Microstructural analysis and XPS investigation of nodular oxides formed on Zricaloy-4

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1. Introduction

Zircaloy-4, which is zirconium (Zr) primarily alloyed with tin and iron is one of the most commonly used fuel-cladding materials in nuclear industry due to its fairly good resistance to corrosion, a very low absorption cross-section of thermal neutrons, adequate strength, and formability. In the nuclear reactors, this Zircaloy-4 or other Zr based alloys would experience corrosion and hydrogen uptake under various oxidizing environments, such as water chemistry during a normal operation and steam at high temperature under transient or accident condition. Protective black oxide layers are usually formed on the surface of cladding tube in those normal corrosion processes; however, nodular oxidation or breakaway oxidation which is another type of corrosion can also be observed under certain oxidation conditions. The term of nodular oxidation or nodular corrosion can be explained by local, white, thick, and spotty ZrO2 layers which were formed by permeation of water or steam through cracks in the local area of intact uniform black oxide layer. When compared with usual uniform black oxides, there are various negative influences of nodular oxides on fuel cladding such as more susceptibility to delamination, interaction with crud deposits, local metal wall thinning, and increase in the rate of hydrogen uptake. This whitish nodular oxide with lenticular shape in cross-sectional view is most pronounced in the boiling water reactors (BWRs) [1-3].

On the basis of previous results [1, 2], Likhanskii et. Al reported that this nodular oxide growth on the surface of cladding in BWRs is related, mainly, to two factors resulting in increase of oxygen content in coolant: water boiling and radiolysis. In case of pressurized water reactors (PWRs) or heavy water reactors, on the other hand, uniform oxide layers were normally grown on the surface of cladding because suppression of water radiolysis and decrease in concentrations of oxidizing radiolytic species resulted from rather high contents of dissolved hydrogen in the coolants of them [4]. But they also insist that nodular oxidation phenomenon of zirconium fuel claddings could be a crucial problem for the PWRs in case when the steam phase is formed between the oxide and coolant. Therefore, it can be expected that oxidation condition of high temperature and steam atmosphere under loss of coolant accident (LOCA) situation would be another possible cause of nodular oxides occurrence. This possibility is supported by a few previous studies reporting nodular oxidation phenomenon of Zr-base alloy cladding during LOCA conditions [5-8]. Even though several mechanisms with different explanation for formation of nodular corrosion in BWRs or relatively low temperature oxidation tests (300~500℃) have been proposed in the literatures, there remain controversies and it’ s still unclear how theses nodule oxide occurs.

We investigated growth evolution of nodular oxides and found that there is a correlation between Sn additive and nodular oxides formation on the Zircaloy-4 tube.

2. Methods and Results

2.1 Experimental Procedure

A Zircaloy-4 tube which has a 200 mm length was used in this study. Direct heating by an ohmic resistance enabled the specimen to heat up to temperatures from 1000℃ to 1200℃. Specimen temperature was measured by a pyrometer. The specimen was oxidized in a flowing steam with different exposure times in the range of 300 s to 4000 s. Finally, the specimen was cooled at an intermediate temperature of 700℃ for 200 s after oxidation and then quenched. The metallographic study and cross sectional morphology of the oxide layer was investigated by optical microscopy (OM) with a polarized filter. X-ray photoelectron spectroscopy (XPS , SIGMA PROBE (ThermoVG, U.K.) with an monochromatic Al Ka source of 200–300 W under a pressure of 6.2 X 10^{-7}Pa) have been used to measure the stoichiometry, surface composition, ionic valence of Zr oxides layer.

2.2 Results

Figure 1 shows a typical overview spectrum together with relevant element spectra obtained from different area of Zr oxide layers formed on Zircaloy-4 tube. XPS spectra from white nodular oxide shows two clear Sn 3d photopeaks in addition to the Zr (3d and 3p) and Oxygen(1s) photopeaks while XPS spectra from normal black oxide layer shows only Zr (3d and 3p) and Oxygen photopeaks(1s). The further Zircaloy-4 components, Fe, Cr, and Ni, were below the detection limit of XPS. These results indicate that Sn additive may have an effect on nodular oxidation phenomenon, but exact mechanism of nodular oxide formation is not clear at this time.

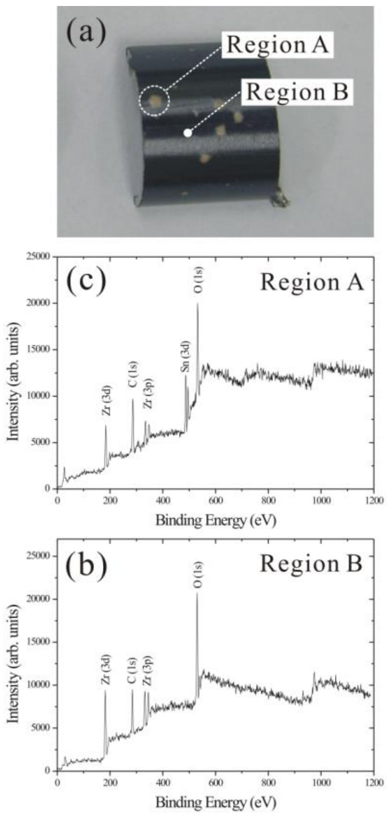

Fig. 1. (a) Zircaloy-4 cladding tube with nodular oxides on the surface. XPS survey scans in the binding energy

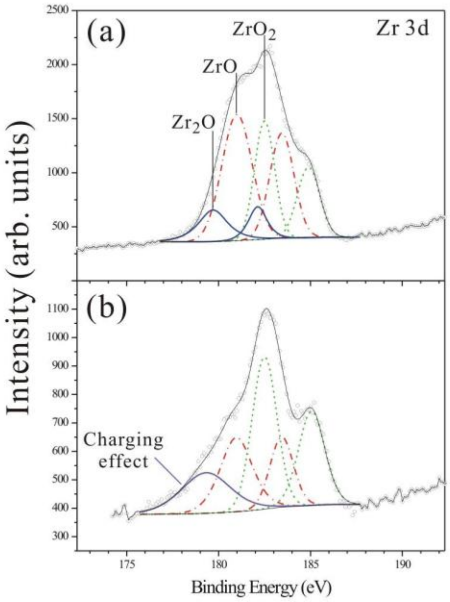

Fig. 2. Multi-peak fitted Zr3d spectra taken from surface of the oxidized Zircaloy-4 cladding tube: (a) black oxide region; (b) white nodular oxide.

Multi-peak fitted Zr3d spectra were taken from white nodular oxide and black oxide region [Figure 2]. The best fit to the experimental data was obtained when two suboxide peaks were added to the ZrO_2 peaks. Figure 2 indicates clear evidence of suboxide formation during high temperature oxidation in both regions. Figure 2 also shows that unit cell of nodular oxides is more stoichiometric structure than that of normal oxides. Sn additive in the unit cell promotes a lower concentration of O vacancies, and therefore, a stoichiometric oxide. This may cause the oxide layer susceptible to local microcracking and the cladding becomes susceptible to nodular oxidation.

3. Conclusions

The nodular oxides phenomenon of Zircaloy-4 has been investigated by XPS measurement. Even though two suboxides of Zr_2O and ZrO accompanied with ZrO_2 in both nodular oxides and normal oxides, nodular oxides were more stoichiometric than normal oxides. We think that susceptibility of Zircaloy-4 to nodular oxidation caused by Sn additive.

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