INFLUENCE OF PRE-OXIDATION ON MICROSTRUCTURE AND LOCAL MECHANICAL PROPERTIES OF ZIRCONIUM ALLOYS

Olga BLÁHOVÁ a, Jan ŘÍHA a

a NEW TECHNOLOGY RESEARCH CENTRE, University of West Bohemia, Univerzitní 8, 306 14 Plzeň, Czech Republic, blahova@ntc.zcu.cz

Abstract

The paper deals with evaluation of a zirconium alloy developed for production of cladding tubes for nuclear reactor fuel rods. The specimens were subjected to high-temperature oxidation (at various exposure times and temperatures) and subsequently cooled. The process was a simulation of the loss of coolant accident (LOCA). Before this treatment, some specimens had been pre-oxidized at lower temperatures to simulate the state of material after certain period of service. The microstructure was documented by means of light and scanning electron microscopes. Parameters and lattice volumes of individual phases have been analysed by means of X-ray diffraction. Local mechanical properties (indentation hardness and modulus of elasticity) were tested by means of nanoindentation.

1. INTRODUCTION

Zirconium alloys are used in nuclear power generation primarily due to their low thermal neutron absorption cross section, good mechanical properties and corrosion resistance. They are used, for instance, for production of cladding tubes serving as the primary barrier between the fuel and the surrounding environment. Zirconium (\(T_f = 1,860°C\)) is an allotropic metal with a low-temperature form \(α\) (hcp) stable up to about 860°C and a high-temperature form \(β\) (bcc).

Zirconium shows a high affinity for hydrogen, oxygen and nitrogen, forming stable hydrides, oxides, nitrides and interstitial solid solutions. Other alloying elements are added to Zr for the purpose of improvement of mechanical and corrosion-related properties: Sn, Nb, Al, Cu, V... High corrosion resistance in alloys containing Nb (0.1 to 2 wt %) can be achieved by preparing a microstructure with finely distributed \(β\)-Nb precipitates on the \(α\)-phase grain boundaries and within the matrix [1].

During the operation of the VVER pressurised-water reactor, the outer wall of the tube is in contact with the cooling water at the temperature of 320°C and the pressure of 16 MPa, which results in Zr oxidation and release of hydrogen, part of which is absorbed by the alloy. The forming oxide creates a water-metal barrier inhibiting the corrosion.

A LOCA-type accident may occur in water-cooled reactors, which involves a failure of the main piping and a leak of the coolant. The loss of moderator then occurs within less than 10 seconds and the fission stops. The temperature of the fuel cladding rises to about 1,000°C. A reaction between the steam and the cladding tube occurs, resulting in high-temperature oxidation with parabolic kinetics. After certain delay, emergency systems flood the reactor with water and the fuel cladding tubes will be cooled down rapidly.

UJP Praha a.s. carries out simulations of this type of accident under laboratory conditions [2]. During heating, a portion of oxygen forms oxides, while the other portion dissolves in the metal. The amount of oxygen dissolved in the metal increases with temperature and an oxygen concentration gradient forms. At higher temperatures, the \(α\)-phase transforms to the \(β\)-phase, where \(β\) might contain certain maximum proportion of dissolved oxygen. Even at high temperatures, oxygen causes the transformation of the \(β\)-phase back to the hcp-phase termed \(α\)-Zr(O) which remains stable during cooling. On cooling, the remaining \(β\)-
phase undergoes a transformation to the \( \alpha \)-phase (prior \( \beta \)-phase). Microstructure of the material upon high-temperature oxidation and cooling consists of the \( \text{ZrO}_2 \) oxide layer, oxygen-stabilized \( \alpha \)-Zr(O)-phase and the \( \alpha \)-phase (enriched with H, Fe and Cr). The \( \alpha \)-Zr(O) layer is very brittle, and thus it is the \( \alpha \)-phase which provides the residual ductility and toughness of material. Cooling down from higher temperatures leads to hydride precipitation [3].

2. EXPERIMENTAL MATERIALS

The evaluated \( \text{Zr} \)-alloy contains: 1.0 - 1.1 wt.% Nb, 3 ppm H, 20 ppm N, 100 ppm C and 840 ppm O. Tubes with the length of 30 mm, an outer diameter of 9 mm and a wall thickness of 0.6 mm were used as experimental samples. Specimens were subjected to high-temperature oxidation in steam (exposure temperature: 1,000°C and 1,150°C, exposure time: 0 to 30 min) and quenched in a mixture of water and ice. Upon high-temperature oxidation and quenching, the tubes were sectioned with a diamond-disc cutter at UJP to annular rings with the height of 3 mm and then embedded in resin and polished for metallographic observation. The specimen preparation and evaluation are described in the report [2].

3. EXPERIMENTAL METHODS

Nanoindentation measuring was carried out using an Nano Indenter XP and a Berkovich indenter. With this equipment, it is possible to conduct an instrumented indentation test recording the load-indentation depth curve (\( F - h \)) during loading and unloading phases and thus determine the indentation hardness, elastic modulus and other characteristics. The indentation hardness is defined by the standard [4]:

\[
H_{IT} = \frac{F_{\text{max}}}{A_p}
\]

where \( F_{\text{max}} \) is the maximum loading force and \( A_p \) is the projected indentation contact area. Indentations were made under the load of 8 mN in three parallel rows starting at the oxide-metal interface with a pitch of 5 \( \mu \)m. Indentations were documented with light and scanning electron microscopes, see [5].

X-ray diffraction measuring was carried out using an AXS Bruker D8 Discover diffractometer with a cobalt-target X-ray tube (\( \lambda_{K\alpha} = 0.179021 \) nm) and an area detector Hi-Star with position sensitivity. Upon integration along the radial profile of the diffraction line, one can obtain a one-dimensional diffraction pattern (radial profile of lines) with this detector, like with conventional powder diffractometers. With using XRD analysis the coarseness and biaxial stress were evaluated. The coarseness \( C \) was calculated as a ratio of the area under diffraction lines and the area under linear background \( A_B \):

\[
C = \frac{A_L}{A_B}
\]

The area under diffraction lines \( A_L \) represents the coarse-grained phase, the area under the background \( A_B \) refers to the fine-grained phase. The biaxial stress is calculated from the diffraction line shift compared to the reference diffraction line position:

\[
\sigma_1 + \sigma_2 = -\frac{E}{\mu} \cdot \frac{d - d_0}{d_0^2}
\]

where \( d_0 \) is the reference lattice spacing, \( d \) is the lattice spacing obtained from the experiment, \( E \) is Young’s modulus and \( \mu \) is Poisson’s ratio of the material investigated.

RESULTS

Fig. 1 shows microstructure documented by a light microscope. In this alloy, containing Nb (stabilizing the \( \beta \)-
phase) the layer Zr(O) is non-uniform, in a needle-like form. Upon long exposure times, individual grains of this phase can be observed in the $\alpha$-phase (prior $\beta$). Fig. 1 shows rows of indentations. The chart contains indentation hardness in dependence on the distance from the oxide-metal interface. The chart shows an interval (green lines) of values for the $\alpha$-phase. Of these, mean values (blue line) were calculated (Table 1).

**Table 1.** Measured values of indentation hardness $H_{IT}$ [GPa] shown in dependence on exposure temperature, thickness of pre-oxide and exposure time.

<table>
<thead>
<tr>
<th>Temp. [°C]</th>
<th>Thickness of pre-oxide [µm]</th>
<th>Time [min]</th>
<th>$H_{IT}$ [GPa]</th>
<th>$C$ [-]</th>
<th>$\sigma_1 + \sigma_2$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>0</td>
<td>3</td>
<td>3.76 ± 0.28</td>
<td>1.931</td>
<td>-343.93</td>
</tr>
<tr>
<td>1100</td>
<td>0</td>
<td>6</td>
<td>3.98 ± 0.28</td>
<td>2.205</td>
<td>-50.89</td>
</tr>
<tr>
<td>1100</td>
<td>0</td>
<td>9</td>
<td>4.11 ± 0.24</td>
<td>1.627</td>
<td>-119.79</td>
</tr>
<tr>
<td>1100</td>
<td>0</td>
<td>30</td>
<td>4.34 ± 0.26</td>
<td>1.667</td>
<td>-71.38</td>
</tr>
<tr>
<td>1100</td>
<td>2</td>
<td>3</td>
<td>3.50 ± 0.51</td>
<td>1.875</td>
<td>-62.89</td>
</tr>
<tr>
<td>1100</td>
<td>2</td>
<td>6</td>
<td>3.96 ± 0.25</td>
<td>2.978</td>
<td>-74.17</td>
</tr>
<tr>
<td>1100</td>
<td>2</td>
<td>9</td>
<td>3.86 ± 0.22</td>
<td>1.910</td>
<td>-92.67</td>
</tr>
<tr>
<td>1100</td>
<td>2</td>
<td>15</td>
<td>4.23 ± 0.29</td>
<td>1.264</td>
<td>-103.02</td>
</tr>
<tr>
<td>1150</td>
<td>0</td>
<td>0</td>
<td>3.14 ± 0.27</td>
<td>2.311</td>
<td>-71.53</td>
</tr>
<tr>
<td>1150</td>
<td>0</td>
<td>3</td>
<td>3.98 ± 0.22</td>
<td>1.902</td>
<td>-141.25</td>
</tr>
<tr>
<td>1150</td>
<td>0</td>
<td>6</td>
<td>4.97 ± 0.32</td>
<td>1.564</td>
<td>-149.42</td>
</tr>
<tr>
<td>1150</td>
<td>0</td>
<td>9</td>
<td>4.62 ± 0.24</td>
<td>2.354</td>
<td>-84.77</td>
</tr>
<tr>
<td>1150</td>
<td>0</td>
<td>30</td>
<td>4.83 ± 0.33</td>
<td>3.417</td>
<td>-85.59</td>
</tr>
<tr>
<td>1150</td>
<td>10</td>
<td>0</td>
<td>3.28 ± 0.26</td>
<td>2.614</td>
<td>1.11</td>
</tr>
<tr>
<td>1150</td>
<td>10</td>
<td>3</td>
<td>3.90 ± 0.25</td>
<td>4.409</td>
<td>-13.42</td>
</tr>
<tr>
<td>1150</td>
<td>10</td>
<td>6</td>
<td>4.30 ± 0.24</td>
<td>3.504</td>
<td>-24.12</td>
</tr>
<tr>
<td>1150</td>
<td>10</td>
<td>9</td>
<td>4.27 ± 0.26</td>
<td>3.511</td>
<td>-61.71</td>
</tr>
<tr>
<td>1150</td>
<td>10</td>
<td>15</td>
<td>4.01 ± 0.32</td>
<td>4.103</td>
<td>-81.18</td>
</tr>
<tr>
<td>1150</td>
<td>10</td>
<td>30</td>
<td>4.50 ± 0.37</td>
<td>3.786</td>
<td>-91.40</td>
</tr>
</tbody>
</table>
Fig. 1a). Indentations on the sample with an exposure time of 9 min and exposure temperature of 1,150°C.

b) Measured values of indentation hardness in dependence on the distance from the oxide-metal interface.
The biaxial stress results show an influence of pre-oxidation. The course of stress for pre-oxidized samples is unambiguous at both temperatures. The compressive stress is increasing with the exposure time. This is caused by partial material relaxation during the pre-oxidation. The ambiguous course of stress in samples without pre-oxidation is caused by different plastic deformation rates during production of the semi-products (Fig. 3).

The course of coarseness is ambiguous regardless of the exposure temperature or pre-oxidation. This is caused by conditions of the measurement. The accuracy of the measurement is strongly influenced by a small amount of crystallites diffracting in the irradiated volume (Fig. 4).
The Fig. 5 shows the dependence of indentation hardness on biaxial stress. Results for samples exposed at 1,100°C have relatively low dispersion. The hardness of pre-oxidized samples is increasing with compressive stress. The dispersion of values for samples exposed at 1,150°C is markedly higher, but even here the hardness of pre-oxidized samples is increasing with stress.

![Fig. 5 a. Indentation hardness in dependence on biaxial stress: 1,100°C](image1)

![Fig. 5 b. Indentation hardness in dependence on biaxial stress: 1150°C](image2)

### 3. CONCLUSION

The study deals with the effect of pre-oxidization at lower temperatures to simulate the state of material after certain period of service temperature, time of high-temperature oxidation and subsequent quenching on mechanical properties of a Zr-alloy.

Measured values and correlations will be used for enhancement of accuracy of safety criteria in case of the LOCA accident.

**ACKNOWLEDGEMENT**

*The study was prepared with the support of the MPO ČR 2A - 1TP1/037 project.*

### REFERENCES


