TEM analysis of δ-hydride in Zircaloy-4 cladding

Ju-Seong Kim [a], Sung-Dae Kim [b], Jonghun Yoon [c*]

[a]Korea Atomic Energy Research Institute, 989-111 Daedeokdaero, Yuseong-gu, Daejeon, 305-353, Republic of Korea
[b]Korea Institute of Material Science (KIMS), 797 Changwondaero, Changwon, Gyeongnam, 642-831, Republic of Korea
[c]Department of Mechanical Engineering, Hanyang University, 1271 Sa3-dong, Sangrok-gu, Ansan, Gyeonggi-do 426-791, Republic of Korea
[*]*Corresponding author yooncsmd@gmail.com*

1. Introduction

Zirconium alloys have been used as cladding and other structural material in the nuclear reactor due to a good corrosion resistance, a low neutron cross section and a proper mechanical property in the radiation environment. However, corrosion of zirconium alloys with coolant water incurs oxide formation with hydrogen absorption. The hydrogen precipitates when the hydrogen concentration exceeds the terminal solid solubility (TSS) of H in α-Zr matrix. In Zr-matrix, three types of hydride phases can exist in α-Zr matrix [1]: face centered cubic (FCC) δ-hydride, face centered tetragonal (FCT) ε-hydride and one metastable FCT γ-hydride. Hydride habit plane has critical importance to verify hydride embrittlement because most of the commercial zirconium alloys have a typical texture distribution. One of the most convincing relationship between Zr hydride and α-matrix has been reported as follows in the case of δ-hydride [2-10]:

$(111)_\delta \parallel (0001)_\alpha$ or $(111)_\delta \parallel (10\bar{1}7)_\alpha$

It is well known that habit plane of δ-hydride is basal or near basal plane.

2. Methods

Cold worked stress-relieved (CWSR) Zirclaoy-4 with an outside diameter of 9.5 mm and wall thickness of 0.57 mm was used. The specimen was charged with hydrogen in Sieverts-type apparatus at 400 ºC and slowly cooled to room temperature. The hydrogen concentration of the specimen was determined by hydrogen analyzer (LECO RH-404) using an inert gas fusion method. Hydrogen concentration in the bulk specimen was around 209 wppm.

Internal microstructures of the hydrogen charged Zricaloy-4 (HC-Zr-4) specimens were analyzed by a transmission electron microscope (JEM-2100, JEOL. Ltd.) with acceleration voltage of 200kV. To identify the phase of the hydrides and confirm the crystallographic relations between the Zr matrix and the hydrides, selected area electron diffraction (SAED) patterns were taken. Also, the dark-field TEM imaging technique was utilized to clearly visualize the hydrides formations by choosing the diffraction spots of the hydrides in the SAED.

3. Results

The microstructure of the hydrided Zircaloy-4 sample was analyzed by transmission electron microscope (TEM). Selected area electron diffraction (SAED) patterns of the sample were taken for phase analysis. The SAED pattern in Fig.1 contains two types of diffraction patterns, i.e., electron diffraction pattern of the hexagonal α-Zr matrix and that of the FCC δ-hydride. From the SAED pattern, we could confirm that the orientation relationships between the δ-hydride and the Zr matix as

$$(111)_\delta // (0001)_\alpha \,;\, [1\bar{1}0]_\delta // [11\bar{2}0]_\alpha$$

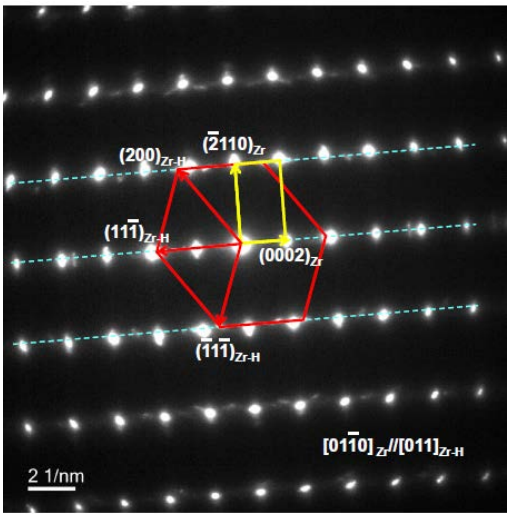

Fig.1 Selected area diffraction patters (SADPs) in hydride-Zircaloy-4 sample

Fig.2 shows the dark-field images taken by selecting each diffraction spots of the δ-hydrides (Fig. 2(a)) and the Zr matrix (Fig. 2(b)) reveal that the platelet type of δ-hydrides are evenly dispersed in the Zr matrix. Dealing with its size, however, the δ-hydrides are bimodally distributed.

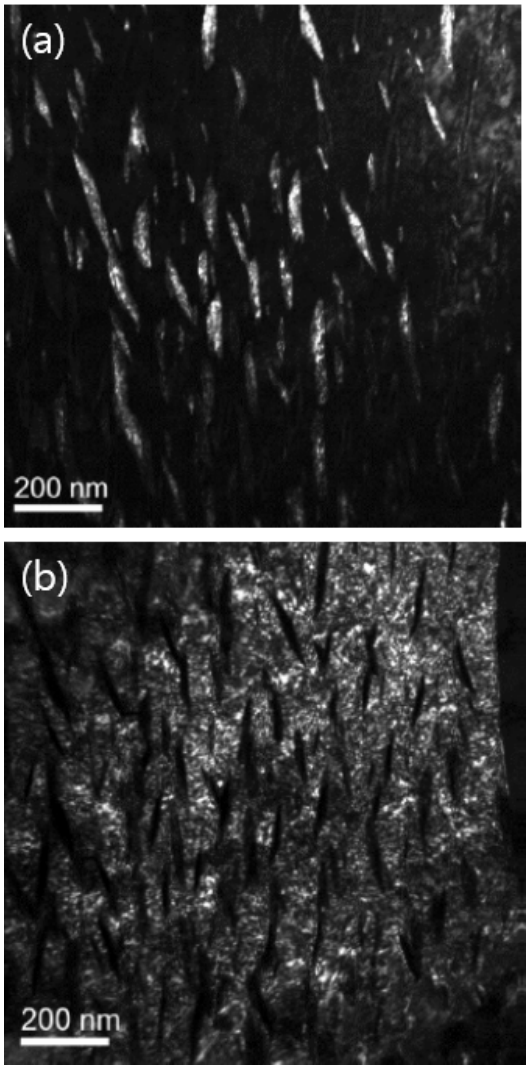

Fig. 2. Dark-field image of specimen: (a) Selecting (0001) diffraction spot for Zr and (b) Selecting (111) diffraction spot for microscopic δ–hydride

Based on the SAED patterns in the δ-hydrides, it is concluded that the relation between the δ-hydride and the α-Zr matrix has been analyzed as follows:

$$(111)_\delta \parallel (0001)_\alpha\,;\ [1\bar{1}0]_\delta \parallel [11\bar{2}0]_\alpha$$

In addition, small fraction of the macroscopic hydrides [11] with micrometer scale are observed. However, there are several controversial literatures concerning habit planes of the Zr hydrides with the form of $\{10\bar{1}m\}_\alpha$ [12-14] in which Chung et al. [11, 15] demonstrated that the microscopic hydrides formed on or near <c>-type dislocations on $\{0002\}_\alpha$ plane, and they have aligned and coalesced into the macroscopic hydrides having slightly different habit planes, i.e., the $\{10\bar{1}7\}_\alpha$, a plane 14.7° away from the $\{0002\}_\alpha$.

4. Conclusions

Based on the TEM investigations, it is demonstrated that the δ-hydrides are mainly precipitated over the α-matrix of the Zircaloy-4. Crystallographic relation between the δ-hydride and the α-Zr matrix have been analyzed as $(111)_\delta \parallel (0001)_\alpha\,;\ [1\bar{1}0]_\delta \parallel [11\bar{2}0]_\alpha$.

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