Corrosion Behavior of Cr Alloy Coatings Deposited by DC Magnetron Sputtering on Zircaloy-4

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1. Introduction

After the Fukushima accident in 2011, accident tolerant fuel (ATF) has attracted more attention in the nuclear industry [1]. The purpose of ATF is to improve the high temperature steam oxidation behavior of cladding, thus preventing or delaying 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 [2,3,4]. 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. Because of these problems, many researches are underway to take both stability and economy by coating the surface of zirconium cladding. Coating materials subject to high temperature, corrosion environment, are required for thermal stability, adhesion, and oxidation. In particular, in extreme environments such as nuclear power generation, better oxidation resistance and adhesion are required.

At present, the main coating technology can be divided into three categories: Spray coating, chemical vapor deposition (CVD), and physical vapor deposition (PVD) [5]. Up to now, the PVD coating is widely applied to deposit coating for zirconium cladding. The advantages of the PVD coating are low cost, excellent bonding to substrate, and dense structure.

Cr alloys have high melting point, good thermal conductivity, and excellent oxidation resistance. Thus, it was widely used to surface modified. In this study, we attempted to improve the corrosion resistance of zirconium cladding using magnetron sputtering technology. For this purpose, we coated Cr alloy on Zircaloy-4 claddings and their corrosion behavior in high temperature and steam environment was also investigated.

2. Experimental

The Cr alloy coatings were deposited on the Zircaloy-4 claddings with Cr-Al target (99.5% purity) using direct current (DC) magnetron sputtering, which is schematically illustrated in Fig 1. The main deposition conditions used in this study are summarized in Table 1.

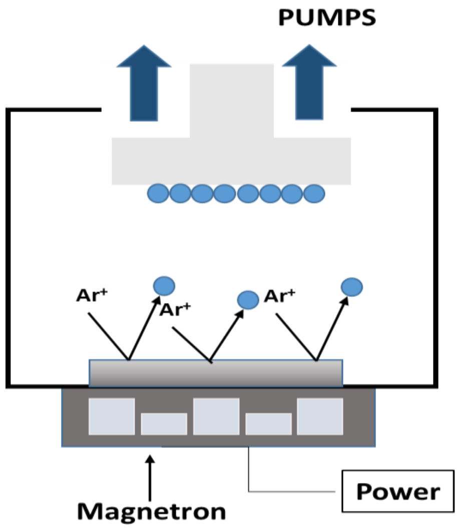

Fig. 1. Schematic representation of DC magnetron sputtering system.

Table 1. Main deposition conditions

Substrate	**Zircaloy-4**
Target-to-substrate spacing	**10cm**
Pre-sputtering time	**10min**
Residual pressure	**10^{-5} Torr**
Working pressure	**5 mTorr**
DC power	**4kW**
Ar flow rate	**100sccm**
Bias	**-50V**
Temperature	**200°C**

To investigate the effect of a sputtered 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 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 X-ray diffraction pattern of the as-deposited Cr-alloy film on Zircaloy-4 is 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. Fig. 2 shows the SEM micrograph of cross-section of Cr alloy coating deposited on a Zircaloy-4 cladding. As seen in fig 2, the coating thickness was approximately 10 μm. Because x-ray could not penetrate the thick film, Zircaloy-4 peaks did not show up. The coatings exhibited dense, homogenous, and crack-free structure.

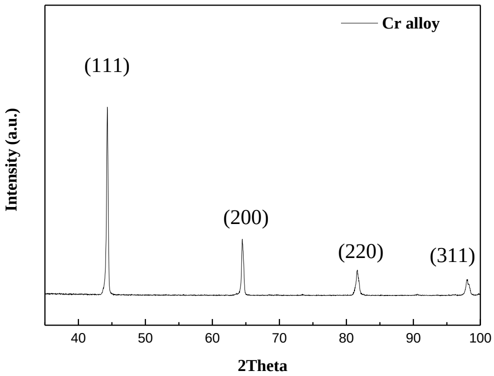

Fig. 2. XRD pattern of the Cr-alloy coated Zircaloy-4

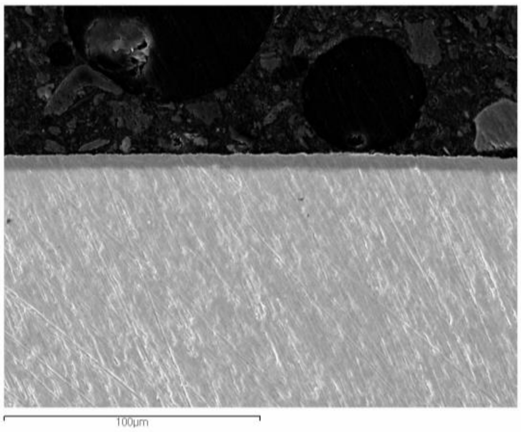

Fig. 3. Cross-sectional SEM image of Cr-alloy coated Zircaloy-4 cladding.

3.2 Corrosion behavior of protective film

Fig. 3 shows the mass gain per unit area versus time curves of the Zircaloy-4 and the Cr-alloy coated Zircaloy-4. The Cr-alloy film showed good oxidation resistance as compared to the pure zircaloy-4. Therefore, the results of the high-temperature oxidation test showed that the sputtered Cr-alloy layer could protect the claddings from a loss of coolant accident.

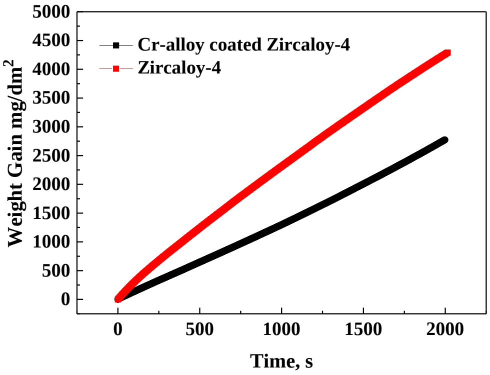

Fig. 4. Corrosion behaviors of the Cr-alloy coated Zircaloy-4 in 1473K steam for 2000s.

3. Conclusions

In this study, the dense and homogeneous Cr alloy film as a protecting layer was successfully deposited on the Zircaloy-4 claddings by the DC magnetron sputtering system. Compared to the pure Zircaloy-4, Cr alloy coated Zircaloy-4 exhibited high oxidation resistance. The structure of the coating layer after oxidation will be investigated.

ACKNOWLEGEMENT

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