

Effect of Thickness on Oxidation Behavior of Cr coated Zircaloy-4 using Arc Ion Plating

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1. Introduction

Ever since the Fukushima accident, accident tolerant fuel (ATF) has been widely studied [1]. To increase the life time and safety of nuclear claddings, there are increasing demands for protective coatings exhibiting excellent oxidation resistance. Therefore, coating methods, providing a dense and highly adherent coating layer, should be required.

Among the surface coating methods, Arc ion plating (AIP) is an important deposition technique that utilizes a cathode vacuum arc discharge to deposit film of high performance [2]. Many metal and oxide films are produced by using this method because of the high kinetic energy of the ions, ionization efficiency and deposition rate.

Candidate materials for a protective layer have higher thermal neutron absorption cross sections than Zr[3]. However, there is no systematic study of thickness effect on oxidation resistance of protective layer. In this study, Cr films with different thickness (from 1 μm to 50 μm) were deposited on the cladding surfaces by AIP. The high temperature oxidation resistance of Cr films with different thicknesses has been investigated.

2. Methods and Results

2.1 Growth and characterization of Cr film on Zircaloy-4 by AIP

The Cr coatings were deposited on the Zircaloy-4 claddings using arc ion plating method with Cr target (99.9%, purity). The claddings were cleaned ultrasonically in ethanol and acetone, and the claddings were then mounted in a vacuum chamber. Fig.1 is a diagram of arc ion plating (AIP) system.

In the beginning, the chamber was evacuated down to a base pressure of less than 1×10^{-5} Torr meanwhile the chamber and the substrates were rapidly heated and kept at the temperature 473 K to eliminate tiny liquid contaminants and solid pollutants.

For the 10 min plasma cleaning, high purity argon (Ar, 99.99% purity) was introduced and the substrate negative bias voltage was fixed at -600 V. The argon flow rate was determined by the total pressure. When the deposition began, the Cr target was burnt by the triggers, and the arc current was kept at 150 A.

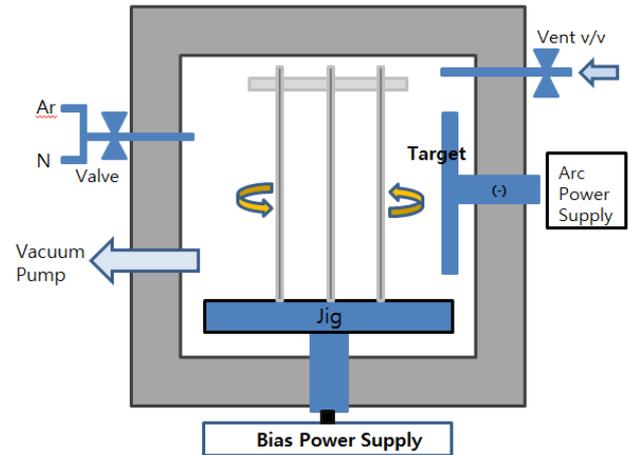


Fig.1 Schematic diagram of AIP system

The partial pressure of Ar was kept at 1×10^{-2} Torr. The samples were negatively biased at 50V and the substrate temperatures were kept constant a 473 K during the deposition. Detailed conditions of the process are shown in Table 1.

Table 1. Coating conditions for Cr coated Zircaloy-4

| | Process Pressure | Ar Flow rate | Bias Voltage | Cleaning Time | Arc Power |
|-----------------|------------------|--------------|--------------|---------------|-----------|
| Ion bombardment | 1.5 mTorr | 50 sccm | -600 V | 10min | 60A |
| | Process Pressure | Ar Flow rate | Bias Voltage | Coating Time | Arc Power |
| Cr coating | 20 mTorr | 100 sccm | -50V | 6h~14h | 150A |

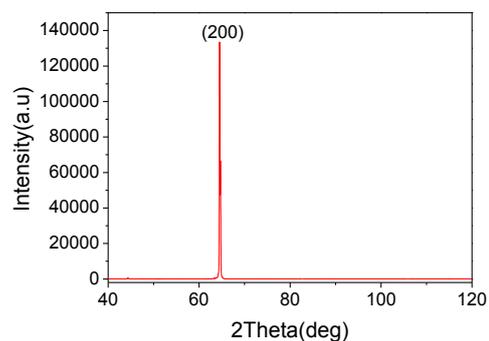


Fig.2 X-ray diffraction pattern of Cr coated Zircaloy-4

Fig.2 is shown the microstructure of the Cr coated Zircaloy-4 samples using a glancing angle X-ray diffractometer with filtered $\text{Cu K}\alpha$ radiation. The incident X-ray beam angle was 2° . The detected diffraction angle (2θ) was scanned from 40° to 120° . The scan rate and the step size were $2^\circ/\text{min}$ and 0.01° .

The XRD result shows that only the diffraction peaks of Cr can be observed without oxide phases (CrO, Cr₂O₃).

Fig.3 shows the cross-sectional SEM images of the Cr-coated Zircaloy-4 cladding. The Cr layers with the thickness of 1 μm to 50 μm were deposited on Zircaloy-4.

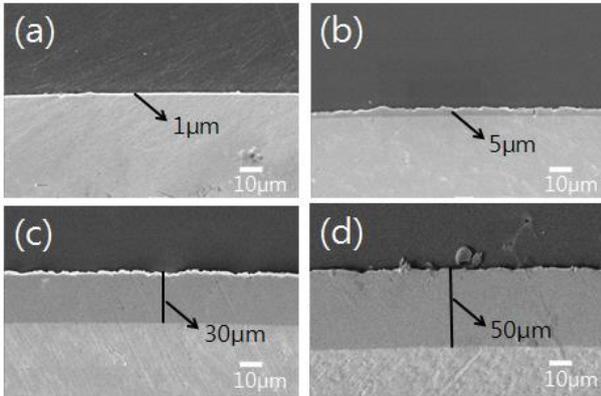


Fig.3 SEM micrographs showing coating thickness

2.2 Oxidation behavior of Cr coated Zircaloy-4

The high-temperature oxidation tests for the pristine and Cr-coated Zircaloy-4 were performed in a 1473 K steam environment using a thermo-gravimetric analyzer for up to 2000 sec [4]. The oxidation test specimens with an outer diameter, inner diameter, and length of 9.5, 8.3 and 3 mm, respectively, were cut from the longer tubes, deburred, grounded at the both ends, and cleaned in an ultrasonic bath of acetone and ethanol. The temperature increased at a heating rate of 50 K/min for up to 1473 K. The Ar gas flowed at a rate of 200ml/min in order to minimize the initial oxidation during the heating process. After the temperature reached 1473 K, the flow rate of Ar gas as carrier gas was set at 20 ml/min and the steam was supplied at a constant rate during the oxidation test. The oxidized samples were cooled down to room temperature by air cooling.

Fig. 4 shows the weight gain as function of the film thickness for Cr films. The weight gain is about 4000 mg/dm² for pristine Zircaloy-4, and the dramatically decreases to 1300 mg/dm² for 30 μm Cr film. However, the weight gain does not change much between 30 μm and 50 μm.

Fig. 5 show Cr-coated Zircaloy-4 before and after the high-temperature oxidation tests. As shown Fig.5, spalling phenomenon was not observed after the high temperature oxidation tests. It is assumed that the adhesion property of the Cr layer by the AIP can be guaranteed regarding the thermal expansion point at up to 1473 K

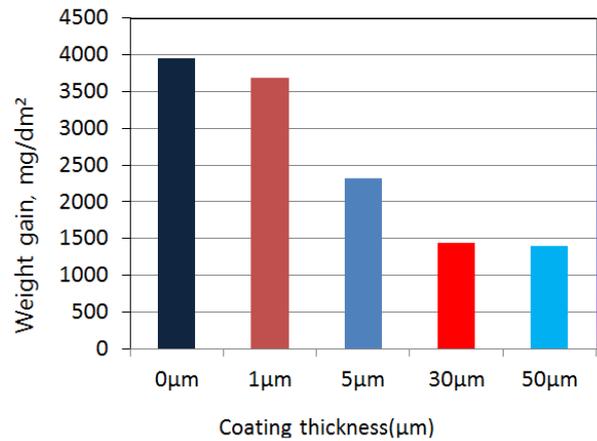


Fig.4 Results of high temperature steam oxidation test

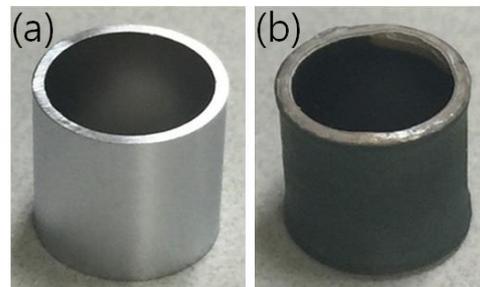


Fig.5 Cr coated Zircaloy-4 before (a) and after (b) the high temperature oxidation tests.

3. Conclusions

In conclusion, Cr films with different thicknesses (1-50 μm) were deposited on Zircaloy-4 by AIP method. With increase of thickness of Cr film, the oxidation resistance of Zircaloy-4 was improved. The weight gain of 30 μm film is 1300 mg/dm² and the weight gain does not change between 30 and 50. Therefore, to obtain Cr films with good oxidation resistance, it is suggested that the thickness of Cr film is better to be thicker than 30 μm.

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