

High Temperature Oxidation Behavior of Cr Layer Coated on Zr Fuel Cladding Using Arc Ion Plating Technique

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1. Introduction

Zirconium based alloy have been generally used for nuclear fuel cladding due to their fairly good resistance to corrosion from water at elevated temperatures and a very low absorption cross-section of thermal neutrons. After Fukushima nuclear reactor accident, however, the development of new concept of fuel cladding is required because the aggressive oxidation and significant heat production of existing zirconium-based alloys in a high-temperature steam environment could significantly increase the risk of explosion caused by hydrogen gas [1-7].

In this study, we aim to develop surface coated zirconium cladding with Cr to enhance safety of nuclear reactor during accident. We found that Cr has an excellent oxidation resistance at high temperature. For Cr layer coating, arc ion plating technique was used. To investigate efficiency of the Cr coating to act as oxidation resistant barrier, high temperature oxidation test as well as metallurgical investigation were carried out. Cr coated zirconium-based alloy claddings oxidized at 1200°C in a steam environment showed much lower weight gain compared to bare zirconium-based alloy cladding samples. The microstructure of the oxide layers formed on coated zirconium tubes during high temperature oxidation test is characterized systematically by using various analyzing tools.

2. Methods and Results

In this section some of the experimental procedure and technical details of apparatus are described. Highlight data obtained from high temperature oxidation test and analyzed results from microstructural characterization study are also presented.

2.1 Coating Technique

Fig. 1 shows the surface modification technology using arc ion plating. Regarding the arc ion plating, the property of coated layers was controlled by arc current, partial pressure of Ar, and bias during coating. The Zircaloy-4 (Zry-4) cladding temperature kept constant at 200°C. The advantage of arc ion plating is to form the coating layer without deforming or damaging the base material.

2.2 High Temperature Oxidation Test

For the high temperature oxidation tests, 400 mm long tubular Zr alloy cladding samples were filled with 10 mm long alumina pellets to simulate the heat capacity of the fuel. The furnace was heated to a pre-test hold temperature of 300°C within 240 s, where the steam flow and sample temperature were stabilized for 500 s. A heating rate of 14°C/s from 300°C to 1200°C was used. After exposure at 1200°C for 300 s, the tube was cooled slowly to 800°C and then quenched by flooding from the bottom of the chamber with water. The Specimen temperature was measured by type-R thermocouple located near the sample center and the quartz tube provides an enclosed volume for steam flow and water quench, both of which are introduced through the bottom. Further details of the test equipment and experimental procedures can be found in our previous paper [7].

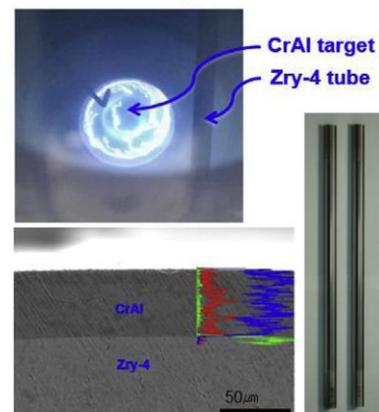


Fig. 1. Manufacturing example of surface modification technology using arc ion plating.

2.3 Results

Fig. 1(a) and (b) show photographs of the Cr-coated and uncoated Zr alloy cladding tubes after high temperature oxidizing test at 1200°C for 300 s where the color difference due to different oxides formation are clearly visible. The Cr-coated tube showed a much smaller burst opening than the Zr alloy cladding sample. Although the Cr-coated tube showed small axial cracks on the surface near the ballooned region, significant cracking or spallation of the Cr coating was not observed after the integral LOCA test. This indicates that the rapid temperature change during the LOCA experiment had little effect on the adhesion between the

Cr layer and the Zr matrix despite their different thermal expansion coefficients.

Fig. 2 represents the experimental and calculated XPS spectra of the oxide layer of the corroded sample in the binding energy range of 572–582 eV, which includes the Cr 2p_{3/2} peaks. Spectral decompositions of the Cr 2p_{3/2} peaks were conducted to quantitatively evaluate the oxidation process. The Cr 2p_{3/2} lines were fitted to two oxidation states at 575.36 (CrO₂), 576.61 eV (Cr₂O₃), 578.16 (Cr(OH)₃) and 579.06 eV (CrO₃).



Fig. 2. Photographs of Zr cladding specimens (a) with and (b) without Cr coating after high temperature oxidation.

Thus, the XPS spectra may confirm the presence of CrO₂, Cr₂O₃, CrO₃, and Cr(OH)₃ phases in the oxide layer on the surface of the oxidized Cr coated specimen. The primary phase was Cr₂O₃.

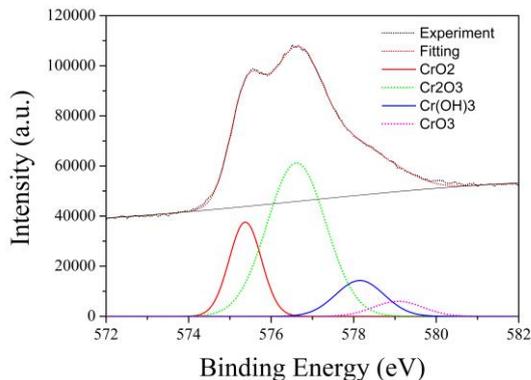


Fig. 3. Fraction of counts lost with voltage and charge sensitive preamplifiers as a function of the true count rate.

However, another characterization technique, X-ray diffraction, may have to be used to differentiate the structures of the Cr oxides; these results will be discussed later.

3. Conclusions

To investigate the oxidation of the Cr layer coated Zr alloy cladding in accident condition of LWR, cladding samples were oxidized at 1200°C for 300 s. After the test, the oxidation of the Cr layer coated Zr alloy cladding and the microstructure of the oxide layer were

examined by various analytical techniques. Based on the results, the following conclusions were drawn.

1. The Cr coated Zr alloy cladding showed superior corrosion and oxidation resistance compared to Zr-based alloys used as current nuclear-fuel cladding.
2. The Cr coated Zr alloy cladding that was oxidized at 1200°C. Although various chromium oxide phases such as CrO₂, Cr₂O₃, CrO₃, and Cr(OH)₃ were present near the outer oxide surface, the primary phase was a- Cr₂O₃.

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