

Phase Transformation of the Oxidized Zirconium Alloys by Hydriding Effect

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1. Introduction

It has been reported that the hydride redistribution induces micro-structural changes during the zirconium alloy oxidation process. Tetragonal phase ZrO_2 formed near the metal-oxide interface in the early stage of zirconium oxidation is very protective against further oxidation. However, as the oxide grows the stress built up during the oxidation process relieves then the tetragonal phase turns into a monoclinic phase which is non-protective and stable at low stress. If the phase transformation is accelerated by any stress-lowering factor, the oxidation process would be faster. Therefore, it is believed that the zirconium oxidation process depends on the ZrO_2 phase transformation. In this study, the effects of hydride precipitates on the phase transformation and the micro-structural changes in the zirconium alloy oxide have been investigated quantitatively using Raman spectroscopy.

2. Methods and Results

Specimens used in Raman spectroscopy analysis were plate type, pre-hydrided/unhydrided Zry-4 and Zr-1.5Nb alloys. Pre-hydriding of each specimen was performed using gaseous charging apparatus. Hydrogen contents were measured by the hydrogen determinator (model:RH-404) from LECO Corp. Specimens were oxidized in the muffle furnace system on the condition of 600 °C air to grow different pre-transition region(0~40 mg/dm²) oxide layer. The phase identification of oxide layer surface was investigated using LabRam HR with liquid N₂ cooled CCD detector system supported from Raman laboratory.

2.1 Oxidation Behaviors of zirconium alloys in the Muffle Furnace System

The results of weight gain curves as a function of time are shown in Fig.1. This figure demonstrates that the Zr-1.5Nb alloys have faster oxidation behaviors than Zry-4 alloys. And also the hydrided zirconium alloys have faster oxidation process than the unhydrided ones in both the zirconium alloys.

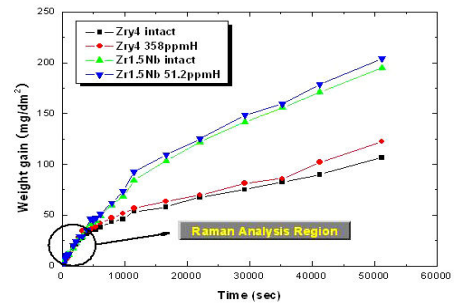


Figure 1. Oxidation behaviors of Zry-4 and Zr-1.5Nb (600 °C, 0.1MPa, air condition)

2.2 Raman Spectroscopy Analysis

First of all, the dominating peak position of tetragonal and monoclinic ZrO_2 was checked from the result of the reference Raman shifts(Fig.2). And Fig. 3 and Fig. 5 show the Raman spectra of pre-hydrided/unhydrided Zry-4 and Zr-1.5Nb as a function of weight gain from zero to 40 mg/dm² analysis region. These results revealed that the tetragonal ZrO_2 peak intensities become weaker as the oxide grows. Especially the pre-hydrided specimens have lower fraction of the tetragonal ZrO_2 phase than that of the unhydrided ones. Fig. 4 and Fig. 6 clearly demonstrate the fractional changes of tetragonal ZrO_2 phase quantitatively.

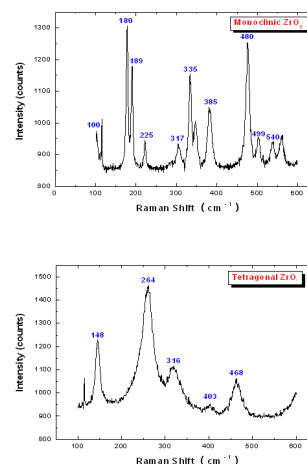


Figure 2. Raman spectra of the pure tetragonal and monoclinic ZrO_2

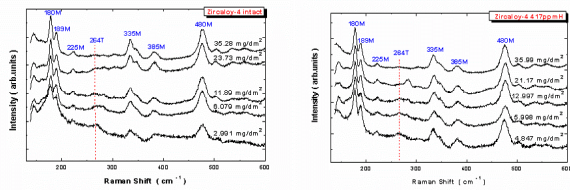


Figure 3. Raman spectra of Zry-4 as a function of weight gain (Left : intact, Right : 417 ppmH)

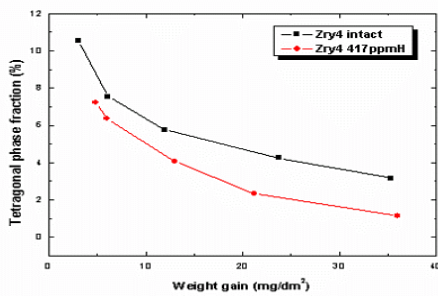


Figure 4. Tetragonal phase fraction changes of Zry-4 as a function of weight gain

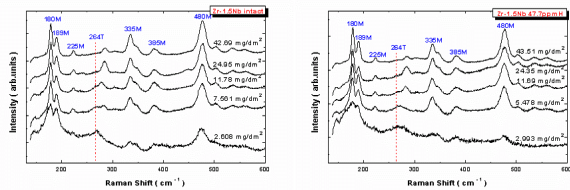


Figure 5. Raman spectra of Zr-1.5Nb as a function of weight gain (Left : intact, Right : 47.7 ppmH)

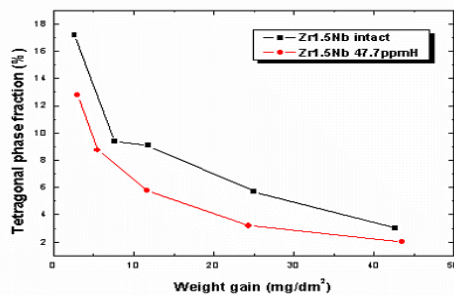


Figure 6. Tetragonal phase fraction changes of Zr-1.5Nb as a function of weight gain

3. Conclusions

Phase transformation analysis of the hydrided and unhydrided zirconium alloys was carried out using Raman spectroscopy. Also the quantitative phase fraction changes of protective tetragonal ZrO_2 due to the hydride precipitates were obtained. First, these results show that tetragonal ZrO_2 phase fraction decrease as oxidation proceeds. Second, especially the pre-hydrided specimens have more rapid decrease tendency in the phase fraction curve. Finally, it is described that the hydride precipitations in the zirconium alloy matrix play an important role in the acceleration of oxidation kinetics by changing the oxide micro-structure.

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