Effect of Hydrides Formed by Electrochemical Methods in Zry-2 Cladding Tubes on Tensile Strength

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ABSTRACT

Tensile test was conducted on cladding tubes of Zry-2 charged with hydrogen. Hydrogen pick-up and subsequent hydride precipitation in zircaloy cladding materials was conducted by electrochemical cathodic charging. Electrochemical cathodic charging of hydrogen in Zry-2 tubes was accomplished in 5% sulfuric acid, at a current density of 2 mA/cm². Some of specimens were heat treated at 750ºC for 5 minutes to precipitate hydrides; other specimens were not heat treated to keep hydrogen un-precipitated.

Tensile test was performed on hydrogen charged Zry-2 tubes at cross head strain rate 0.009 mm/Sec. Uncharged Zry-2 tubes were also tested at the same cross head strain rate.

The results showed that the unhydrided specimens were fractured at load equal 13501 N and strain of 15.2mm, while specimens charged with hydrogen and hydrides precipitated at 750ºC, the fracture load was 8719 N and elongation 13.6mm. The third type of specimens, which were charged with hydrogen and oxidized in air at 700ºC, the fracture load is 9888.77N and elongation 16mm to investigate the combined effect of thin oxide formation and hydride precipitation on tensile properties. Some Zry-2 tubes were oxidized in air at 700ºC for 2hrs and tested, the fracture load is10031.43N and the strain is 17.44mm. Scanning Electron Microscopy was used to examine the fracture surface of specimens.

Key Words: Nuclear Cladding / Zirconium alloy / Hydrogen Embrittlement

INTRODUCTION

The adsorption of hydrogen in materials is a wide and important. In many metals and alloys, it can lead to premature failure under stresses (1-2), in a phenomena referred to as hydrogen embrittlement. The mechanism of such embrittlement is believed to be different depending on whether or not stable hydrides are formed. Metal hydrides and the precipitation of hydrides are important factor in studding the material failure. The precipitation of hydrides embrittle the alloys and lead delayed hydride cracking, which in turn lead to failure (3).

The low alloyed zirconium alloy Zry-2 and Zry-4 were developed for fuel rod claddings and fuel assembly and other in-core structure components of light water reactors (BWR&PWR), due to a combination of desirable properties such as good strength and ductility at reactor operating temperatures, good corrosion resistance at high temperature in aqueous environments and good compatibility with the fuel materials.

However, zirconium alloys have several serious drawbacks, the most critical of which is the phenomenon of hydrogen embrittlement. Zr-alloys can pick up hydrogen during the service corrosion.

Hydrogen has very limited solubility in zirconium alloys (4), when the terminal solid solubility is exceeded in a component high stressed for long period of time, hydride cracking failure may occur (5).
The hydrides have either of two crystallographic structures $\delta$-hydrides (ZrH$\text{1.5}$ to ZrH$\text{1.66}$) with face centered cubic structure exist for lower concentrations whereas $\varepsilon$-hydrides (ZrH$\text{1.66}$ to ZrH$_2$) with a face centered tetragonal structure exist at higher hydrogen concentration ($^6$). The aim of the present work is to investigate the effect of precipitated hydrides and dissolved hydrogen in cladding alloy Zry-2 on the tensile properties.

**EXPRIMENTAL**

Electrochemical cathodic charging was used to charge cladding tubes of Zry-2 hydrogen; the nominal composition is given in Table (1). The electrochemical cathodic charging method is simple because it can be conducted at room temperature. The required equipments are constant current power supply and charging cell, the model of the power supply is Hewlett-Packard model 6028A DC-power supply, 0-60V/10A, and 200w.

The charging cell is a double wall; the circulating water was at 25°C to keep the temperature constant during charging process. The charging solution was 5% concentration sulfuric acid and the charging current density was 2mA/cm$^2$ and charging time was 24hrs.

The charged tubes have outer diameter 10.8mm and 80mm length. The tubes were plugged from the two ends with stainless steel plugs with 10mm each. The gage length of tube was 60mm.

After charging some specimens were heat treatment at 700°C for 5 minute to precipitate hydrides, another type of specimens were not heat treated to keep hydrogen in solid solution. Some of heat treated specimens were oxidized in air at 700°C for 2hrs to investigate the combined effect of hydrides and oxidation on tensile properties.

The process of gaseous hydriding of zirconium and zirconium alloys is complicated and many problems faced it, as the presence of thin oxide film, which prevent the ingress of hydrogen to alloy.

The gaseous hydriding of zirconium alloys depends on hydrogen pressure, sample temperature and the environmental hydrogen purity. But, on the other side, and besides its simplicity, cathodic hydriding represents to some extent the hydriding of zirconium alloys in side the nuclear reactor due to the water radiolysis and proton formation, i.e. by hydrogen ions.

<table>
<thead>
<tr>
<th>%</th>
<th>Zr</th>
<th>Sn</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>O</th>
</tr>
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<tbody>
<tr>
<td>Zr-2</td>
<td>98.2-97.7</td>
<td>1.2-1.7</td>
<td>0.07-0.2</td>
<td>0.05-0.15</td>
<td>0.03-0.08</td>
<td>0.13</td>
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**RESULTS & DISCUSSION**

During reactor operation, zirconium and its alloys are susceptible to a slow corrosion that leads to a gradual pick up of hydrogen from environment. As hydrogen concentration reaches the solubility limit, hydrides will start to form and grow. Because of the brittleness of the hydrides, fracture can initiate at the hydrides depending on the stress level, the distribution and the orientation hydride. The original strength of the alloy can be reduced by order of magnitude ($^7$). It is known that the shape and distribution of hydrides are critical to hydride induced fracture; in situ experimental study of the evolution of hydride morphology is relatively difficult. Most of examinations were conducted on the surface of specimen, where stress state is in plane stress ($^8$). Also, it is very expensive to study experimentally to evaluate the morphology of precipitated hydrides in irradiated materials because of the costs involved in irradiation protection.

Fig. (1) Show the results of this test, the fracture load was 13249 N, and elongation was 14.9 mm. Second tensile test was conducted at cross head speed 0.009 mm/sec, which is corresponding to strain rate $1.5\times10^{-4}$ sec$^{-1}$. In the tensile test of tubes, the effective forces are tangent forces in the same direction and parallel to each other. The fracture will be under plane stresses condition ($^9$).
Fig. (2) show the result of tensile test on hydrogen charged specimen and hydrides were precipitated at 750°C for 5 minutes, the fracture load was 8719.7 N, and elongation of 13.95 mm, which mean a reduction in fracture load by 1.5 times than that of uncharged specimen and a reduction in elongation by 1.2 times.

Fig. (3) shows the results of tensile test of specimens charged with hydrogen and hydrides precipitated then oxidized in air at 700°C for 2hrs, the fracture load was 9888.7 N and elongation 16.00mm, the reduction in fracture load was 1.4 times than that of uncharged specimens, and the elongation was decreased by 0.97 times than that of uncharged specimens.

Fig (4) shows the tensile test results of oxidized specimens in air at 700°C, the fracture load is 10031N and elongation is 17.77mm. Hydrogen embrittlement caused by the formation of hydrides at stress concentration, has been examined in electronmicroscope studies of vanadium and niobium (10).
In present study, hydride platelets oriented normal to the axial direction of the tension panel and located at edge or center position of the panel as shown in Fig.(5). Since failure stress of solid hydride is low, the hydride platelet was modeled as micro-crack (9).

Fig.(6) shows the fracture surface of unhydrided specimens tested at 0.009mm/sec cross head speeds, the fracture surfaces show brittle fracture.

Fig.(7) shows the fracture surface of hydrided specimens, it shows also brittle fracture.

**CONCLUSIONS**

1. The fracture load of hydride precipitated specimens decreased by 1.5 times and by 1.4 times for specimens hydrides precipitated then oxidized in air, than uncharged specimens.
2. The fracture load of charged and oxidized specimens in air at 700°C for 2 hrs Zry-2 tubes was lower than that of uncharged specimens.
REFERENCES


