Research Article

Study on the Influence of Introducing Al Transition Layer on Deuterium Resistance of Al_2O_3 Coating

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The $\text{Al}/\text{Al}_2\text{O}_3$ composite deuterium barrier was deposited on the polished side of 316 L stainless steel by the method of radio-frequency magnetron sputtering. The influence of the introduction of Al transition layer on the deuterium resistance performance of Al_2O_3 ceramic coating was studied. The field emission scanning electron microscope (SEM), the grazing incident X-ray diffraction technique (GIXRD), and the auger electron spectroscopy (AES) were used to analyze the microscopic morphology, phase, and element distribution in the depth direction of the $\text{Al}/\text{Al}_2\text{O}_3$ coating, and the gas-driver permeation method was used to measure the deuterium permeation behavior of the coating sample. The results show that Al_2O_3 is amorphous after annealing at 873 K. Due to the oxidation of the Al transition layer, the connection between the coating and the substrate is tightly connected. Under the combined action of permeation temperature and pressure of 873 K and 80 kPa, the deuterium permeability of $\text{Al}/\text{Al}_2\text{O}_3$ coating is $6.35 \times 10^{-14} \text{ mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-0.5}$, which shows that the $\text{Al}/\text{Al}_2\text{O}_3$ coating has excellent deuterium permeation resistance. Furthermore, deuterium permeability of the $\text{Al}/\text{Al}_2\text{O}_3$ coating was diminished by about 2 orders of magnitude compared with 316 L stainless steel, and it is reduced 2~3 times compared with the single Al_2O_3 coating sample. The study indicates that the introduction of the Al transition layer can significantly enhance the barrier effect of the $\text{Al}/\text{Al}_2\text{O}_3$ coating sample.

1. Introduction

Nuclear energy, as a clean energy source, has been received extensive attention in recent decades. For nuclear fusion reactions, deuterium and tritium with tiny atomic radius have the very strong permeability in metallic structure materials, which will lead to hydrogen embrittlement and surface corrosion of the materials. In fusion power plants, tritium with high radioactivity, as a fusion fuel, contacts directly with the inner wall of the vessels and pipes. The high permeation and leakage of tritium not only lead to waste of nuclear fuel but also could cause radioactive contamination to the surroundings. Therefore, the suppression of tritium permeation is required in the operation process. The preparation of tri-

tium permeable barriers (TPBs) on the inner wall of metallic structural materials has been considered a promising solution. A large number of research show that the ceramic coatings, including Al_2O_3 [1–3], Y_2O_3 [4–6], Er_2O_3 [7–9], Cr_2O_3 [10], other metal oxide coatings, AlN [11] and Si_3N_2 , other nitride coatings, TiC and SiC [12], and other carbide coatings and their composite coatings, have been demonstrated to be beneficial to reduce tritium permeation flow. Among these TPBs, the Al_2O_3 ceramic coating, as a promising candidate, has been attached much more attention because of its high permeation resistance performance, outstanding compatibility with Pb-Li, good thermal stability with irradiation and corrosion resistance, and excellent comprehensive properties [13–16]. However, the structure of Al_2O_3 ceramic coating is

not compact, there are microcracks being located in it, the internal stress is large, and when the coating is thicker, its bonding with substrate is not firm because of the characteristics of the ceramic material itself, making it unable to withstand the test of high temperature thermal shock cycle. By introducing Al metal transition layer, not only can the bonding force between the coating and substrate be enhanced but also the high temperature stability can be improved.

In this work, the Al/Al₂O₃ composite coating was deposited on the polished side of 316 L stainless steel by physical vapor deposition (PVD) and radio-frequency magnetron sputtering. The microstructure, phase, and element distribution in depth of the coating with before and after deuterium permeation measurement were separately investigated. More importantly, the influence of the introduction of the metal transition layer on the deuterium resistance of the Al₂O₃ ceramic coating and the permeation mechanism of deuterium in the Al/Al₂O₃ composite coating have been studied, which provide experimental support for subsequent coating design.

2. Experimental Details

2.1. Preparation of Samples. The disk-shaped 316 L stainless steel samples were cut from the mechanical polishing 316 L stainless steel plate with mechanical polishing. The samples size specification was $\Phi 29 \times 0.5$ mm. Before preparing the coating, the bare samples were orderly washed with acetone, deionized water, and absolute ethanol for 10 min in the ultrasonic cleaner. Then these samples were blown to be dry for use. The method of radio-frequency magnetron sputtering was used to deposit Al/Al₂O₃ composition coatings at room temperature on the one side of the mirror-polished 316 L stainless steel substrates. The Al₂O₃ ceramic target and Al metal target were chosen in this work. The base pressure is about 2×10^{-4} Pa in a magnetron sputtering chamber. When the Al transition coating was deposited, argon with a purity of 99.999% was introduced into the chamber, where the total gas pressure was maintained at the set point, that was ignited to the argon plasma with a power density of $4.98 \text{ W}\cdot\text{cm}^{-2}$ by radio-frequency power. The method of Al₂O₃ coating deposition is similar to the previous research, and the specific preparation process parameters were shown in the previous study [17]. Table 1 shows the specific process parameters by radio-frequency magnetron sputtering, which has a serious impact on the quality of coating. The coated samples were heat treated in vacuum tube furnace for 2 h at 873 K to eliminate inherent stress generated by the coating during the deposition process.

2.2. Permeation Flux Measurement. Tritium has strong radioactivity, and the abundant hydrogen in the atmosphere will affect the measurement results. Thus, deuterium was selected as the permeate gas. The deuterium permeation property was measured by the gas-driven permeation method. An experimental equipment was set up to carry out the permeation measurement in this work. The sample was sealed with two O-ring copper gaskets, whose inside diameter, outside diameter, and thickness were 17 mm,

29 mm, and 0.5 mm, respectively. The effective permeation area was calculated to be $1.43 \times 10^{-3} \text{ m}^2$ by measuring impression of the seal gaskets on the sample after permeation measures. Prior to the measurement, the uncoated side of the samples was polished with an abrasive paper in order to remove the oxide layer, which ensured the accuracy of the experiment. The sample was mounted in a resistance furnace to maintain constant temperature. A thermocouple was inserted through a hole in order to directly contact with the sample room to monitor the sample temperature in real time. The measurement temperature range was between 773 K and 873 K. The specific experimental steps and process parameters were detailed in Ref. [17].

2.3. Characterization Methods. The microtopography of the Al/Al₂O₃ composite coating was observed by the field scanning electron microscope (SEM, Hitachi-S4800). The crystallographic properties of the composite coating were analyzed using Grazing incidence X-ray diffraction (GIXRD, SmartLab 9 kW), and the incidence angle was 3° . The element distribution in depth of the coating was analyzed by the auger electron spectroscopy (AES, PHI-700), and the sputtering rate was 15 nm/min.

3. Results and Discussion

3.1. Microstructure and Phase. Low deuterium permeation requires dense structure and integrity of the coatings [18, 19]. In the previous measurements, it was found that the thickness of the coating was basically similar when the coatings were deposited on the surface of the 316 L stainless steel and Si wafer for the same batch of samples. Therefore, the Si substrate sample was used to characterize the microstructure of the coating. The surface and cross-section morphology of the deposited Al/Al₂O₃ coating are shown in Figure 1. From the surface image (Figure 1(a)), the coating is compact and dense. There are no cracks and voids on the surface of the coatings. The composite layer with a fairly uniform thickness of 542 nm can be observed from Figure 1(b), of which the Al transition layer and Al₂O₃ ceramic coating have the thickness of 135 nm and 407 nm, respectively. The interface of Al/Al₂O₃ composite coating is clear, and the coating has good adhesion with substrate. However, due to different coating preparation methods in applications, there are differences in the optimal thickness range. But it must be ensured that the coating structure is dense and has good adhesion to the substrate.

Figure 2 shows the EDS spectrum of the element distribution along the depth direction and the element weight percent. It can be seen from Figure 2 that the Al element showed an increasing trend. When the scanning distance was 400 nm, reaching the Al metal transition layer, the Al element was basically stable, and the O element content dropped sharply. When scanning to the Si substrate, the content of Si increases, and the content of Al and O decreases. However, it can be seen from the element weight percent located in the lower right corner of Figure 2 that when the EDS was used to analyze the element content, it cannot be accurately detected because it is affected by the carbon

TABLE 1: The specific process parameters of coating preparation by radio-frequency magnetron sputtering.

Process parameters	Coating	
	Al	Al ₂ O ₃
Target type	Metal	Ceramic
The target diameter (mm)	101.5	101.5
The target-substrate distance (mm)	75	75
The base pressure (Pa)	2×10^{-4}	2×10^{-4}
The sputtering power (W)	250	350
The sputtering power density ($\text{W} \cdot \text{cm}^{-2}$)	4.98	6.67
Coating deposition pressure (Pa)	0.5	0.5
Sputtering atmosphere and flow (sccm)	Ar (5 N) = 20	Ar (5 N): O ₂ = 20 : 1
Coating deposition time (h)	0.5	6

FIGURE 1: SEM images of the Al/Al₂O₃ composite coating: (a) surface and (b) cross-sectional. FIGURE 2: The AES spectrum of Al/Al₂O₃ coating in depth element distribution.

element. The subsequent element content test was carried out by AES.

In addition, the deuterium permeation properties of the coating are influenced on the crystal structure. The GIXRD

spectra of Al/Al₂O₃ composite coating are shown in Figure 3, which includes three different state spectra, respectively, the deposited, the annealed, and the deuterium permeation measured. The peaks of the crystalline Al₂O₃ were not observed, which indicated that the coating was still amorphous after the 873 K high temperature measurement. However, compared with the deposited samples, the peaks corresponding to the (111) and (311) orientations of the Al metal transition layer disappeared, indicating that the Al metal transition layer was oxidized during the permeation measurement process. Comparing the annealed and deuterium penetration measured samples, there is no new diffraction peak in the XRD spectrum, which indicates that the coating structure has basically reached a stable state after the high temperature anneal. Besides, the peaks marked with solid circles in the spectra correspond to the diffraction peaks of the 316 L stainless steel substrate.

3.2. Element Distribution. Figure 4 shows the element distribution along the depth direction of the Al/Al₂O₃ in three different states. The coating surface was etched for 5 nm before the measurement in order to avoid surface contamination. For the deposited coating, the atomic ratio of Al : O was about 1.4 in the top Al₂O₃ layer, which was slightly less than the stoichiometric ratio of 1.5. In the bottom metal transition layer, the content of O element became almost zero, and the content of Al element increased significantly. After

FIGURE 3: GIXRD spectra of the deposited, annealed and measured Al/Al₂O₃ composite coatings.

873 K anneal treatment, it can be seen from Figure 4(b) that the metal transition layer was completely oxidized to form Al₂O₃ coating. In addition, the atomic ratio of Al:O was 1.5, which met the stoichiometric. It can be seen that the atomic ratio of Al:O remains stable and is fairly constant throughout the coating after deuterium penetration measurement at the 773 K-873 K. Compared with the annealed coating and deuterium permeation measured coating, the atomic ratio of Al and O remained unchanged, so it was considered that the structure of the coating tends to be stable after annealing at 873 K, which is consistent with the analysis result of GIXRD in Figure 3. It is found that the thickness of the measured Al₂O₃ coating sample increases by about 50 nm compared with the annealed. The main reason is that the thickness of the diffusion layer between the coating and the substrate decreases due to the more complete oxidation of the Al element in high temperature, which can be seen from the decreasing slope of the O element.

The comprehensive analysis of the GIXRD and AES test results shows that the deposited coating is composed of an Al metal transition layer and an Al₂O₃ coating, and the coating interface is obvious. After 873 K annealing treatment, the Al metal transition layer was oxidized, but the coating was not completely oxidized because the Al metal phase was present in the coating. After 773 K-873 K high temperature deuterium permeation measurement, the Al metal transition layer disappears, the coating was completely oxidized, and the coating structure tended to be more stable.

3.3. Measurement of Deuterium Permeation. The permeability, as the most important factor in evaluating the quality of permeation barriers, was measured. It is noted that 3 to 5 samples are prepared per batch. To ensure the reliability and repeatability of the experimental data, at least three samples were used to measure deuterium resistance, and the average value was taken as the experimental value of permeability. Figure 5 shows the relationship curve of the deuterium ion flow through the Al/Al₂O₃ composite coating

sample with permeation time at 773 K-873 K. It can be seen from the curve in Figure 5 that the deuterium ion flow increased with increasing permeation temperature. The process of deuterium permeation was divided into two states, namely the permeation state and the steady state. For the permeation state, the slope of the curve represents the sensitivity of the coating to deuterium permeation. In terms of the curve of 773 K, its slope was not remarkable and the deuterium ion current changed slightly during the entire process. But the slope increased as the permeation temperature goes up. Because the temperature increases, the movement of deuterium atoms intensifies, which leads to an increase in the permeation ion current and a shorter time to arrive the steady state. The results show that the sensitivity of the coated samples to deuterium is enhanced at high temperatures.

Figure 6 displays the relationship curves between the logarithm of deuterium permeability and the inverse temperature for the Al/Al₂O₃ coating samples and the bare 316 L stainless steel substrate [10], and Al₂O₃ single coating samples are given in order to contrast. The logarithm of deuterium permeability changes linearly with the increase of permeation temperature at 773 K-873 K, which satisfies Arrhenius law. Compared with the bare 316 L stainless steel, the deuterium permeability of the Al/Al₂O₃ coating sample was decreased by about 2 orders, and it is reduced 2~3 times compared with the single Al₂O₃ coating sample. During the high temperature annealing process at 873 K, the metal Al layer was fully oxidized, which improves the tightness of the connection between the coatings, and it is beneficial to the release of high temperature thermal stress. Therefore, the densification of the coating structure can improve the deuterium resistance performance, and the high temperature stability can extend the service life of the coating to a certain extent.

With the permeation of deuterium in materials, it acts as a thermal activation process in a certain temperature range which satisfies the Arrhenius' equation [20].

$$P = P_0 \times e^{\left(-\frac{E_a}{RT}\right)}, \quad (1)$$

where P_0 is the permeation frequency factor ($\text{mol} \cdot \text{m}^{-1} \cdot \text{s}^{-1} \cdot \text{Pa}^{-n}$); E_a is the permeation activation energy ($\text{J} \cdot \text{mol}^{-1}$); R is the gas constant, equal to $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$; and T is the deuterium permeation temperature (K). Taking the logarithm of both sides of formula (1), formula (2) can be obtained. It can be seen from formula (2) that the logarithm of the permeability has a linear relationship with the reciprocal of the temperature, which verifies the accuracy of the experimental data in Figure 6.

$$\ln P = \ln P_0 - \frac{E_a}{RT}. \quad (2)$$

Levchuk et al. [21] prepared the Al-Cr-O thin coating as a deuterium permeation barrier on Eurofer. The results showed that deuterium permeability of the Al-Cr-O film was 1/3500~1/2000 of the Eurofer at 973 K. It is noted that

FIGURE 4: AES depth profile of the Al/Al₂O₃ composite film: (a) the deposited Al/Al₂O₃, (b) the annealed Al/Al₂O₃, and (c) the coating after deuterium permeation measured.

the deuterium permeability of the Al/Al₂O₃ coating in this work is not the best, compared with literature reports [15–21, 22]. The main reason is that the crystalline state of the coating has a certain impact on the deuterium resistance performance [7, 15]. The researches have shown that the coating has a good and stable crystalline state, then its deuterium resistance performance is stronger [15, 23], but the Al₂O₃ layer is amorphous in this work. Therefore, under the premise of ensuring the density and structural integrity of the coating, increasing the coating deposition temperature and subsequent heat treatment is aimed at obtaining crystalline Al₂O₃ coating in the next study.

4. Conclusion

Microstructure analyses and deuterium permeation experiments were carried out for the bare 316L stainless steel and the Al/Al₂O₃ coating samples prepared by radio-frequency magnetron sputtering. The Al₂O₃ coating of Al/Al₂O₃ composite coating was found to be amorphous by GIXRD. The coating was deposited densely, without cracks, holes, peeling, and other microscopic defects. In the direction perpendicular to the substrate, the interface between the metal transition layer and the Al₂O₃ ceramic layer was clear and tightly connected for the deposited

FIGURE 5: Deuterium ion current of Al/Al₂O₃ samples with different permeation temperature.

FIGURE 6: Deuterium permeability through the Al/Al₂O₃ coating and bare 316L stress steel as a function of the permeation temperature. The test deuterium permeation pressure is 80 kPa.

coating. The total thickness of the coating was 542 nm. After annealing at 873 K, the metal transition layer was oxidized and transformed into Al₂O₃ coating. The chemical composition of the coating remains stable before and after the deuterium penetration measurement. The deuterium permeation experiments of the coating show that the deuterium permeability of the Al/Al₂O₃ coating was decreased by about 2 orders of magnitude compared with 316L stainless steel, and it is reduced 2~3 times compared with the single Al₂O₃ coating sample. With the stable structure and the low permeability, the Al/Al₂O₃ film could be considered a promising tritium permeation barrier for blanket application in nuclear fusion reactions.

Data Availability

Some of the data used in this study are included within the article, and the rest are derived from the references that have been cited in the article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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