OXIDATION-INDUCED EMBRITTLEMENT AND STRUCTURAL CHANGES OF ZIRCALOY-4 TUBING IN STEAM AT 700 - 1000 °C

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Abstract

The oxidation-induced embrittlement and structural changes of Zircaloy-4 (KWU-Type) tubing was investigated under light water reactors (LWR) Loss-of-Coolant Accident conditions (LOCA) in the temperature range 700-1000°C. The effect of hydrogen addition to steam was also investigated in the temperature range 800-1000°C.

The oxidation-induced embrittlement was found to be a function of both temperature and time. Fractography investigation of oxidized tubing showed a typical brittle fracture in the stabilized-alpha zone. The microhardness measurements revealed that the alpha-Zr is harder than that near the mid-wall position. The oxidation-induced embrittlement at 900°C was found to be higher than at 1000°C. The results also indicated that the addition of 5% by volume hydrogen to steam resulted in an increase in the degree of embrittlement.

1. INTRODUCTION

The oxidation behaviour of Zircaloy-4 cladding tube material in steam is an extremely important factor to be considered in the safety analysis of LOCA and Severe Fuel Damage (SFD) accidents. The oxidized cladding tube wall consumption determines cladding embrittlement and influences fuel-clad interaction [1-8]. The lack of enough data for the high temperature reaction kinetics of Zircaloy and steam and the experimental difficulties associated with accurately determining the reaction rates were the main reasons for proposing the conservative Baker-Just (BJ) correlation[1] to calculate the Zircaloy-steam oxidation and the
equivalent cladding reacted (ECR). However an extensive amount of work has been performed afterwards on the oxidation of Zircalloys in steam at high temperatures. Some examples, of numerous publications addressing the embrittlement criteria (associated with oxide formation and oxygen-containing sub-surface layers) under LOCA conditions can be cited [9-13].

This work presents the results of Zircaloy-4 tubing oxidized in flowing steam under isothermal conditions at 700 to 1000°C. The results presented in this paper specifically address the oxidation-induced embrittlement of Zirealoy-4 cladding tubes.

2. EXPERIMENTAL

Zircaloy-4 KWU-type tubing (10.75 mm OD, 0.725 mm thick, 10 mm long specimens) of standard composition (Table I) were used for the investigation. After degreasing and pickling in a mixture of hydrofluoric acid, nitric acid and water the specimens were oxidized in an open, non-pressurized loop under a steam flow rate of 520 mg/cm² min. The effect of hydrogen addition (5% by volume of the steam) was also investigated. Oxidation time ranged between several minutes and few hours depending on temperature.

Fractographic investigation and microhardness measurements were made across the thickness of the oxidized tube. Microhardness testing (using SHIMATZU-V) was performed using 300 g load for 10 seconds. The microhardness indentation was done at various locations making sure that the distance between each two successive indentations is greater than 4 times the indentation diameter.

Table I: Chemical Analysis of Zircaloy-4 KWU-Tubing

<table>
<thead>
<tr>
<th>Material</th>
<th>Sn</th>
<th>Fe</th>
<th>Cr</th>
<th>O</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zircaloy-4</td>
<td>1.35-1.47</td>
<td>0.19-0.21</td>
<td>0.09-0.10</td>
<td>0.12</td>
<td>98.1-98.25</td>
</tr>
</tbody>
</table>
3. RESULTS

The microhardness measurements taken across oxidized tubing are shown in Figures 2-7 and tables II and III. A hardness gradient exists across the tube wall, with the material nearest to the metal-oxide (M/O) interface being harder than that near the center of the tubing. The results indicated that the microhardness increases with both temperature and time. The degree of embrittlement for specimens oxidized for short durations (10 to 30 min) were high only near the metal-oxide interface through a small thickness layer (about 50 μm) at 900 and 1000°C. The thickness of the brittle layer was found to increase with time at all test temperatures. The embrittlement was found to the higher at 900 than at 1000°C. The results also indicated an enhancing effect of hydrogen to embrittlement. It is noted that the microhardness results were not precisely symmetric around the mid-wall position of the tube thickness, particularly for cases of high temperature and long durations of oxidation. Metallographic examinations substantiated that, revealing that the outerside oxide film thickness is slightly greater than the inner side film thickness.
Fig. 2. Variation of microhardness with distance from metal/oxide interface (700°C).

Fig. 3. Variation of microhardness at 800°C.
Fig. 4. Variation of microhardness at 900°C.

Fig. 5. Variation of microhardness at 1000°C.
Fig. 6. Variation of microhardness for steam and hydrogen mixture at 800°C.

Fig. 7. Variation of microhardness at 1000°C and 10 min. for steam and steam+H₂.
Table II: Vicker Hardness Number (V.H.N) at the inner and the outer surface oxide/metal interface, and the mid-wall position of the tube for oxidation times 1/2 and 1 hr. in steam +5% H mixture.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>1/2 hr inner</th>
<th>1/2 hr outer</th>
<th>1/2 hr mid</th>
<th>1 hr inner</th>
<th>1 hr outer</th>
<th>1 hr mid</th>
</tr>
</thead>
<tbody>
<tr>
<td>800°C</td>
<td>320</td>
<td>580</td>
<td>220</td>
<td>400</td>
<td>620</td>
<td>260</td>
</tr>
<tr>
<td>900°C</td>
<td>550</td>
<td>820</td>
<td>320</td>
<td>700</td>
<td>720</td>
<td>350</td>
</tr>
<tr>
<td>1000°C</td>
<td>350</td>
<td>500</td>
<td>200</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Table III: Vicker Hardness Number (V.H.N) at the inner and the outer surface oxide/metal interface of the tube, and in the mid-wall position for oxidation times 1/2, 1 and 3 hrs. in pure steam.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>1/2 hr inner</th>
<th>1/2 hr outer</th>
<th>1/2 hr mid</th>
<th>1 hr inner</th>
<th>1 hr outer</th>
<th>1 hr mid</th>
<th>3 hr inner</th>
<th>3 hr outer</th>
<th>3 hr mid</th>
</tr>
</thead>
<tbody>
<tr>
<td>700°C</td>
<td>200</td>
<td>200</td>
<td>100</td>
<td>180</td>
<td>190</td>
<td>180</td>
<td>230</td>
<td>320</td>
<td>200</td>
</tr>
<tr>
<td>800°C</td>
<td>240</td>
<td>290</td>
<td>200</td>
<td>250</td>
<td>330</td>
<td>200</td>
<td>350</td>
<td>480</td>
<td>230</td>
</tr>
<tr>
<td>850°C</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>550</td>
<td>650</td>
<td>350</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>900°C</td>
<td>510</td>
<td>650</td>
<td>210</td>
<td>800</td>
<td>900</td>
<td>400</td>
<td>700</td>
<td>1060</td>
<td>600</td>
</tr>
<tr>
<td>1000°C</td>
<td>350</td>
<td>550</td>
<td>150</td>
<td>400</td>
<td>600</td>
<td>200</td>
<td>500</td>
<td>740</td>
<td>320</td>
</tr>
</tbody>
</table>

The results also indicated that the addition of 5% by volume hydrogen to steam resulted in an increase in the degree of embrittlement.

The microstructural features of the oxidized Zircaloy-4 tubings are shown in Fig. 1. The outermost layer is ZrO₂. Adjacent to the oxide is a layer of α-Zr (O) (stabilized-alpha) overlying a transformed β-Zr matrix.
Fractography investigation of the oxidized tubing reveals the brittle fracture of the tubing wall which is mostly stabilized α-Zr (O) (Fig. 8). Figure 9 reveals a severe crack extending from the oxide through the underlying metal.

4. DISCUSSION

The oxidation-induced embrittlement of Zircaloy tubings, as indicated by the microhardness and structural measurements, was shown to increase with increasing time and temperature of oxidation. The results also indicated the enhancing effect of hydrogen addition to steam on the oxidation-induced embrittlement. It has been shown earlier [8] that when Zircaloy-4 tubings are oxidized in air at 850°C and 1000°C for a typical LOCA duration (5 min.), the amount of ductility exhausted increases from 14% at 850°C to 95% at 1000°C.

The present results as well as previous work [6, 8] reveal the dependence of the degree embrittlement on the amount of

![Fractograph of Zircaloy-4 tubing oxidized at 1200°C under transient conditions for the typical LOCA duration (300 sec.)](image)

Fig. 8. Scanning electron microscopy (SEM) fractograph of Zircaloy-4 tubing oxidized at 1200°C under transient conditions for the typical LOCA duration (300 sec.) (x150).
oxidation. The ductility of Zircaloy is a direct function of its oxygen content which is a function of temperature and time. The results indicated that temperature is more effective in promoting embrittlement; in agreement with the results of Hobson and Rittenhouse [14].

Fracture surface investigation of the oxidized Zircaloy-4 tubings, by scanning electron microscopy (SEM), reveals the severe brittle fracture within the stabilized-alpha phase width. The results of this work and those of others [6, 15, 16] indicate that the metallurgical characteristics of the oxidized Zircaloy, generally, consist of an outer layer of ZrO$_2$, a central layer of oxygen-stabilized alpha Zircaloy and a base of transformed beta phase. Microhardness measurements revealed that $\alpha$-Zircaloy material is extremely hard and that $\beta$-Zircaloy region exhibits an increase in hardness, with that material nearest to the $\alpha$-phase being harder than that near the center of the tube.

The increasing amount of the stabilized-alpha phase with both temperature and time in addition to the increased
thickness of the oxide would be responsible for the enhancing
effect of both temperature and time on the degree of
embrittlement. The comprehensive microstructural investigation
performed by Aly [6] for Zircaloy-4 tubings oxidized in steam
reveals the enhancing effect of oxidation on both oxide and
stabilized \(\alpha\)-phases. The results of this work are also in
agreement with those of Hobson and Rittenhouse [14] and others
[5] indicating that the increasing degree of embrittlement with
oxidation could be explained in terms of the increasing thickness
of the combined \(\text{ZrO}_2/\alpha\)-Zircaloy layer.

The increase in oxygen content of zirconium is known to
increase the hardness of the material and modify other relevant
mechanical properties. Treco [17] reported that the extensive
hardening effect of oxygen might be due in part to the lattice
distortion accompanying its introduction and possibly the
preferred positions may inhibit the normal slip processes of the
zirconium hexagonal lattice during plastic deformation.

The change in the metallurgical characteristics of Zircaloy
tubing due to oxidation has been considered by many
investigators to play the predominant role in determining its
ductility [5, 14, 15]. These investigators pointed out that the
lower the value of the ratio of the transformed-\(\beta\) thickness to the
total thickness of the cladding the lower would be the ductility.

Due to the importance of oxygen embrittlement, as one of
the modes of cladding failure, several embrittlement criteria have
been proposed and are now in use in the USA [11-13, 18]. Based
on the fraction of the cladding wall thickness which is beta
phase, Scatena [19] suggested an embrittlement criterion which
states that the material is considered embrittled if the fraction of
the remaining beta-phase thickness to the original unoxidized
wall thickness is \(\leq 0.5\). Pawel [20] considered the cladding
embrittled if the oxygen content of the \(\beta\)-phase exceeded 95
percent of the saturation level. The presently used acceptance
criteria specify that the oxide thickness which would result if all the oxygen uptake produced ZrO$_2$ (Called "equivalent cladding reacted") must not exceed 17% of the original cladding wall thickness [18].

The enhancing effect of hydrogen on the oxidation-induced embrittlement could be attributed to the hydride formation as well as the hydrogen effect on the oxide growth mechanism. The results are in agreement with those of Leistikow et al. [21] and Eklom [22].

5. CONCLUSION

The oxidation induced embrittlement of Zircaloy-4 tubings is a function of both temperature and time. The embrittlement is related to the detrimental effect of oxygen on both the mechanical and structural characteristics of Zircaloy tubing. Fractography investigation of oxidized tubings revealed severe embrittlement indicated by a typical brittle fracture of the stabilized-α zone of the oxidized tubing.

REFERENCES


