The time of the oxidation to rich similar weight gains was noticeably different: at 1000 °C by an older; - at 1100 °C by 20-50 %; - at 1200 °C by 10-15 %.

One of the important characteristics for assessing safe the operation of water cooled reactor fuel rods is residual ductility of claddings after high temperature steam oxidation that simulates LOCA type accidents. Previous investigations have shown the adverse effect produced by the high temperature oxidation of the integrated content of some impurities that are usually available in the alloy on the behaviour of E110 (Zr-1Nb) alloy cladding tubes [1-3]. This work continued studies into the influence effected by the impurity compositions on the behaviour of Zr-1Nb cladding tubes when oxidized in steam at 1000-1200 °C. The primary emphasis in this case is put on C, N, F and Cl impurities that are most dangerous for the corrosion resistance of the Zr-1Nb type alloys operated under normal conditions.

In the investigated tubes the impurity content of which complies with the specification for the E110 alloy the total content of C, N, F and Cl impurities differed and was at the level of 65-205 ppm.

In the investigated tubes the impurity content of which complies with the specification for the E110 alloy the total content of C, N, F and Cl impurities differed and was at the level of 65-205 ppm.

Testing conditions:
1. Steam environment, atmospheric pressure;
2. Double side oxidation;
3. Steam flow rate ~ 20 g/h;
4. The error of temperature keeping is ~ ±1 °C;
5. The instrumental error of a mass measurement is ±0.1 mg;
6. The heating rate is about 50 °C;
7. The cooling rate in steam is about 20 °C;
8. Sample length of 30 mm.

The investigation was carried on using samples of cladding tubes (outer diameter of 9.10 mm, wall thickness of 0.68 mm) of three lots having different impurity contents and fabricated from experimental ingots ~ 50 kg in mass. The cladding tubes were fabricates at JSC ChMZ according to the effective specifications and as delivered had etched outer and inner surfaces.

Originally the samples of all the lots had a recrystallized structure with grain sizes of ~ 3 μm and the average βNb phase precipitates of ~ 55 nm.

In the investigated tubes the impurity content of which complies with the specification for the E110 alloy the total content of C, N, F and Cl impurities differed and was at the level of 65-205 ppm.

The content of the other impurities such as Cu, Mn, Mg, Be, Cd, Pb, Ti, K, Ca, Sn of the all tubes was the same.

Chemical composition determination

Metals – spectral method
N – restoration melting method
C – infrared absorption method
F and Cl – photometrical method (pyrohydrolysis)
O – neutron activation method

<table>
<thead>
<tr>
<th>Element</th>
<th>Lot</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>55-60</td>
<td>340-360</td>
<td>160-170</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>44-56</td>
<td>13-15</td>
<td>26-27</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>20-30</td>
<td>30-35</td>
<td>68-73</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>35-50</td>
<td>80-100</td>
<td>120-140</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>19-25</td>
<td>23-35</td>
<td>27-50</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>18-30</td>
<td>18-22</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>32-37</td>
<td>48-50</td>
<td>21-23</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>1.0-1.7</td>
<td>1.0-1.9</td>
<td>4.1-4.2</td>
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<tr>
<td>Cl</td>
<td>1.1-1.9</td>
<td>3.0-3.2</td>
<td>2.5-3.1</td>
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<tr>
<td>O</td>
<td>&lt;70</td>
<td>590</td>
<td>680</td>
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</tr>
</tbody>
</table>

Chemical composition of tubes from Zr-1Nb alloy

**High Temperature Steam Oxidation**

The U-127 facility scheme

- Electronic balance;
- Platinum suspension of a sample;
- Quartz tube of a working zone;
- Upper flange of the furnace;
- Furnace;
- Sample;
- Warmed hub;
- Insulating hub;
- Water;
- Steam generator;
- Thermocouple;
- Intermediate suspension;
- Heat-reflecting disk;
- Electronic balance lower suspension.

**Appearance of the oxidized samples**

<table>
<thead>
<tr>
<th>$T_{ox}$, °C</th>
<th>ECR, %</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>10</td>
<td>8120 s</td>
<td>10190 s</td>
<td>830 s</td>
</tr>
<tr>
<td>1000</td>
<td>18</td>
<td>25770 s</td>
<td>37120 s</td>
<td>1350 s</td>
</tr>
<tr>
<td>1100</td>
<td>10</td>
<td>540 s</td>
<td>540 s</td>
<td>1070 s</td>
</tr>
<tr>
<td>1100</td>
<td>18</td>
<td>1780 s</td>
<td>1800 s</td>
<td>2130 s</td>
</tr>
<tr>
<td>1200</td>
<td>10</td>
<td>200 s</td>
<td>200 s</td>
<td>200 s</td>
</tr>
<tr>
<td>1200</td>
<td>17</td>
<td>500 s</td>
<td>500 s</td>
<td>500 s</td>
</tr>
</tbody>
</table>
Microstructures of oxidized tubes

<table>
<thead>
<tr>
<th>Lot</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 °C</td>
<td>10 % ECR</td>
<td>10 % ECR</td>
<td>10 % ECR</td>
</tr>
<tr>
<td>ZrO2</td>
<td>ZrO2</td>
<td>ZrO2</td>
<td></td>
</tr>
<tr>
<td>1100 °C</td>
<td>18 % ECR</td>
<td>18 % ECR</td>
<td>18 % ECR</td>
</tr>
<tr>
<td>ZrO2</td>
<td>ZrO2</td>
<td>ZrO2</td>
<td></td>
</tr>
<tr>
<td>1200 °C</td>
<td>17 % ECR</td>
<td>17 % ECR</td>
<td>17 % ECR</td>
</tr>
<tr>
<td>ZrO2</td>
<td>ZrO2</td>
<td>ZrO2</td>
<td></td>
</tr>
</tbody>
</table>

- In oxide coat on a sample of lot C as steam oxidized at 1000 and 1100 °C tangential cracks were revealed;
- As the oxidation temperature increases to 1100-1200 °C differences of the oxide coat thicknesses and α-Zr(O) layer depths decrease in all tube lots.
- Differences in "ex-β" grain sizes after steam oxidation at 1100 and 1200 °C are: 130-140 μm in samples of A lot; 60-70 μm in samples of B and C lots.
- In samples of the investigated lots as steam oxidized at 1000-1200 °C the availability of hydrogen containing phase was revealed.

Hydrogen in oxidized samples

- Oxidized samples hydrogen content were analyzed using LECO instrumentation (TCH 600, TC 436, RHEN 600).

- Maximal hydrogen content was revealed in C lot samples oxidized in steam at 1000-1100 °C.

Compression Tests of Oxidized Samples at 20 °C

- Samples of A and B lots as steam oxidized at 1000-1100 °C to 18 % ECR had a higher residual ductility level in comparison to samples of C lot.
- At 1200 °C the residual ductility of the all tube samples oxidized to 17 % ECR was similar.

Microhardness of oxide tube wall

- Typical microhardness profiles

Microhardness H50, kg/mm²

- Increase in oxygen content of oxidized βZr phase is explained by hydrogen pick up

Conclusions

1. The influence of the impurities on the behaviour of cladding tubes was corroborated under LOCA simulating conditions in the range of the contents permissible by the specifications.

2. The impurity content of Zr-1Nb alloy steam oxidized at 1000-1200 °C to 18 % ECR influenced the type of the resulting oxide coats and the structures of α-Zr(O) and "ex-β" layers.

3. The impurities C, N, F and Cl influenced the behaviour of Zr-1Nb tubes steam oxidized at 1000-1200 °C:
   - at the contents of (C+N)>180 ppm and (F+Cl)>5ppm the tubes oxidized to form white crumbling coats, noticeably picked up hydrogen and residual ductility was drastically decreased;
   - at the contents of (C+N)<130 ppm and (F+Cl)<5ppm the tubes demonstrated a better corrosion behavior and a high level of residual ductility.

References