# Corrosion behavior of Cr-alloy coated Zircaloy-4 in water vapor environment at 1573K

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## 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 [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 [2].

In order to eliminate or reduce the risk of hydrogen explosion cause by zirconium water reaction under accident conditions, accident tolerant fuel (ATF) has been widely studied in the nuclear industry. 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]. 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.

Among the reported coating for accident tolerant fuel cladding, Cr is one of the most candidate materials for ATF application. Bischoff and Brachet tried to deposit Cr coating on M5 by a special PVD process [4]. Park et al. used arc ion plating and studied the high temperature steam oxidation performance of Cr-coated zirconium alloy [5]. Zhong et al deposited Cr coating and Cr-Al alloy coating on Zircaloy-2 alloy, and studied the steam oxidation properties of two coatings at 700°C [6].

Because of the excellent high temperature oxidation resistance and corrosion resistance of Max phase, nitride and other ceramic materials, many researchers also use this kind of materials for protective coating on zirconium alloy. Ma et al prepared CrN coating and uncoated zirconium alloy, and compared the oxidation resistance [7]. The results show that at 1160°C, the CrN coating shows no signs of cracking and falling off, and the weight gain is 97.7% less than that of uncoated zirconium alloy.

In this study, Cr-Al coating is deposited on Zircaloy-4 as protective layer. The surface morphology, thickness and crystalline phase are characterized by SEM and XRD. The high temperature steam oxidation performances of Cr alloy coating under 1573K in steam atmosphere are investigated.

## 2. Methods and Results

### *2.1 Coating procedure*

Cr-alloy coating was deposited on Zircaloy-4 tube by using cathodic arc ion plating, which is schematically illustrated in Fig 1. Before the coating, the Zircaloy-4 tubes were cleaned ultrasonically in acetone and an ethanol solution, and the substrates were then mounted in a vacuum chamber. Cr-alloy target was used to deposit the coating. 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 an 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. After deposition, the coatings were polished to reduce the influence of the roughness, as well as for more precise measurements. Fig 2 shows a Cr-alloy coated sample by CAIP.

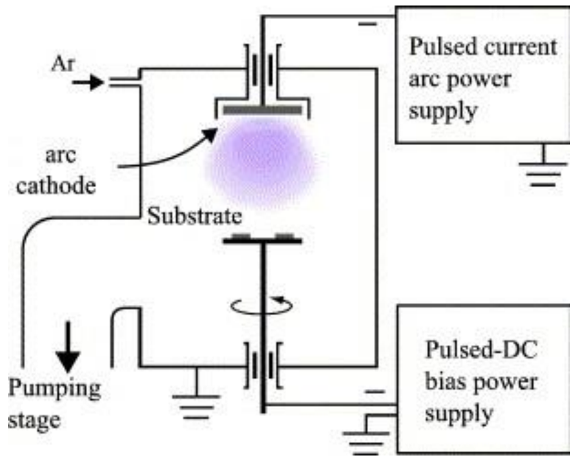


Fig. 1. Schematic representation of cathodic arc ion plating system.

Fig. 2. Cr-alloy coated Zircaloy-4 specimen.

### *2.2 Microstructural properties*

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. Figure. 2 Shows the cross-sectional SEM images 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 20 μ m.

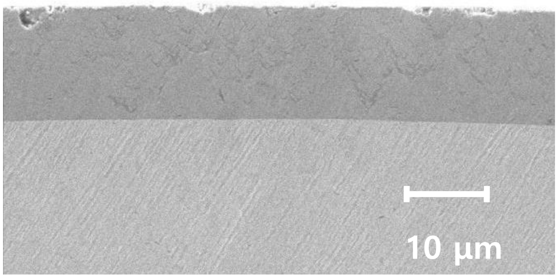


Fig. 3. SEM image of the Cr-alloy coated Zircaloy-4 by AIP

X-ray diffraction pattern of the as-deposited Cr and Cr-alloy films on Zircaloy-4 are shown in Fig. 4. 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 (111) preferred orientation was observed for protective films.

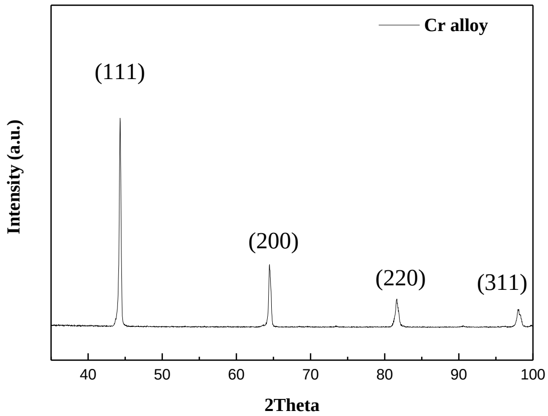


Fig. 4. XRD pattern of the Cr-alloy coated Zircaloy-4

### *2.3 Corrosion behavior of protective film*

High temperature steam oxidation performance test was carried out in thermo-gravimetric analyzer. 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 1573K 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 1573K. The steam supply was maintained constant at 1573K for 1000s before the temperature was decreased by air cooling.

The weight gain of the Cr-alloy coated Zircaloy-4 and Zircaloy-4 is shown in Fig. 5. The Cr-alloy films showed excellent oxidation resistance.

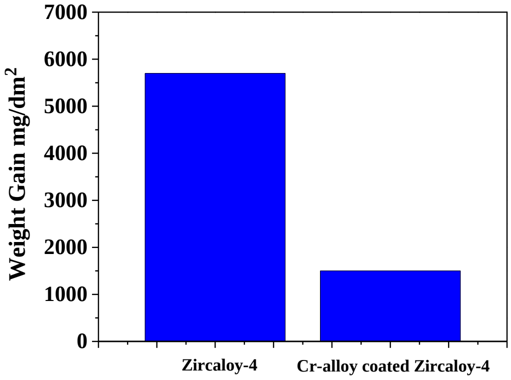


Fig. 4. Corrosion behaviors of the Cr and Cr-alloy coated

## 3. Conclusions

In this study, the Cr alloy film as a protecting layer was successfully deposited on the Zircaloy-4 claddings by the AIP system. The results of this study that the oxidation resistance of Cr-alloy coating is better than that of Zircaloy-4. And Cr-alloy coating plays an excellent protective role on the internal Zircaloy-4 under 1573K in steam atmosphere

## ACKNOWLEGEMENT

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