

Characterization of FeCrAlY Thin Film Deposited by Magnetron Sputtering and Its Corrosion Resistance under High-temperature Water Vapor Environment

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ABSTRACT: The work aims to deposit FeCrAlY thin film on Zr alloy substrate and use it as a protection layer to alleviate the corrosion under high-temperature water vapor environment. The FeCrAlY thin film was deposited on Zr and glass substrate via magnetron sputtering method. The XRD and SEM were used to characterize the structure and morphology of FeCrAlY thin film. The XPS was employed to investigate the valence states change before and after corrosion under high-temperature water vapor environment. The corrosion property of Zr and FeCrAlY thin film coated on Zr was tested under high-temperature water vapor environment of 900 °C. The results showed that FeCrAlY thin film coated on Zr displayed better anticorrosion property compared to Zr. The weight gain of FeCrAlY thin film coated on Zr was nearly 30% less than that of Zr. The FeCrAlY thin film deposited on Zr via magnetron sputtering method plays the role of protection layer under high-temperature water vapor environment. During the process of corrosion, Al₂O₃ passivation layer separates out with help of Cr because of “third element effect”. The separated Al₂O₃ layer plays as protection layer and inhibits corrosion.

KEY WORDS: magnetron sputtering; Zr alloy; FeCrAlY thin film; high temperature water vapor environment; Al₂O₃ passivation layer; corrosion property

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磁控溅射法制备 FeCrAlY 薄膜表征及其在高温水环境中的抗腐蚀性能研究

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摘要: 目的 在锆合金基底上沉积 FeCrAlY 薄膜, 研究其高温水蒸气环境中的抗腐蚀性能。方法 采用磁控溅射的方法在锆合金基底与玻璃基底上沉积 FeCrAlY 薄膜。使用 XRD、SEM 对沉积的 FeCrAlY 薄膜进行结构、形貌表征, 使用 XPS 对 FeCrAlY 薄膜高温水蒸气腐蚀前后的元素价态变化进行表征和分析。结果

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在 900 °C 高温水蒸气环境中测试了锆合金与锆合金沉积 FeCrAlY 薄膜的腐蚀性能。发现与锆合金相比, 锆合金沉积 FeCrAlY 薄膜的样品表现出了良好的抗腐蚀性能, 氧化增重少于锆合金样品的 30%。结论 磁控溅射法制备的 FeCrAlY 薄膜在高温水蒸气环境下对锆合金基底起到了很好的保护作用。高温水蒸气腐蚀过程中, 由于第三元素效应的发生, 即 FeCrAlY 薄膜中的铬元素促使铝元素析出到 FeCrAlY 薄膜表面, 在高温水蒸气环境下氧化生成氧化铝钝化膜, 氧化铝钝化膜起到了阻挡层的作用, 减缓了腐蚀的进行。

关键词: 磁控溅射法; 锆合金; 铁铬铝钇薄膜; 高温水蒸气环境; 氧化铝膜; 腐蚀性能

1 Introduction

Zr alloy, because of its excellent overall property, such as: good mechanical properties, anti-corrosion property and low thermal-neutron capture cross-section, had been chosen to use as cladding material in the thermal neutron reactors. However, Zr would rapidly oxidize under water vapor environment at high temperature when the coolant system was no longer efficient. At this time, the oxide layer of Zr would form, overall mechanical property would degrade, and Zr would react with hydrogen that formed ZrH₂, which was brittle product that could cause the Zr cladding crack. The mixture of hydrogen and oxygen in the air was source of explosive accident. In 2011, Fukushima nuclear leakage accident happened by this way^[1]. Since then, how to avoid hydrogen explosion and development of accident tolerant fuel became significant research topics in the nuclear security field^[2].

The long-term way for the cladding materials in the nuclear reactor was to find substituted materials. Now the candidate materials were FeCrAl alloy^[3], ODS steel^[4-6], Mo^[7-8] and SiC/SiC_f composite^[9]. Every material had its pros and cons. Before the above candidate materials came into the final application in the nuclear reactor, there were still many tests to be done in the future. The relevant nuclear security research, development and evaluation were also required. Under this background, surface coating on Zr was a short-term solution for cladding materials^[10]. FeCrAl and Cr were the metal candidates for the coating materials^[11-13]. FeCrAl, due to the good oxidation resistance exposed to the high temperature vapor, was considered the most promising coating material for the accident tolerant fuel (ATF) program^[14]. It had been attracted a lot of attention and widely investigated in the recent years.

In this manuscript, FeCrAlY thin film deposited on the Zr surface via magnetron sputtering approach along with different substrate temperature (room temperature, 200 °C, 400 °C). The corrosion resistance of Zr deposited with FeCrAlY thin film was studied under water vapor environment at high temperature. For the FeCrAlY thin film, due to the “third element effect”, Cr would accelerate Al to diffuse to the surface of

FeCrAlY thin film, and Al₂O₃ passivation layer would form with help of Cr under water vapor environment at high temperature. The existence of Y would promote to form stable α -Al₂O₃. The Al₂O₃ passivation layer was an effective layer to protect Zr alloy from corrosion^[15-21]. The high temperature water vapor corrosion test demonstrated that FeCrAlY thin film deposited on Zr substrate could efficiently slow the corrosion rate under water vapor environment at high temperature.

2 Experimental details

2.1 Deposition of FeCrAlY thin film

The Fe-18Cr-5Al-0.2Y target was prepared by vacuum melt, solidification. After material processing, the thickness of the Fe-18Cr-5Al-0.2Y target was 1 mm. The chemical composition was as follows: Fe 76.8%, Cr 18%, Al 5%, Y 0.2% (weight percent ratio). The Fe-18Cr-5Al-0.2Y thin film was deposited on Zr alloy substrate by magnetron sputtering method. The composition of Zr alloy was in the following: Sn 1.5%, Fe 0.2%, Cr 0.1%, O 0.013%, Zr 98.187%. The parameters for the Fe-18Cr-5Al-0.2Y thin film deposition were in the following. The voltage was 220 V, and the current was 1 A, and the sputtering time was 45 min. The thin film deposited on the Zr substrate at room temperature, 200 °C and 400 °C.

2.2 Characterization of FeCrAlY thin film

The FeCrAlY thin film sample was characterized by Scanning Electron Microscopy (SEM, FEI Inspect F50). The phase composition of the FeCrAlY thin film before and after corrosion was characterized by X-ray diffraction (XRD, RIGAKU D/max-2500PC) with CuK α radiation. The adhesive force between FeCrAlY thin film and Zr substrate was evaluated by measuring the adhesive strength. A Quad Group Sebastian Five tensile tester (Quad Group Inc, Spokane WA) was applied where a 2.7 mm diameter stud with a thin film of epoxy was bonded on FeCrAlY thin film. The valence states and depth profiles of the FeCrAlY thin film sample were estimated by X-ray photoelectron spectroscopy (XPS) with MgK α (1253.6 eV) and AlK α (1486.6 eV) twin anode X-ray using an ESCALAB250 system. The Ar⁺-ion repetitive bombarded etching was applied to obtain the quantification and valence states of the elements along the film depth. The sputtering rate was

0.1 nm/s for the Ar⁺-ion gun of 3 kV and 2 μ A. The FeCrAlY thin film deposited on the Zr substrate at room temperature was chosen to conduct the high temperature water vapor environment test. The detail water vapor corrosion test was performed at 900 °C for 8 hours. The pressure of the water vapor was 0.1 MPa. All the specimens for corrosion test were 15 mm \times 10 mm \times 1 mm.

3 Result and discussion

3.1 XRD analysis of FeCrAlY thin film deposited by magnetron sputtering method

Fig.1 displayed the structure of as-deposited FeCrAlY thin film on the Zr and glass substrate at room temperature, 200 °C and 400 °C. The FeCrAlY thin film deposited

on the Zr and glass substrate showed uniform cubic structure (Fig.1a, Fig.1b). Because the content of Y in the target was 0.2% (wt), it was too difficult to detect Y in thin film. Compared the as-sputtered FeCrAl and FeCrAlY thin film under the same sputtering condition, the main peaks of FeCrAlY shifted to the low angles (Fig.1c). It illustrated that the crystal cell of FeCrAlY was larger than the FeCrAl, which demonstrated that Y was in the thin film. The XPS result (Fig.1d) also proved above result. The 3d peaks at 156.5 eV and 157.7 eV showed that Y existed in the thin film. The adhesive force of the FeCrAlY thin film was tested, which were 76 MPa, 82 MPa, 84 MPa, respectively. It showed that the higher of the substrate temperature, the higher of the adhesive force for the thin film.

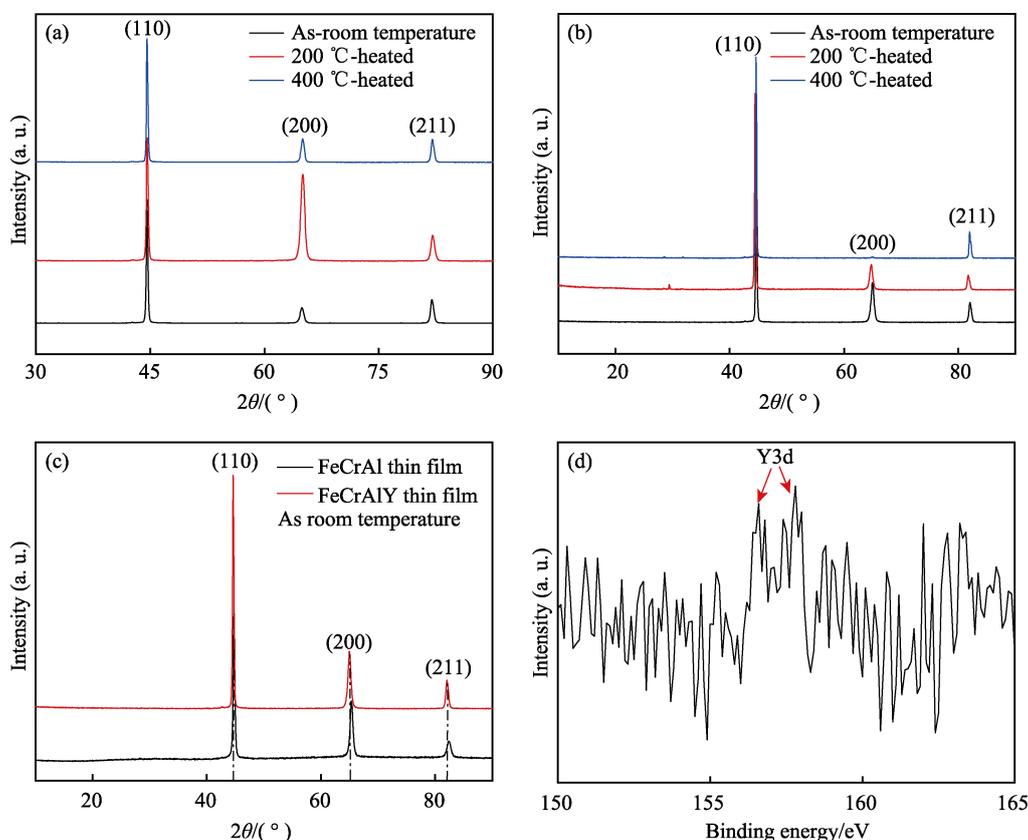


Fig.1 (a) XRD patterns of FeCrAlY thin film deposited on the Zr substrate, (b) XRD patterns of FeCrAlY thin film deposited on the glass substrate, (c) XRD patterns of FeCrAl and FeCrAlY thin film deposited on the Zr substrate, (d) Y 3d XPS peaks of FeCrAlY thin film

3.2 SEM analysis of FeCrAlY thin film

Fig.2 showed surface view and cross-section images of FeCrAlY thin film deposited on the glass and Zr substrate at room temperature, 200 °C and 400 °C. When the substrate temperature was higher for glass and Zr substrate, the grain grew larger in situ during the deposition process. From the images of surface view and cross-section, small pinholes could be seen (Fig.2k). It

illustrated that the higher deposited temperature was, the more pinholes were. The pinholes would become diffusion channel under high temperature and high pressure water vapor environment. The corrosion rate would accelerate. The role FeCrAlY thin film cannot efficiently protect Zr substrate from water vapor corrosion. When the temperature was high to deposit FeCrAlY thin film, the quality of the thin film was not good enough to protect Zr substrate to resist water vapor corrosion.

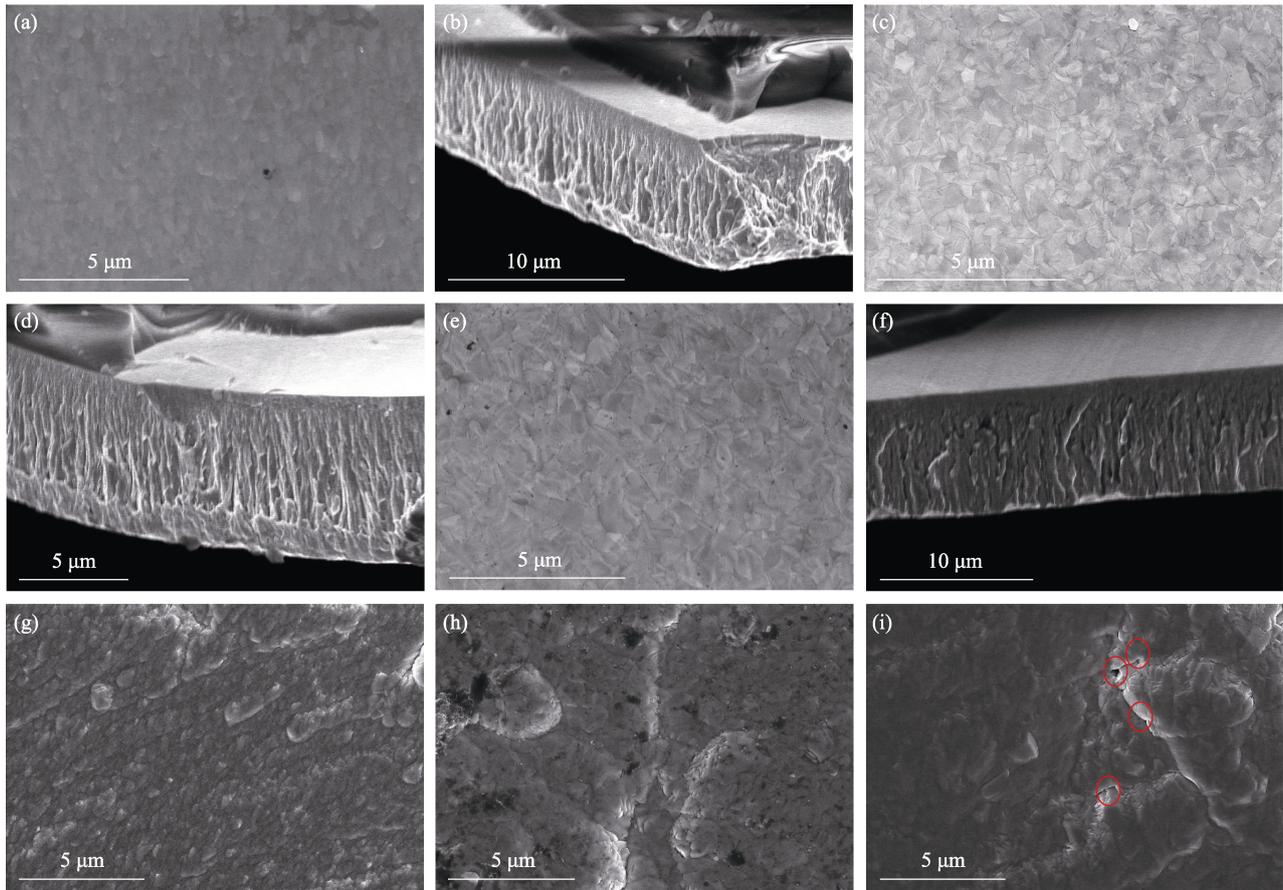


Fig.2 (a, c, e) Surface view images of FeCrAlY thin film deposited on the glass substrate at room temperature, 200 °C and 400 °C; (b, d, f) Cross-section images of FeCrAlY thin film deposited on the glass substrate at room temperature, 200 °C and 400 °C; (g, h, i) Surface view of FeCrAlY thin film deposited on the Zr substrate at room temperature (g), 200 °C (h) and 400 °C (i)

3.3 XRD analysis of FeCrAlY thin film after corrosion test at 900 °C water vapor environment

In the Fig.3, after corrosion test at 900 °C water vapor environment, metal oxide compounds, such as Al_2O_3 , Cr_2O_3 , Fe_2O_3 , and FeCr_2O_4 were formed. In the

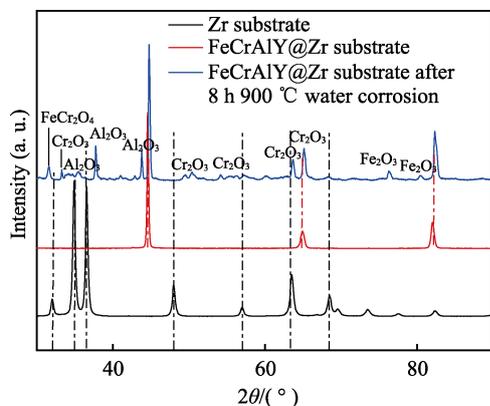


Fig.3 XRD patterns of Zr (black line), FeCrAlY thin film deposited on Zr substrate (red line), FeCrAlY thin film deposited on Zr substrate after 8 h water vapor corrosion test at 900 °C (blue line)

beneficial to alleviate the corrosion rate. According to previous work, the as-formed Al_2O_3 , Cr_2O_3 layer were the XRD pattern, the as-formed Al_2O_3 layer was $\alpha\text{-Al}_2\text{O}_3$. During the process of FeCrAlY thin film under water vapor environment at high temperature, metastable $\gamma\text{-Al}_2\text{O}_3$ was formed because $\gamma\text{-Al}_2\text{O}_3$ could exist at 550 °C. When the temperature elevated, they transformed to stable $\alpha\text{-Al}_2\text{O}_3$ ^[22-23]. As for Zr substrate with out FeCrAlY thin film, ceramic ZrO_2 was formed during the process of water vapor corrosion. However, when the FeCrAlY thin film was deposited on the Zr substrate, the as-formed metal oxide could retard corrosion rate, and the weight gain for the tested sample was smaller than the Zr sample in the Fig.6.

3.4 XPS analysis of FeCrAlY thin film after corrosion test at 900 °C water vapor environment

Fig.4 showed the element valence states of Fe, Cr, Al, respectively. It illustrated that after water vapor test at 900 °C for 8 hours, the Fe^{3+} , Cr^{3+} , and Al^{3+} formed. The three metal cations corresponded to the compounds of Fe_2O_3 , Cr_2O_3 , Al_2O_3 and FeCr_2O_4 . Under water vapor environment at high temperature, Fe, Cr, Al would oxi-

de by high temperature water vapor. The stable metal oxide could form. As for FeCrAlY thin film, the as-formed metal oxide would protect Zr substrate from water vapor corrosion. Among the as-formed metal oxide, Al_2O_3 played the key role because the Al_2O_3 was a kind

of robust metal oxide which possessed high corrosion resistant property. For the FeCrAlY alloy, the existence of Cr would accelerate Al to diffuse to the surface of thin film. This phenomenon was “the third element effect”. It had been demonstrated by the previous research^[22].

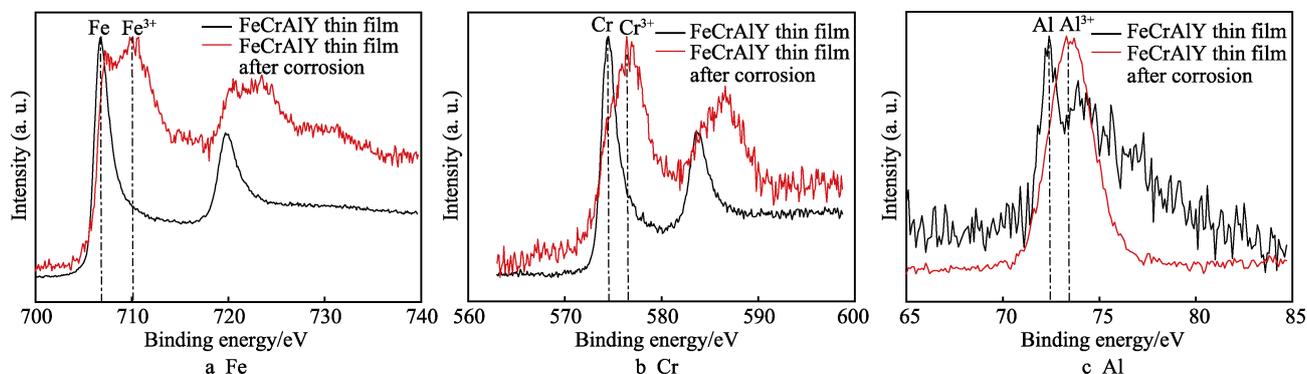


Fig.4 X-Ray photoelectron spectroscopy of FeCrAlY thin film before and after 8 h water vapor corrosion test at 900 °C

3.5 Elemental change with depth of FeCrAlY thin film before and after corrosion test at 900 °C water vapor environment

Fig.5 displayed the Fe, Cr, Al element content changed with surface depth. Because the content of Y was too small to detect, there was no Y element content changed in the Fig.5. As can be seen from the Fig.5a, the content of Fe was in good accordance with the

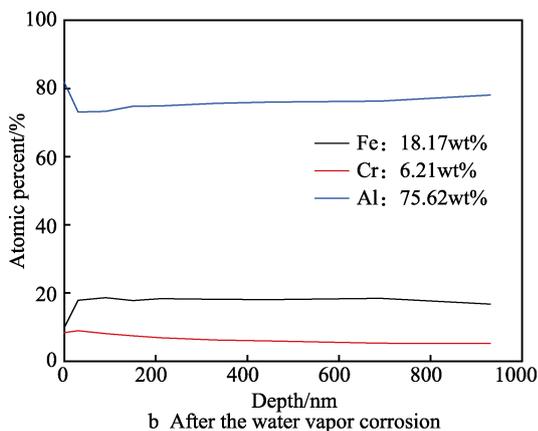
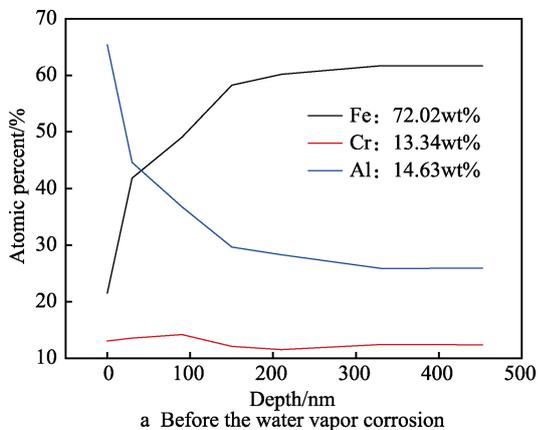


Fig.5 XPS surface depth profiles of as-sputtered FeCrAlY thin film

target; however, the Cr was less than the target, and the Al was higher than the target. When the content of Al was higher than the target, it was beneficial that Al would separate out during the water vapor corrosion and Al_2O_3 was useful layer that protected the Zr substrate from the corrosion. In the Fig.5b, after the water vapor corrosion test, the Al content rapidly increased to 75.62% from 14.63% on the surface of the thin film. The phenomenon could be taken into account that Cr would accelerate Al to diffuse to the surface under water vapor environment at high temperature.

3.6 Corrosion data of FeCrAlY thin film deposited on the Zr substrate and Zr

Fig.6 illustrated the weight gain of Zr and FeCrAlY thin film deposited on the Zr substrate. As can be seen from the Fig.6, The weight gain of Zr was 34 mg/cm², however the weight gain of FeCrAlY was only 25 mg/cm². The weight gain of FeCrAlY was nearly 30% less than that of Zr. It showed that FeCrAlY could use as protection thin film that alleviated water vapor to corrode Zr substrate.

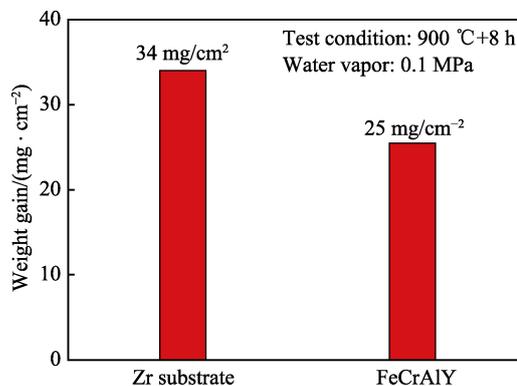


Fig.6 Corrosion data of Zr and FeCrAlY thin film deposited on the Zr substrate after 8 h water vapor environment corrosion test at 900 °C

3.7 SEM analysis of FeCrAlY thin film deposited on the Zr substrate after corrosion test at 900 °C water vapor environment

Fig.7 showed surface and cross-section images of FeCrAlY thin film deposited on the Zr substrate under water vapor environment at high temperature. From the surface images of Fig.7a and b, metal oxide films were formed during the corrosion process. Some pinholes and cracks could observe. These pinholes and cracks could be the channel for water vapor to diffuse into the Zr substrate and corrode it. From the cross-section images Fig.7c and d, the Zr substrate did not corrode seriously. It demonstrated that FeCrAlY thin film could

effectively retard the water vapor diffusion and alleviate the corrosion rate of Zr substrate. In the Fig.7g and h, Cr_2O_3 and Al_2O_3 thin film could observe. These two thin films played the vital roles to resist water vapor corrosion to Zr substrate. The existence of Cr would accelerate Al to separate out and the separated Al would oxide to form Al_2O_3 protection film. Element Y could also promote Al to form stable $\alpha\text{-Al}_2\text{O}_3$ when Al content was above 5% in the thin film under water vapor environment at high temperature^[21]. Cr_2O_3 and Al_2O_3 were efficiently protection layers to retard corrosion rate in 900 °C water vapor environment. Therefore, the overall weight gain of FeCrAlY thin film deposited on the Zr substrate slowed down.

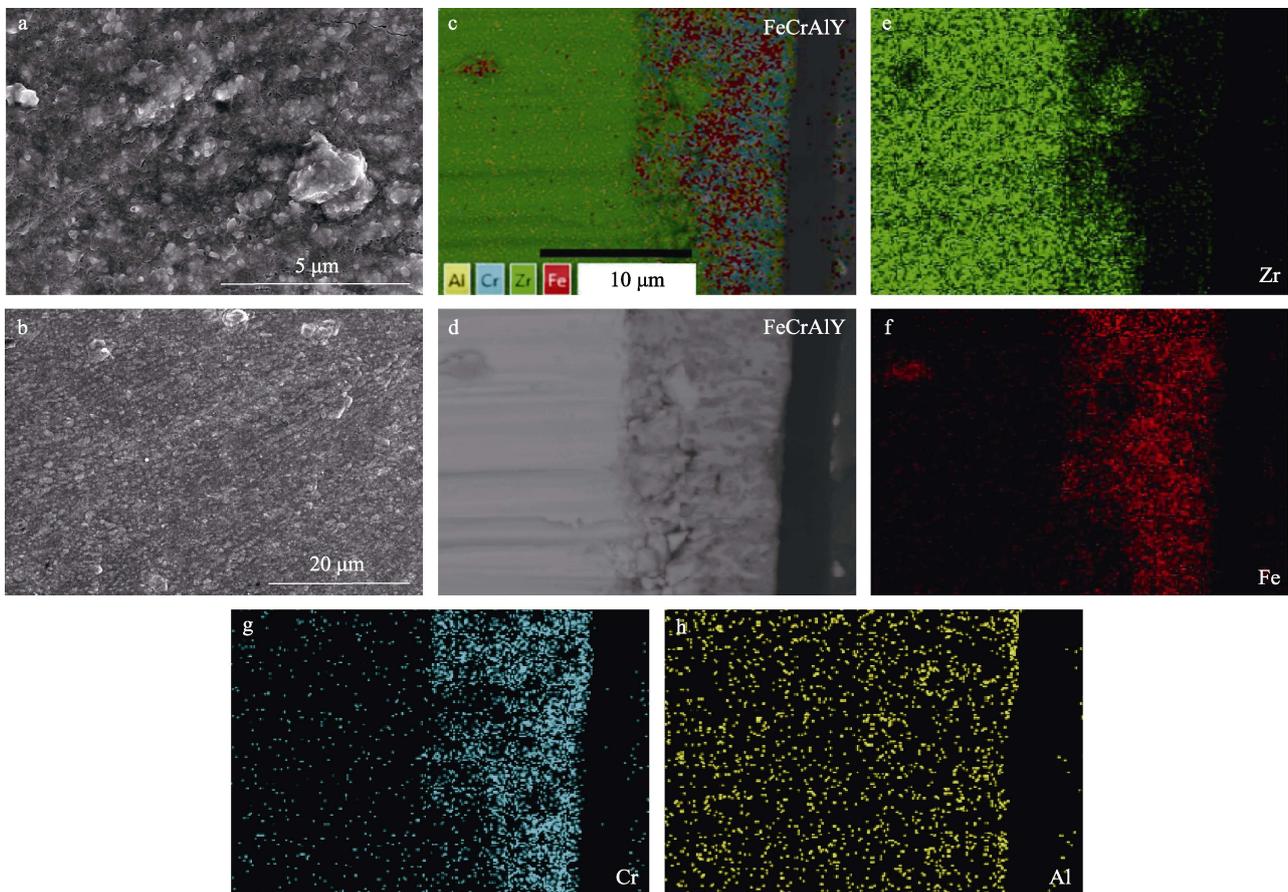


Fig.7 a, b: Surface-view images of FeCrAlY thin film after 8 h water vapor environment corrosion test at 900 °C (the scale bar of 5 μm and 20 μm); c, d: Cross-section SEM images of FeCrAlY thin film after 8 h water vapor environment corrosion test at 900 °C; e: Zr; f: Fe; g: Cr; h: Al

4 Conclusions

FeCrAlY thin film was deposited on glass and Zr alloy substrate via magnetron sputtering approach under different temperature. The grain of the as-deposited FeCrAlY thin film was larger increased with the temperature of substrate. FeCr_2O_4 、 Fe_2O_3 、 Al_2O_3 and Cr_2O_3 were formed in 900 °C high temperature water vapor

environment after 8 h corrosion test. Passivation layers of Cr_2O_3 and Al_2O_3 were separated out to protect Zr substrate and slowed down the corrosion rate of the FeCrAlY thin film deposited on Zr substrate. FeCrAlY thin film deposited on Zr substrate paved the way to slow the corrosion rate under water vapor environment at high temperature.

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