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ARTICLE

Microstructure Evolution of FeCrAl Coating with Low Al Content Under High-Temperature Air Oxidation

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Abstract: FeCrAl coating with thickness of 18 μm was deposited on Zr-4 alloy substrate by magnetron sputtering in order to improve the high-temperature oxidation resistance of Zr alloys. The oxidation resistance of FeCrAl coating with low Al content was investigated by air oxidation tests. Field emission scanning electron microscope, energy dispersive spectrometer, and grazing incidence X-ray diffraction were used to evaluate the relationship between interfacial evolution and element migration. Results show that although the FeCrAl coating is layered and gradually peels off after air oxidation at 1000 °C, the coating still effectively protects the Zr-4 substrate from oxidation. The performance degradation of FeCrAl coatings is mainly caused by the severe outward diffusion of Al element and the inward diffusion of Fe and Cr elements at high temperatures, which results in the layering and peeling inside the coating. The air oxidation behavior of FeCrAl coating at 800, 900, and 1000 °C was also discussed.

Key words: accident-tolerant fuel coating; magnetron sputtering; FeCrAl coating; low Al content; high-temperature air oxidation

FeCrAl alloy is commonly considered as an accident-tolerant fuel (ATF) cladding material due to its excellent mechanical properties and oxidation resistance at high temperatures[1–3]. However, the thermal neutron absorption cross-section of FeCrAl alloy is much larger than that of Zr alloy cladding material, resulting in restricted application in nuclear fuel field[4–6]. FeCrAl-coated Zr alloy cannot only inherit the excellent properties of FeCrAl and Zr alloys, but also be compatible with the existing equipment and process of Zr alloy fuel cladding, showing great potential[7–8].

Currently, it is reported that the high-temperature oxidation resistance of the FeCrAl coating mainly depends on the formation of dense protective films of Cr_2O_3 and Al_2O_3 during the oxidation process, which prevents oxygen diffusion to the Zr alloy substrate[9–10]. Some failure mechanisms of FeCrAl coatings have also been discussed in steam environments[11–12]. However, the oxidation behavior of FeCrAl coatings under high-temperature air oxidation is rarely researched. Air oxidation conditions are more severe than the steam oxidations, because Zr oxidation in air releases more heat by approximately 85% than that under steam oxidation[13]. Therefore, during the loss-of-water accident in a spent fuel pool or during handling operations, fuel assemblies may result in the air exposure with serious consequences[14–15]. Furthermore, the FeCrAl coatings with high Al content may lead to worse corrosion resistance, low strength, and high brittleness, thereby restricting their application in nuclear reactors[16]. In conclusion, it is crucial to study the air oxidation performance and behavior for composition control and structural design of FeCrAl coatings with low Al contents.

In order to satisfy the engineering applications of ATF coating, the coating deposition rate and coating quality should be considered. The magnetron sputtering is a commonly used method due to its low deposition temperature, good bonding strength, and high deposition rate, which is normally used for preparation and performance study of ATF coatings. In this

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research, a FeCrAl coating with low Al content was prepared on Zr-4 substrate by magnetron sputtering. The high-temperature oxidation resistance of FeCrAl coating at different air oxidation temperatures was studied, and the oxidation mechanism of the coatings was discussed from the perspective of interfacial evolution and element migration. This research provides guidance for investigation of accident-tolerant fuel coatings.

1 Experiment

FeCrAl coating with thickness of 18 μm was deposited on Zr-4 alloy substrate by magnetron sputtering method. The oxidation experiments were conducted in a muffle furnace at three different temperatures (800, 900, and 1000 °C) for 60 min under air condition and ambient pressure. The heating rate was 10 K/min, and all coatings were furnace-cooled. To avoid the influence of substrate, the phase structure and oxidation products of the oxidized FeCrAl coating were characterized by grazing incidence X-ray diffractometer (GIXRD, Empyrean, PANalytical) with Cu Kα radiation (wavelength λ=0.154 06 nm), and the incident angle used for GIXRD measurements was 3°. The high-temperature oxidation resistance of the FeCrAl coating was evaluated through surface morphology by field emission scanning electron microscope (SEM, FEI Inspect F50, FEI) equipped with an energy dispersive spectrometer (EDS). Additionally, the oxidation behavior was also discussed.

2 Results and Discussion

2.1 Air oxidation test

Fig.1 shows SEM cross-sectional morphologies and appearances of FeCrAl coatings after air oxidation at different temperatures for 60 min. After air oxidation at 800 and 900 °C for 60 min, the color of local FeCrAl coating surfaces changes, and the coating remains intact, indicating that the FeCrAl coatings can well protect the Zr-4 substrates. Additionally, the interface between FeCrAl coating and Zr-4 substrate can be clearly observed, as shown in Fig. 1a – 1b. When the temperature increases to 1000 °C, only a small amount of spalling occurs at the edges and corners of the FeCrAl coating surface. This is because the edges of Zr-4 substrate cannot be completely coated during the deposition process. These unprotected edges are oxidized during experiment, therefore leading to the peeling phenomenon. However, the middle area and the cross-sectional morphologies of the coating are still intact without obvious cracks and spalling. Only the FeCrAl coating thickness decreases to a certain extent. In conclusion, the FeCrAl coating can effectively protect the Zr-4 substrate at elevated temperatures.

Fig.2 shows SEM surface morphologies and EDS analysis results of the oxidized FeCrAl coatings at different temperatures. After air oxidation at 800 °C, the surface morphology changes dramatically, as shown in Fig. 2a: the plate-like structural oxides are formed on the coating surface, which may be a transition phase, such as γ-Al_2O_3[17]. According to EDS results in Fig. 2d, the content of Fe, Cr, Al, and O elements is 28.9at%, 20.8at%, 3.3at%, and 47.0at%, respectively. When the temperature increases to 900 °C, the FeCrAl coating surface is flat without any spalling, as shown in Fig.2b. According to Fig.2e, no microcracks can be observed in FeCrAl coating. Moreover, the content of Fe, Cr, Al, and O elements in Fig. 2e is 43.7at%, 11.3at%, 11.6at%, and 33.4at%, respectively. It can be seen that the contents of Fe and Cr elements on the coating surface decrease after air oxidation, whereas the content of Al element obviously increases, compared with those of the as-deposited coating. According to the thermodynamic data, the order of Gibbs free energy of the formation of involved oxides is $Al_2O_3<ZrO_2<Cr_2O_3<Fe_2O_3$[18]. Therefore, Al content increases because Al has a much higher affinity for oxygen than Fe and Cr do, and thus the outward migration of Al element occurs during the high-temperature oxidation process[19–20]. In addition, the FeCrAl coating surface becomes rougher after air oxidation at 1000 °C for 60 min, as shown in Fig.2c. A small number of microcracks and a large amount of particulate matter can be observed in Fig. 2f. Combined with EDS analysis results, the particles are Cr-rich oxides, and the planar regions between the particles are mainly composed of Al-rich oxides. Notably, a small amount of Zr exists on the FeCrAl coating surface, inferring that Zr can diffuse to the coating surface during air oxidation at 1000 °C. However, based on the small content of Zr element, the existence of Zr inside the substrate is probably caused by the penetration of electron beam.

The phase structures of the oxidized products on FeCrAl

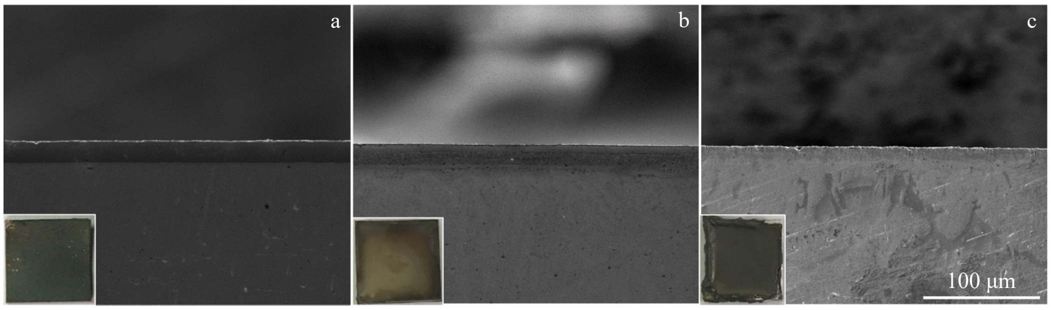

Fig.1 SEM cross-sectional morphologies and appearances of FeCrAl coatings after air oxidation at 800 °C (a), 900 °C (b), and 1000 °C (c) for 60 min

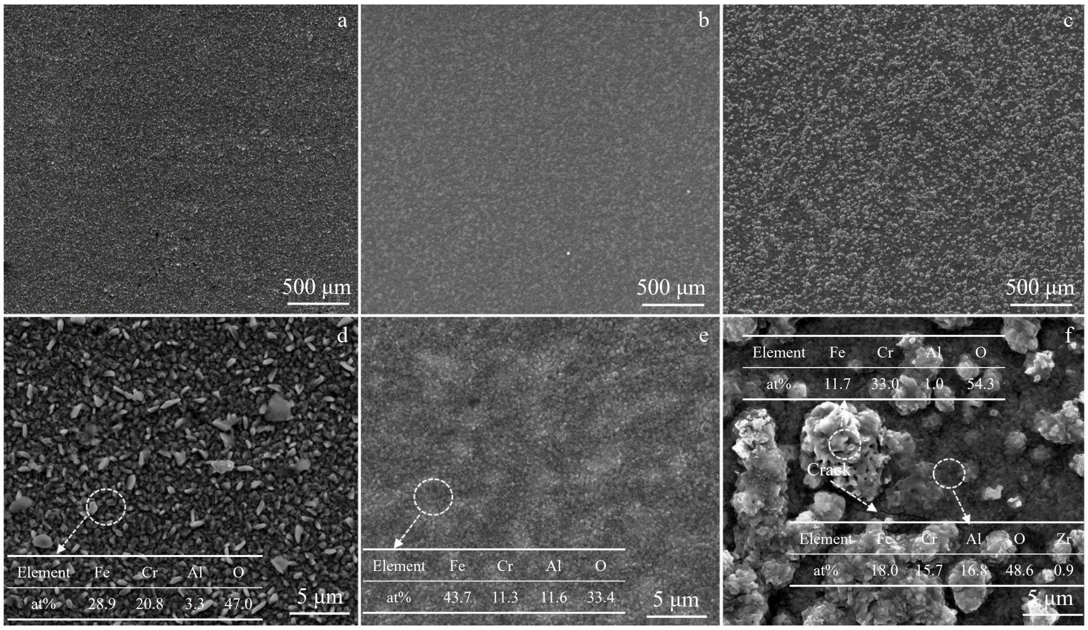

Fig.2 SEM surface morphologies (a–c) and magnified images with EDS analysis results (d–f) of FeCrAl coatings after air oxidation at 800 °C (a, d), 900 °C (b, e), and 1000 °C (c, f) for 60 min

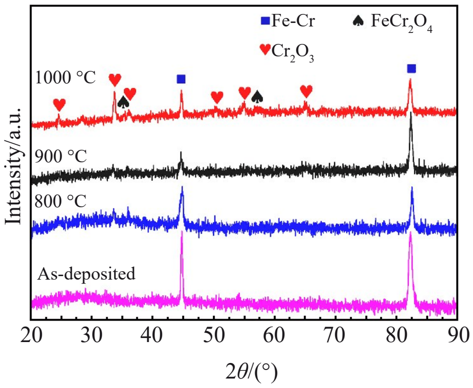

Fig.3 GIXRD patterns of FeCrAl coatings before and after air oxidation at different temperatures for 60 min

coatings were further analyzed by GIXRD, and the results are shown in Fig. 3. The as-deposited FeCrAl coating is mainly composed of Fe-Cr phase with a body-centered cubic (bcc) structure[20]. After air oxidation at 800 and 900 °C, the weak diffraction peaks of Cr_2O_3 can be detected in the FeCrAl coating. Additionally, the Fe-Cr peaks still exist in the FeCrAl coating, indicating that the coating is not completely oxidized. After air oxidation at 1000 °C, the oxide phases of $FeCr_2O_4$ and Cr_2O_3 are formed on the FeCrAl coating, and no Al_2O_3 peaks appear. This may be related to the thin oxide layer of Al_2O_3.

Fig. 4 shows SEM cross-sectional morphologies and EDS line scanning results of the FeCrAl coatings after air oxidation at different temperatures. Table 1 shows EDS results of as-deposited FeCrAl coating and selected points in Fig. 4. According to Fig.4a and 4d, a uniform Al oxide film is formed on the surface of FeCrAl coating after air oxidation at 800 °C. Besides, it can be seen that the Al element in the near-surface layer migrates more severely to the surface area. After air oxidation at 900 °C for 60 min, the dense Al oxide film, Al-rich layer, Fe/Cr/Al/O interface layer, Cr-rich layer, and mixed layer containing Fe, Cr, and Zr are successively formed from the surface to the substrate, according to EDS line scanning results of Fig.4e. This phenomenon is caused by the diffusion of Fe and Cr elements to the substrate. The high oxygen content in the Fe/Cr/Al/O interface layer may be related to the trapping of oxygen caused by the high defect concentration at the interface between the Cr-rich and Al-rich layers[21]. Brittle intermetallic compounds (Fe_2Zr, $FeZr_2$, and $ZrCr_2$) are inevitably formed in the mixed layer containing Fe, Cr, and Zr at high temperatures[22–23]. Because GIXRD detection depth does not reach the place of diffusion layer or there is no crystallization, these compounds cannot be detected. Moreover, a large number of pores are formed in the Cr-rich layer, as shown in Fig.4b.

When the oxidation temperature rises to 1000 °C (the Fe-Zr eutectic temperature is about 928 °C), the Al-rich layer disappears, but the Cr-rich layer and a small amount of Fe/Cr/Al/O interface layer are retained on the coating surface. Besides, large holes are formed. The coating is significantly thinned, and the mixed layer is obviously thickened, as shown in Fig. 4c and 4f. Therefore, the Al-rich layer peels off with increasing the temperature. However, no obvious oxygen can be detected in the Zr-4 substrate, as shown in Fig. 4f, which demonstrates that the FeCrAl coating can still protect the Zr-4 substrate from oxidation. Notably, the interface evolution caused by diffusion inside the coating results in the peeling off of the Al-rich layer. This phenomenon is different from the oxidation failure or degradation at the coating-substrate interface under traditional high-temperature steam

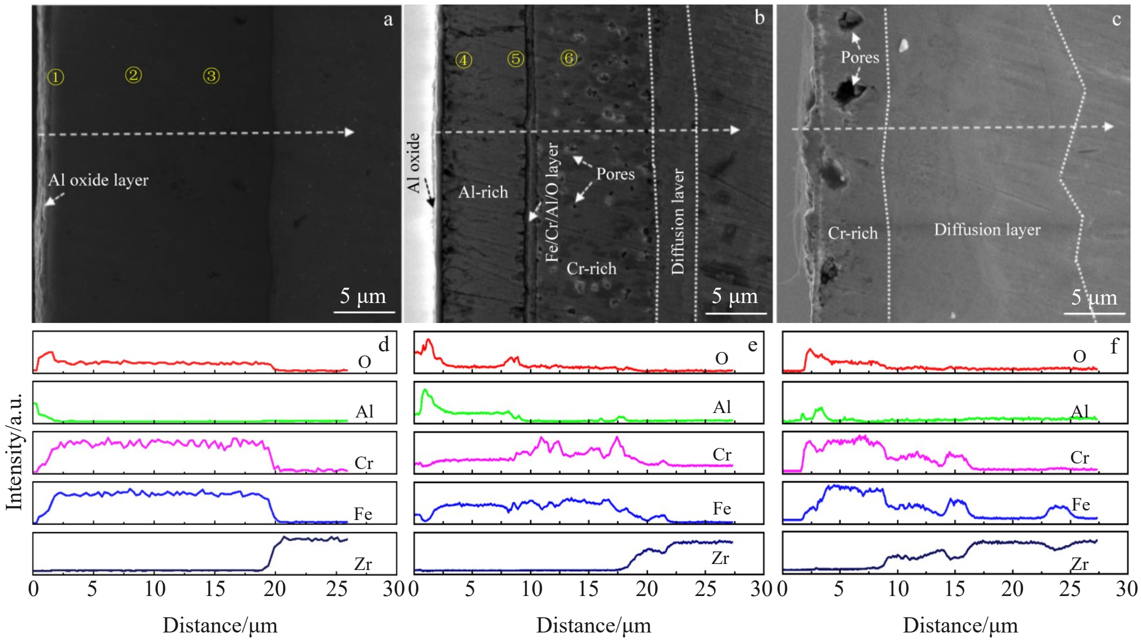

Fig.4 SEM cross-sectional morphologies (a–c) and EDS line scanning results along dashed arrow lines (d–f) of FeCrAl coatings after air oxidation at 800 °C (a, d), 900 °C (b, e), and 1000 °C (c, f) for 60 min

Table 1 EDS results of as-deposited FeCrAl coating and selected points in Fig.4 (at%)

Point	Fe	Cr	Al	O
As-deposited	80.2	16.7	3.1	-
1	77.8	18.4	1.6	2.2
2	77.4	18.2	2.0	2.4
3	77.2	17.4	2.1	3.3
4	48.5	6.2	36.6	8.7
5	46.8	8.0	32.5	12.7
6	67.4	20.8	6.8	5.0

oxidation conditions, indicating that the mechanism of air oxidation of the FeCrAl coating may be different from that under steam oxidation[19].

2.2 Oxidation process

The schematic diagrams of the air oxidation process for FeCrAl coatings is shown in Fig.5. After FeCrAl coating is air-oxidized at 800 °C, Al near the surface side diffuses outward to form a dense oxide film, as shown in Fig.5a. According to Table 1, the Al content near surface side obviously decreases after air oxidation, compared with that of as-deposited coating. When the temperature reaches 900 °C (Fig.5b), the formation of Al-rich layer induces the outward diffusion of Al element due to the high affinity of Al to O in the FeCrAl coating[12,19–20]. Additionally, the Al content of the outer Al-rich layer is higher than that in the inner Cr-rich layer. The formation of the oxide layer is mainly attributed to the reaction between Al element on the surface and O element from the air. Moreover, the Fe and Cr in the FeCrAl coating diffuse to the Zr-4 substrate side above 900 °C, and the formation of brittle Fe-Zr and Cr-Zr intermetallic compounds occurs[24–25]. These phenomena lead to the formation of diffusion layers containing Fe, Cr, and Zr on one side of the Zr-4 substrate, as shown in Fig.4e–4f. However, the outward diffusion of Al element and the inward diffusion of Fe and Cr elements lead to the formation of a large number of vacancies in the Cr-rich layer. Zhang et al[25] found that there is a concentration tendency for vacancies in bcc metals by the modified analytical embedded-atom method. Therefore, the vacancy aggregation is conducive to the formation of pores by Kirkendall effects, as shown in Fig.4b[20].

Meanwhile, the compressive stress is generated in the Al-rich layer due to the outward diffusion of Al element and the inward diffusion of O element[26–27]. With increasing the oxidation temperature, the stress concentration between Al-rich layer and Cr-rich layer leads to the separation of the two layers at the Fe/Cr/Al/O interface layer[28], as shown in Fig.5c. The Al-rich layer peels off, the interfacial oxide layer is exposed, and a dense oxide layer composed of spinel $FeCr_2O_4$ and Cr/Al oxides is formed on the surface. Furthermore, the gradual evolution and integration of the pores inevitably lead to the degradation of coating properties[20]. The pores are caused by the diffusion of Fe and Cr elements to the substrate at the temperature above Fe-Zr eutectic temperature (928 °C), thereby resulting in holes, as shown in Fig.5d.

The FeCrAl coating can restrict the inward diffusion of oxygen at 800 °C by forming a dense oxide layer of Al and Cr elements, which greatly enhances the oxidation resistance of Zr-4 alloys. When the temperature increases to 900 °C, the oxidation kinetics of the coating intensifies, and Al element migrates outward, which inevitably leaves a large number of vacancies inside the coating, thus promoting the inward migration of oxygen and leading to the enrichment in Al-rich

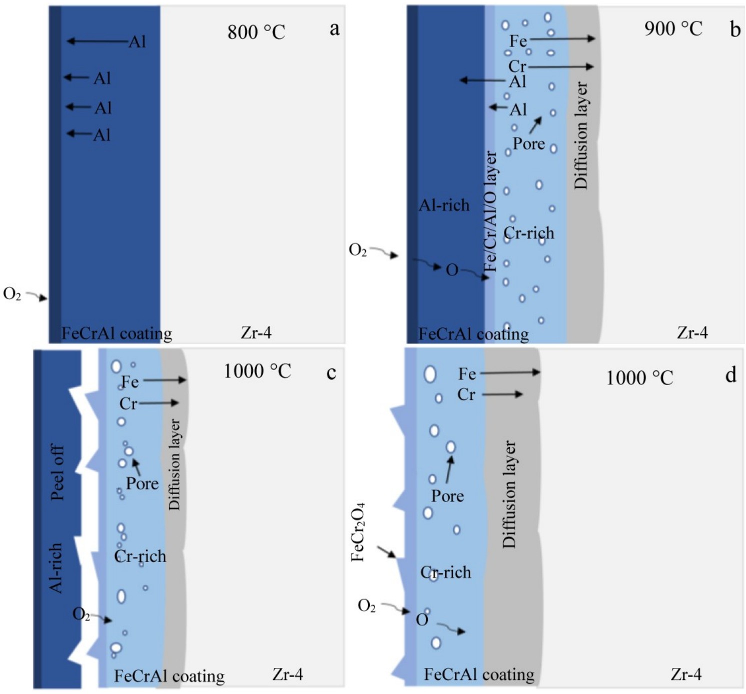

Fig.5 Schematic diagrams of interfacial evolution of FeCrAl coating during air oxidation at 800 °C (a), 900 °C (b), and 1000 °C (c–d)

and Cr-rich layers. When the oxygen continues to accumulate, the oxygen potential increases, leading to the oxidation at the interface. Because this temperature is close to the Fe-Zr eutectic temperature (928 °C), Fe and Cr continue to diffuse into the inner part of the Zr-4 substrate, forming the Fe-Zr diffusion layer. Al element diffuses outward. These phenomena are consistent with the morphology in Fig. 3b: a large number of voids can be observed in the Cr-rich layer. The oxidation reaction and diffusion effect become more obvious when the temperature increases to 1000 °C (above the Fe-Zr eutectic temperature of 928 °C), leading to the formation of larger voids in the Cr-rich layer, as shown in Fig.3c. In this case, it is necessary to introduce a diffusion barrier layer between the FeCrAl coating and Zr-4 substrate to prevent the formation of holes and brittle intermetallic compounds[19–20,24]. However, the barrier layer cannot completely eliminate the interfacial diffusion. The element diffusion between the barrier layer and Zr-4 substrate still occurs to some extent. The outward migration of Al element may be the main reason for the deterioration of coating performance. Hence, the composition design of FeCrAl coating is necessary to restrain the dramatic migration of Al element to the surface and the aggregation of vacancies in the FeCrAl coating. This amelioration can be accomplished by adding specific elements, such as Y or Hf, which can improve the oxidation resistance of the coating.

3 Conclusions

1) The air-oxidized FeCrAl coating has a dense Al oxide film, an Al-rich layer, a Fe/Cr/Al/O interface layer, a Cr-rich layer, and a mixed layer containing Fe, Cr, and Zr elements.

2) Although the Al-rich layer peels off at 1000 °C, it can still prevent oxygen from interacting with the substrate, thus inhibiting the oxidation of Zr-4 substrate.

3) The main reason for the performance degradation of FeCrAl coatings is the layering and peeling phenomena inside the coating caused by the severe outward diffusion of Al element and the inward diffusion of Fe and Cr elements at high temperatures.

4) Appropriate composition and structural design of FeCrAl coating can prevent the diffusion and migration of alloy elements, therefore achieving the FeClAl coating with long service life and application in accident-tolerant fuel field.

References

1 Zhao H, Yang C, Guo D X *et al. Rare Metal Materials and Engineering*[J], 2022, 51(7): 2460

2 Bai Guanghai, Xue Fei, Liu Erwei *et al. Rare Metal Materials and Engineering*[J], 2020, 49(9): 3071 (in Chinese)

3 Tang C, Stieber M, Seifert H J *et al. Corrosion Reviews*[J], 2017, 35(3): 141

4 George N M, Terrani K, Powers J *et al. Annals of Nuclear Energy*[J], 2015, 75: 703

5 Wu X, Kozlowski T, Hales J D. *Annals of Nuclear Energy*[J], 2015, 85: 763

6 Younker I, Fratoni M. *Progress in Nuclear Energy*[J], 2016, 88: 10

7 Duan Z, Yang H, Satoh Y *et al. Nuclear Engineering and Design*[J], 2017, 316: 131

8 Terrani K A. *Journal of Nuclear Materials*[J], 2018, 501: 13

9 Wang Y D, Zhou W C, Wen Q L *et al. Surface and Coatings Technology*[J], 2018, 344: 141

10 Cui Y, Liang Z Y, Wang G *et al*. *Journal of Nanoscience and Nanotechnology*[J], 2019, 19(5): 2732

11 Park D, Mouche P A, Zhong W *et al*. *Journal of Nuclear Materials*[J], 2018, 502: 95

12 Zhong W, Mouche P A, Han X *et al*. *Journal of Nuclear Materials*[J], 2016, 470: 327

13 Steinbrück M. *Journal of Nuclear Materials*[J], 2009, 392(3): 531

14 Duriez C, Dupont T, Schmet B *et al*. *Journal of Nuclear Materials*[J], 2008, 380(1–3): 30

15 Duriez C, Drouan D, Pouzadoux G. *Journal of Nuclear Materials*[J], 2013, 441(1–3): 84

16 Dong P, Zhang R Q, Wang H *et al*. *Journal of Alloys and Compounds*[J], 2016, 684: 549

17 Berthomé G, N'Dah E, Wouters Y *et al*. *Materials and Corrosion*[J], 2005, 56(6): 389

18 Rumpf I B. *Thermochemical Data of Pure Substances*[J], 1997, 4(55): 359

19 Wang Y, Tang H, Han X C *et al*. *Surface & Coatings Technology*[J], 2018, 349: 807

20 Han X C, Wang Y, Peng S M *et al*. *Corrosion Science*[J], 2019, 149: 45

21 Lesage B, Marechal L, Huntz A M *et al*. *Defect and Diffusion Forum*[J], 2001, 194: 1707

22 Bhanumurthy K, Kale G B, Khera S K. *Journal of Nuclear Materials*[J], 1991, 185(2): 208

23 Yeom H, Maier B, Johnson G *et al*. *Journal of Nuclear Materials*[J], 2018, 507: 306

24 Gigax J G, Kennas M, Kim H *et al*. *Journal of Nuclear Materials*[J], 2019, 519: 57

25 Zhang J M, Wen Y N, Xu K W. *Surface and Interface Analysis*[J], 2007, 39(6): 542

26 Huntz A M. *Materials Science & Engineering A*[J], 1995, 201(1–2): 211

27 Evans H E. *International Materials Reviews*[J], 1995, 40(1): 1

28 Chen Q S, Liua C H, Zhang R Q *et al*. *Corrosion Science*[J], 2020, 165: 108 378

高温空气氧化作用下低铝含量FeCrAl涂层的组织演变

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摘　要：通过磁控溅射技术在Zr-4合金基体上沉积了厚度约为18 μm的FeCrAl涂层，以提高Zr合金的高温抗氧化性能。通过空气氧化实验研究了低Al含量的FeCrAl涂层抗氧化性能。为了评估涂层界面演变和元素迁移之间的关系，采用了场发射扫描电子显微镜、能谱仪和掠入射X射线衍射仪进行了深入分析。结果表明，尽管FeCrAl涂层在1000 ℃空气氧化后会出现分层剥落，但该涂层仍然有效地保护了Zr-4合金基体不被氧化。FeCrAl涂层性能下降的主要原因是高温下Al元素严重向外扩散以及Fe、Cr元素向内扩散，最终导致涂层内部分层和剥落。此外，还讨论了FeCrAl涂层在800、900和1000 ℃时的空气氧化行为。

关键词：耐事故容错燃料涂层；磁控溅射；FeCrAl涂层；低Al含量；高温空气氧化

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