On the tensile fracture behavior of Cr coating for ATF cladding considering the effect of pre-oxidation

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Abstract: In this study, the fracture mechanisms of Cr-coated Zr4 alloy samples were studied by in-situ tensile testing with high-resolution observations. Both original sample and pre-oxidized sample were studied to study the effects of pre-oxidation on the cracking and failure behavior. For the Cr-coated Zr4 sample, with the increase of tensile strain, multiple surface cracks were dominant and less interfacial cracks were formed, indicating good interfacial strength of Cr coating. For the pre-oxidized samples, there was a thin oxide layer formed on the Cr coating surface, revealing improved oxidation resistance and protection effects. However, a brittle ZrCr2 diffusion layer was formed in the same while at the Cr/Zr4 interface underneath the Cr coating, which would lead to earlier micro-cracks formed under tensile stress and evidently degrade the interfacial strength. The findings in the study indicated the importance of optimizing coating microstructure in future study to avoid forming the above-mentioned brittle diffusion interlayer and the associated premature failure.

1. Introduction
Since the Japanese Fukushima accident, accident tolerant fuel (ATF) has attracted increasing interests from both nuclear industry and academy. Among the ATF research activities all around the world, ATF coatings have been regarded as favorable candidate methods for enhancing the oxidation resistance and corrosion resistance [1-5] of zirconium cladings. In the previous studies, the Nuclear Materials Laboratory (NuMat Lab) of Sun Yat-sen University has successfully fabricated several ATF coatings, in which Cr coatings have exhibited very promising balance between high temperature resistance and mechanical properties [6-8]. There is quite limited study on the mechanical deformation and failure of Cr coatings [9]. Regarding the effects of Cr coating on the mechanical behaviors of Zr4 alloy, the authors’ recent studies indicated that Cr coating could improve the tensile properties and especially the low-cycle fatigue properties of Zr4 alloy under some conditions. At 400 ºC, Zr4 alloy coated with 15μm Cr showed much longer fatigue life, which is an order of magnitude higher than that of Zr4 alloy [9].

One important concern of ATF cladding is the resistance to loss of coolant accident (LOCA) condition; hence, it is important to study the effects of high temperature oxidation on the performance and failure mechanisms of ATF cladding [2, 10]. In this study, pre-oxidation was used to simulate the effects of LOCA. Subsequently, the associated effects on the mechanical properties of ATF coating system were studied, using a novel in-situ testing machine [9]. The objective is to reveal the effects of oxidation on the deformation and failure mechanisms of Cr coated Zr4 alloy, which will help to
understand the beneficial or detrimental effects of Cr coatings. It will also benefit the R&D of better ATF cladding coatings with optimized properties under simulated LOCA conditions.

2. Materials and experimental procedure

2.1. Materials
The material used in this study is a Zr4 alloy designed for nuclear reactor use. Then, about 13 μm thick Cr coating was prepared on the Zr4 substrate by magnetron sputtering technique. The initial microstructure of Cr coating is shown in Figure. 1. In Figure. 1a, the surface morphology of Cr coating revealed no evident porosity, indicating good quality of Cr coating, which was confirmed by the compact interface and small roughness as shown in Figure. 1b. Electronic Backscattering Scanning Diffraction (EBSD) scan indicated that the surface Cr coating exhibited evident (001) texture, i.e. the Cr coating has columnar grains with [001] along the coating growth direction.

![Figure 1 Microstructure of Cr coating on Zr4 alloy: (a) surface morphology of Cr coating; (b) cross section of Cr coating showing a thickness of about 13 μm](image)

2.2. Pre-oxidation test
The Cr-coated Zr4 tensile sample was pre-oxidized at 1060°C for 1h (hereafter referred to as the pre-oxidized sample) to study the effect of oxidation on the microstructure and mechanical degradation. It is used to simulate the exposure to high temperature in a loss of coolant (LOCA) accidental scenario.

2.3. In-situ tensile test
To study the deformation and fracture behavior of Cr-coated Zr4 samples with or without pre-oxidation effects, an in-situ tensile testing system was used, equipped with optical microscope of up to ×2500 magnification (Figure. 2a). For the tensile tests, displacement control was used, at a tension speed of 0.005 mm/s. The load clamp was shown in Figure. 2b. The sample has a dog-bone shape and the sample geometry was shown in Figure. 2c. To capture the plastic deformation and cracking behavior of Cr coatings, the optical microscope was placed above the sample, which can provide detailed information on the grain level. The captured images will be used to analyze the crack density and deformation features.

3. Results and discussion
With the help of in-situ observations under high-magnification microscope, the surface deformation and onset of micro-cracks in Cr coating can be observed and captured during the in-situ tensile tests (Figure. 3). Hence, the occurrence and features of the cracks were recorded and analyzed by the optical microscope system.
Figure 2 (a) In-situ test machine; (b) tensile clamp of samples; (c) tensile sample geometry

Figure 3 shows the surface crack evolution in the Cr coating at different tensile strains. In Figure 3a, at a tensile strain of 0.47%, micro-cracks appeared in the Cr coating. With the increase of tensile strain, the cracks began to increase in both quantity and length (Figure 3b). Multiple cracks phenomenon was evident. With the further increase of tensile strain, the crack density increased and finally approached saturation at about 11.6%, as shown in Figure 3c. Figure 3d shows the cracking behavior of the Cr coating. The underneath Zr4 substrate was exposed after the final fracture. It is noted that there is no evident stripping of Cr coatings from the substrate as shown in Figure 3, indicating that Cr coating has good adhere properties on Zr4 alloy in the present study.

Jiang et al. [7, 8] pointed out that there is a critical strain value for the occurrence of cracks on the coating surface. In this study, it is noted that when the tensile strain reached about 0.40-0.47%, the Cr coating started to crack. According to the previous studies on coating-substrate system, it indicated that the present Cr-Zr4 sample had a good toughness with a higher critical crack value.

Figure 4 shows an in-situ observation of the deformation behavior of the Cr-coated Zr4 sample after pre-oxidation. The first micro-crack appeared at a tensile strain of about 0.24% (see Figure 4a). This value of pre-oxidized sample is much smaller than that of the original in Cr-coated Zr4 sample, indicating that cracks formed earlier due to pre-oxidation effects. This phenomenon can be rationalized by the fact that a brittle oxidized layer of Cr2O3 was formed on the Cr coating surface after oxidation.

In Figure 4, the oxide layer of Cr coating appeared dark green and covered the whole coating surface. When the tensile strain reached about 2.4%, the spallation of oxidized layer started. Figure 4b showed the cracking behavior of oxidized layer under tensile strain of 4.23% and the underlying coating was exposed. The width of the multiple cracks was about 30 μm. The cracks appeared first in the oxide layer and then penetrated into the coating, which developed in the same direction as that in the non-oxidized sample in Figure 3. With the further increase of tensile strain, the crack density increased and finally came to almost saturation. Figure 4c showed that a macroscopic crack was formed at the edge of the sample and there was increased spallation of oxidized layer on the sample surface. Figure 4d is the corresponding contour map of the fractured sample, showing that there was large tensile crack opening in the sample.
To understand the effects of pre-oxidation on the tensile fracture mechanism of Cr-coated Zr4 alloy, both types of samples were sectioned along the longitudinal sections and subjected to examination under SEM, as shown in Figure 5. Figure 5a shows the detailed morphology of tensile cracks of the Cr-coated Zr4. It can be seen that the surface cracks were perpendicular to the tensile loading direction due to tensile stress. Some of the cracks extended into the substrate, but the cracks generally appeared...
blunt without evident crack tips (see Figure 5b). No secondary long cracks were observed in the Zr4 substrate.

For the Cr-coated Zr4 sample with pre-oxidation, the sample section was composed of four layers, the surface oxide layer, the Cr coating, the diffusion layer, and the Zr4 substrate. The oxide layer is about 5 μm thick, which primarily composed of Cr2O3, according to the XRD result the authors conducted. Figure 5c and d show the fracture features and the crack morphology after tensile fracture. It is seen that the oxide layer formed on the pre-oxidized Cr coating had multiple cracks with much higher density than the sample in Figure 5a. The Cr coating showed protection of Zr4 substrate against the oxidation. What is more, there were many micro cracks formed in the ZrCr2 diffusion layer between the Cr coating and the Zr4 substrate. This ZrCr2 interlayer was known to have brittle property compared with Cr and Zr4, according to our previous studies [7, 8]. Some of the microcracks extended and penetrated into the substrate (see Figure 5c), others formed interfacial cracks (see Figure 5d). Both cracks would affect the integrity of the Cr coating and Cr/Zr interface, which led to premature failure of the coating. Hence, the microscopic studies here explained the underlying mechanisms of how pre-oxidation degraded the mechanical performance of Cr-coated Zr4 alloy.

![Cracking features on the longitudinal sections after tensile fracture](image)

Figure 5 Cracking features on the longitudinal sections after tensile fracture: (a) Cr-coated Zr4, multiple cracks (b) Cr-coated Zr4, a representative crack; (c) pre-oxidized Cr-coated Zr4, multiple cracks on the section; (d) pre-oxidized Cr-coated Zr4, a representative crack

4. Conclusions
In this study, the fracture mechanisms of Cr-coated Zr4 alloy samples with and without pre-oxidation were studied by in-situ tensile testing with high-resolution observations, to reveal the effects of pre-oxidation on the cracking behavior. The main conclusions are obtained as follows:

(1) For the Cr-coated Zr4 sample, more surface cracks and less interfacial cracks were formed with the increase of tensile strain, indicating good interfacial strength of Cr coating.

(2) For the Cr-coated Zr4 sample after pre-oxidation, there is a thin oxide layer formed on the Cr coating surface, showing protection of Zr4 substrate against oxidation; however a brittle ZrCr2
Diffusion layer was formed beneath the Cr coating in the same while, which would lead to earlier micro-cracks formation and hence degrade the interfacial strength.

(3) For future studies of accidental tolerant coatings, countermeasures should be taken to optimize the coating microstructure and avoid the above-mentioned brittle diffusion interlayer.

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