Development of Protective Layer Coating for Accident Tolerant Fuel Cladding

Jung-Hwan Park*, Yang-Il Jung, Dong-Jun Park, Hyun-Gil Kim, Byoung-Kwon Choi, Young-Ho Lee, Jae-Ho Yang
Nuclear Fuel Safety Research Division, *Korea Atomic Energy Research Institute, 989-111 Daedeok-daero,*
Yuseong-gu, Daejeon 305-353, Korea
**Corresponding author: Junghwan@kaeri.re.kr*

1. Introduction

Zirconium alloys such as Zircaloy-4, Zirlo, and HANA6 have been used as nuclear fuel claddings in pressurized water reactors (PWRS) because of their low neutron capture cross sections, good corrosion resistance under operating conditions, and satisfying mechanical properties [1]. However, a major problem with zirconium alloys is their reactivity with water, releasing a large amount of hydrogen gas and heat at > 1473K [2]. Moreover, a massive hydrogen explosion by zirconium-steam interaction occurred at the Fukushima Daiichi nuclear power plant.

Since the Fukushima accident, the safty of nuclear power plants has become one of the main issues. Hydrogen, which is generated from the oxidation of the cladding by water or steam at high temperature, is one of the major concerns of reactor safety. Thus, accident-tolerant fuel (ATF) for decreasing the oxidation rate of Zr-alloy at high temperature has been widely studied. As a short-term solution for the development of ATF, protective coating such as cathodic arc ion plating can be considered. It has been previously reported that an arc ion plated Cr film on zircaloy-4 enhances the high-temperature oxidation resistance significantly.

In this study, Cr and Cr-alloy coatings were fabricated on a Zircaloy-4 by cathodic arc ion plating and their microstructure was investigated using X-ray diffraction. The coated samples were also tested in a high-temperature steam environment at 1473K for 2000s.

2. Methods and Results

2.1 Coating procedure

Cr and Cr-alloy coatings were deposited on Zircaloy-4 using the cathodic arc ion plating, which is schematically illustrated in Fig 1. The substrates were cleaned ultrasonically in acetone and an ethanol solution, and the substrates were then mounted in a vacuum chamber. Prior to the deposition, the chamber was evacuated to a pressure of 1 x 10^{-5}Torr, and meanwhile the chamber and substrates were rapidly heated and kept at a temperature of 473K. The substrates were then sputtered and cleaned by ion bombardment to attain sufficient adhesion of the films. The deposition of Cr and Cr-alloy was carried out in a Ar atmosphere with a pressure of 20mTorr. The samples were negatively biased at 150 V during the deposition. Deposition time was 2 h, and the rotation speed of substrate was 2rpm.

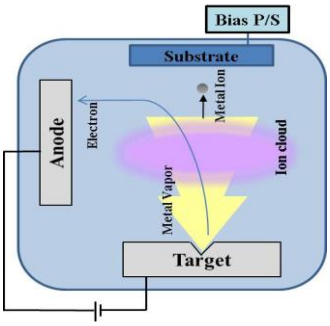

Fig. 1. Schematic representation of cathodic arc ion plating system.

2.2 Characterization of protective film on cladding

The X-ray diffraction pattern of the as-deposited Cr and Cr-alloy films on Zircaloy-4 are shown in Fig. 2. All of the diffraction peaks in both samples can be indexed as the cubic phase of Cr, and chromium oxide phases were not observed. A strong (200) preferred orientation was observed for protective films.

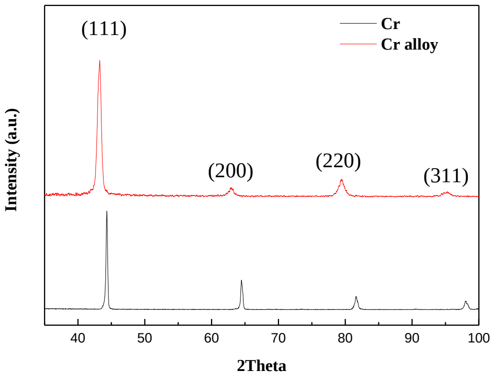

Fig. 2. XRD pattern of the Cr and Cr-alloy coated Zircaloy-4

The residual stress of the films was measured by the $2\theta - \sin^2\psi$ method of XRD. This method was performed by measuring a diffraction angle of 2θ in the tilt axis against the direction of stress measurement, and generating $2\theta - \sin^2\psi$ diagrams (fig.3). The stress value was calculated as [3]

$$\sigma = \frac{E}{2(\upsilon \quad 1)} \cot\theta_0 \frac{\pi}{180} \frac{\partial(2\theta)}{\partial(\sin^2\psi)}, \qquad (1)$$

where $\partial(2\theta)/\partial(\sin^2\psi)$ is the gradient of the 2θ – $\sin^2\psi$ diagrams that approach a linear relationship. In addition, θ_0, E, and ν are the standard Bragg diffraction angle, Young's modulus, and Poisson ratio of the films.

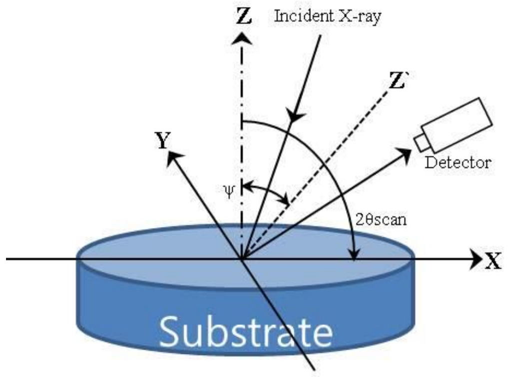

Fig. 3. The optic system for X-ray stress measurement.

After the 2θ-$\sin^2\psi$ measurement, the residual stress and strain were estimated using Eq. (1). As the results of the calculation, the estimated residual stress of Cr films is 0.06%, and that of Cr-alloy film is about 0.09%.

2.3 Corrosion behavior of protective film

To investigate the effect of a protective Cr and Cr-alloy film on the high-temperature oxidation behavior of Zircaloy-4, the high-temperature oxidation tests were performed in a 1473K steam environment using a thermo-gravimetric analyzer for up to 2000s. The oxidation test specimens with an outer diameter, inner diameter, and length of 9.5, 8.3 and 30mm, respectively, were cut from the longer tubes, deburred, grounded at the both ends, and cleaned in an ultrasonic bath of acetone and ethanol. The polished specimens were placed in a basket made of Pt inside the furnace. The temperature was increased at a heating rate of 50 K/min for up to 1473K with Ar gas to prevent oxidation during the heating process. Steam was supplied into the furnace with Ar carrier gas immediately after the temperature reached 1473K. The steam supply was maintained constant at 1473K for 2000s before the temperature was decreased by air cooling.

The weight gain of the Cr and Cr-alloy coated Zircaloy-4 is shown in Fig. 4. The Cr and Cr-alloy films showed excellent oxidation resistance. However, the weight gain of the Cr coated Zircaloy-4 cladding was larger than that of the Cr-alloy coated Zircaloy-4. Therefore, the results of the high-temperature oxidation test showed that the Cr-alloy layer can effectively protect the claddings from a loss of coolant accident (LOCA).

Fig. 5 shows Cr and Cr- alloy coated samples after the high temperature oxidation test. Despite of the difference in the thermal expansion coefficients between film and Zr, the spalling phenomenon was not observed after the high-temperature oxidation test. It can be assumed that the adhesion property of the Cr and Cr alloy layer by the AIP can be guaranteed at up to 1473 K.

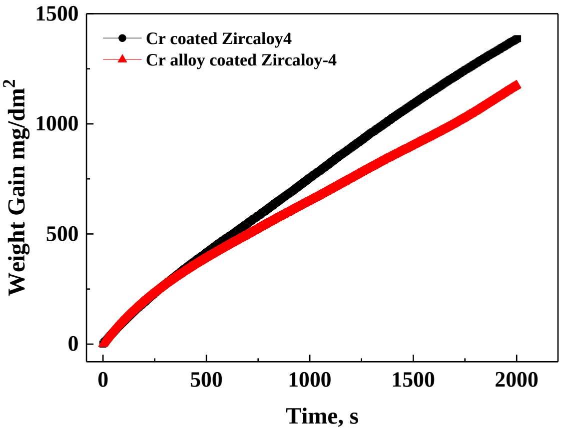

Fig. 4. Corrosion behaviors of the Cr and Cr-alloy coated Zircaloy-4 in 1473K steam for 2000s.

Fig. 5. The Cr and Cr-alloy coated Zircaloy-4 after high temperature steam oxidation tests.

3. Conclusions

In this study, the dense and homogeneous Cr and Cr alloy film as a protecting layer was successfully deposited on the Zircaloy-4 claddings by the AIP system. Compared to the Cr, and Cr alloy coated Zircaloy-4 exhibited superior oxidation resistance. Based on the result of high temperature steam test, the Cr alloy is suitable for protective film. The cladding performance, such as corrosion, creep and irradiation growth, will be investigated.

ACKNOWLEGEMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2017M2A8A5015058).

REFERENCES

[1] K. A. Terrani, C. M. Parish, D. Shin, B. A. Pint, Protection of zirconium by alumina- and chromia-forming iron alloys under high-temperature steam exposure, J. Nucl. Mater. Vol. 438, pp64-71, 2013.

[2] H. G. Kim, I. H. Kim, Y. I. Jung, D. J. Park, J. Y. Park , Y. H. Koo, High-temperature oxidation behavior of Cr-coated zirconium alloy, TopFuel 2013, pp842-846, 2013.

[3] I. C. Noyan, J.B. Cohen, An X-ray diffraction study of the residual stress-strain distributions in shot-peened two-phase brass, Mater. Sci. Eng. Vol.75, pp1799-193, 1985.