

XRD Analysis of Oxide Layers Formed on Zirconium Alloys at 360°C in Water with Different pH

Galina Gosmanová,¹ Ivo Kraus,² Michal Kolega,³ Věra Vrtílková⁴

Abstract: Two types of differently manufactured Zr1Nb alloy were investigated after exposition in the water at 360° C with different pH. The residual stresses σ , crystallite size D and micro strains ϵ in oxide layers were examined by means of XRD. It was shown that the oxide layers of alloys investigated have had the different characteristics in the same oxidizing environments. The so-called “dry” and “wet” samples were investigated. The comparative study was shown that the decrease of macroscopic stresses in the “wet” samples during some exposures could be related to change of microstructure of the oxide layers. This effect indicate the changes in oxidation kinetics of the alloys under investigation.

Keywords: Zr-Based Alloys, Oxide Layers, Gel, Stresses, Microstructure, Corrosion Kinetics

1. Introduction

Corrosion properties of zirconium alloys are intensively investigated because its main using as fuel claddings in the primary circuits of nuclear reactors. However the corrosion mechanism of zirconium alloys is still not quite understood. The characterization of the oxide properties such as macroscopic stresses and microstructure and its changes through the different stages of oxide growth may contribute to a better understanding of corrosion mechanism. The present work has been performed in cooperation with UJP PRAHA, Inc., where the corrosion behavior of Zr-based alloys in the different environments is studied in long-time tests. The paper deals with the properties of oxide layers formed on the Zr1Nb alloy of two modifications during oxidation at 360° C in the environments with different pH. Characteristics of oxide layers such as macroscopic stresses σ , crystallite size D and microstrains ϵ were obtained by means of X-ray diffraction analysis.

¹ RNDr. Galina Gosmanová, Czech Technical University in Prague, Faculty of Nuclear Sciences and Engineering, Trojanova 13, 120 00 Praha 2, Czech Republic, galina.gosmanova@jfifi.cvut.cz

² Prof. RNDr. Ivo Kraus, DrSc., Czech Technical University in Prague, Faculty of Nuclear Sciences and Engineering, Trojanova 13, 120 00 Praha 2, Czech Republic, ivo.kraus@jfifi.cvut.cz

³ Ing. Michal Kolega, PhD, New Technologies Research Centre, West Bohemian University, Univerzitní 8, 306 14 Plzeň, Czech republic

⁴ Ing. Věra Vrtílková, UJP PRAHA Inc., Nad Kamínkou 1345, 156 10 Praha-Zbraslav, Czech Republic

2. Experimental

2.1. Specimens investigated

The cladding tubes were prefabricated from two types Zr1Nb alloy denoted 6 and 7. The Zr1Nb alloy 6 was manufactured from Kroll Zr and alloy 7 from Van Arkel Zr. The tubular specimens under investigation were oxidized at 360°C in pure water and VVER water with exposures varied from 105 to 357 days. Corresponding adherent oxide thicknesses were ranged from 1.6 µm to 6.22 µm. In the 70ppm Li added water exposures were varied from 42 to 126 days. Corresponding adherent oxide thicknesses were ranged from 2µm to 21.22µm.

The measurements were carried out on two types of oxide layers so-called “wet” and “dry”. Where the “dry” samples were dehydrated on air after corrosion exposure, the “wet” samples were permanently kept in water. It is known that ZrO₂ is gradually hydrated forming hydrated oxide of a gel character, when exposed to water. This process is reversible. The gel represents a two-phase system forming a joint structure composed of solid and liquid components [1]. It can be assumed that “wet” samples correspond to the oxide state in-situ. Since X-rays cannot detect the amorphous gel, the obtained characteristics are related only to the crystalline part of the hydrated layer.

2.2. Diffraction method and experimental conditions

The „sum of the surface principal stresses“ technique with a reference substance was used with regard to the specific experimental conditions, especially to the marked texture of oxide layers and the shape of specimens. The method is based on the determination of lattice strains ϵ_{hkl} perpendicular to the surface of the samples, where with regard to the origination a centrally symmetrical state of stress (i.e. $\sigma_1 = \sigma_2 = \sigma$) is assumed. Thus, $\epsilon_{hill} = (d_s - d_0)/d_0 = -(v/E)(\sigma_1 + \sigma_2) = -(v/E) 2\sigma$ and $\sigma = (E/2v)(\delta\theta \text{ctg}\theta_0)$ because $\epsilon = -\delta\theta \text{ctg}\theta_0$. In the expressions above σ , v and E stand for the stress parallel to the sample surface, the Poisson's ratio and the Young's modulus respectively; a_{ds} is stressed and d_0 unstressed spacing of (hill) planes parallel to the surface, θ is the Bragg's angle [2].

It should be noticed that measured values ϵ_{hkl} are supposed as average within the effective X-ray penetration depths T_e , which values are usually calculated to produce 63% of the overall diffracted intensity. The same presumption is valid for values of crystallite size D and microstrains ϵ . The stress values were calculated by using macroscopic Young's modulus $E = 20.7 \times 10^4$ MPa for ZrO₂. The evaluation of the crystallite size D and microstrains ϵ was performed by using „single-line“ method with the Pearson VII approximation of the profiles shape [3]. A D-8 Discovery powder diffractometer with CoK α radiation was used to measure diffraction patterns⁵. The measurements were performed on {10-4} planes with $2\theta \approx 85.2^\circ_{\text{tab}}$ for CoK α radiation. The appropriate effective X-ray penetration depth $T_e(10-4) = 3.68$ µm. Four partially overlapping diffraction lines were recorded into

⁵ The measurements of diffraction patterns was performed on NTC, West Bohemian University, Plzeň

the 2θ range of measurement: (10-4) of ZrO_2 and (112), (201), (004) of α -Zr; thus, the fitting procedure had to be used to obtain the accurate characteristics of diffraction line i.e. peak positions 2θ , integral breadth W_{int} and integral intensity I_{int} . The error of stress determination was about a 10% of calculated stress values; the error of size and strain evaluation was about of 20% of calculated values.

3. Results and discussion

The recent XRD research was focused on the properties of gel-like oxide layers [4]. It was shown that

- a) the values of macroscopic stresses σ in the crystalline part of hydrated layers increase in comparison with those of dry samples. The effect can be caused by the increase of the hydrated layer volume provided a mechanical stability stays in the oxide/metal system,
- b) the values of crystallite size D in the crystalline part of hydrated layers decrease in comparison with those of dry samples. The effect can be caused by dissolution of the mosaic blocks boundaries.

The present investigation indicates that exceptions occur from this observation. The above-mentioned relations between characteristics of wet and dry oxide layers are reversed during some exposures (Table 1) i.e. $\sigma_w < \sigma_d$ and $D_w > D_d$.

For an explanation of this effect it should be considered the diffracted intensity. The increase of crystallite size D in the hydrated layers can be caused by stress induced recrystallization. On the assumption that whole mass of the crystalline component remains the same, the reorientation of crystallites should occurs if the diffracted intensity decreases for hydrated layers. Such changes of microstructure are accompanied with decrease of macroscopic stresses and the pores evaluation in observed oxide layers. With regard to diffusion character of the oxidation process both the factors contribute to acceleration of oxidation. Consequently the changes in the corrosion kinetics can be expected whether the temporary or steady state character (from parabolic to linear for example).

Graphs in Figs. 1.– 4. illustrate corrosion kinetics and courses of observed characteristics of monoclinic ZrO_2 component for “wet” samples of alloy Zr1Nb (types 6 and 7) exposed in VVER water for example. Points related to kinetics changes whether the temporary or steady state character are highlighted.

Table 1. Exposures with reverse relations between characteristics σ and D for dry and wet samples respectively. R denotes the difference between absolute values. Tox is oxide layer thickness; I_{int} is integral intensity of (10-4) reflection

Alloy 7 exposed in VVER water								
Sample	Exp (days)	Tox (μm)	σ (MPa)	D (nm)	I int.(R.U.)	R σ (d-w)	R D (d-w)	R I (d-w)
Dry	105	2.7	-1198	10	646			
Wet	105	2.7	-1036	14	571	-163	-4.3	85
Dry	146	1.6	-1317	12	469			
Wet	146	1.7	-1205	14	405	-159	-2.1	64
Dry	147	3.5	-1300	14	674			
Wet	147	3.4	-1155	15	559	-145	-1.0	115
Dry	255	5.2	-948	17	888			
Wet	255	5.3	-885	17	816	-63	-1.0	92

Alloy 7 exposed in 70 ppm Li added water								
Sample	Exp (days)	Tox (μm)	σ (MPa)	D (nm)	I int.(R.U.)	R σ (d-w)	R D (d-w)	R I (d-w)
Dry	42	2.4	-1282	15	664			
Wet	42	2.4	-1205	17	602	-77	-2.3	82
Dry	126	3.9	-1248	15	823			
Wet	126	9.5	-1158	16	734	-91	-1.0	89

Alloy 6 exposed in VVER water								
Sample	Exp (days)	Tox (μm)	σ (MPa)	D (nm)	I int.(R.U.)	R σ (d-w)	R D (d-w)	R I (d-w)
Dry	105	2.7	-1193	11	756			
Wet	105	2.7	-1108	13	588	-68	-2.6	168
Dry	210	3.5	-1147	12	838			
Wet	210	3.6	-957	14	645	-190	-1.9	193
Dry	316	5.5	-1046	16	1077			
Wet	316	5.6	-832	17	858	-214	-1.2	219

Alloy 6 exposed in 70 ppm Li added water								
Sample	Exp (days)	Tox (μm)	σ (MPa)	D (nm)	I int.(R.U.)	R σ (d-w)	R D (d-w)	R I (d-w)
Dry	42	3.6	-1076	13	608			
Wet	42	2.0	-980	17	508	-97	-3.3	100
Dry	49	2.1	-1099	14	605			
Wet	49	5.3	-1044	14	530	-55	-0.9	86
Dry	63	2.3	-1187	14	624			
Wet	63	2.4	-1093	15	510	-95	-0.6	115
Dry	105	2.7	-1212	13	728			
Wet	105	2.7	-1112	14	656	-101	-1.0	92

Alloy 6 exposed in pure water

Sample	Exp (days)	Tox (μm)	σ (MPa)	D (nm)	I int.(R.U.)	R σ (d-w)	R D (d-w)	R I (d-w)
Dry	252	4.1	-1092	13	895			
Wet	252	4.1	-960	15	721	-132	-1.8	174

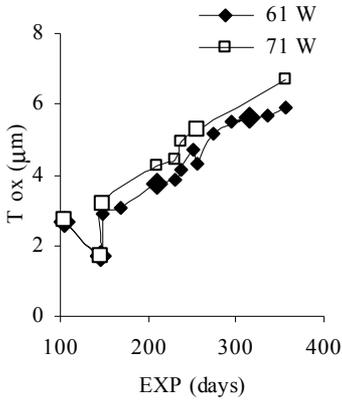


Fig. 1. Corrosion kinetics of Zr1Nb alloy (types 6 and 7) oxidized in VVER water.

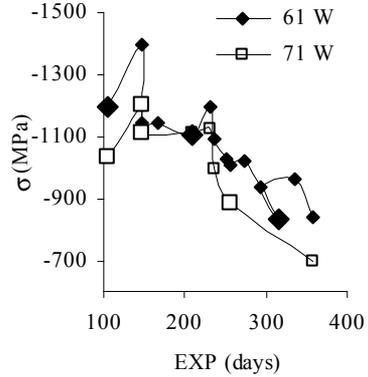


Fig. 2. Macroscopic residual stresses σ determined in „wet“ oxide layers of Zr1Nb alloy (types 6 and 7) oxidized in VVER water.

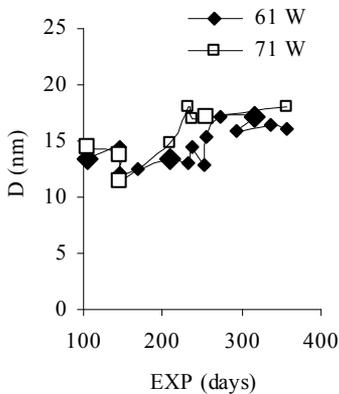


Fig. 3. Crystallite size D determined in „wet“ oxide layers of Zr1Nb alloy (types 6 and 7) oxidized in VVER water.

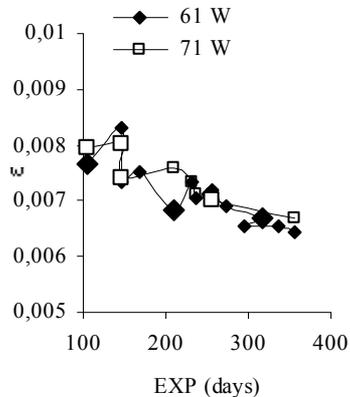


Fig. 4. Microdeformations ε determined in „wet“ oxide layers of Zr1Nb alloy (types 6 and 7) oxidized in VVER water.

The behavior of two types alloys oxidized under different conditions can be qualitatively compared using average values of quantities investigated which were calculated for the corresponding ranges of exposures excluding “critical” points (Tables 2, 3). It should be noticed that all the results was obtained by measurements on the adherent dark oxide.

Table 2. Average values of macroscopic stresses σ determined for hydrated (w) and dehydrated (d) oxide layers of alloys oxidized at 360° C in the different environments. The difference R between d and w values and the error of measurement are tabled as well. All the values are in MPa

Environment	Water	VVER	VVER	70ppmLi	70ppmLi
Alloy	60	61	71	63	73
Average σ "w"	-1015	-1059	-1089	-1118	-1273
Average σ "d"	-875	-934	-1003	-1000	-1218
R σ (d - w)	139	125	85	118	55
Measurement error	82	58	72	70	53

Table 3. Average values of crystallite size D and microdeformations ϵ determined for hydrated (w) and dehydrated (d) oxide layers of alloys oxidized at 360° C in the different environments. The difference R between d and w values and the error of measurement are tabled as well. Values of D are in nm

Environment	Water	VVER	VVER	70ppmLi	70ppmLi
Alloy	60	61	71	63	73
Average. D "w"	11	14	14	13	14
Average D "d"	14	16	15	14	15
R D (d - w)	2.9	1.6	1.5	1.0	1.0
Measurement error	1.3	1.4	2.0	1.4	1.5
Average ϵ "w"	0.0053	0.0069	0.0074	0.0076	0.0079
Average ϵ "d"	0.0067	0.0072	0.0075	0.0077	0.0080
R ϵ (d - w)	0.0015	0.0003	0.0001	0.0001	0.0001
Measurement error	0.0002	0.0002	0.0001	0.0001	0.0001

The average values of oxide layers thicknesses calculated for whole range of exposures in the appropriate oxidizing environment are given in Table 4.

Table 4. Average values of the oxide thicknesses T_{ox} . All the values are in μm

Environment	Water	VVER	VVER	70ppmLi	70ppmLi
Alloy	60	61	71	63	73
Average T_{ox} "w"	4.34	3.49	4.54	4.11	9.86
Average T_{ox} "d"	4.31	3.64	4.31	4.40	9.11

It follows from data tabulated that

the recent conclusions about the relation between the characteristics σ and D in the dehydrated and hydrated oxide layers respectively are surely valid. Moreover it can be seen that values of the microdeformations ϵ for hydrated layers are systematically smaller than for dehydrated layers even if effect inhere in the error range just like as for crystallite size D ,

the average values of macroscopic stresses σ and microdeformations ϵ in the oxide layers for both the types of alloy increase in the lithiated water in comparison with VVER water. This effect is typical for pretransition mode of oxidation Zr-based alloys as was found in earlier investigation [5],

the values of crystallite size D decrease in the lithiated water especially in the “wet” layers. This effect corresponds with the hypothesis proposed by Cox [6] that LiOH causes the preferential dissolution of zirconia at the grain boundaries,

the largest thicknesses of oxide layers belong to alloy of type 7 oxidized in lithiated water.

4. Conclusions

It can be concluded from the results of XRD analysis that the changes in the kinetics of oxidation whether temporary or steady state can be related to changes in microstructure of oxide layers such as stress induced recrystallization together with reorientation of crystallites. This presumption is in good agreement with diffusion model of corrosion.

Another physical factors (as tetragonal - monoclinic transformation for example) can contribute to steady state kinetics transition as well.

Acknowledgements

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