

INFLUENCE OF MACROSCOPIC STRESSES IN OXIDE LAYERS ON CORROSION KINETICS OF ZR-BASED ALLOYS

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

Keywords: zirconium alloys, oxide layers, stresses, XRD

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 of long-term corrosion behavior of Zr-based alloys in different corrosion environments is carried out, exposing all alloys under identical conditions.

The aim of the present study is focused on the relation between 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 tubular specimens of Zr1Nb and Zircaloy 4 alloys under temperature transient conditions.

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 unoxidized specimens and on 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 336 days. The specimens of both the alloys, which had not undergone the temperature

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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 [1] was used with regard to the specific experimental conditions, especially to the marked texture of oxide layers and the shape of specimens to determine stresses in oxide layers. The method is based on determination of lattice strains ϵ^{hkl} from which, subsequently, the stresses were calculate using appropriate macroscopic Young's module. Evaluation of the crystallite size was performed by using a "single-line" method with the Pearson VII approximation of the profiles' shape [2]. It should be noticed that the measured values ϵ^{hkl} are supposed to be average within the effective X-ray penetration depths T^{ef}, whose values are usually calculated to produce 63% of the overall diffracted intensity. The same assumption is valid for values of crystallite size D.

2.3 Experimental conditions

A Bruker D8 Discover powder diffractometer with CoK α radiation was used to measure diffraction patterns. In oxide layers of the samples investigated the measurements were performed on {10-4} planes with $2\theta_{tab} = 85.24^{\circ}$ for CoK α radiation. With regard to the appearance of X-ray patterns the value of T^{ef} can be calculated as 9.77 µm (i.e., for 97% of the overall diffracted intensity).

Four partially overlapping diffraction lines were recorded within the 2 θ range of measurement: (10-4) of ZrO2 and (112), (201), (004) of α -Zr; thus, the fitting procedure had to be used to obtain the accurate profile characteristics such as peak position 2 θ , integral intensity I_{int} and integral breadth W_{int}. The same procedure was applied to standard oxide samples of both the alloys under investigation. The error in stress determination was about 10% of the calculated stress values; the error in crystallite size evaluation was about 20% of the 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. Corrosion kinetics of Zr1Nb alloy under different oxidation conditions (A), macroscopic stresses σ 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 σ 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 qualitatively compared using average values of measured and calculated quantities. For this purpose, the range of exposures from 1 to 255 days has been chosen.

Alloy	T _{ox} . (μm)	σ (MPa)	D (nm)
Oxidation in pure water			
Zr1Nb	2.85	-830	12
Zry-4 S	3.23	-780	12
Transient oxidation in water + steam + water			
Zr1Nb	3.74	-816	8
Zry-4 S	3.29	-804	11
Transient oxidation in steam + water			
Zr1Nb	4.82	-849	9
Zry-4 S	6.48	-617	9

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

It follows from Figures 1, 2 and the data tabulated that:

- oxidation of the alloys under transient conditions leads to the increase in weight gain (or T_{ox}) which is especially rapid in the case of oxidation in water steam 500 °C + water 360 °C (with the exception of Zry-4 S in water-steam-water conditions),

- at initial stages of water-steam-water oxidation the stresses in oxide layers of both the alloys dropped rapidly but reached the previous high values in a short period of time of subsequent oxidation in water,

- the average value of macroscopic stresses in oxide layers of Zr1Nb alloy keeps the high level in all the cases of oxidation,

- the 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 the decrease in crystallite size D values in oxide layers of Zr1Nb alloy for both cases of transition. The decrease in D in oxide layers of Zry-4 s alloy is remarkable in the case of steam-water transition only,

- the smaller increment of oxide thickness for Zry-4 S alloy in comparison with Zr1Nb under transient oxidation in water-steam-water can be related to the considerable difference between the average values of crystallite size D. Note that the average values of stresses are the same for the two alloys in this case of oxidation.

- therefore, the protectiveness of oxide layers is closely related to such factors being superimposed as microstructure and stress characteristics of the oxide.

3.1 The relation between 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 σ is the experimental value of stresses and t – the oxidation time for appropriate experimental oxide thickness T_{ox} . This quantity has a gradient character and is related to the whole oxide formed during the exposure time.

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

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



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



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 Gt vs. exposure (B) for Zr1Nb and Zry-4 S alloys oxidized under steam-water transition

It can be seen from the figures that there exists a qualitative relation $T_{ox} \sim 1/G$ in all cases of oxidation. Thus, the gradient of macroscopic stresses in oxide layer plays a important part in the oxidation process.

The effect of stress gradient G on oxidation kinetics of the 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 the alloys reaches the same average values (Tab. 1) in this case.

4. Conclusions

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

- there exists a qualitative relation between the gradient of macroscopic residual stresses in oxide layers and oxidation kinetics of Zr-based alloys,

- the protectiveness of oxide layers is closely related to such factors being superimposed as microstructure and stress characteristics of the oxide.

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