Effects of Negative Bias Voltage on the Corrosion Properties of Cr-alloy Coatings by Cathodic Arc Ion Plating for Accident Tolerant Fuel Cladding

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1. Introduction

Zirconium alloys such as Zircaloy-4, Zirlo, and HANA6 are widely used as nuclear energy materials owing to their low neutron capture cross sections, high mechanical strength, creep resistance, and corrosion resistance in boiling water and steam environment. The major application of zirconium alloys in PWR and BWR type reactors is fuel cladding tubes [1].

Since the Fukushima accident, the safty of nuclear power plants has become one of the main issues. However, Zirconium alloys are vulnerable to high-temperature steam oxidation, because zirconium reacts with water at high temperature, releasing a large amount of hydrogen gas and heat above 1473 K. Therefore, accident tolerant fuel (ATF) has been widely studied. To minimize the fuel cladding failures, the oxdation rate of Zirconium alloys at high temperature should be decreased. As a short-term solution for the development of ATF, corrosion resistance coatings can be considered. Recently, Bischoff *et al.* reported the oxidation resistance of Cr for protecting zirconium alloys from the rapid oxidation in a high-temperature steam environment [2]. Park et al. also reported the corrosion behavior of Cr-coated Zircaloy-4 [3]. All of these Cr coatings showed excellent corrosion resistance. FeCrAl alloys also showed a low weight change after LOCA test, because of the protective Al_2O_3 scale formed on the surface [4]. However, it is well known that eutectic interaction or inter-diffusion between FeCrAl and Zr at high temperature [1].

Coating methods can be divided into two major categories: physical vapor deposition (PVD) and chemical vapor deposition (CVD) [5]. So far, PVD has been widely used to deposit coatings for Zr-based fuel cladding because it shares several advantages of other techniques, including high deposition rate, low deposition temperature, and excellent bonding with substrate,

Among the PVD coating methods, cathodic arc ion plating (CAIP) is one of the promising methods to develop protective coatings on Zr-based fuel cladding because cathodic arc ion plated films tend be denser and have better adhesion characteristics than films produced using other method [3].

Cr and Cr-based alloy have high melting point and good corrosion resistance. Thus, they were widely used as protective films. In this study, we attempted to improve the corrosion resistance of Zr-based nuclear cladding using CAIP. It was investigated the influence of the negative bias voltage on the corrosion resistance of the Cr-alloy films exposed to high temperature and steam environment. .

2. Methods and Results

2.1 Coating procedure

Cr-alloy coating was deposited on the Zircaloy-4 using the CAIP with Cr-alloy target (99.5% 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 x 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 -500V 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-alloy 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 -150 to -250V 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.

2.2 Characterization of the coatings

The thickness and surface micrograph of the deposited coatings were analyzed using a SEM. The cross-sectional SEM image of the Cr-alloy 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-alloy coated Zircaloy-4 cladding. From the cross-sectional SEM image, it shows obviously that the deposited coating is very dense and the Cr-alloy coating is bonded tightly to Zircaloy-4 cladding. The thickness of Cr-alloy coatings is was about 40 μ m

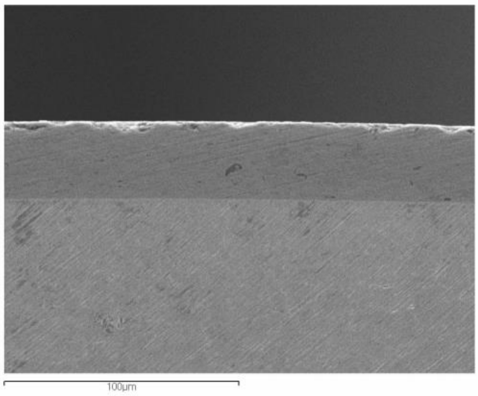

Fig. 2. SEM image of the Cr-alloy coated Zircaloy-4 by AIP

The pristine microstructure of the deposited coating was investigated using a glancing angle X-ray diffractometer with filtered Cu Kα radiation. The incident X-ray beam angle was 2°. The detected diffraction angle (2θ) was scanned form 20° up to 90°. The scan rate and the step size were 2°/min and 0.01°.

Fig. 3 shows structure analysis of Cr-alloy film on Zircaloy-4. The XRD result exhibits that all of the diffraction peaks can be indexed as the cubic phase of Cr, and chromium and aluminum based oxide phases were not observed.

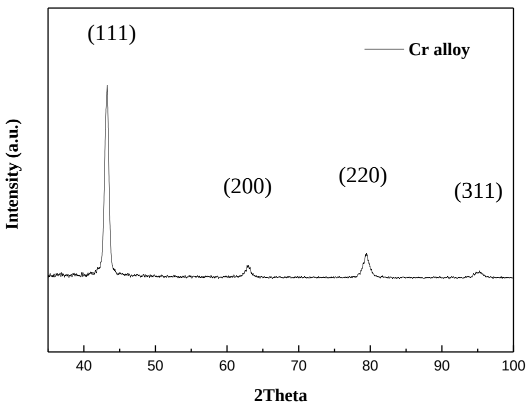

Fig. 3. XRD pattern of the Cr-alloy coated Zircaloy-4

2.3 High-temperature steam oxidation test

To investigate the effect of a protective 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 2000 s. 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 1473 K 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 1473 K. The steam supply was maintained constant at 1473 K for 2000 s before the temperature was decreased by air cooling.

The weight gain of the Cr-alloy coated Zircaloy-4 is shown in Figure. 4. 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-alloy coated Zircaloy-4 cladding decreases when the negative bias voltage increases form 150V to 250V. However, all the Cr-alloy films showed excellent oxidation resistance. Moreover, the oxidation resistance of a Cr-alloy surface is expected to be better than the weight gain data, because the Cr-alloy coated area is only outside the surface of the claddings. 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).

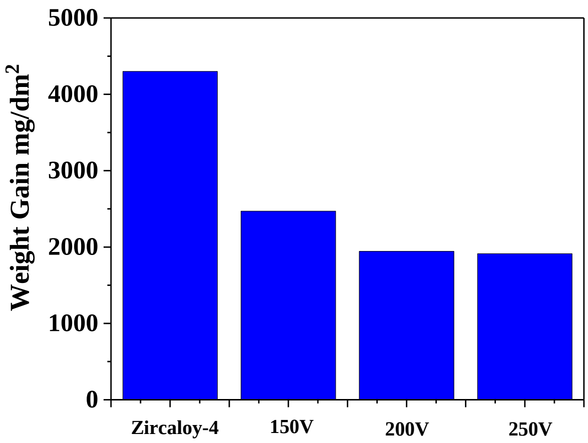

Fig. 4. Corrosion behaviors of the Cr-alloy coated Zircaloy-4 with different negative bias voltages.

3. Conclusions

In this study, the dense and homogeneous Cr-alloy 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-alloy 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-alloy coatings will be investigated

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