

Corrosion Properties of Cr Coating Deposited on Nuclear Fuel Cladding

Jung-Hwan Park*, Yang-Il Jung, Dong-Jun Park, Hyun-Gil Kim, Byoung-Kwon Choi, Young-Ho Lee
ATF Technology Development 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 have been used as primary materials for fuel cladding which protect the nuclear fuel from the outside in the nuclear power system. Zirconium alloys have very low absorption cross-section of thermal neutrons, high hardness, ductility, and corrosion resistance [1]. However, they had problems with nuclear reactor safety as they reacted violently with steam at high temperature, producing large amounts of hydrogen and heat, and having low mechanical strength at high temperature. Moreover, a massive hydrogen explosion by zirconium-steam interaction occurred at the Fukushima Daiichi nuclear power plant.

The development of accident-tolerant fuel cladding has been widely studied since the Fukushima nuclear reactor accident [2]. Ideas and new concepts have been proposed for accident-tolerant fuel cladding to prevent hydrogen explosion by inhibiting reaction with steam in the accident environment. Therefore, the ATF research was actively carried out in the early development period to replace zirconium alloys using materials such as SiC, FeCrAl, etc., which have oxidation resistance better than zirconium [3,4]. However, the phenomenon of dissolution in cooling water under normal operating conditions was observed, and some materials had lower economic feasibility because the neutron absorption cross-section area was larger than zirconium. To overcome these problems, many researches are underway to take both stability and economy by coating the surface of zirconium cladding. By applying coating technology to zirconium cladding, it is easy to obtain corrosion resistance without a change in the base materials. Recently, Terrani et al. reported the oxidation resistance of Fe-based alloys for protecting zirconium alloys from the rapid oxidation in a high-temperature steam environment. Kim and co-workers also reported the corrosion behavior of Cr-coated zirconium alloy using a plasma spray and laser beam scanning [5].

In the present work, Cr anti-oxidation coating was fabricated on a commercial Zircaloy-4 cladding using cathodic arc ion plating (CAIP) because cathodic arc ion plated films tend to be denser and have better adhesion characteristics than films produced using other methods [6]. The Cr system was selected because of its good corrosion resistance. The microstructures of arc ion plated Cr coating were characterized. The oxidation behavior of the coating was analyzed.

2. Experimental

CAIP is a well recognized method of producing protective coatings due to its high ionization efficiency and excellent film adhesion. It is a promising method for depositing oxidation-resistant coatings on nuclear fuel claddings.

Pure Cr coating was deposited on the Zircaloy-4 using the CAIP with Cr target (99.59% purity). Figure 1 shows the CAIP system which was designed to coat protective film onto the surface of a nuclear cladding.

The substrates were cleaned ultrasonically in acetone and an ethanol solution, and the substrates were then mounted in a vacuum chamber. The chamber was evacuated to a pressure of 1×10^{-5} Torr, and heated simultaneously to 1473 K to remove the residual gas adsorbed on the chamber wall and substrates. Prior to the deposition, the substrates were sputter cleaned using Ar^+ ions under -400V negative bias voltage for 5 min. Cr ion bombardment was applied to remove contaminants and ensure good adhesion of deposited coatings. The deposition of Cr was carried out in an Ar atmosphere with a pressure of 20mTorr. In order to study the effects of negative bias voltage, different negative bias voltages ranging from -25 to -100V were applied. After deposition, the coatings were polished to reduce the influence of the roughness, as well as for more precise measurements.



Fig. 1. Cathodic arc ion plating system for ATF claddings.

To investigate the effect of a sputtered Cr 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 50mm, 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.

3. Result and discussions

3.1 Characterization of protective film on cladding

The thickness and surface micrograph of the deposited coatings were analyzed using a SEM. The cross-sectional SEM image of the Cr coated Zircaloy-4 sample was used to detect the thickness of the deposited film. At the same time, the thickness of the deposited coating can also be analyzed by cross-sectional SEM image. Figure. 2 Shows the cross-sectional SEM image of the Cr coated Zircaloy-4 cladding. From the cross-sectional SEM image, it shows obviously that the deposited coating is very dense and the Cr coating is bonded tightly to Zircaloy-4 cladding. The thickness of Cr-alloy coatings is was about 20 μ m

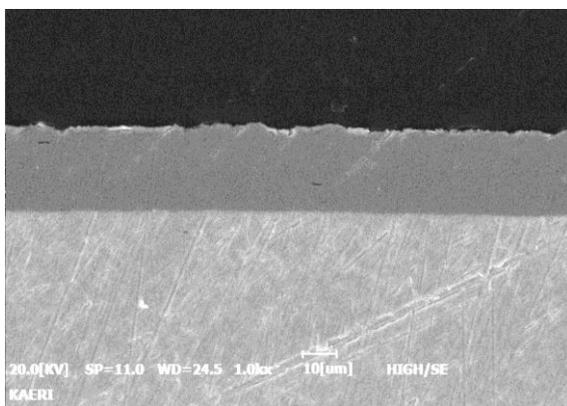


Fig. 2. Cross-sectional SEM image of Cr coated Zircaloy-4 cladding.

The XRD pattern of the Cr layer is shown in Fig. 2. According to our peak assignment based on the JCPD data, the Cr layer does not contain impurity phase and chromium oxide phases. All of the diffraction peaks can be indexed as the cubic phase of Cr (JCPDS card No. 06-0694). Therefore, a pure Cr coating was successfully formed on the Zircaloy-4 cladding by the arc ion plating.

3.2 Corrosion behavior of protective film

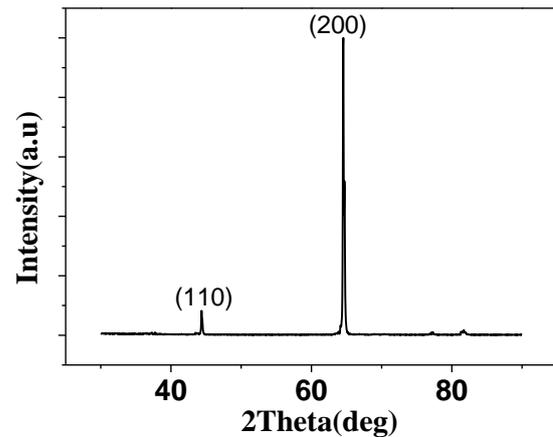


Fig. 2. XRD pattern of the Cr-alloy coated Zircaloy-4

The weight gain of the Cr-alloy coated Zircaloy-4 is shown in Figure. 3. Generally, Adhesion is improved by increasing negative bias voltage because the kinetic energy of the striking adatoms is increased with the increase in the bias voltage. Therefore, the weight gain of the Cr coated Zircaloy-4 cladding decreases when the negative bias voltage increases from 25V to 100V. . However, all the Cr films showed excellent oxidation resistance.

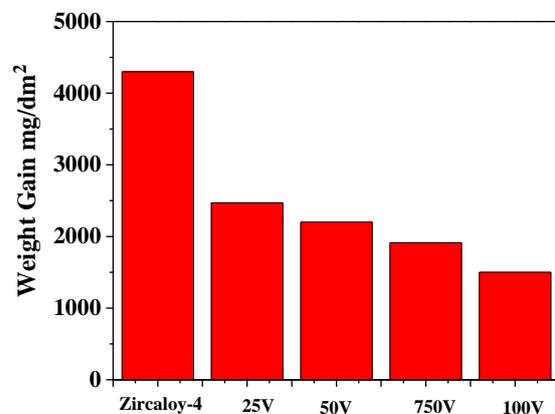


Fig. 4. Corrosion behaviors of the Cr-alloy coated Zircaloy-4 in 1473K steam for 2000s.

3. Conclusions

In this study, the dense and homogeneous Cr film as a protecting layer was successfully deposited on the Zircaloy-4 claddings by the AIP system and the influence of negative bias voltages on the corrosion property are studied through high-temperature steam oxidation test. Compared to the Zircaloy-4, Cr coated Zircaloy-4 exhibited superior oxidation resistance. The Corrosion resistance is obviously influenced by negative bias voltage. The influence of negative bias voltage on

the microstructure and adhesion property of the Cr coatings will be investigated

ACKNOWLEDGEMENT

This work was supported by the National Institute of Energy Technology Evaluation and Planning (KETEP) funded by the Korea government (MOTIE) (No. 20171510101990).

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] C.C. Tang, M. Stueber, H.J. Seifert, M. Steinbrueck, Protective coatings on zirconium-based alloys as accident-tolerant fuels (ATF) claddings. *Corrosion Reviews* 2017, 35(3):141-165.
- [3] J.D. Stempien, D.M. Carpenter, G. Kohse, M.S. Kazimi, Characteristics of Composite Silicon Carbide Fuel Cladding After Irradiation Under Simulated PWR Conditions. *Nuclear Technology* 2013, 183:13-29.
- [4] K.A. Terrani, S.J. Zinkel, L.L. Snead, Advanced oxidation-resistant iron-based alloys for LWR fuel cladding. *Journal of Nuclear Materials* 2013, 448:420-435.
- [5] 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.
- [6] T. Nishikiori, T. Nohira, Y. Ito, Electrochemical evaluation of high temperature hydrogen impermeability of TiN films and its dependence on film thickness. *Thin Solid Films*, Vol. 408, pp148-154,