

Hydrothermal Corrosion Behavior of TiN and TiCrN as an Environmental Barrier Coating for ATF claddings

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1. Introduction

In the Fukushima nuclear power plant, a large amount of hydrogen from the rapid oxidation of the Zr-alloy fuel cladding caused an explosion, which caused a serious accident. It has motivated the research of the accident tolerant fuel (ATF) cladding, a concept that reduces the hydrogen or heat due to oxidation to delay damage to the reactor core and securing the coping time in the event of an accident. In the short-term of the ATF cladding development, the Environmental Barrier Coating (EBC) has been considered [1]. This is a technology that prevents oxidation of Zr by depositing an oxidation-resistant coating on surface of Zr cladding. Since it can be applied without changing the current design, it has the advantage of shortening development time and cost.

In this study, TiCrN was considered as EBC materials. TiN has been attempted to be applied to fuel cladding [2, 3], and TiCrN is known to have better oxidation resistance than TiN [4]. In addition, the EBC on ATF cladding such as Zr alloy and SiC composite should give excellent corrosion resistance not only in hot-steam but also in high-temperature and pressurized water, which is a normal operating conditions of reactor. Therefore, in this experiment, the corrosion behavior of TiN and TiCrN in the Pressurized Water Reactor operating environment was evaluated.

2. Experimental

The Zr-alloy tube cut to 300 mm was used for EBC deposition. TiN and TiCrN was deposited on the outer surface of the cladding using an arc ion plating and sputtering system for coating with high density and adhesion. The deposition process was performed at 200 °C to minimized the stress caused by the mismatch of the thermal expansion coefficient. The argon, an inert gas, and the nitrogen, a reaction gas, were injected into the chamber in a 1:1, and nitride coating was deposited by reacting Cr and Ti vaporized from the target with nitrogen. Since the arc target Ti and sputter target Cr are located opposite each other in the chamber, the sample was rotated during the process for uniform deposition. TiN and TiCrN were deposited approximately 6 μm and 3 μm, respectively.

The corrosion test was conducted in water chemistry at 360 °C, 20 MPa condition which is simulating a PWR operating condition. A dissolved oxygen was

maintained at <5 ppb, hydrogen was maintained at 25 ccH₂/kgH₂O, and H₃BO₃ and LiOH were added 1250 ppm, 2.2 ppm, respectively. The samples were put into a loop while being hung in a sample holder made of SUS-304.

The samples were exposed for 120 days and weight was measured using an electronic balance with an 0.01 mg error range every 30, 60, 120 days. Based on measurement, a change in weight over time of exposure was observed. The phase change of the sample surface due to corrosion was analyzed by X-ray diffraction analysis, and the microstructure was observed using an electron microscope.

3. Results and Discussion

Fig.1 is a graph showing the weight change of the samples with increasing corrosion time. The measurement results included an oxidation of Zr exposed to water without coating on the inner diameter. TiN had a higher corrosion rate than Zr at the beginning of corrosion, but the increase rate tended to decrease with time. TiCrN had a lower corrosion rate than TiN and Zr. Even when the corrosion effect of uncoated Zr is removed, the all samples gained weight after corrosion. The weight of TiN increased rapidly at the beginning of exposure, which is twice that of Zr. After 120 days, the weight gain was saturated and finally increased by 0.51 mg/cm². On the other hand, TiCrN had a lowest weight gain at the beginning of corrosion, which is 1/4 times lower than Zr-alloy and 1/7 times lower than TiN. Even after 120 days, it increased by 0.23 mg/cm² and showed the lowest corrosion rate.

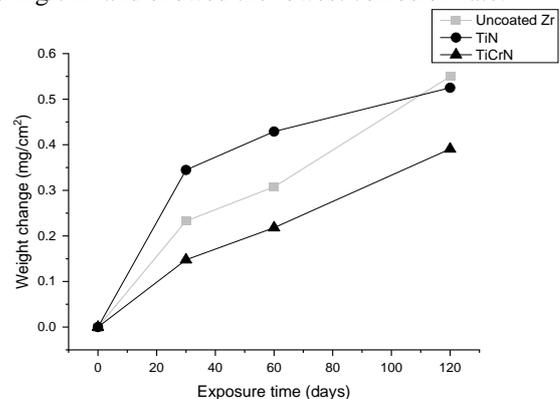


Figure 1. Weight change of uncoated Zr-alloy, TiN coating, TiCrN coating after the PWR simulated corrosion test for 120 days

Fig.2 shows the XRD results of TiN and TiCrN corroded for 120 days. The major phase of the TiN after corrosion is FeTiO_3 . Fe, from the sample holder, participated in the reaction. TiO_2 and remaining TiN peak were weakly detected. TiN has been reported to increase the weight by forming an oxide on the surface under the static autoclave and BWR conditions [2, 3, 5], and it was confirmed that in this experiment, TiN was also formed oxide with a large weight gain. In the results of TiCrN (Fig.2.b), only TiCrN peak was detected. Although the X-ray incident angle was very low (0.5°), no oxide peak was detected. It shows that Cr has a great influence on improving corrosion resistance.

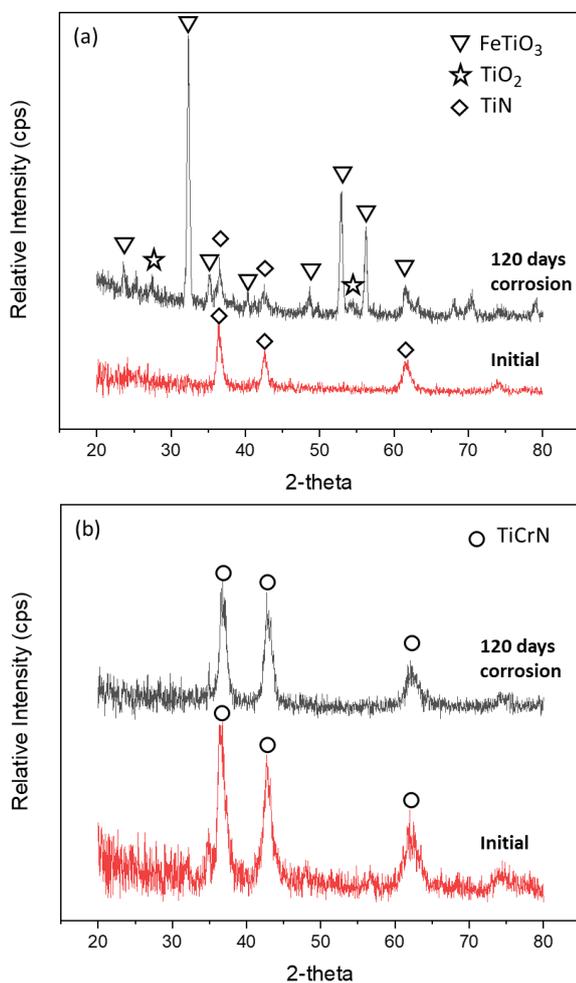


Figure 2. XRD patterns of the coatings before and after 120 days corrosion : (a) TiN, (b) TiCrN

Fig.3 is a micrographs of the oxide formed on the surface of the TiN and TiCrN corroded for 120 days using TEM. TiN formed a thick oxide by corrosion. The oxide was bi-layer of FeTiO_3 and TiO_2 . On the other hand, an oxide layer having a thickness of about 20 nm was formed on the surface of TiCrN. The oxide layer is very thin and dense. It shows that Cr contributes to the formation of a thin and dense oxide film.

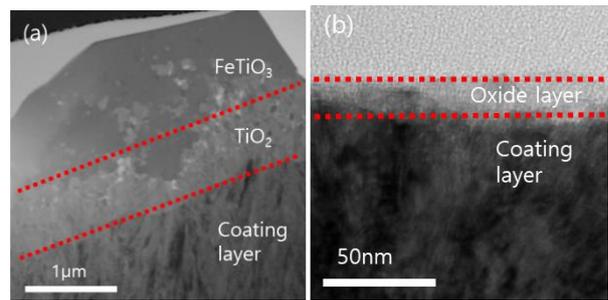


Figure 3. TEM micrographs of oxide formed on the surface of (a)TiN and (b)TiCrN corroded for 120 days

Fig.4 is a cross-section image showing the Zr tube and overall coating thickness of the TiCrN after corrosion test for 120 days. Even after exposure for 120 days, TiCrN coating layer remained, but Zr oxide was formed under the coating layer partially. It is assumed that Zr oxide contributed to the overweighting of the weight gain.

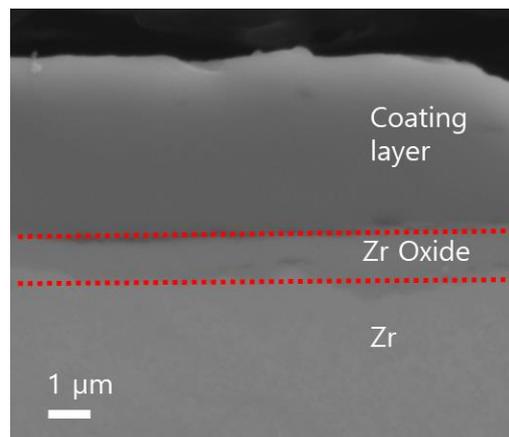


Figure 4. The cross-sectional SEM image of TiCrN after 120 days corrosion

4. Conclusions

The corrosion behavior of TiN and TiCrN were evaluated under the conditions of simulated PWR primary water. TiN deposited about $6\ \mu\text{m}$ on the Zr-alloy cladding had a high corrosion rate at 360°C , 20 MPa. FeTiO_3 formed due to Fe originating from the sample holder, and this corrosion product is a possibility because the Fe is actually dissolved in the reactor coolant due to structural corrosion. On the other hand, TiCrN deposited about $3\ \mu\text{m}$ had lowest corrosion rate. A very thin and dense oxide film was formed on the surface and coating layer survived after 120 days corrosion. This results indicates that the addition of Cr to TiN significantly improves the corrosion resistance. In the further work, it is necessary to deposit a thicker coating layer by optimizing the deposition process to improve the integrity of the coating layer in the PWR conditions.

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