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Micro-structural analysis of the metal-oxide interface formed on Zircaloy-4

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1. Introduction

It is known that the effect of thermal redistribution of hydrides across the zirconium metal-oxide interface, coupled with thermal feedback on the metal-oxide interface, is a dominating factor in the accelerated oxidation in zirconium alloys cladding PWR fuel. Also it has been reported that the hydride redistribution induces microstuctural changes. In fact, it is well-known that tetragonal ZrO_2 forms in the metal-oxide interface in the early stage of zirconium oxidation that is protective against further oxidation. However, as the oxide grows the stress built up during the oxidation process relieves then the tetragonal phase turns into the monoclinic phase which is non-protective and stable at low stress. Therefore, it is believed that the zirconium oxidation kinetics depends on the phase transformation. In other words, if the transformation is accelerated by any stress-lowering factor, the kinetics would be fast. It has been proposed that hydride precipitates and their redistribution lower the stress built up in the metal-oxide interface and thus promote the phase transformation, ending up with the oxidation-enhancement. Therefore, in this study the effects of hydride precipitates on the phase transformation and the microstructural changes have been investigated using TEM and EDX.

2. Methods and Results

TEM specimen was made by FIB (Focused Ion Beam) system. The specimen has about 2 ㎛ thickness oxide film which was grown in the muffle furnace. Hydrogen content in the hydrided specimen was analyzed with the hydrogen determinator (model:RH-404) from LECO Corp. The oxide layer and metal matrix were examined using JEM-ARM1300S HVEM (High Voltage Electron Microscope) instruments and JEOL JEM2100F TEM with EDX system in KBSI (Korea Basic Science Institute). FFT patterns and lattice images were obtained by digitalmicrograph program.

2.1 TEM Investigations

The results of TEM analysis on the microstructural changes in the hydrided pure Zr specimen are shown in Fig.1. This figure clearly demonstrate that the hydride precipitates induce the amorphous layer in the metal-oxide interface, which must lower the stress build-up in the interface. More abundant monoclinic phases in the hydrided specimen than those in the unhydrided one shown in the figure support the phase transformation mechanism in the zirconium oxidation kinetics. Similar analysis was carried out for Zircaloy-4 specimen. Fig.2 shows BFI (Bright Field Image) of oxide-metal interface of the Zircaloy-4 and Fig.3 shows the lattice image of interface. Both figures demonstrate the microstrucural and morphological changes between hydrided and unhydrided Zircaloy-4 specimens, though amorphous layer is not clearly seen in the hydrided zircaloy-4 specimen. The matrix texture of the pre-hydrided specimen is rougher and more unstable than that of the unhydrided one.

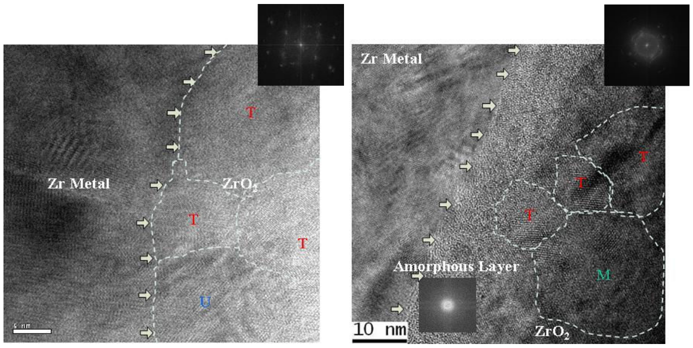

Figure 1. Lattice Image of pure zirconium interface region (Left : unhydrided 0.916 ㎛ oxide layer, Right : 2.15 ㎛ oxide layer, 607ppm hydrided)

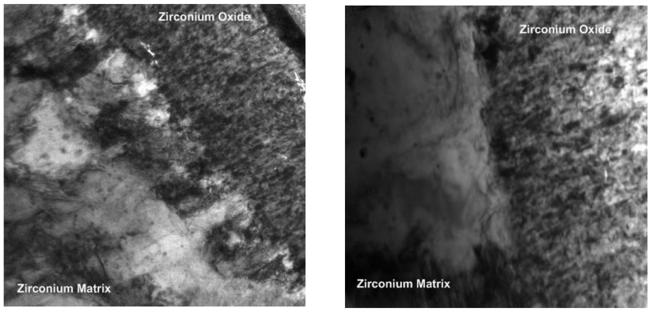

Figure 2. Bright Field Image of Zry-4 interface region (Left : unhydrided 2.31 ㎛ oxide layer, Right : 1.72 ㎛ oxide layer, 651ppm hydrided)

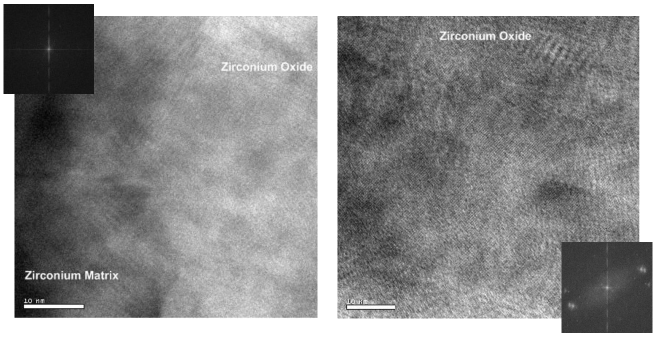

Figure 3. Lattice Image of hydrided Zry-4 oxide region (Left : interface region, Right : 300nm away from interface, 1.72 ㎛ oxide layer, 651ppm hydrided)

2.2 Energy Dispersive X-ray microanalysis

JEOL JEM2100F TEM with EDX system was used to investigate the microstructural changes and chemical composition changes in the unhydrided and the hydrided Zircaloy-4 specimens. Fig.4 shows grain boundaries and precipitates distributions in both of the Zircaloy-4 matrixes. Fig.5 shows the results of EDX chemical composition analysis in the identical specimens in Fig.4. These figures clearly demonstrate the microstructural changes of the matrix and hydrided precipitates redistribution and their composition changes.

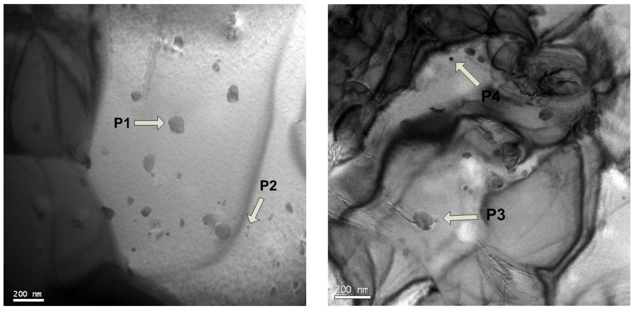

Figure 4. Microstructure of Zry-4 matrix
(Left : unhydrided, Right : 476ppm hydrided)

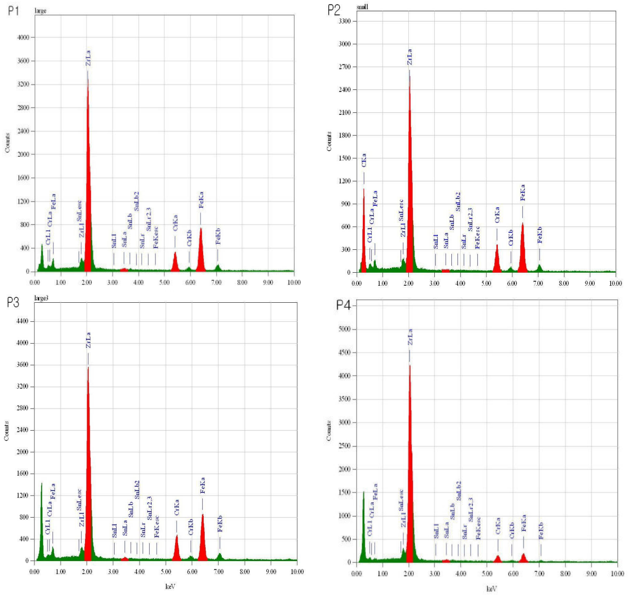

Figure 5. X-ray microanalysis spectra of precipitates

3. Conclusions

Microstructural analysis of metal-oxide interface in the hydrided and unhydrided Zircaloy-4 specimen was carried out using HVEM. Also the morphological and the chemical composition changes due to the hydride precipitates were analyzed by TEM and EDX system. TEM results from the hydrided pure Zr specimen clearly demonstrate the micro-structural changes, showing even the amorphous layer developed in the metal-oxide interface. Following results on the Zircaloy-4 specimens also show the microstructural, morphological, and compositional changes due to the hydrides precipitation in the zirconium matrix.

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