Three-point bending study on the microscopic fracture behavior of pre-oxidized Cr-coated Zr-4 alloys

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Abstract—In this study, an in situ three-point bending test was carried out to study the mechanical properties and cracking behavior of the Cr-coated Zr-4 alloy considering the effect of pre-oxidation. The results showed that high temperature pre-oxidation led to the formation of intermetallic ZrCr₂ at the coating/substrate interface and an α-Zr(O) layer beneath the interface. During the three-point bending test, the Cr coating and Zr-4 substrate showed good plastic deformation. However, the brittle intermetallic ZrCr₂ diffusion layer exhibited cracks in the early stage, which accelerated the crack penetration to the Cr coating and the Zr-4 substrate, leading to the pre-failure of the pre-oxidized sample.

1. Introduction
Developing accident tolerant fuel (ATF) cladding materials has drawn worldwide attention to enhance the accident resistance of the light water reactor under beyond design basis events [1]. ATF coating technology is one of the most favorable methods to enhance the oxidation and corrosion resistance of nuclear fuel claddings under severe accident conditions [2]. The ATF coatings effectively protect the underlying Zircaloy claddings from oxidation in hot steam environment, eliminating the risk to dramatic hydrogen explosion under loss-of-coolant accident (LOCA) scenarios. Despite this, the severe high temperature oxidation environment might greatly affect the microstructures and mechanical properties of ATF coatings, leading to different fracture mechanisms from those under service conditions.

A variety of ATF coating materials have been studied recently, including metallic materials (e.g. Cr[1-3], FeCrAl[4]), ceramic materials (e.g. CrN[5], SiC[6]), MAX phases (e.g. Ti₂AlC[7], Ti₃SiC₂[8]), and multilayer composite coatings (e.g. Cr-Zr/Cr/CrN[9]). Among them, Cr coatings have been regarded as one of the most promising candidate coatings. The good corrosion and oxidation resistance of Cr coatings under high temperature steam environment has been confirmed in previous work [10-15]. However, there are few studies on failure mechanisms of ATF coating systems under service and accidental conditions. Under accident conditions, a dense Cr₂O₃ oxide layer formed on the Cr coating surface, acting as a barrier to oxygen diffusion into the substrate [16]. Simultaneously, inter-diffusion between Cr and Zr occurs at the coating/substrate interface, forming a brittle intermetallic layer. In addition, the β-Zr phase transforms to an α-Zr(O) phase in the Zr substrate at high temperature. Ultimately, the bilayer structure of the Cr-coating-Zr substrate system varies to a multilayer structure consisting of Cr₂O₃, Cr, ZrCr₂, α-Zr(O) and prior β-Zr layers. There is significant difference in thermal and mechanical properties among these layers, which greatly alters the mechanical properties and fracture mechanisms of the coated Zr alloys.
In order to investigate the effect of oxidation on the fracture mechanism of the Cr coatings, an in-situ three bending test was conducted in this work. The vertical and interfacial cracking in the pre-oxidized Cr coating was observed, and the microstructure-dependent fracture mechanism of the Cr coating was disclosed.

2. Materials and experiment

2.1. Materials and pre-oxidation test

The Zr-4 alloy was used as the substrate material in this study, with the main chemical composition listed in Table 1 and the sample processed by electrical discharge machining (EDM) cutting to the shape shown in Fig. 1 was pre-sanded with SiC sandpapers (#360, #600, #1000, #1200 and #1500) on the surface and sides of the samples step by step to retain a certain roughness on the surface, which could improve the adhesion of the coating/substrate interface.

| Element | Sn    | Fe    | Cr     | N     | O    | H    | Zr     |
|---------|-------|-------|--------|-------|------|------|--------|
| Wt.%    | 1.2-1.7 | 0.18-0.24 | 0.07-0.13 | 0.008 | 0.16 | 0.01 | Bal.    |

A magnetron sputtering ion plating method was used to prepare the Cr coated samples for the experiments in three steps: substrate material pre-treatment, ion cleaning and coating deposition. The sample was washed with anhydrous ethanol (approx. 10 minutes), rinsed with deionized water and then blown dry before being placed in the ionization chamber. In order to suspend the substrate sample in the chamber, a small 1.5 mm diameter hole was drilled in one side of the sample. As ultrasonic cleaning is difficult to completely remove stubborn impurities from the substrate surface. The substrate was therefore cleaned with argon ions at -600 V, 0.5 A and 8 × 10⁻⁴ Torr for 30 minutes and the target was cleaned at -200 V, 4 A and 8 × 10⁻⁴ Torr for 10 minutes prior to formal coating. For the deposition of the Cr coating, a bias voltage of -60 V and an arc target current of 7 A was used and the sputtered target particles were allowed to reach the substrate for 700 minutes to deposit the film.

A pre-oxidation test of the Cr-coated Zr-4 alloy was carried out in a Muffle furnace at 1000°C. The procedure was as follows: the temperature in the Muffle furnace was first raised to the target temperature, then the samples were placed in the Muffle furnace, heated for 60 minutes and then...
removed from the muffle and cooled in air.

2.2. Three-point bending test
In-situ three-point bending tests of pre-oxidized coated samples were carried out on the servo-hydraulic test system. Before testing, the observed surface of the sample needs to be polished in order to observe the crack evolution behavior. Before testing, the sample was fixed to the grippers with a pre-tightening force of 20 N. The test was in a displacement control mode at a constant rate of 0.005mm/s. The load-deflection (P-w) curve was acquired by a data acquisition system, and the evolution of vertical and interfacial cracks was captured by a scanning electron microscope (SEM).

2.3. Microstructure characterization
The composition in the pre-oxidized coated samples was analyzed by the position and intensity of the X-ray diffraction (XRD) peaks, and the morphology of the surface and longitudinal cross-section of the samples was observed by SEM. The effect of high temperature and oxidation on the grain size, grain orientation and other characteristics of the coating and substrate was analyzed by means of electron backscatter diffraction (EBSD). The type and content of elements in the different layers of the sample were characterized by energy dispersive X-ray spectroscopy (EDS) in combination with SEM.

3. Results and discussion

3.1. Surface morphology
Figure 2 demonstrates the surface morphology of the Cr-coated Zr-4 substrate pre-oxidized at 1000°C for 1 h. The surface Cr2O3 oxide layer is dense in Fig. 2(a). Some microcracks appeared on the oxide layer, and even local buckling and spallation occurred. The local failure of oxide layer was mainly driven by the internal stresses due to the mismatch of thermal expansion coefficients between all layers upon cooling.

![Fig. 2 Images of the Cr coating surface after pre-oxidization at 1000°C for 1 h.](image)

Figure 3 shows the XRD patterns of the as-deposited and 1000°C pre-oxidized Cr coatings. From the XRD pattern of the as-deposited Cr coating it can be found that the primary orientation of the as-deposited Cr coating was (200). In contrast to the as-deposited XRD pattern, the high temperature oxidation product Cr2O3 of Cr was detected in the pre-oxidized coating. At the same time, the Cr peak was still detectable, probably due to the thinner oxide layer which is easily penetrated by X-rays. In addition, the Cr (200) peak became weaker after 1 h of oxidation at 1000 °C.
3.2. In-situ observation of the crack evolution

Figure 4 shows the in-situ observations of the pre-oxidized Cr coating during the three-point bending test. The cracks appeared first in the brittle oxide layer and at the coating/substrate interface after the load has been applied. The high density of vertical cracks at the interface indicates that a brittle intermetallic layer was formed at the interface, which was due to the pre-oxidation and the diffusion between Cr coating and Zr-4 substrate. Continued loading and stress concentration at the crack tip induced coating crack sprouting. At deflection w = 1.361mm, the substrate near the interface cracked and continued to propagate deeper into the substrate as the load increased.

Compared with the authors’ previous work [16], there is a large difference of crack evolution between the as-deposited and pre-oxidized samples. The crack density on the coating of the pre-oxidized sample is significantly lower than that of the as-deposited sample. The phenomenon may be due to the alteration of the microstructure of the layers caused by the heat treatment, therefore EBSD scans was carried out on the longitudinal section of the coating and indicates that the grains of the pre-oxidized sample are no longer the columnar grains exhibited in the as-deposited sample, while the grain size to increase significantly. This indicates that the high temperature oxidation environment leads to recrystallization and grain growth of the Cr coating, which releases internal stresses and increases plasticity through recrystallization. In addition to this we can also observe cracks in the coating as transgranular cracks.
Fig. 4 In situ observation of the crack evolution of the pre-oxidized Cr-coated Zr-4 sample under three-point bending: (a) w = 0.584 mm, (b) w = 0.995 mm, (c) w = 1.361 mm, (d,e) w = 1.701 mm and (f) the corresponding load–deflection (P–w) curve.

Additionally, as seen from the longitudinal section of pre-oxidized sample in Fig. 5, oxidation-diffusion behavior has a significant influence on the crack initiation and extension mechanism of the coated samples. From the SEM images of the longitudinal sections, pre-oxidized samples did not crack from the Cr coating, but mainly cracked from the Cr2O3 oxide layer and the coating/substrate interface, and then appeared in the Cr coating because of local stress concentration at the crack tips. In addition, the crack path deflected in the coating, which might be affected by the grain boundaries of the Cr coating. To explain the new process of crack evolution, the elemental composition of the different layers was analyzed by EDS mapping, which indicates that a brittle intermetallic layer is formed at the coating/substrate interface due to diffusion at high temperature.
where micro-cracks are more likely to occur. Furthermore, a small amount of oxygen is dissolved into the substrate beneath the interface during high temperature pre-oxidation, which might induce a phase transition from $\beta$-Zr to $\alpha$-Zr(O). The $\alpha$-Zr(O) has lower fracture toughness than $\beta$-Zr, which raised the risk to crack in the substrate, and thus lead to pre-failure of the coated sample. The schematic of the degradation and failure mechanism is shown in Fig. 6. Hence, the present study emphasized the importance of interface fracture in the strength evaluation of Cr coated Zr-4 alloy under high temperature for accident tolerant fuel claddings.

Fig. 5 Longitudinal morphologies of the pre-oxidized Cr-coated Zr-4 alloy after three-point bending test.

Fig. 6 Schematics of the longitudinal cross-section of the (a) as-deposited Cr coating (b) pre-oxidized Cr coating before three-point bending test and (c) pre-oxidized Cr coating after three-point bending test.

4. Conclusions
In this study, the effects of pre-oxidation on the mechanical properties and fracture mechanisms of Cr-coated Zr-4 alloys were investigated by in situ three-point bending tests. A multi-layer structure was formed in the pre-oxidized Cr coating, consisting of a dense oxide layer, a residual Cr coating, a diffusion ZrCr$_2$ layer, and the Zr-4 substrate. Some microcracks were distributed in the diffusion layer after the pre-oxidation. With the increase of bending load, the Cr coating and Zr-4 substrate alloy showed plastic deformation. Meanwhile, many microcracks were formed at the brittle oxide layer and the interfacial diffusion layer, which finally penetrated to the Cr coating and the $\alpha$-Zr(O) layer. Interfacial cracks were formed and Cr coating was broken through the thickness, leading to the final failure of the pre-oxidized sample.

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References

[1] S.J. Zinkle, K.A. Terrani, J.C. Gehin, L.J. Ott, L.L. Snead, Accident tolerant fuels for LWRs: a perspective, J. Nucl. Mater. 448 (1–3) (2014) 374–379.
[2] K.A. Terrani, Accident tolerant fuel cladding development: promise, status, and challenges, J. Nucl. Mater. 501 (2018) 13–30.
[3] C. Tang, M. Stueber, H.J. Seifert, M. Steinbrueck. Protective coatings on zirconium-based alloys as accident-tolerant fuel (ATF) claddings, Corros. Rev., 2017, 35(3): 141-165.
[4] K.A. Terrani, C.M. Parish, D. Shin, B.A. Pint, Protection of zirconium by aluminia and chromia-forming iron alloys under high-temperature steam exposure, J. Nucl. Mater. 438 (1–3) (2013) 64–71.
[5] C. Meng, L. Yang, Y. Wu, J. Tan, W. Dang, X. He, X. Ma, Study of the oxidation behavior of CrN on Zr alloy in air, J. Nucl. Mater. 515 (2019) 354–369.
[6] T. Usui, A. Sawada, M. Amaya, A. Suzuki, T. Chikada, T. Terai, SiC coating as hydrogen permeation reduction and oxidation resistance for nuclear fuel cladding, J. Nucl. Sci. Tech. 52 (10) (2015) 1318–1322.
[7] B.R. Maier, B.L. Garcia-Diaz, B. Hauch, L.C. Olson, R.L. Sindelar, K. Sridharan, Cold spray deposition of Ti2AlC coatings for improved nuclear fuel cladding, J. Nucl. Mater. 466 (2015) 712–717.
[8] D.J. Tallman, J. Yang, L. Pan, B. Anasori, M.W. Barsoum, Reactivity of Zircaloy-4 with Ti3SiC2 and Ti2AlC in the 1100–1300° C temperature range, J. Nucl. Mater. 460 (2015) 122–129.
[9] A.S. Kuprin, V.A. Belous, V.N. Voyevodin, V.V. Bryk, R.L. Vasilenko, V.D. Ovcharenko, E.N. Reshetyuk, G.N. Tolmachova, P.N. V'yugov, Vacuum-arc chromium-based coatings for protection of zirconium alloys from the high temperature oxidation in air, J. Nucl. Mater. 465 (2015) 400–406.
[10] J.C. Brachet, E. Rouesne, J. Ribis, T. Guilbert, E. Pouillier. High Temperature Steam Oxidation of Chromium-Coated Zirconium-Based Alloys: Kinetics and Process, Corros. Sci., 2020, 167:108537.
[11] X. Han, C. Chen, Y. Tan, W. Feng, S. Peng, H. Zhang. A Systematic Study of the Oxidation Behavior of Cr coatings on Zry4 substrates in High Temperature Steam Environment, Corros. Sci., 2020, 174:108826.
[12] B. Maier, H. Yeom, G. Johnson, T. Dabney, J. Walters, P. Xu, J. Romero, H. Shah, K. Sridhara. Development of cold spray chromium coatings for improved accident tolerant zirconium-alloy cladding, J. Nucl. Mater., 2019, 519:247-254.
[13] X. He, Z. Tian, B. Shi, X. Xu, C. Meng, W. Dang, J. Tan, X. Ma, Effect of gas pressure and bias potential on oxidation resistance of Cr coatings, Ann. Nucl. Energy, 2019, 132: 243-248.
[14] M. Sevecek, A. Gurgen, A. Seshadri, Y. Che, M. Wagih, B. Phillips, V. Champagne, K. Shirvan. Development of Cr cold spray-coated fuel cladding with enhanced accident tolerance, Nucl. Eng. Technol., 2018, 50:229-236.
[15] J.C. Brachet, I. Idarraga-Trujillo, M. Le Flem, M. Le Saux, V. Vandenberghe, S. Urvoy, E. Rouesne, T. Guilbert, C. Toffolon-Mascele, M. Tupin, C. Phalippou, F. Lomello, F. Schuster, A. Billard, G. Velisa, C. Ducros, F. Sanchette, Early studies on Cr-Coated Zircaloy-4 as enhanced accident tolerant nuclear fuel claddings for light water reactors, J. Nucl. Mater., 2019, 517: 268-285.
[16] J.S. Jiang, H.L. Zhai, P.F. Gong, W.J. Zhang, X.J. He, X.F. Ma, B. Wang. In-situ study on the tensile behavior of Cr-coated zircaloy for accident tolerant fuel claddings, Surf. Coat. Tech., 2020, 394:12547.