X-RAY DIFFRACTION ANALYSIS OF OXIDIZED ZR-BASED ALLOYS

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Abstract

The results of X-ray diffraction analysis of macroscopic stresses $\sigma$ and crystallite size $D$ in oxide layers are presented in this contribution. The oxide layers was formed on the tubular specimens of Zircaloy 4 and Zr1Nb alloys which were simultaneously oxidized for various time under temperature transient conditions (oxidation in water at 360 °C with a short-time shock in steam at 500 °C). The qualitative relation was outlined between the residual stresses in oxide layers and corrosion kinetics of alloys under investigation.

1. INTRODUCTION

Zirconium alloys are widely used in nuclear power engineering as fuel cladding materials in nuclear reactors. The description and understanding of their corrosion behaviour under the conditions of primary circuits are of prime importance for optimization of both operation and safety of nuclear reactors. Therefore corrosion behavior of Zr-based alloys has been extensively studied all over the world. Non-destructive investigation of corrosion properties of these alloys is also performed at the Faculty of Nuclear Sciences and Physical Engineering, Czech Technical University. The investigation has been performed in cooperation with UJP Praha Inc., where the comparative out-of-pile experimental study on long-term corrosion behavior of Zr-based alloys in different corrosion environments is carried out exposing all alloys under identical conditions.

The aim of present study is focused on the relation between the corrosion kinetics and such characteristics of the oxide layers as residual macroscopic stresses and crystallite size $D$, which have been investigated by means of XRD. The characteristics under examinations have been determined for the oxide layers formed on the tubular specimens of Zr1Nb and Zircaloy 4 alloys under temperature transient conditions. The preliminary results have been published earlier [1], [2].

2. EXPERIMENTAL

2.1 Oxidation conditions

Transition oxidation in water steam at 500 °C (1 day for Zr1Nb and 0,003 day for Zry-4S) was applied on the unoxidized specimens and on the specimens preoxidized in water at 360 °C for 21 days. All the specimens were further oxidized in pure water at 360 °C for various times up to 170 days. The specimens of both the alloys which had not undergone the temperature transition were also studied. The kinetics of oxidation of the alloys under investigation were represented by weight gain (or $T_{ox}$) being measured after each exposure.
2.2 Diffraction method used

The „sum of the surface principal stresses“ technique with a reference substance [3] was used with regard to the specific experimental conditions, especially to the marked texture of oxide layers and the shape of specimens to determine the stresses in oxide layers. The method is based on the determination of lattice strains \( \varepsilon^{hkl} \) from which, subsequently, the stresses were calculated by using appropriate macroscopic Young’s moduli. The evaluation of the crystallite size was performed by using a „single-line“ method with the Pearson VII approximation of the profiles’ shape [4].

2.3 Experimental conditions

A Bruker D8 Discover powder diffractometer with CoK\( \alpha \) radiation was used to measure diffraction patterns. In oxide layers of the samples investigated the measurements were performed on the \{10-4\} planes with \( 2\theta_{tab} = 85.24^\circ \) for CoK\( \alpha \) radiation. Four partially overlapping diffraction lines were recorded within the 20 range of measurement: (10-4) of \( \text{ZrO}_2 \) and (112), (201), (004) of \( \alpha \)-Zr; thus, the fitting procedure had to be used to obtain the accurate profile characteristics such as peak position 20, integral intensity \( I_{int} \) and integral breadth \( W_{int} \). The same procedure was applied on standard oxide samples of the both alloys under investigation. The error of stress determination was about of 10% of calculated stress values; the error of crystallite size evaluation was about of 20% of calculated values.

3. RESULTS AND DISCUSSION

The results of measurements and calculations are depicted in Fig. 1 for Zr1Nb alloy and Fig. 2 for Zry-4 alloy.

![Fig. 1](image_url)

Fig. 1 Corrosion kinetics of Zr1Nb alloy under different oxidation conditions (A), macroscopic stresses \( \sigma \) vs. oxide thickness (B) and crystallite size \( D \) vs. oxide thickness (C) of samples investigated
Fig. 2 Corrosion kinetics of Zircaloy-4 under different oxidation conditions (A), macroscopic stresses $\sigma$ vs. oxide thickness (B) and crystallite size $D$ vs. oxide thickness (C) of samples investigated.

The behavior of the two alloys oxidized under different conditions can be qualitative compared using average values of measured and calculated quantities.

Table 1 Average values of oxide thickness $T_{ox}$, macroscopic stresses $\sigma$ and crystallite size $D$ determined for oxide layers of the alloys oxidized within the range of exposures from 1 to 255 days.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_{ox}$ (μm)</th>
<th>$\sigma$ (MPa)</th>
<th>$D$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation in pure water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr1Nb</td>
<td>2.85</td>
<td>-830</td>
<td>12</td>
</tr>
<tr>
<td>Zry-4 S</td>
<td>3.23</td>
<td>-780</td>
<td>12</td>
</tr>
<tr>
<td>Transient oxidation in water + steam + water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr1Nb</td>
<td>3.74</td>
<td>-816</td>
<td>8</td>
</tr>
<tr>
<td>Zry-4 S</td>
<td>3.29</td>
<td>-804</td>
<td>11</td>
</tr>
<tr>
<td>Transient oxidation in steam + water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr1Nb</td>
<td>4.82</td>
<td>-849</td>
<td>9</td>
</tr>
<tr>
<td>Zry-4 S</td>
<td>6.48</td>
<td>-617</td>
<td>9</td>
</tr>
</tbody>
</table>

It follows from the figures 1, 2 and data tabulated that:
- oxidation of the alloys under transient conditions leads to increase in weight gain (or $T_{ox}$) especially rapid for case of oxidation in water steam 500 °C + water 360 °C (with except of Zry-4 S at water-steam-water conditions),
- at the initial stages of water-steam-water oxidation the stresses in oxide layers of the both alloys dropped rapidly but was reaching the previous high values at the short time of subsequent oxidation in water,
- average value of macroscopic stresses in oxide layers of Zr1Nb alloy keeps the high level for the all cases of oxidation,
- average value of macroscopic stresses in oxide layers of Zry-4 S alloy is smallest in the case of steam-water transition,
oxidation in steam leads to decrease of crystallite size D values in oxide layers of Zr1Nb alloy for the both cases of transition. The decrease of D in oxide layers of Zry-4 s alloy is maricable for case of steam-water transition only.

3.1 The relation between the residual stresses in oxide layers and corrosion kinetics of alloys under investigation

Let us define a quantity \( G^t = \sigma^t / T_{ox}^t \) where \( \sigma \) is the experimental value of stresses and \( t \) – oxidation time for appropriate experimental oxide thickness \( T_{ox} \). This quantity has a gradient character and related to the whole oxide formed during exposure time.

With regard to the nature of XRD measurements the values of \( G \) have to be affected by the penetration of applied radiation as well as by morphology of external part of oxide layer where the relief of growth stresses is occurred. Nevertheless this quantity can be used to illustrate the influence of residual macroscopic stresses \( \sigma \) on the oxidation kinetics.

The comparison of the oxidation kinetics and the relevant \( G^t \) vs. exposure \( t \) is given in Figs. 3 – 5 for two alloys oxidized under different conditions.

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**Fig. 3** Oxidation kinetics (A) and gradients \( G^t \) vs. exposure (B) for Zr1Nb and Zry-4 S alloys oxidized in pure water at 360 °C

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**Fig. 4** Oxidation kinetics (A) and gradients \( G^t \) vs. exposure (B) for Zr1Nb and Zry-4 S alloys oxidized under water-steam-water transition
Fig. 5 Oxidation kinetics (A) and gradients $G$ vs. exposure (B) for Zr1Nb and Zry-4 S alloys oxidized under steam-water transition

It can be seen from figures that qualitative relation $T_{\text{ox}} \sim 1/G$ exists in all cases of oxidation. Thus the gradient of macroscopic stresses in oxide layer takes more important part in the oxidation process then the absolute value of stresses.

The effect of stress gradient $G$ on the oxidation kinetics of alloys under investigation is clearly obvious in the case of steam-water oxidation (Fig. 5) for example. The crystallite size $D$ in oxide layers of both alloys in this case acquires the same average values (Tab. 1).

4. CONCLUSIONS

From the results of comparative XRD analysis of oxide layers formed on Zr-based alloys oxidized under different conditions, it can be stated that

- the qualitative relation exists between the gradient of macroscopic residual stresses in oxide layers and oxidation kinetics of Zr-based alloys,
- the protectiveness of oxide layers is closely correlated with such factors being superimposed as microstructure and stress characteristics of the oxide.

5. REFERENCES

[3] I.Kraus and V.V.Trofimov, Rentgenová tenzometrie, Academia, Prague, 1988

6. ACKNOWLEDGEMENTS

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