surface pretreatment is performed through the following steps: gradually sand the surface and edges of the cut zirconium hydride sample using SiC water sandpaper. The SiC water sandpapers of 400#, 800#, 1200#, 2000# were used sequentially for grinding the substrate surface. After ultrasonic cleaning, the average surface roughness of  $\text{ZrH}_2$  specimens was measured to be  $R_a \approx 0.25 \mu\text{m}$ ; ultrasonically clean the sample in acetone first for 20 minutes, then in ethanol for another 20 minutes, rinsing with deionized water after each cleaning; finally, allow the sample to air-dry before use.

In an n-propanol solution of aluminum isopropoxide (supplied by Sinopharm Chemical Reagent Co., Ltd.), a mixture of acetylacetone and isopropanol was added. The mixture was refluxed under  $95^\circ\text{C}$  conditions for 4 hours to prepare an aluminum sol (with V-n-propanol:V-mixed solution:V-water = 1:1:1). A oxalic acid solution was then refluxed at  $95^\circ\text{C}$  with an inorganic zirconium salt (zirconium oxychloride) solution for 1 hour. Polyvinyl alcohol (PVA) and glycerol were subsequently added to obtain a zirconium sol (with an inorganic zirconium salt:oxalic acid molar ratio of 3:1)[9]. The zirconium sol and aluminum sol were mixed, and a film-forming promoter, polyethylene glycol (PEG) was added. After aging for 12 h, a zirconium-aluminum composite sol was obtained. This study investigated the effect of  $\text{ZrO}_2$  addition on composite oxide coating performance by adjusting the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio in the sol-gel process. The selected  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratios were 1:1, 1:2, 1:3, 1:4, and 1:5. Table 1 presents the process parameters for preparing composite oxide coatings with different  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratios.

The zirconium hydride matrix was coated by the immersion and drawing method followed by staged heat treatment. For preparing 100 mL aluminum sol: n-propanol 40 mL, isopropanol-acetylacetone mixed solution 40 mL, deionized water 40 mL, aluminum isopropoxide dosage matched to 0.4 mol/L concentration, refluxed at  $95^\circ\text{C}$  for 4 h. For preparing 100 mL zirconium sol: zirconium oxychloride fixed at 0.2 mol/L, oxalic acid molar ratio 3:1 relative to Zr salt, with a small amount of glycerol and PVA added. After mixing Al sol and Z sol, PEG film-forming agent was incorporated, and the composite sol was statically aged for

24 h at 25 °C under a sealed environment. The dip-coating operation was carried out at room temperature: each ZrH<sub>2</sub> substrate was immersed in the composite sol for 30 s, and then pulled out vertically at a constant withdrawal speed of 10 cm/min. After each coating layer, the sample was dried at 120 °C for 15 min in air, and the above coating-drying cycle was repeated three times to obtain the target composite coating.

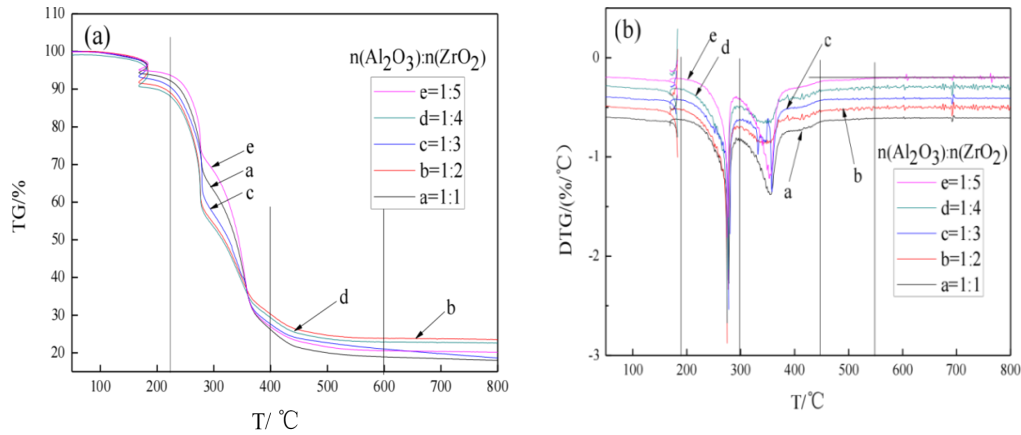
**Table 1.** Processing parameters of composite oxide coatings with different Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> molar ratio.

| No. | c(ZrOCl <sub>2</sub> )/mol·L <sup>-1</sup> | c(Al(OPr <sup>i</sup> ) <sub>3</sub> )/mol·L <sup>-1</sup> | n(Al <sub>2</sub> O <sub>3</sub> ):n(ZrO <sub>2</sub> ) |
|-----|--------------------------------------------|------------------------------------------------------------|---------------------------------------------------------|
| 1   | 0.2                                        | 0.4                                                        | 1:1                                                     |
| 2   | 0.2                                        | 0.4                                                        | 1:2                                                     |
| 3   | 0.2                                        | 0.4                                                        | 1:3                                                     |
| 4   | 0.2                                        | 0.4                                                        | 1:4                                                     |
| 5   | 0.2                                        | 0.4                                                        | 1:5                                                     |

<sup>1</sup> The molar ratios are controlled by mixing two fixed-concentration precursor sols with different volumes, and the total volume of mixed sol is kept consistent for all groups.

To investigate the structural and compositional changes of composite oxide coatings with different Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> molar ratios during heat treatment, thermogravimetric-trend thermograms (TG-DTG) were performed on the composite gel, as shown in Figure 1. Figure 1(a) reveals significant weight loss of the composite gel between 220-400°C, followed by gradual weight loss between 400-550°C. The weight loss rate stabilized at 550-800°C. Figure 1(b) indicates that the gel with different composite ratios exhibited maximum weight loss rates around 270°C and 360°C. Prior to 200°C, solvent evaporation caused initial weight loss. Between 200-440°C, substantial weight loss occurred due to zirconium oxalate dehydration, thermal decomposition, and boehmite hydroxyl removal. From 440-550°C, the weight loss slowed as some film-forming promoters and binders underwent combustion decomposition. After 550°C, the weight loss plateaued, indicating complete reaction formation of oxides followed by crystalline transformation.

The performance of composite coatings is influenced not only by the quality of the sol but also critically by the setting of heat treatment process parameters. According to the TG-DTG curve, three temperature zones are established in the heat treatment process to ensure more complete reactions at each stage. The endpoint temperatures within these zones are maintained at constant temperatures for 1-2 hours.



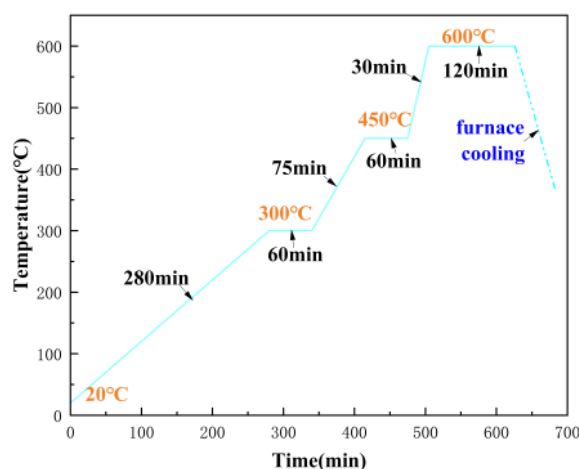
**Figure 1.** TG-DTG curves of composite gels with different  $\text{Al}_2\text{O}_3$  molar ratios (1:1-1:5). Test conditions: heating rate  $10^\circ\text{C}/\text{min}$ , air atmosphere, temperature range  $25\text{--}800^\circ\text{C}$ , sample mass 8-10 mg; (a) TG mass loss curves; (b) DTG differential thermal weight loss rate curves.

As shown in Figure 1, composites with different gel ratios exhibit significant weight loss during heat treatment at a relatively high rate. After drying, the composite gels still contain physically adsorbed water, alcohols, and inorganic acids as solvents. The volatilization of these solvents causes coating volume shrinkage, leading to cracking and delamination that impair the hydrogen barrier properties of zirconium hydride surface coatings. To control solvent evaporation rates and achieve crack-free coatings, a slower heating rate should be adopted to reduce stress in the composite coatings. Between  $50\text{--}300^\circ\text{C}$ , the heating rate is controlled at  $1^\circ\text{C}/\text{min}$ . At  $300\text{--}450^\circ\text{C}$ , where significant weight loss occurs rapidly, the heating rate should be reduced to  $2^\circ\text{C}/\text{min}$ . Beyond  $450^\circ\text{C}$ , partial organic decomposition occurs, allowing a moderate increase in heating rate to  $4^\circ\text{C}/\text{min}$ . After  $550^\circ\text{C}$ , when no significant weight loss remains and most volatile components have been removed, the heating rate can be appropriately increased to  $10^\circ\text{C}/\text{min}$  to shorten treatment time. The final heat-treatment temperature was determined as  $600^\circ\text{C}$  based on TG-DTG results: nearly all organic solvents, binders, and oxalate decomposition products were completely volatilized below  $550^\circ\text{C}$ . Heating above  $600^\circ\text{C}$  would aggravate  $\text{ZrO}_2$  grain growth and cause excessive coating shrinkage, leading to more microcracks. Maintaining  $600^\circ\text{C}$  for 2 h can fully complete oxide crystallization while avoiding severe coating defects. In summary, the heat treatment process parameters for composite gels specified in this study are presented in Table 2, with the thermal treatment sequence illustrated in Figure 2.

**Table 2.** Heat treatment process parameters of composite coatings.

| T range/°C | Heating rate/°C·min <sup>-1</sup> | Holding time/min |
|------------|-----------------------------------|------------------|
| 20~300     | 1                                 | 280              |
| 300~300    | 0                                 | 60               |
| 300~450    | 2                                 | 75               |
| 450~450    | 0                                 | 60               |
| 450~600    | 5                                 | 30               |
| 600~600    | 0                                 | 120              |

<sup>2</sup> The temperature holding stages are set according to TG-DTG weight loss characteristics to fully remove organic solvents and complete oxide crystallization.



**Figure 2.** Heat treatment schedule for Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> composite coatings, including segmented heating rates, constant temperature holding stages and furnace cooling procedure after 600 °C sintering.

Composite sols were dried at 80 °C and sintered at 600 °C under atmospheric pressure. The heat treatment parameters matched those applied to zirconium hydride-coated samples. The sintered powder was ground into fine particles for X-ray diffraction (XRD) phase analysis. The primary phase structure was determined by analyzing characteristic peaks' positions and intensities in the diffraction patterns. The Japanese D/MAX 2500/C X-ray diffractometer operated at 40 kV voltage with 35mA current, employing a 0.02°step scan. The Cu target produced K $\alpha$  radiation corresponding to an X-ray wavelength of 0.15418 nm.

The surface morphology and cross-sectional morphology of the zirconium hydride composite oxide coating were analyzed using a Sigma 500 field emission scanning electron microscope (FE-SEM). During the analysis of the cross-sectional morphology, areas with uniform coating thickness distribution were identified, and the coating thickness was determined by averaging five different thickness measurements. The surface morphology of the composite oxide coating was further observed using a Zeiss LSM-700 laser confocal microscope (CLSM) at 500x

magnification to characterize its uniformity. The elemental distribution on the composite oxide coating surface was analyzed using an EDX-type electron energy-dispersive spectrometer (EDS), an accessory device for the field emission scanning electron microscope.

The critical load of the coating was tested by the WS-2005 scratch method [25]. The specific parameters were set as follows: loading load 100 N, loading speed 100 N/min, scratch speed 5mm/min and scratch length 5mm. For each  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio group, 3 independent  $\text{ZrH}_2$  substrates were separately prepared as parallel specimens. Each substrate underwent 3 cycles of dip-coating and heat treatment. All thickness, critical scratch load, and PRF values were averaged from 3 parallel samples, and the standard deviation was calculated as the uncertainty of the measured data.

For the high-temperature dehydrogenation experiments, specimens were placed in a quartz reactor and purged with argon for 30 minutes prior to heating to establish a protective atmosphere, which was maintained throughout the test. Following evacuation, samples were heated from ambient temperature to  $750^\circ\text{C}$  at  $5^\circ\text{C}/\text{min}$ , held at this temperature for 10 hours, then furnace-cooled. The hydrogen barrier efficacy was determined by comparing the hydrogen loss between coated and uncoated zirconium hydride samples, where higher PRF values indicated superior barrier performance. The hydrogen permeation reduction factor (PRF) was adopted to quantitatively evaluate the hydrogen barrier capacity of coatings, and the calculation formula is defined as:

$$PRF = \frac{\text{Hydrogen loss in the non-coated zirconium hydride}}{\text{Hydrogen loss in the coated zirconium hydride}} \quad (1)$$

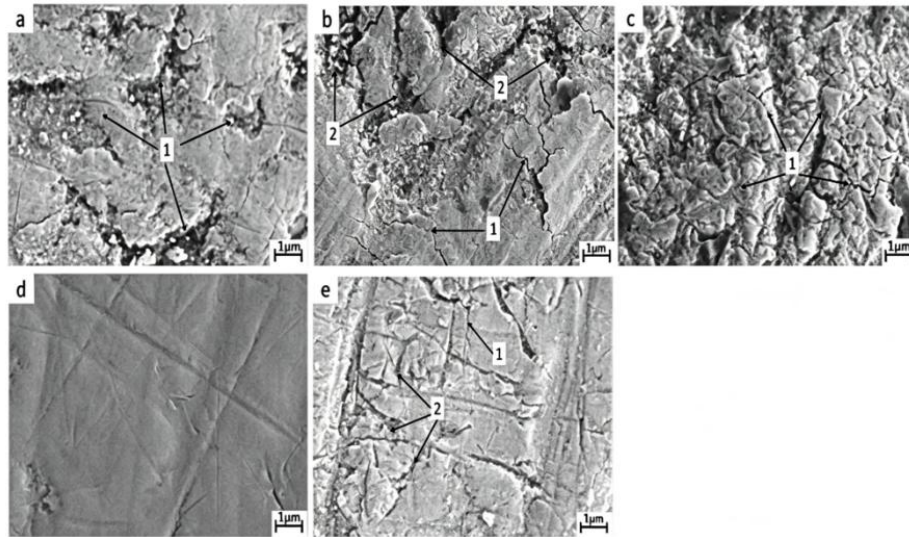
After 10 h of constant-temperature treatment at  $750^\circ\text{C}$ , the net hydrogen mass loss of the bare  $\text{ZrH}_2$  substrate is 12.6 mg, while the specimen coated with  $\text{Al}_2\text{O}_3/\text{ZrO}_2=1:4$  only loses 0.79 mg of hydrogen. This test data yields a PRF of 15.9, and the hydrogen escape of the coated sample accounts for only 6.3% of bare  $\text{ZrH}_2$ .

### 3. Results

Figure 3 displays the surface morphology of composite oxide coatings with varying  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratios. The 1:1 coating presents numerous micropores. With increasing  $\text{ZrO}_2$  content, the 1:2 and 1:3 coatings show obvious cracks and delamination. The 1:4 coating is uniform, dense, and free of cracks and pores. Further increasing  $\text{ZrO}_2$  to 1:5 leads to minor cracks and reduced density[10].

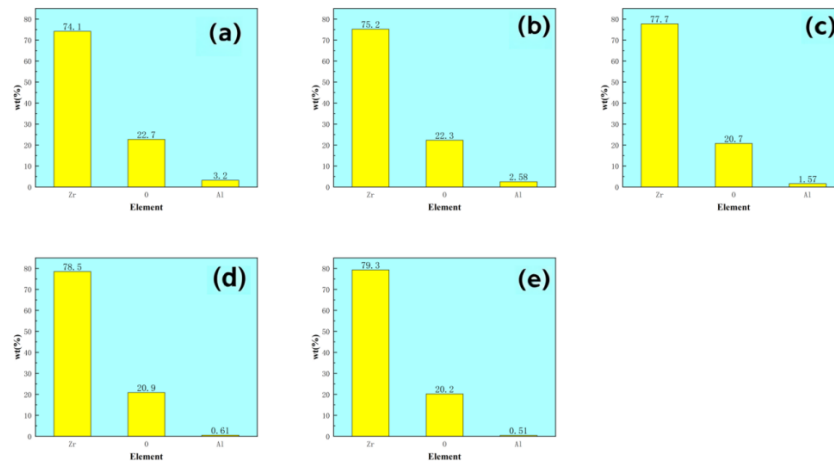
These defects provide rapid diffusion channels for hydrogen atoms and reduce the interfacial critical load between the coating and the substrate, thus significantly impairing the hydrogen barrier performance[11].

The  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio changes the sol viscosity. Low  $\text{ZrO}_2$  content leads to higher viscosity and thicker coatings, causing defects during heat treatment. High  $\text{ZrO}_2$  content reduces viscosity and hinders the formation of continuous coatings.



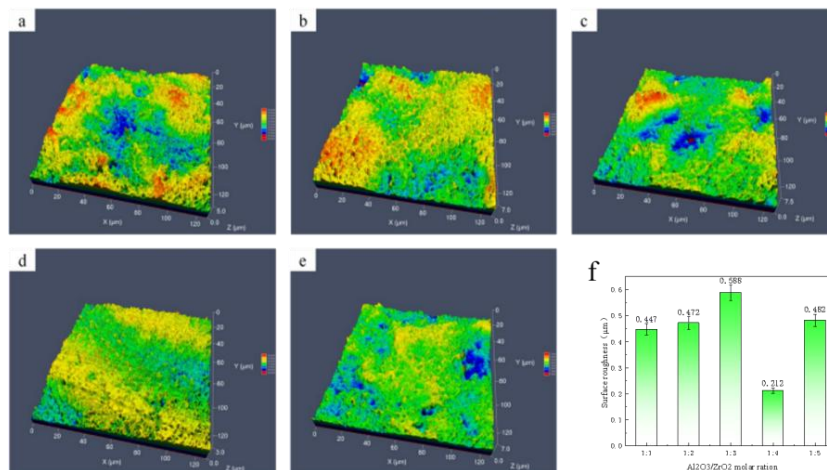
**Figure 3.** Surface FE-SEM morphologies of  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  composite coatings deposited on  $\text{ZrH}_2$  substrates (molar ratios 1:1–1:5). Test parameters: accelerating voltage 15 kV, magnification  $\times 5000$ ; (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4, (e) 1:5.

Figure 4 presents the surface energy spectrum analysis of composite oxide coatings with varying  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratios on zirconium hydride surfaces. The results demonstrate that as the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio decreases (indicating increased  $\text{ZrO}_2$  content), the Zr element exhibits progressively enhanced intensity and higher concentration. Conversely, the Al element shows decreasing intensity and reduced proportion. The actual chemical composition of the composite coating was characterized by EDS (Figure 4), which verified that the element ratio of the coating was consistent with the initial sol molar ratio design.



**Figure 4.** EDS mass fraction analysis of Zr, O and Al elements on the surface of  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  composite coatings with molar ratios of 1:1–1:5; EDS equipped on Sigma500 FE-SEM, accelerating voltage 15 kV.

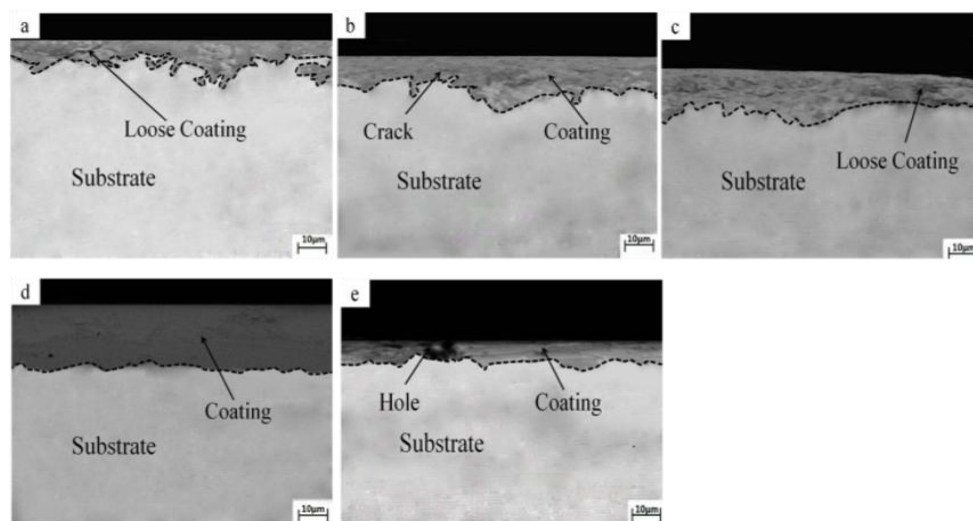
Figure 5 displays the 3D surface morphology of composite oxide coatings with different  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratios on  $\text{ZrH}_2$  surfaces. As shown in Figure 5(a), the coating exhibits an uneven surface with a roughness ( $R_a$ ) of  $0.447\mu\text{m}$ . At an  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  ratio of 1:2, the coating surface becomes less uniform, with a roughness value of  $0.472\mu\text{m}$  (Figure 5(b)). As zirconia content increases, surface uniformity sharply declines, reaching a maximum roughness of  $0.588\mu\text{m}$  (Figure 5(c)). Figure 5(d) reveals optimal coating quality at an  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  ratio of 1:4, featuring a smooth, uniform surface with minimal roughness ( $R_a$   $0.212\mu\text{m}$ ).



**Figure 5.** 3D Morphology of composite oxide coatings on the surface of  $\text{ZrH}_2$  with different  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio: (a)  $\text{Al}_2\text{O}_3/\text{ZrO}_2=1:1$ ; (b)  $\text{Al}_2\text{O}_3/\text{ZrO}_2=1:2$ ; (c)  $\text{Al}_2\text{O}_3/\text{ZrO}_2=1:3$ ; (d)  $\text{Al}_2\text{O}_3/\text{ZrO}_2=1:4$ ; (e)  $\text{Al}_2\text{O}_3/\text{ZrO}_2=1:5$ ; (f) surface roughness.

However, as zirconia content rises further to  $0.482\mu\text{m}$  (Figure 5(e)), surface flatness deteriorates. The increasing zirconia content reduces composite sol viscosity, hindering the formation of continuous coatings on zirconium hydride surfaces. Conversely, lower zirconia content results in higher sol viscosity, leading to thicker coatings with greater internal stress and compromised quality. Comprehensive analysis of Figures 5(a)-(e) demonstrates that the composite oxide coating on zirconium hydride surfaces exhibits optimal uniformity at an  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  ratio of 1:4.

Figure 6 shows the cross-sectional morphology of coatings with different  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  ratios. The 1:1 coating is loose; the 1:2 and 1:3 coatings show micro-cracks and obvious boundaries. The 1:4 coating is dense and tightly bonded with the  $\text{ZrH}_2$  substrate. The 1:5 coating becomes discontinuous and thinner. The cross-sectional quality is determined by sol viscosity and thermal expansion mismatch between the coating and substrate.

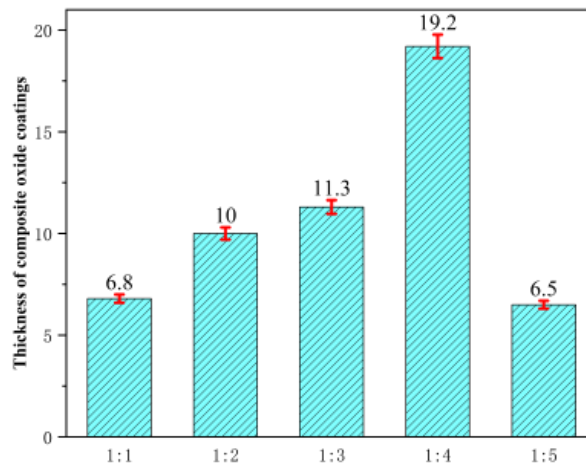


**Figure 6.** Cross-section morphology of composite oxide coatings on the surface of  $\text{ZrH}_2$  with different  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio: (a)  $\text{Al}_2\text{O}_3/\text{ZrO}_2=1:1$ ; (b)  $=1:2$ ; (c)  $\text{Al}_2\text{O}_3/\text{ZrO}_2=1:3$ ; (d)  $\text{Al}_2\text{O}_3/\text{ZrO}_2=1:4$ ; (e)  $\text{Al}_2\text{O}_3/\text{ZrO}_2=1:5$ .

In this study, as the heat treatment temperature increases,  $\text{ZrOC}_2\text{O}_4$  in the coating undergoes thermal decomposition to form  $\text{CO}_2$ , which reacts with zirconium hydride to form a protective coating on the surface. However, the cross-sectional morphology and quality of the zirconium hydride composite oxide coating vary depending on the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio. In this experiment, the coating's cross-sectional quality reached its optimal level but subsequently declined. The analysis reveals two primary reasons: First, the amount of  $\text{ZrO}_2$  sol added affects the viscosity of the composite sol, thereby influencing the coating's application

performance. Second, the thermal expansion coefficients of  $\text{ZrO}_2$  and  $\text{ZrH}_2$  are similar, while those of  $\text{Al}_2\text{O}_3$  differ significantly. Variations in  $\text{ZrO}_2$  content lead to different thermal expansion coefficients in the composite oxide coating. This mismatch between the coating's thermal expansion coefficient and the substrate causes the  $\text{ZrH}_2$  surface coating to become loose, crack, or even peel off.

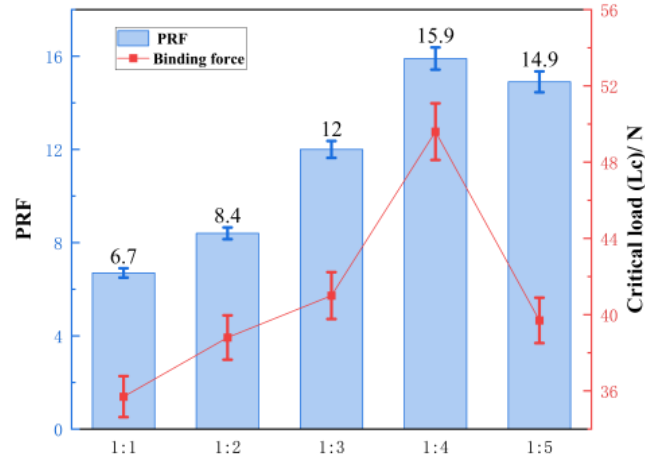
Figure 7 shows the thickness of composite oxide coatings with different  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratios. The sol-gel method enables the preparation of coatings of specific thickness on substrate surfaces. As illustrated in Figure 7, the coating thickness ranges from 6.5 to 19.2  $\mu\text{m}$ . Notably, the coating thickness first increases and then decreases as the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio decreases. When the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio is between 1:1 and 1:4, the coating thickness gradually increases. The coating reaches its maximum thickness of 19.2  $\mu\text{m}$  at an  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio of 1:4. Subsequent decreases in the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio further reduce the thickness. The  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio significantly affects coating thickness. Low  $\text{ZrO}_2$  content leads to coating delamination, while increased  $\text{ZrO}_2$  content facilitates coating formation. However, higher  $\text{ZrO}_2$  content hinders coating formation for two reasons: First, thermal expansion coefficient mismatch between the substrate and coating causes cracking and delamination [12]. Second, volume shrinkage and internal stress caused by volatilization of water and organic components during heat treatment lead to coating defects [9,13].



**Figure 7.** Thickness of composite oxide coatings with different  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratios.

Figure 8 demonstrates the critical load between zirconium hydride surface composite oxide coatings and substrates with varying  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratios, along with the hydrogen permeation barrier factor (PRF). The composite coatings prepared via the sol-gel method on zirconium hydride surfaces exhibit strong

bonding with substrates and demonstrate significantly enhanced hydrogen permeation resistance.



**Figure 8.** Critical load and PRF of composite oxide coatings with different  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ration.

As shown in Figure 8, the critical load and PRF values of the composite oxide coatings range from 35.69 N to 49.55 N and 6.7 to 15.9, respectively. Both parameters initially increase with increasing  $\text{ZrO}_2$  content before showing a decreasing trend. When the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio is between 1:1 and 1:4, the critical load and PRF values of the coatings gradually increase. Among the five tested  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratios, the coating with a ratio of 1:4 delivers the highest critical load (49.55 N) and PRF value (15.9). Further increasing the  $\text{ZrO}_2$  proportion leads to a gradual decline in both indicators.

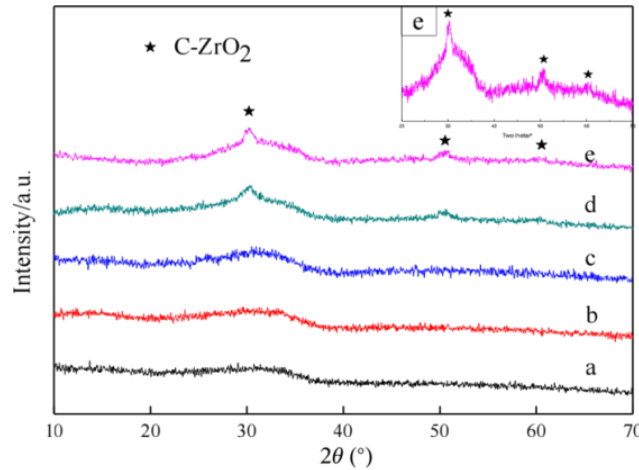
Generally, the critical load between composite oxide coatings and substrates is determined by three factors: coating surface quality, cross-sectional characteristics, and coating thickness. In this study, the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio significantly influences the bond strength. This phenomenon arises because lower  $\text{ZrO}_2$  content leads to higher sol-gel viscosity, resulting in thicker coatings. During heat treatment, the zirconium hydride-coated surfaces tend to become loose and crack, thereby weakening the bond strength. Conversely, higher  $\text{ZrO}_2$  content reduces sol-gel viscosity, hindering coating formation and consequently decreasing bond strength. Additionally, variations in  $\text{ZrO}_2$  content cause differences in thermal expansion coefficients between the composite oxide coatings and substrates, which further contribute to variations in critical load due to thermal expansion rate differences.

The hydrogen resistance of composite oxide coatings is closely related to coating quality and the critical load between the coating and substrate. As shown in Figures 3, 5, and 6, when the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio is 1:4, the zirconium hydride surface exhibits a smoother, more continuous, and denser coating with excellent adhesion to the substrate. Therefore, compared to other process parameters, the composite oxide coating prepared with an  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio of 1:4 demonstrates superior hydrogen resistance. Figure 8 reveals that although the composite coating with a  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio of 1:5 has the smallest thickness, its PRF value is not the lowest, indicating that hydrogen resistance cannot be solely determined by coating thickness [14].

The quantitative dehydrogenation comparison results verify that the composite coating with  $\text{Al}_2\text{O}_3/\text{ZrO}_2=1:4$  can reduce the hydrogen release of the  $\text{ZrH}_2$  matrix by 93.7% under long-term high-temperature service conditions, which quantitatively demonstrates its outstanding hydrogen permeation resistance.

The heat treatment process for composite sols is identical to that of oxide coatings. Powder sintered at  $600^\circ\text{C}$  was characterized by XRD, with results shown in Figure 9. As observed in Figure 3, a distinct broad diffraction peak appears around  $2\theta=30^\circ$ . The diffraction peaks become progressively narrower as the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio decreases. When the  $\text{ZrO}_2$  content increases to a  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  ratio of 1:3, a bun-shaped peak emerges around  $2\theta=30^\circ$ , indicating amorphous characteristics in the experimental product (Figures 9(a), 9(b), and 9(c)). When the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio is 1:1, 1:2 and 1:3 (curves a, b, c), the composite gel shows a wide diffuse peak near  $2\theta=30^\circ$  without obvious sharp diffraction peaks, which indicates that the composite material is still in an amorphous state. Amorphous structure has no long-range ordered lattice arrangement, so it cannot produce characteristic crystal diffraction peaks. When the molar ratio decreases to 1:4 and 1:5 (curves d, e), amorphous zirconia gradually transforms into cubic zirconia (C- $\text{ZrO}_2$ ), and three strong characteristic diffraction peaks appear at about  $30^\circ$ ,  $50^\circ$ , and  $60^\circ$ , indicating the formation of a crystal structure. At  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  ratios of 1:4 and 1:5, three diffraction peaks appear at  $2\theta\approx 30^\circ, 50^\circ$ , and  $60^\circ$ , mainly assigned to cubic-phase zirconia, as shown in Figures 9(d) and 9(e). Generally, zirconia remains stable as a monoclinic phase at low temperatures and forms a tetragonal crystal system at high temperatures, with cubic-phase zirconia (C- $\text{ZrO}_2$ ) existing above  $2370^\circ\text{C}$ . However, during heat treatment of zirconia coatings prepared via sol-gel methods, the transformation from amorphous to crystalline zirconia occurs. The preferential formation of tetragonal zirconia (T- $\text{ZrO}_2$ ) and cubic-phase zirconia (C- $\text{ZrO}_2$ ) dominates. As heat treatment temperature increases, the T- $\text{ZrO}_2$  phase transitions to M- $\text{ZrO}_2$  (monoclinic zirconia), with the proportion of monoclinic zirconia gradually increasing [16,17](Figure 9). In this experiment, the C- $\text{ZrO}_2$  transition was preferred because the structure of cubic zirconia is more similar to that of

amorphous zirconia, and the Al<sup>3+</sup> doping into ZrO<sub>2</sub> grains can increase the oxygen vacancies to play a stabilizing role [18,19].



**Figure 9.** XRD patterns of composite oxides with different Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> molar ratios: (a) Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> = 1:1; (b) Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> = 1:2; (c) Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> = 1:3; (d) Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> = 1:4; (e) Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> = 1:5.

Combining the surface/cross-sectional morphology and XRD phase results, the performance trend can be fully explained: the 1:1–1:3 amorphous coatings contain abundant pores and cracks, leading to low critical load and poor hydrogen isolation; when the ratio reaches 1:4, the coating transforms into dense cubic ZrO<sub>2</sub> crystalline structure with complete, crack-free morphology, which extends hydrogen diffusion paths and eliminates rapid transmission channels, thus achieving the maximum critical scratch load and PRF value; further increasing ZrO<sub>2</sub> to 1:5 breaks coating continuity and introduces tiny defects, resulting in declined barrier performance. This reveals that coating microstructure and crystal phase jointly determine the final hydrogen-blocking capacity.

#### 4. Discussion

The results of this study demonstrate that different Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> molar ratios significantly influence the microstructure and hydrogen barrier performance of composite films. When the Al<sub>2</sub>O<sub>3</sub>:ZrO<sub>2</sub> ratio is 1:4, the film exhibits optimal critical load (49.6N) and a hydrogen permeability reduction factor (PRF = 15.9). This phenomenon can be attributed to Al<sub>2</sub>O<sub>3</sub> promoting the transformation of zirconia from amorphous to cubic zirconia (C-ZrO<sub>2</sub>). It is hypothesized that Al<sup>3+</sup> substitution in ZrO<sub>2</sub> grains may boost the stabilization effect of oxygen vacancies. These oxygen vacancies not only inhibit the phase transition from T-ZrO<sub>2</sub> to M-ZrO<sub>2</sub> but also reduce hydrogen diffusion rates through the pinning effect [20].

However, when the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio exceeds 1:4, the performance of the thin film layer shows a slight decline. It is speculated that excess  $\text{Al}^{3+}$  might accumulate oxygen vacancies, resulting in elevated local lattice stress and more hydrogen diffusion paths. Furthermore, analysis of surface morphology and cross-sectional morphology in Figures 3 and 6 reveals that excessive  $\text{Al}_2\text{O}_3$  content leads to defects such as cracks and pores in the coating, further confirming the decisive influence of the  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratio on material properties [19,22].

The hydrogen barrier performance of  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  composite coatings originates from the four synergistic mechanisms:

- *Physical Barrier Effect*

The dense, crack-free microstructure formed at the optimal ratio (1:4) eliminates hydrogen diffusion channels. The thick and compact coating prolongs the diffusion path of hydrogen atoms and increases the diffusion activation energy, which fundamentally restrains the outward diffusion of hydrogen from the  $\text{ZrH}_2$  matrix.

- *Chemical Trapping Effect*

We speculate that  $\text{Al}^{3+}$  doping could introduce plenty of oxygen vacancies in the  $\text{ZrO}_2$  lattice. Hydrogen atoms are adsorbed by oxygen vacancies and combine with  $\text{O}^{2-}$  to form O–H bonds, which effectively capture hydrogen and slow down its migration rate in the coating[23–25].

- *Phase Stabilization Mechanism*

$\text{Al}_2\text{O}_3$  inhibits the phase transformation of  $\text{ZrO}_2$  from the tetragonal phase to the monoclinic phase, and stabilizes the C- $\text{ZrO}_2$  structure. This avoids coating cracking caused by volume expansion during heating–cooling cycles, maintaining the structural integrity of the hydrogen barrier layer [26–28].

- *Interface Optimization Mechanism*

The appropriate  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  ratio reduces the thermal expansion coefficient mismatch between the coating and the  $\text{ZrH}_2$  substrate. This lowers interfacial thermal stress, improves critical load, and prevents interfacial defects from becoming rapid hydrogen diffusion paths[29–31].

## 5. Conclusions

Using zirconium oxychloride and aluminum isopropoxide as precursors, a composite oxide coating was prepared on zirconium hydride surfaces through the sol–gel method. The thermal treatment process for the composite coating was formulated based on the TG–DTG curves of composites with different  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratios. This study investigated the effects of  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  molar ratios on the phase structure, microstructure, thickness, interfacial critical load between the coating and substrate, and hydrogen-barrier properties of composite oxide coatings prepared by the sol–gel method. Key findings are summarized as follows:

Composite gels with different Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> molar ratios remained in a weight-loss state between 100–550 °C. After 550 °C, the gels showed minimal weight loss. The maximum weight loss occurred around 270 and 360 °C. Between 230–450 °C, significant weight loss resulted from zirconium oxalate thermal decomposition and boehmite hydroxyl removal-induced dehydration.

The thermal treatment process for composite oxide coatings was formulated based on the TG–DTG curves of composites with different Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> molar ratios. Specifically: from room temperature to 300 °C at a heating rate of 1 °C/min; hold at 300 °C for 1 hour; from 300 °C to 450 °C at a heating rate of 2 °C/min; hold at 450 °C for 1 hour; from 450 °C to 600 °C at a heating rate of 5 °C/min; hold at 600 °C for 2 hours.

The Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> molar ratio significantly influences the microstructure of composite oxide coatings. When the ratio is between 1:1 and 1:3, zirconium hydride fails to form a dense coating on the surface. At an Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> ratio of 1:4, the composite oxide coating exhibits excellent uniformity with a surface roughness of 0.212 μm and demonstrates strong bonding with the substrate. However, as the ZrO<sub>2</sub> content increases, continuous and intact coatings become difficult to form on the zirconium hydride surface when the Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> ratio reaches 1:5.

Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> molar ratio significantly influences the phase structure of composite gels. As ZrO<sub>2</sub> content increases, the diffraction peaks of the composite gel gradually narrow from broad to narrow. When the Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> molar ratio ranges between 1:1 and 1:3, the composite gel exists in an amorphous state. At Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> molar ratios of 1:4 and 1:5, the composite gel primarily undergoes a transition from amorphous zirconia to C-ZrO<sub>2</sub>.

The critical load between the composite oxide coating and substrate, coating thickness, and hydrogen barrier performance exhibit a trend of initial increase followed by decrease as the Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> molar ratio decreases. The critical load of the composite oxide coating ranges between 35.69 and 49.55 N, with coating thickness varying from 6.5 to 19.2 μm and PRF values between 6.7 and 15.9. When the Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> molar ratio reaches 1:4, the coating thickness reaches its maximum value of 19.2 μm, demonstrating an excellent critical load (49.55 N) and superior hydrogen barrier performance with a PRF value of 15.9. EDS results show that the actual element ratio of the coating is consistent with the initial Al<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> molar ratio design of the sol, which ensures the accuracy of ratio regulation.

#### **Data Availability Statement**

The raw experimental data, including TG-DTG, SEM, EDS, XRD, scratch test, and hydrogen-barrier test results generated in this study, are available upon reasonable request from the corresponding author.

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### Conflicts of Interest

The authors declare no conflict of interest.

### Artificial Intelligence Disclosure

No artificial intelligence-based or generative tools were used in the preparation of this manuscript.

## REFERENCES

- [1] Sprouster, D.J.; Ouyang, M.; Cetiner, N.; Negi, P.; Sharma, A.; Bhardwaj, D.; Huang, Y.; Hu, X.; Shirvan, K.; Snead, L.L. Low temperature neutron irradiation stability of Zirconium hydride and Yttrium hydride. *J. Nucl. Mater.* **2025**, *609*, 155770, <https://doi.org/10.1016/j.jnucmat.2025.155770>.
- [2] Shirvan, K.; Kazimi, M. Superheated Water-Cooled Small Modular Underwater Reactor Concept. *Nucl. Eng. Technol.* **2016**, *48*, 1338-1348. <https://doi.org/10.1016/j.net.2016.06.003>.
- [3] Wang, H.; Ruan, Z.S.L.; Wang, X.; Li, J.D.; Ma, M.W. Hydrogen desorption kinetics of yttrium hydride under isothermal and non-isothermal conditions. *J. Alloys Compd.* **2026**, *188093*, <https://doi.org/10.1016/j.jallcom.2026.188093>.
- [4] Torres, J.R.; Mizzi, C.A.; Rehn, D.A.; Smith, T.; Paisner, S.W.; Terricabras, A.J.; Parkison, D.M.; Vogel, S.C.; Kohnert, C.A.; Hayne, M.L.; Nizolek, T.J.; Torrez, M.A.; Munroe, T.T.J.; Maiorov, B.; Saleh, T.A.; Shivprasad, A.P. High-temperature structure, elasticity, and thermal expansion of  $\epsilon$ -ZrH<sub>1.8</sub>. *J. Nucl. Mater.* **2025**, *603*, 155437. <https://doi.org/10.1016/j.jnucmat.2024.155437>.
- [5] Wu, M.; Chen, Y.; Peng, J.Q.; Yan, G.Q.; Wang, L.J. Hydrogen permeation resistance and characterization of Si-Al and Si-Zr composite sol oxide coating on surface of zirconium hydride. *Rare Met.* **2017**, *36*, 55-60. <https://doi.org/10.1007/s12598-016-0724-5>.
- [6] Carrasco-Amador, J.P.; Diaz-Parralejo, A.; Macías-García, A.; Díaz-Díez, M.Á.; Olivare, M.; et al. Preparation and characterization of ZrO<sub>2</sub>/Y<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>-based microstructured multilayer sol-gel coatings. *Ceram. Int.* **2017**, *43*, 14890-14898, <https://doi.org/10.1016/j.ceramint.2017.07.166>.
- [7] Wang, P.; Li, J.P.; Guo, Y.C.; Wang, J.L.; Yang, Z.; Liang, M.X. The formation mechanism of the composited ceramic coating with thermal protection feature on an Al12Si piston alloy via a modified PEO process. *J. Alloys Compd.* **2016**, *688*, 730-738, <https://doi.org/10.1016/j.jallcom.2016.04.195>.
- [8] Malka, I.E.; Danelska, A.; Kimmel, G. The influence of Al<sub>2</sub>O<sub>3</sub> content on ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nanocomposite formation: Comparison between sol-gel and microwave hydrothermal method. *Mater. Today: Proc.* **2016**, *3*, 2713-2724. <https://doi.org/10.1016/j.matpr.2016.06.018>.
- [9] Xu, L.M. Preparation and high-temperature stability of zirconium oxide composite membranes. Master's Thesis, Tianjin University, Tianjin, China, **2005**.
- [10] Huang, J.; Xie, H.; Luo, L.-M.; Zan, X.; Liu, D.-G.; Wu, Y.-C. Preparation and properties of FeAl/Al<sub>2</sub>O<sub>3</sub> composite tritium permeation barrier coating on surface of 316L stainless steel. *Surf. Coat. Technol.* **2020**, *382*, 125282, <https://doi.org/10.1016/j.surfcoat.2019.125282>.

- [11] El Hallani, G.; Nasih, S.; Fazouan, N.; Liba, A.; Khuili, M.; Sajjeddine, M.; Mabrouki, M.; Laanab, L.; Atmani, E.H. Comparative study for highly Al and Mg doped ZnO thin films elaborated by sol gel method for photovoltaic application. *J. Appl. Phys.* **2017**, 121, 125101, <https://doi.org/10.1063/1.4979724>.
- [12] Wang, Z.G.; Chen, W.D.; Yan, S.F.; Chen, Y.; Wu, M. Microstructure and hydrogen permeation resistance of zirconium hydride coated by micro arc oxidation. *Rare Met. Mater. Eng.* **2015**, 44, 2877-2881.
- [13] Tong, Z.; Zou, L.; Cui, S.K.; Dong, X.J.; Zhang, H. Influence of sol-gel preparation process parameters on quality of Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> thin films. *Mater. Sci. Eng. Powder Metall.* **2012**, 17, 818-824.
- [14] Bouhattate, J.; Legrand, E.; Feaugas, X. Computational analysis of geometrical factors affecting experimental data extracted from hydrogen permeation tests: I—Consequences of hydrogen trapping. *Int. J. Hydrogen Energy* **2011**, 36, 12644-12652. <https://doi.org/10.1016/j.ijhydene.2011.06.043>.
- [15] Su, X.H.; Zhou, J.; Wang, B.P.; Liu, Y. Synthesis and electric field-assisted sintering behavior of Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> composite nanopowders by polyacrylamide gel method. *J. Sol-Gel Sci. Technol.* **2016**, 80, 126-132. <https://doi.org/10.1007/s10971-016-4085-1>.
- [16] Platt, P.; Frankel, P.; Gass, M.; Wenman, M.R. Finite element analysis of the tetragonal to monoclinic phase transformation during oxidation of zirconium alloys. *J. Nucl. Mater.* **2014**, 454, 290-297. <https://doi.org/10.1016/j.jnucmat.2014.08.020>.
- [17] Gocmez, H.; Tuncer, M.; Uzulmer, I. Particle formation and agglomeration of an alumina-zirconia powder synthesized by supercritical CO<sub>2</sub> method. *Ceram. Int.* **2012**, 38, 1215-1219. <https://doi.org/10.1016/j.ceramint.2011.08.051>.
- [18] Parkes, M.A.; Tompsett, D.A.; D'Avezac, M.; Offer, G.J.; Brandon, N.P.; Harrison, N.M. The atomistic structure of yttria stabilised zirconia at 6.7 mol%: an ab initio study. *Phys. Chem. Chem. Phys.* **2016**, 18, 31277-31285. <https://doi.org/10.1039/C6CP04694K>.
- [19] Chen, W.D.; Wang, L.J.; Han, L. Properties of hydrogen permeation barrier on the surface of zirconium hydride. *Rare Met.* **2008**, 27, 473-478.
- [20] Wu, M.; Peng, J.Q.; Yan, G.Q.; Chen, Y.; He, Z.Y.; Xu, Z.G.; Wang, L.J. Preparation and properties of composite hydrogen permeation barrier on ZrH<sub>1.8</sub> by sol-gel technique. *Surf. Coat. Technol.* **2018**, 352, 159-165. <https://doi.org/10.1016/j.surfcoat.2018.07.079>.
- [21] Duffin, T.G.; Palomares, K.B.; Zinkle, S.J. Characterization of Yttria-Stabilized Zirconia (YSZ) following high temperature hydrogen exposures of molybdenum-YSZ composites. *J. Nucl. Mater.* **2024**, 591, 154894. <https://doi.org/10.1016/j.jnucmat.2023.154894>.
- [22] Zhang, Y.F.; Wang, T.Y.; Mei, L.; Yang, R.J.; Guo, W.W.; Li, H.; Zeng, Z.Y. Rational Design of Cost-Effective Metal-Doped ZrO<sub>2</sub> for Oxygen Evolution Reaction. *Nano-Micro Lett.* **2024**, 16, 180. <https://doi.org/10.1007/s40820>.
- [23] Liu, L.; Chu, C.; Chen, C.; Huang, S. MarineYOLO: Innovative deep learning method for small target detection in underwater environments. *Alexandria Eng. J.* **2024**, 104, 423-433. <https://doi.org/10.1016/j.aej.2024.07.126>.
- [24] Wang, X.; Zhao, P.; Yue, S.; Gu, Y. An improved cross algorithm edge detection method and its application in coal gangue identification. Available online: <http://www.tandfonline.com/doi/full/10.1080/19392699.2025.2481147>.
- [25] Yin, X.; Chen, L. Image Object Detection Method Based on Improved Faster R-CNN. *J. Circuits Syst. Comput.* **2024**, 33. <https://doi.org/10.1142/s0218126624501305>.
- [26] Zheng, L.; Xu, A.M.; Li, F.; Zhang, Y.; Liu, Y.; Chen, W.D.; Wu, M. Improving Hydrogen Permeation Resistance in Ultrathin ZrO<sub>2</sub> Coating via Y Dopant Tuning. *ACS Appl. Mater. Interfaces* **2025**, 17, 50011-50023. <https://doi.org/10.1021/acsami.5c11792>.
- [27] Ehrhart, G.; Capoen, B.; Robbe, O.; Boy, Ph.; Turrell, S.; Bouazaoui, M. Structural and optical properties of n-propoxide sol-gel derived ZrO<sub>2</sub> thin films. *Thin Solid Films* **2006**,

- 496, 227-233. <https://doi.org/10.1016/j.tsf.2005.08.309>.
- [28] Li, Z.L.; Kang, Y.X.; Yan, S.F.; Yang, S.H.; Chen, W.D.; Guo, C.X.; Ma, W. Enhanced hydrogen barrier performance of  $\text{ZrH}_{1.8}$  via yttria-zirconia composite film developed through the ECD-MAO technique. *Corros. Sci.* **2024**, *232*, 112013. <https://doi.org/10.1016/j.corsci.2024.112013>.
- [29] Wu, J.M.; Xie, J.Q.; He, M.Y.; Zhang, J.Y.; Li, S.J. Yttria-Stabilized Zirconia Composite Coating as Barrier to Reduce Hydrogen Permeation into Steel. *Materials* **2024**, *17*, 3017. <https://doi.org/10.3390/ma17133017>.
- [30] Wang, W.K.; Yan, G.Q.; Zhang, J.D.; Ma, Z.H.; Wang, L.J.; Guo, Z.C.; Zhang, S.L.; Wu, Y.K. Hydrogen Permeation Behavior of Zirconium Nitride Film on Zirconium Hydride. *Materials* **2022**, *15*, 550, <https://doi.org/10.3390/ma15020550>.
- [31] Laadel, N.-E.; El Mansori, M.; Frederich, N.; Marlin, S. On processing technologies of ceramic coatings for hydrogen-isotope permeation barriers. *Ceram. Int.* **2025**, *51*, 10247–10261, <https://doi.org/10.1016/j.ceramint.2025.01.394>.