Article

Hydrogen Isotope Permeation Behavior of AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi High-Entropy Alloys Coatings

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Abstract: The hydrogen permeation behavior of novel AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi high-entropy alloy (HEA) coatings were investigated. The hydrogen permeability of HEA coatings prepared by magnetron sputtering technology were tested using gas-driven deuterium permeation and electrochemical hydrogen permeation methods. The gas-driven permeation results show that the deuterium permeation resistance of the AlCrFeTiNb coating is the worst because of the unstable structure at a high temperature. Scanning electron microscope (SEM) and X-ray Diffraction (XRD) analysis proved a loose surface morphology of the AlCrFeTiNb coating and demonstrated the formation of iron-based oxides after deuterium permeation experiments. A high content of iron in HEA coating is disadvantageous for improving the hydrogen permeability. Differently, electrochemical hydrogen permeation reveals that the AlCrMoNbZr coating could resist hydrogen permeation better in a corrosive environment (0.2 mol/L KOH solution). The AlCrFeMoTi coating was peeled off after an electrochemical hydrogen permeation test due to the poor corrosion resistance. The hydrogen behavior of HEA coatings was discussed in detail. Our study provides a promising thought on hydrogen permeation of HEA coatings.

Keywords: high-entropy alloy coatings; gas-driven permeation; electrochemical hydrogen permeation; corrosion

Citation: Hong, Z.; Wang, L.; Zhang, W.; Yang, J.; Feng, Y.; Yang, J.; Li, H.; Yin, H.; Zhang, L.; Wang, X.

Hydrogen Isotope Permeation

Behavior of AlCrFeTiNb,

AlCrMoNbZr and AlCrFeMoTi

High-Entropy Alloys Coatings.

Coatings **2022**, *12*, 171. [https://](https://doi.org/10.3390/coatings12020171)

doi.org/10.3390/coatings12020171

Academic Editors: Ivan Shorstkii and Evgeny Sokolov

Received: 31 December 2021

Accepted: 24 January 2022

Published: 28 January 2022

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1. Introduction

Fusion reactors are fueled by hydrogen isotopes, including deuterium and tritium. As a result of a small atomic radius and high activity, it is easy for hydrogen isotope atoms to diffuse through metal materials by tetrahedral interstices or octahedral interstices, especially for the structural material of a tritium breeder blanket, where lithium atoms combined with fusion neutrons for producing tritium. Due to hydrogen isotope permeation and retention, the mechanical properties, service stability and service life of structural materials can be degraded. To avoid potential safety accidents, the permeation of hydrogen isotopes through a structural material should be controlled to the limit. As far as we concerned, the common practice is to prepare a tritium permeation barrier on the surface of the structural materials.

Tritium barrier coatings are generally divided into three groups: oxide coatings, non-oxide coatings and composite coatings. Among oxide coatings (Cr₂O₃, Y₂O₃, Al₂O₃, TiO₂, Er₂O₃ and SiO₂, etc.), α -alumina shows great potential [1], but the phase formation temperature can reach 1200 °C [2], which will degrade the mechanical properties of the

substrate materials [3,4]. For non-oxide coatings (TiN, TiC and SiC, etc.) and composite coatings ($\text{Cr}_2\text{O}_3/\text{SiO}_2$, $\text{Al}_2\text{O}_3/\text{SiO}_2$, $\text{Al}_2\text{O}_3/\text{SiC}$, $\text{Er}_2\text{O}_3/\text{Al}_2\text{O}_3/\text{W}$ [5,6]), cracking can still be a problem due to the misfit between the substrate and coating or sub-layers, which is disadvantageous for improving the hydrogen permeability. Thus, it is urgent to explore new tritium permeation barriers, as the existing coatings still need to be further developed to meet the application requirements for future commercial fusion reactors.

High-entropy alloys are novel systems [7,8], which contain at least five main elements, and the atomic percentage of each main element is between 5 at% and 35 at%. As a result of special effects [9], including a lattice distortion effect, cocktail effect, hysteresis diffusion effect and high-entropy effect, high-entropy alloys behave with superior mechanical properties [10–13], good corrosion resistance [14,15] and good irradiation stability [16–19]. Recently, high-entropy alloy coatings, which behave with an outstanding comprehensive performance, have also been developed. Zhang Wei et al. [20] studied the preparation, structure and properties of an AlCrMoNbZr HEA coating; the nano-indentation test showed that the hardness of the coating was 11.8 GPa, and the coating had good hydrophobicity and corrosion resistance. Nagase et al. [21] prepared a nanocrystalline CoCrCuFeNi HEA coating, which can remain in a constituent phase when irradiated to 40 dpa at a temperature range from 25 to 500 °C. Li et al. [22] studied the NbMoCrTiAl HEA coating, and its compressive fracture strength is significantly improved (1542 MPa). However, studies on the hydrogen permeability of HEA coatings was limited besides our recent work [23]. We reported an AlCrTaTiZr coating, which can serve as a hydrogen permeation barrier [23]. However, the hydrogen permeability of other HEA coatings with different main elements is unknown at present and needs to be further studied.

In this study, three new types of AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi HEA coatings were prepared on a CLF-1 substrate by magnetron sputtering. The hydrogen isotope permeation behavior of HEA coatings was analyzed by electrochemical hydrogen permeation and gas-driven permeation methods. The morphology and microstructure of the HEA coatings were characterized in detail.

2. Materials and Methods

2.1. Materials and Coating Preparation

The substrate material chosen in this experiment was CLF-1 steel (8.5% Cr, 1.5% W, 0.3% V, 0.5% Mn, 0.08% Ta and the balance Fe), which has been researched and developed by the Southwestern Institute of Physics (SWIP) [3]. The disc specimens with a diameter of 12 mm and a thickness of 0.5 mm are used in deuterium permeation experiments and another shape of the disc specimens with a diameter of 29 mm and a thickness of 0.5 mm for electrochemical hydrogen permeation experiments. Before coating, the substrates were first polished to a mirror finish, and cleaned in acetone and ethanol by an ultrasonic bath. Then, three kinds of HEA coatings were deposited on the CLF-1 steel substrate by a radio frequency (RF) magnetron sputtering technique. Three types of alloy targets, including AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi, were used. Etching cleaning of the target surface was also done with Ar ions in the chamber before deposition. The distance between the sample holder and metal targets was maintained at 9 cm. The background pressure was 8.0×10^{-4} Pa before the experiments. The flow rate of Ar gas was fixed at 48 standard cubic centimeters per minute (sccm). The sputtering deposition power was 200 W, and the sputtering time was 2 h for HEA coatings to ensure a certain thickness of the high-quality coating. An annealing treatment of HEA coatings was performed at 600 °C for 1 h in an Ar gas atmosphere.

2.2. Deuterium Permeation Experiment and Methods

Gas-driven deuterium permeation experiments were carried out for the three types of HEA coatings and the uncoated CLF-1 steel. Deuterium was introduced into the upstream chamber at pressures ranging from 50 kPa to 100 kPa, and the measurement temperature

was 500–600 °C. A detailed description of the procedure was described in our previous paper [23].

When the diffusion reaches a steady state ($t \rightarrow \infty$), the permeation flux of deuterium through a material can be expressed as follows:

$$J_{\infty} = \frac{\Phi}{l} (P_{in}^n - P_{out}^n) \quad (1)$$

J_{∞} is deuterium permeation flux, $\text{Pa} \cdot \text{m}^3/\text{s}$. l is film thickness and m . Φ is the permeability of deuterium through the material, $\text{mol}/(\text{m} \cdot \text{s} \cdot \text{Pa}^n)$. P_{in} is deuterium pressure at the input side of the upstream. P_{out} is deuterium pressure at the output side of downstream (in this experiment, $P_{in} \gg P_{out}$, P_{out} can be regarded as 0 Pa). n is a constant for deuterium in a certain material, which is defined as 0.5 for a diffusion-limited process and is 1 for a recombination reaction-limited process.

I (ion current) has a liner relation with the permeation flux (J_{∞}); the expression is as follows:

$$J_{\infty} = \lambda I \quad (2)$$

2.3. Electrochemical Hydrogen Permeation

The hydrogen permeation measurements were performed using an electrochemical cell (Devanathan–Stachurski double electrolyzer model [24]). A sample was sandwiched between the cathode chamber and anode chamber; the hydrogen charging side facing the coating was the cathode chamber, and the hydrogen permeation side facing the polished surface was the anode chamber. Each unit was filled with 0.2 mol/L KOH solution. Saturated Ag/AgCl reference electrodes and Pt counter electrodes were used as auxiliary electrodes. The property of hydrogen permeation resistance of the material could be evaluated by the steady-state current density.

2.4. Characterization

The phase structure of the coatings was analyzed by grazing incidence X-ray diffraction (GIXRD, Empyrean, PANalytical, Zaragoza, Spain), with an incidence angle of 1°. The microstructure and chemical composition of the samples were characterized by a field emission scanning electron microscope (FESEM, Inspect F50, FEI, Hillsboro, OR, USA). The chemical composition of the coatings was identified by using energy dispersive X-ray spectrometry (EDS, Octane Super, EDAX, Pleasanton, CA, USA).

3. Results and Analysis

3.1. Gas-Driven Permeation Results

Figure 1a–c shows the deuterium ion current–time curves at different temperatures and gas pressures. All coatings used for hydrogen permeation experiments had the same thickness. The details of the preparing parameters are presented in our previous paper [23]. The deuterium ion current–time curve formed a platform, indicating that the permeation process reached a steady state. By comparing with the uncoated CLF-1 steel, the permeation reduction factor (PRF) of the AlCrFeMoTi coatings was calculated to be 63 at a temperature of 600 °C [25]. It indicates that the deuterium permeability of the HEA coating should be further improved by optimizing the structure and composition. We also observed a slight decrease of the deuterium ion current for AlCrMoNbZr and AlCrFeMoTi coatings at a temperature of 600 °C with D_2 pressure of 30 kPa, as shown in Figure 1c, which attributes to crystallization [26,27] and a trap site effect [28]. Compared with AlCrFeTiNb and AlCrMoNbZr, the AlCrFeMoTi coating had a much lower deuterium ion current intensity under all different testing conditions, which indicates that the AlCrFeMoTi coating has a better deuterium permeation resistance.

Figure 1. Deuterium ion current–time curves of the HEA coatings at different temperatures and gas pressures. (a) 500 °C, 30–70 kPa. (b) 550 °C, 30–70 kPa. (c) 600 °C, 30–70 kPa.

The pressure exponents of the coatings calculated by Equation (1) are shown in Figure 2. The results show that the pressure exponent (n) of the HEA coatings is higher than 0.5. It demonstrates combined diffusion- and recombination-limited processes [29,30] for the AlCrFeMoTi and AlCrMoNbZr coatings during permeation at different temperatures. For the AlCrFeTiNb coating, the pressure exponent n is close to 1, indicating a recombination-limited process. Therefore, HEA coatings with a different chemical composition behave with distinguishing deuterium permeation behavior. More research should be conducted to obtain a better understanding of HEA coatings' hydrogen isotope permeation behavior in the future. As hydrogen is easily absorbed by Ti and Nb [25], that recombination becomes the controlled process for the AlCrFeTiNb coating during permeation.

3.2. SEM Analysis

Figure 3(a₁–c₁) shows the surface morphologies of AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi coatings before deuterium permeation tests. As Figure 3(a₁) depicts, the surface of the coating presents irregular particles with a size of 30–60 nm. The coating surface shown in Figure 3(b₁,c₁) has even finer particles, despite the scratches of the substrate formed during polishing. Figure 3(a₂–c₂) shows the surface morphologies of AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi coatings after deuterium permeation tests. There are no cracks and voids on the coating surface, suggesting a good adhesion of the coatings. It is obvious that the surface of the AlCrFeTiNb coating became much coarser after deuterium permeation. By contrast, no obvious changes could be observed

for AlCrMoNbZr and AlCrFeMoTi coatings, except some small particles. Therefore, the structures of AlCrMoNbZr and AlCrFeMoTi coatings are more stable in a high temperature environment, which could be reason for the better deuterium permeation resistance shown in Figure 1.

Figure 2. Driving pressure dependence of deuterium permeation ion current for AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi coatings at a temperature of 500 °C.

Figure 3. Surface Scanning Electron Microscopy (SEM) images of samples. (a₁–c₁) AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi coatings before deuterium permeation. (a₂–c₂) AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi coatings after deuterium permeation.

3.3. EDS Analysis

Figure 4 shows EDS results of AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi coatings before and after deuterium permeation tests. The elements were homogeneously distributed and demonstrated a homogeneous HEA coating formed on the CLF-1 steel. Table 1 shows

the surface chemical compositions before and after deuterium permeation tests of AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi coatings. As Table 1 presents, there were negligible differences in the elemental composition of the AlCrMoNbZr and AlCrFeMoTi coatings before and after deuterium permeation tests. It proves that AlCrMoNbZr and AlCrFeMoTi coatings have good structural stability at a high temperature, which is consistent with the SEM results shown in Figure 3. In particular, it can be seen that the oxygen content in the AlCrFeTiNb coating increased significantly after deuterium permeation tests. Oxidation of AlCrFeTiNb coatings occurred during deuterium permeation. Compared to AlCrMoNbZr and AlCrFeMoTi coatings, the AlCrFeTiNb coating is more sensitive to oxygen.

Figure 4. Surface EDS images of samples. (a₁–c₁) AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi coatings before deuterium permeation. (a₂–c₂) AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi coatings after deuterium permeation.

Table 1. Surface chemical compositions of HEA coatings before and after deuterium permeation tests. The values are in weight percent (wt%).

Samples		Elements Contents					
		Al	Cr	Nb	Ti	Fe	O
AlCrFeTiNb	As-deposited	7.86	20.94	20.18	13.97	36.83	-
	After permeation test	6.67	16.73	16.66	11.64	29.99	18.31
AlCrMoNbZr	As-deposited	6.71	17.24	26.46	26.97	22.61	-
	After permeation test	6.99	17.50	25.99	27.41	22.12	-
AlCrFeMoTi	As-deposited	10.90	19.94	30.38	14.81	23.97	-
	After permeation test	9.90	20.30	29.90	15.95	23.95	-

3.4. XRD Analysis

Figure 5a,b shows the XRD characterization results of AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi coatings before and after deuterium permeation tests. Figure 5a shows a similar broad peak at a diffraction angle of 35–45°, indicating an amorphous nanocrystalline structure of all coatings [31]. It is noted that new diffraction peaks appeared for the AlCrFeTiNb coating after deuterium permeation, as shown in Figure 5b. It proves that the structure of the AlCrFeTiNb coating was changed after a gas-driven permeation test. The newly occurred peaks were indexed to be $(\text{Fe, AlCrTiNb})_x\text{O}_y$, being corresponding with the EDS results. The increase of Fe content is not good for improving the hydrogen permeation resistance due to the loose morphology of iron oxides. In other words, the hydrogen permeability of HEA coatings depends on its principal elements and structure.

Figure 5. XRD patterns of three HEA coatings before deuterium permeation (a) and after deuterium permeation (b).

3.5. Electrochemical Hydrogen Permeation Analysis

An electrochemical hydrogen permeation method was used to test the high temperature effect on the hydrogen permeability of the coatings. Figure 6a–c is the hydrogen permeation current density–time curves of AlCrFeMoTi, AlCrFeTiNb and AlCrMoNbZr coatings at 25 °C, respectively. The steady-state hydrogen permeation current density of AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi coatings are approximately $1.0 \times 10^{-5} \text{ A}\cdot\text{cm}^{-2}$, $8.2 \times 10^{-6} \text{ A}\cdot\text{cm}^{-2}$ and $1.9 \times 10^{-5} \text{ A}\cdot\text{cm}^{-2}$, respectively. Therefore, the AlCrMoNbZr coating performed with better hydrogen permeation resistance at room temperature. Additionally, it took a longer time for AlCrFeTiNb and AlCrMoNbZr coatings to reach the steady-state hydrogen permeation current density.

The time-lag method [24] was used to calculate the hydrogen diffusivity.

$$D = \frac{L^2}{6t_L} \quad (3)$$

The time of t_L corresponds to the point on the permeation curve at which $i_t = 0.63 i_\infty$.

The hydrogen diffusivity in AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi coatings were calculated to be $3.89918 \times 10^{-8} \text{ cm}^2/\text{s}$, $1.82909 \times 10^{-8} \text{ cm}^2/\text{s}$ and $1.46404 \times 10^{-7} \text{ cm}^2/\text{s}$, as shown in Table 2. The AlCrMoNbZr coating had a good hydrogen permeation resistance, while the AlCrFeMoTi coating performed the worst, as it was different with gas-driven permeation results. Structural changes of HEA coatings at a high temperature should be considered.

Figure 6. Electrochemical hydrogen permeation curves of AlCrFeMoTi (a), AlCrFeTiNb (b) and AlCrMoNbZr (c), respectively.

Table 2. Hydrogen diffusivity of AlCrFeMoTi, AlCrFeTiNb and AlCrMoNbZr coatings in 0.2 KOH mol/L solution.

Sample	t_L (s)	Hydrogen Diffusivity (cm^2/s)
AlCrFeTiNb	10,686	3.89918×10^{-8}
AlCrMoNbZr	22,780	1.82909×10^{-8}
AlCrFeMoTi	2846	1.46404×10^{-7}

Furthermore, the surface morphologies of the coatings after electrochemical hydrogen permeation is presented in Figure 7a–c. It is obvious that the HEA coatings behaved different surface morphologies. The surface morphology of the AlCrMoNbZr coating was smooth and dense without cracks and pores. It suggests that the AlCrMoNbZr coating has a good corrosion resistance in 0.2 mol/L KOH solution. The coating with high chemical stability had a superior hydrogen permeation resistance. Pores formed on the surface of the AlCrFeMoTi coating, as shown in Figure 7c, demonstrating severe corrosion. After analyzing the EDS results, we demonstrated that the chemical compositions of AlCrFeTiNb and AlCrMoNbZr coatings stayed unchanged. However, the content of Fe in the AlCrFeMoTi coating was up to 89.17 wt%, and the content of Al, Ti and Mo was less than 1 wt%, as shown in Table 3. It seems that the AlCrFeMoTi coating was mostly peeled off in 0.2 mol/L KOH solution during the electrochemical hydrogen permeation test. In conclusion, the AlCrFeMoTi coating could not serve as an effective hydrogen isotope

permeation barrier in a strong alkali environment but had advantages in a high temperature working condition.

Figure 7. Surface SEM images of AlCrFeTiNb (a), AlCrMoNbZr (b) and AlCrFeMoTi (c) HEA coatings after electrochemical hydrogen permeation tests.

Table 3. EDS results of HEA coatings before and after electrochemical permeation tests. The values are in weight percent (wt%).

Samples		Elements Contents					
		Al	Cr	Nb	Ti	Fe	Al
AlCrFeTiNb	As-deposited	7.86	20.18	13.97	20.94	36.83	7.86
	After permeation test	7.62	20.67	13.84	20.89	36.97	7.62
AlCrMoNbZr	As-deposited	6.71	22.61	26.46	26.97	17.24	6.71
	After permeation test	6.53	22.77	25.02	27.94	17.75	6.53
AlCrFeMoTi	As-deposited	10.90	14.81	23.97	30.38	19.94	10.90
	After permeation test	0.57	0.14	89.17	0.43	9.80	0.57

4. Conclusions

In this work, AlCrFeTiNb, AlCrMoNbZr and AlCrFeMoTi HEA coatings were prepared by RF magnetron sputtering on CLF-1 steel substrates. The hydrogen isotope permeability of HEA coatings were tested using gas-driven deuterium permeation and electrochemical hydrogen permeation methods. The gas-driven deuterium permeation results show that the deuterium permeation resistance of the AlCrFeTiNb coating was the worst because of the unstable structure at a high temperature. SEM and XRD analyses proved a loose surface morphology and demonstrated the formation of iron-based oxides after deuterium permeation experiments. A high content of iron in an HEA coating is disadvantageous for improving the hydrogen isotope permeability. Differently, electrochemical hydrogen permeation reveals that the AlCrMoNbZr coating could resist hydrogen permeation better in a corrosive environment (0.2 mol/L KOH solution). The AlCrFeMoTi coating was peeled off after an electrochemical hydrogen permeation test due to the poor corrosion resistance. The hydrogen isotope permeability of HEA coatings also depends on structural stability and corrosion resistance.

Author Contributions: Conceptualization, L.W.; Funding acquisition, L.W.; Investigation, H.L.; Methodology, W.Z.; Resources, W.Z. and J.Y. (Jian Yang); Supervision, L.W., Y.F. and J.Y. (Jijun Yang); Writing—original draft, Z.H.; Writing—review & editing, L.W., H.Y., L.Z. and X.W. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by Innovation Program of SWIP (No.201901XWCXRC013) and the National Natural Science Foundation of China (Grant No.12005051).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data sharing is not applicable to this article.

Conflicts of Interest: The authors declare no conflict of interest.

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