Estimation on Stress of Oxide layer in Zirconium Alloys

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1. Introduction

It has been reported that the effect of thermal redistribution of hydrides across the 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. Basically this influence determines characteristic of oxide layer. Influence estimation for corrosion oxide layer due to hydrogen / hydride carried out because of investigation on the kinetic on accelerated oxidation due to hydride precipitation was preceded. Experimental result corroborative of concentration of stress at metal-oxide interface through bend test and XRD analysis was confirmed. Mechanical properties due to stress of oxide layer through Nano-indentation and morphology was confirmed.

2. Methods and Results

They are cut to $2.0\times2.5\times0.075$ cm^3 thin plate with a diamond-wafered low speed saw, ground meachanically with 600, 1200, 2000 grit SiC paper, pickled in a solution of 50 % H_2O + 47 % HNO_3 + 3% HF for 3 min to remove pre-filmed surface oxide, and cleaned ultrasonically in acetone. Experiments are carried out with the twin autoclave system in Figure 1. Their weights are measured before and after the tests with electro-micro-balance whose sensitivity limit is 10^{-5}g. Hydrogen pre-charging was carried out with the multi-purpose apparatus in Figure 2. Hydrogen content is analyzed with the hydrogen determinator (RH-404) from LECO Corp.

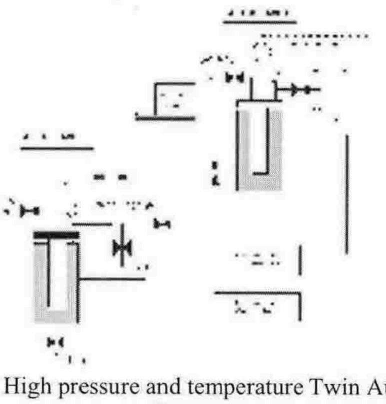

Figure 1. High pressure and temperature Twin Autoclave System

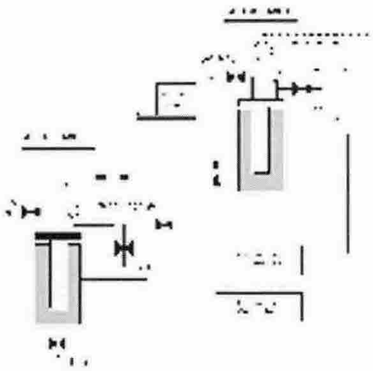

Figure 2. Multi-purpose Apparatus (Hydrogen pre-charging)

2.1 Analysis on Stress of oxide layer

Analysis on stress of oxide layer was carried out with low angle XRD. Figure 3 shows a average stress through oxide thickness of Zircaloy-4. A more thinner oxide are not performed by sensitivity limitation of XRD.

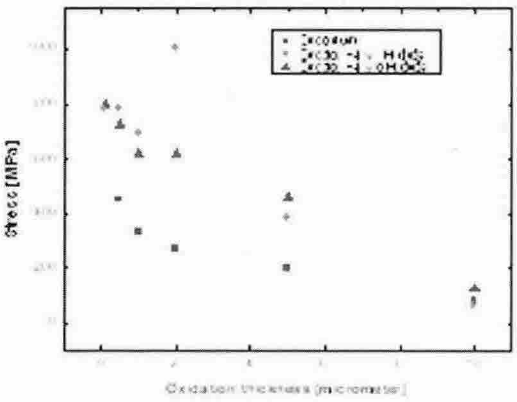

Figure 3.Average stress through oxide thickness of Zircaloy-4

2.2 Microstructure Analysis using AFM / SEM

Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) examinations are performed to analyze microstructure. Figure 4 shows Oxide morphology of Zircaloy-4 using AFM.

Though this paper can not show all figures, as expected, it is not easy to identify microstructure change by hydride in the oxide film.

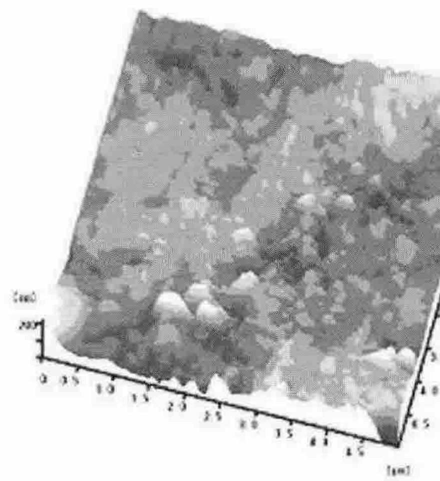

Figure 4. Oxide morphology using AFM (Zircaloy-4 w/o hyd. 10μm)

2.3 Nano-indentation Analysis

Nano-indentation is performed to analyze mechanical properties like hardness, modulus. Figure. 5,6 shows hardness, modulus value through distance from interface , respectively.

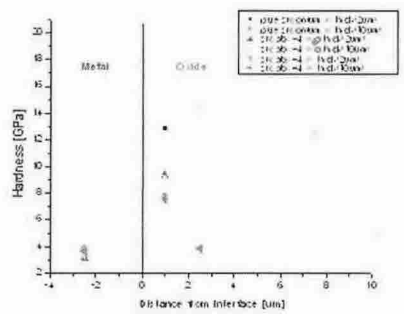

Figure 5.Hardness value through Distance from Interface

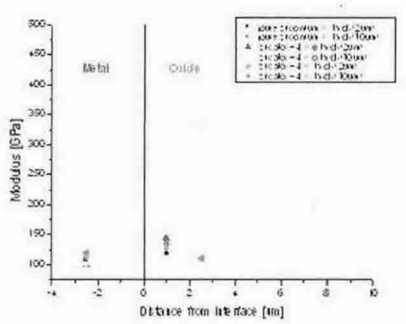

Figure 6.Modulus value through Distance from Interface

The oxidation kinetic mechanism is well-known that due to the high Pilling-Bedworth ratio (1.56) for conversion of zirconium to ZrO_2, tetragonal-ZrO_2 phase oxide film forms in the metal-oxide interface which is protective but only stable at very high stress more than 3 GPa. With the oxide growth the stress is exponentially reduced thus tetragonal phase is transformed into monoclinic-ZrO_2 phase which is non-protective. Later with the accumulated volume expansion micro cracks develope then kinetics turns into linear rate law from cubic rate law.

The accelerated oxidation phenomena due to hydride precipitation may be explained in the following way that the stress developed in the oxide layer on the pre-hydrided zirconium is reduced since Pilling-Bedworth ratio is 1.4 for the conversion of zirconium to ZrH_2 thus protective tetragonal phase formation is suppressed. That is, hydride formation in the zirconium matrix plays certain role that it reduce the stress build-up in between substrate metal and its oxide due to the different volume expansion (ZrH_2: 5.7 g/cm^3, ZrO_2: 5.8 g/cm^3, Zr: 6.5 g/cm^3) as a buffering medium. In other words, the relaxation of the stress due to volume expansion from intermediate density of zirconium hydride retards the formation of tetragonal-ZrO_2 phase and, ultimately, the premature transition of kinetics of protective into non-protective film formation accelerates the zirconium oxidation.

3. Conclusion

Influence estimation for corrosion oxide layer due to hydrogen / hydride carried out because of investigation on the kinetic on accelerated oxidation due to hydride precipitation was preceded. Experimental result corroborative of concentration of stress at metal-oxide interface through bend test and XRD analysis was confirmed. Mechanical properties due to stress of oxide layer through Nano-indentation and morphology was confirmed. Careful and thorough examination of the characteristics of oxide must follow with special techniques to study their effects further.

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