Effect of Nb on hydride embrittlement of Zr-xNb alloys

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Abstract

The effects of Nb on hydride Zr alloys were investigated. Various Zr alloys with different Nb content up to 2.0% were prepared in a sheet shape and charged with hydrogen up to 850 ppms. It was found that the fraction of recrystallized grains was reduced with increasing Nb content during the heat treatment. Intergrain and intragrain hydrides were tangled in unalloyed Zr, which has fully recrystallized grains. On the other hand, Nb containing Zr alloys that have partially cold-worked grains had only intergrain hydrides precipitated along the rolling direction. In tensile tests, elongation was decreased significantly with increasing hydrogen content for unalloyed Zr. However, the reduction of elongation was less significant for Nb-containing alloys. The softening of the Zr matrix was caused by hydrogen, which was arrested in cold-worked grain. And β-Nb precipitates, which have high solubility of hydrogen, retarded the
precipitation of hydrides, thereby enhancing the resistance of hydride embrittlement. Fracture surface of the tensile tested specimen was observed by SEM. From the SEM observation, secondary cracks caused by hydrides were found on the fracture surface of the hydrogen-charged specimens. Cleavage facets were observed on the fracture surface of unalloyed Zr; however, a mixture of dimple and cleavage facets was observed on the surface of the Nb-containing alloys, which indicates that Nb increased the resistance to hydride embrittlement of Zr alloys.

*Keywords: Zirconium; Niobium; Hydride embrittlement; Hydrogen*

1. **Introduction**

Zr based alloys have been used in cladding materials for nuclear power plants because of low neutron absorption, good corrosion resistance and mechanical properties. Zircaloy-4 cladding has been used in pressurized water reactors (PWR) since the 1950s. Recently, cladding materials for high burnup fuels have been developed and are ready to be loaded in nuclear power plants as a way to improve the economy of the plants. When burnup is increased, oxidation and hydrogen concentration in fuel cladding increase exponentially by water side corrosion [1]. In such high burn-up cladding, the thick Zr oxide on its outer surface, hydride rim beneath Zr oxide, and high hydrogen concentration are the main integrity concerns. Advanced fuel cladding materials with better corrosion resistance have been developed to meet the increase in burnup requirements in a nuclear power plant. Compared to the current generation of Zr
cladding materials, most of newly developed alloys have higher Nb and lower Sn contents in order to enhance corrosion resistance [2-4].

High hydrogen concentration due to high burnup operation caused loss of ductility in fuel cladding such that the safety margin at normal operation and accident condition decreased [5]. Therefore, understanding the effects of hydrogen in Zr alloys is very important to developing and assessing the integrity of high burnup cladding. There have been a few studies of the role of Nb on the hydrogen embrittlement of advanced fuel cladding materials. For several decades, a Zr-2.5%Nb alloy, which is the pressure tube material for CANDU reactors, has been the subject of extensive research, including into the role of Nb. However, the Zr-2.5%Nb alloy has a dual phase microstructure consisting of $\alpha$-Zr and Nb-rich $\beta$-Zr, whereas the advanced fuel cladding has a microstructure of $\alpha$-Zr matrix with dispersed Nb-containing precipitates. Therefore, the role of Nb in a Zr-2.5%Nb pressure tube material may not be applicable to that in advanced fuel cladding materials. Recently, the role of alloying elements, including Nb, on the hydride embrittlement of multicomponent Zr alloys was studied [6]. In that study, because of interaction with other alloying elements, the role of Nb alone was not easily understood. Therefore, it is necessary to understand the effect of Nb in advanced fuel cladding material.

The objective of this study is to investigate the effect of Nb on hydrogen embrittlement of hydried Zr alloys. Hydrogen was charged into Zr alloys with different Nb contents. Tensile tests were conducted and alloy mechanical properties such as the strength and elongation were evaluated. Finally, the fracture surfaces were observed under SEM to understand the role of Nb on the fracture mode of Zr alloys.
2. Experimental procedure

2.1. Materials

Materials used in this study are experimental Zr alloys with the different Nb content. Unalloyed Zr was used as a reference material. Chemical compositions of the materials are summarized in Table 1. Zr alloy ingots were prepared by the vacuum arc remelting (VAR) method with sponge Zr from Wah Chang Albany and high purity (99.99%) Nb. From the ingots, 0.88 mm thick sheets were prepared through hot rolling (H/R), cold rolling (C/R), and final annealing at 510°C for 2.5 hours as shown in Fig. 1. The alloys used in this study were manufactured by the same process in order to observe the effect of Nb alone on the hydride Zr alloy.

2.2. Hydrogen charging

The samples were charged with hydrogen using the cathodic hydrogen charging method [7]. Hydrogen was charged up to 850 ppms with a current density of 0.2 A/cm² at 80°C in 1N H₂SO₄ solution; hydrogen concentration was controlled by charging time. After hydrogen charging, samples were homogenized at 400°C for 24 hours. After tensile test, samples were cut by 2 × 2 at test section and then absorbed hydrogen content in each specimen was measured using hydrogen analyzer of LECO Co.,
2.3 Tensile tests

Sheet type tensile test specimens shown in Fig. 2 were cut from samples such that the tensile axis lay parallel to the transverse direction of the plate. The gauge length was 12.5 mm and the thickness 0.88 mm. Tensile test was performed at room temperature with a strain rate of $10^{-4} \text{s}^{-1}$. After the test, fracture surface of tested specimens was observed by SEM.

3. Results and Discussion

3.1 Microstructure observation

Microstructure and hydride morphology of the experimental alloys were observed by optical microscope (OM) as shown in Fig. 3. Unalloyed Zr (P0) had equiaxed grain with grain size of about 10 $\mu$m. On the other hand, Nb-containing alloys showed a mixture of equiaxed and elongated grains parallel to the rolling direction, and the fraction of elongated grains was higher in Zr-2.0%Nb (P2) alloy than in Zr-1.0%Nb (P1) alloy. A similar microstructure was observed in TEM micrographs shown in Fig. 4, such that P2 exhibited a large fraction of cold-worked grains along with recrystallized grains. From the optical and TEM micrographs, it was evident that the ratio of cold-worked grain increased as Nb content increased.

It is known that in HCP metals like Zr and Ti addition of solute atoms retards
recrystallization and increases recrystallization temperature. It is reported that the low solubility of solute atoms increases the recrystallization temperature significantly [8]. In general, the solubility of Nb in a Zr matrix is very low [9]. Therefore, it is thought that Nb solute in a Zr matrix retards recrystallization because the driving force of recrystallization is reduced by the increase of recrystallization temperature. As the solubility of Nb in Zr is about 0.4% and sheets are annealed at the (α-Zr + β-Nb) region (below 610 °C) [10], it is thought that β-Nb could be precipitated in Zr matrix. As shown in Fig. 5, the precipitates have BCC structure by diffraction pattern analysis and Nb contents of precipitates were similar to Zr contents using EDX analysis. However, the result of EDX analysis contains the Zr matrix because the beam size was higher than the precipitates so it is thought that Nb contents in the precipitates is higher than Zr contents. Therefore, we concluded that the precipitates are identified as β–Nb in P2. On the other hand, precipitates were not observed in unalloyed Zr.

3.2 Hydride morphology and orientation

Hydride morphologies of specimens are observed after hydrogen charging; the results are shown in Fig. 6. In all specimens, hydrides were observed aligned parallel to the rolling direction because the hydride platelet normals tended to form in directions perpendicular to the direction of prior specimen strain [11].

Hydride morphology shows a difference with Nb content. Unalloyed Zr had thick and short hydrides and thin and long hydrides were observed at P2. In the case of P1, the hydride morphology shows a mixture of those of unalloyed Zr and P2. Using SEM observation, the detached features of hydrides in Zr alloys with different Nb contents
were observed as shown in Fig. 7. The hydrides of unalloyed Zr show that the single hydride in macroscopic scale consists of short hydrides that were tangled with each other as shown in Fig. 7(a). The thickness of tangled hydrides was thicker than the grain size of unalloyed Zr as shown in Fig. 4(a), so the hydrides were precipitated at and near grain boundaries. The hydrides in polycrystalline Zr alloys are precipitated predominantly at the grain boundary; the available boundaries at which hydrides precipitate were determined by the degree of grain boundary alignment with rolling direction [12]. Therefore, unalloyed Zr with equiaxed and large grain from full recrystallization has less well-aligned grain boundaries available for hydride precipitation than Nb-containing Zr alloys with elongated fine grain. As a result, in unalloyed Zr, the grain boundary hydrides were initially precipitated preferentially at certain grain boundaries, but the well-aligned boundaries were soon exhausted; then, the excess hydrogen contributed to the precipitation of new hydride on the grain boundary with slightly different orientation near the existing hydrides. Consequently, the intergrain and intragrain hydrides were precipitated tangled with each other, which increased the apparent thickness of hydrides.

On the other hand, in P2 as shown in Fig. 7(c), the hydride platelets that connected with each other along the rolling direction made single thin and long hydrides in macroscopic scale without tangled hydrides observed in unalloyed Zr. P2 had a partially recrystallized structure as shown in Fig. 4(c); recrystallized grain (equiaxed and large) and cold-worked grain (fine and elongated) coexist. From this result, thus, the hydrides in P2 precipitated predominantly at cold-worked grain boundaries, which are relatively fine and elongated, rather than at recrystallized ones. Intergrain hydride precipitates were less visible in cold-worked grains. The hydride tended to precipitate normally to
the direction of applied stress [13]. Cold worked grains had residual stress with normal to the rolling direction; however, the residual stress was annihilated during recrystallization. Therefore, hydride precipitation was easier in cold-worked grain than in recrystallized grain in P2 which had a partially recrystallized structure. In P1, as shown in Fig. 7(b), both the tangled hydrides observed in unalloyed Zr and aligned hydrides along the rolling direction observed in P2 are simultaneously present. The fraction of cold-worked grain in P1 was less than that in P2. However, the length of the cold-worked grain boundary at which hydride can be precipitated was short in P1 compared to P2 and some hydrides were precipitated at the recrystallized grain boundary. Therefore, the aligned hydrides which precipitated at cold-worked grain boundary and tangled hydrides which precipitated at recrystallized grain boundary were both visible in P1.

3.3 Tensile properties of hydride Zr alloys

Effect of Nb on the tensile properties

Tensile tests of specimens that had different Nb content were performed at room temperature. Fig. 8 shows the stress-strain curves of as-received specimens and 500 ~ 600 ppm hydrogen charged specimens. In the case of as-received specimens, a discontinuous yield point was observed at all alloys as shown in Fig. 8(a). On the other hand, the yield point disappeared at the stress-strain curve of the hydrogen-charged specimen as shown in Fig. 8(b). The reason is that hydrides act as dislocation sources that lead to an increase of effective dislocation density and thereby suppress the yield
Fig. 9 shows that yield stress, tensile strength and elongation change with Nb content. Yield stress and tensile strength increased with Nb content because of the combined effects of solution strengthening by Nb atoms, precipitation hardening by β–Nb precipitates, and the increased fraction of cold-worked grains. However, elongation decreased with increasing Nb content.

**The effect of Nb on tensile properties of hydrided Zr alloys**

Fig. 10 shows the change of yield stress and UTS with charged hydrogen amount. In the case of unalloyed Zr and P1, the yield stress was nearly independent of hydrogen content. However, yield stress of P2 was reduced slightly by hydrogen. The ultimate tensile strength shows no dependence on hydrogen content as shown in Fig. 10.

Bai observed that yield stress of stress-relieved Zircaloy-4 decreased slightly with hydrogen absorption whereas yield stress of fully-recrystallized Zircaloy-4 was independent of hydrogen content [15]. Similarly, the yield stress of P2 decreased with hydrogen concentration because of the higher fraction of the elongated grains that were retained during the final annealing heat treatment. In steels, hydrogen is arrested when dislocation density is high, and the arrested hydrogen increases the mobility of dislocation because the interaction force between dislocations is relieved by the shielding effect of hydrogen [16, 17]. Also, it has been reported that the tensile properties of pure Zr polycrystalline indicated an increase in ductility with hydrogen addition [18].

In the case of P2, a partially recrystallized structure has high dislocation density as shown in Fig. 4. With an increase of hydrogen concentration, the amount of arrested
hydrogen due to high dislocation density in cold-worked grain would increase, and the arrested hydrogen, in turn, would enhance the mobility of dislocation. Therefore, the yield stress of P2 decreased with hydrogen concentration as shown in Fig. 10.

To exclude the effect of microstructure, P2 was fully recrystallized before the tensile test. To achieve full recrystallization, P2 was heat-treated at 580 °C for 15 hours. Then, the effects of Nb on tensile properties were measured. As shown in Fig. 11, the yield stress and tensile strength of fully recrystallized Zr-2.0%Nb (P2RX) was independent of hydrogen concentration. Thus it was confirmed that the addition of Nb does not affect the yield stress and tensile strength of hydride Zr unless the recrystallization is retarded during the final annealing heat treatment. The retardation of recrystallization results as the Nb addition increases the recrystallization temperature of Zr alloys.

Fig. 12 shows the effect of hydrogen content on elongation. Instead of adding strength, the elongation of all the specimens was significantly reduced with increasing hydrogen content. This indicates the hydrides affect the loss of ductility more strongly than the change of strength in Zr alloys. The degree of elongation reduction is less dependent on hydrogen content when Nb is increased. That is, the elongation of unalloyed Zr was the highest among the tested alloys at low hydrogen content; however the trend was reversed above 500 ppm hydrogen content. Consequently, the addition of Nb enhanced the resistance to hydride embrittlement. As mentioned before, the addition of Nb retarded the recrystallization of Zr alloys, which could have contributed to such behavior. Similar results were reported for Zircaloy-4: the reduction of elongation in stress-relieved Zircaloy-4 by hydrogen was less sensitive than that of fully recrystallized Zircaloy-4 [16]. That is, cold-worked grain is resistant to the loss of ductility brought on by hydride embrittlement. The high dislocation density in cold-worked grains causes the
softening of the Zr matrix. The fraction of cold-worked grains in P2 is highest among the tested alloys, which resulted in a lesser degree of elongation reduction due to the trapping of large amounts of hydrogen in dislocation cores.

In Fig. 12, the change of elongation with hydrogen concentration for unalloyed Zr, P2, and P2RX are also shown. The elongation of P2RX has greater sensitivity to hydride embrittlement than does P2. However, P2RX was less sensitive to hydride embrittlement than was unalloyed Zr, although both have fully recrystallized microstructures. It is thought that the addition of Nb retards the hydride embrittlement by some other mechanism. As the solubility of Nb in Zr is about 0.4%, the excess Nb should be precipitated as $\beta$-Nb as observed in Fig. 5. According to the phase diagram, $\beta$-Nb (BCC) can accommodate hydrogen up to 40–50 at%, whereas $\alpha$-Zr holds up to 5 at% [19]. It is reported that hydrogen solubility in Zr alloys is not affected by solute Nb, but $\beta$-Nb precipitates formed by the addition of Nb lead to an increase in hydrogen solubility because $\beta$-Nb precipitates have higher hydrogen solubility [20]. As $\beta$-Nb predominantly precipitates in the Nb-containing alloys used in this study, hydrogen will preferentially dissolve into the $\beta$-Nb. Thus, in Nb-containing alloys, relatively less hydrogen will be available in the matrix to form hydrides. Therefore, by adding Nb, the reduction of elongation due to hydrogen charging is restrained by $\beta$-Nb precipitation as well as by the retardation of recrystallization.

3.4 Fractography of hydrogen charged Zr alloys

The fracture surface of hydrogen-charged specimens was observed and is shown in Fig. 13. There are secondary cracks which are normal for fracture surface in all
specimens. The length of secondary cracks and the spacing between secondary cracks increased with increasing Nb content. This phenomenon was similar to the hydride morphology of specimens such as small but dense hydride in unalloyed Zr and long hydride in Nb-containing Zr as shown in Fig. 4. Thus it was thought that the secondary cracks emanated from the hydride platelet.

Fracture surface of the specimen was observed at higher magnification and is shown in Fig. 14. Most of the facets in Nb-containing alloys were observed in the neighborhood of secondary cracks, indicating that the hydrides and the secondary cracks due to hydrides caused the cleavage facet of recrystallized grain. Extensive cleavage facets were found at the fracture surface of unalloyed Zr matrix as is shown in Fig. 13(a). In addition, the size of the cleavage facet was similar to the size of grain. On the other hand, in Nb-containing alloys, dimple fractures as well as facet fractures were observed as is shown in Fig. 13(b,c). The number of dimples on the fracture surface increased with Nb content, which is consistent with the lower ductility loss observed in tensile tests. The facet size of Nb-containing alloys was also similar to that of grain. Therefore, it is thought that the cleavage facets of all specimens were caused by hydride that precipitated at the grain boundary.

4. Conclusions

The effects of Nb on hydride Zr alloys were investigated. Various Zr alloys with different Nb content up to 2.0% were prepared in a sheet shape and charged with hydrogen up to 850 ppm. The microstructure and hydride morphology were analyzed and the tensile properties were measured to understand the role of Nb on the hydride
embrittlement of Zr alloy. Based on the results, the following conclusions were drawn:

(1) When heat treated at 510°C for 2.5hr, while unalloyed Zr showed a fully recrystallized structure, but the Nb-containing Zr alloys showed a partially recrystallized structure. With increasing Nb content, the fraction of recrystallized structure was reduced because Nb solute in Zr matrix retarded recrystallization. In addition, while unalloyed Zr had thick and short hydrides, thin and long hydrides precipitated on the boundary of the elongated grains in Nb-containing alloys.

(2) From the tensile test results of as-received specimens, discontinuous yield points were observed in all alloys. However, the yield point disappeared at the stress-strain curve of the hydrogen-charged specimen because the hydrides acted as dislocation sources that led to an increase in effective dislocation density.

(3) In Zr-2.0%Nb alloy, yield stress was reduced slightly at high hydrogen content. The high dislocation density in the partially recrystallized structure is responsible for the softening with hydrogen content in Nb-containing Zr alloys. However, the effects of Nb on yield stress disappear if structure is fully recrystallized at higher temperature.

(4) The addition of Nb enhanced the resistance to hydride embrittlement, such that the reduction of elongation at large hydrogen content became less significant when Nb was added. The resistance to hydride embrittlement of Nb-containing alloys can be explained as the combined effects of β-Nb precipitates with higher hydrogen solubility and the solute Nb causing the retardation of recrystallization.
(5) From fracture surface observation by SEM, secondary cracks caused by hydrides were found. Mostly, the cleavage facets were observed on the fracture surface of the unalloyed Zr matrix, but the number of dimples on the fracture surface increased with Nb addition, which is consistent with the lower ductility loss observed in tensile tests.

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References


Table 11. Chemical composition of Zr alloys

<table>
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<th>ID</th>
<th>Material</th>
<th>Nb [wt%]</th>
<th>Sn [wt%]</th>
<th>Fe [wt%]</th>
<th>H [ppm]</th>
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<td>P0</td>
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<td>0.04</td>
<td>17.35</td>
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Fig. 1. Rolling and annealing process of experimental alloys.

Fig. 2. Schematic drawing of the sample for tensile test. (in mm)
Fig. 3. The microstructure of as-received Zr alloys observed by optical microscope: (a) unalloyed Zr (P0), (b) Zr-1.0%Nb (P1) and (c) Zr-2.0%Nb (P2)

Fig. 4. The microstructure of (a) unalloyed Zr (P0) and (b) Zr-2.0%Nb (P2) by TEM.
Fig. 5. TEM micrograph and EDX result of β-Nb precipitates in P2

Fig. 6. Optical micrographs of the hydride morphology: (a) unalloyed Zr (P0), (b) Zr-1.0%Nb (P1) and (c) Zr-2.0%Nb (P2) with 625, 598 and 462 ppms hydrogen charged respectively.
Fig. 7. SEM micrographs of the hydride morphology at high magnification: (a) unalloyed Zr, (b) Zr-1.0%Nb and (c) Zr-2.0%Nb with 625, 598 and 462 ppm hydrogen charged respectively.

Fig. 8. Stress-strain curves of (a) as-received and (b) hydrogen charged specimens.
Fig. 9. The change of mechanical properties with various Nb contents (as-received).

Fig. 10. The effect of hydrogen concentration on strength of Zr alloys
Fig. 11. Yield stress and UTS of fully recrystallized Zr-2.0%Nb (P2RX) with hydrogen contents.

Fig. 12. Elongation of Zr alloys with hydrogen contents.
Fig. 13. Fracture surface of (a) unalloyed Zr (P0), (b) Zr-1.0%Nb (P1) and (c) Zr-2.0%Nb (P2) which are charged with 625, 500 and 562 ppm of hydrogen, respectively.

Fig. 14. Secondary cracks and fracture surface: (a) unalloyed Zr (P0), (b) Zr-1.0%Nb (P1) and (c) Zr-2.0%Nb (P2) which are charged with 625, 498 and 562 ppm of hydrogen, respectively.