

KOMPARATIVNÍ RENTGENOGRAFICKÉ STUDIUM ZIRKONIOVÝCH SLITIN OXIDOVANÝCH ZA TEPELNĚ PŘECHODOVÝCH PODMÍNEK

COMPARATIVE X-RAY STUDY OF ZR-BASED ALLOYS OXIDIZED UNDER TEMPERATURE TRANSIENT CONDITIONS

Galina GOSMANOVÁ¹, Ivo KRAUS¹, Věra VRTÍLKOVÁ²

Abstrakt

Slitiny na bázi zirkonia patří ke konstrukčním materiálům používaným v jaderné energetice zejména jako obaly palivových článků jaderných reaktorů chlazených vodou. Jejich korozní chování za provozních, extrémních či havarijních podmínek je stále předmětem rozsáhlého celosvětového výzkumu. Obsahem článku je komparativní rentgenové difrakční studium slitin Zr1Nb a Zircaloy 4 (Zry-4S) oxidovaných za podmínek tzv. tepelného přechodu (oxidace ve vodě při 360 °C s krátkodobým šokem v páře při 500 °C). Vzhledem ke vzniku výrazné kvantitativně proměnlivé textury v oxidických vrstvách vzorků se ukázalo, že střední hodnota zbytkových napětí σ v oxidických vrstvách je použitelnou charakteristikou pro porovnání odlišného korozního chování studovaných slitin.

Klíčová slova: zirkoniové slitiny, rentgenová difrakce, zbytková napětí.

Abstract

Zirconium alloys are currently used as cladding materials of fuel elements of water-cooled power reactors. However, their behavior under extreme conditions is still the object of extensive research. The comparative XRD study of Zr1Nb and Zircaloy 4 (Zry-4S) is presented in this paper. The aim of the study was determination of residual stresses σ and analysis of the microstructure of oxide layers formed on tubular specimens oxidized under temperature transient conditions (oxidation in water at 360 °C with a short-time shock in steam at 500 °C). The specimens of both the alloys which had not undergone the temperature transition were also studied. A strongly quantitatively varied texture occurred in oxide layers. Thus, the average values of residual stresses σ in oxide layers represent a useful XRD characteristic for the different behavior of the two alloys.

Key words: zirconium alloys, XRD, residual stresses.

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 have been extensively studied in the world. Non-destructive investigation of corrosion properties of these alloys is performed also at the Faculty of Nuclear Sciences and Physical Engineering, Czech Technical

¹ RNDr. Galina GOSMANOVÁ, prof. RNDr. KRAUS Ivo, DrSc., CTU, Faculty of Nuclear Sciences and Physical Engineering, Praha, gosmanov@troja.fjfi.cvut.cz, kraus@troja.fjfi.cvut.cz.

² Ing. VRTÍLKOVÁ Věra, UJP Praha, Inc., vrtilkova@ujp.cz

Lektoroval: prof. Ing. Svätoboj LONGAUER, CSc., KNoM, HF TU v Košiciach, longauer@tuke.sk

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 (Zr1Nb, ZIRLO, low-tin and standard Zircaloy-4) in different corrosion environments is underway exposing all alloys in identical conditions. The aim of study is focused on the relation between the corrosion kinetics and the microstructural characteristics of the ZrO₂ oxide layers which have been investigated by means of several physical methods including XRD. The following features have been examined using X-ray diffraction techniques [1,2]:

- the evolution of macroscopic stresses σ in oxide layers during oxidation,
- the stress state of the oxide/metal system as a whole,
- the microscopic characteristics such as crystallite size D and lattice strains ε for both the components of oxide/metal system,
- the lattice constants a , c and crystallographic unit cell volume V_b for α -Zr matrix of oxidized specimens.

It would be appeared that the parameters observed can contribute to better understand of the corrosion processes [3,4] and are useful for comparative study the corrosion behavior of Zr-based alloys under both the same or different oxidation conditions [5,6].

EXPERIMENTAL

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 a specimen 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.

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 the stresses in oxide layers and metal underlying. The method is based on the determination of lattice strains ε^{hkl} from which, subsequently, the stresses were calculated by using appropriate macroscopic Young's moduli. The evaluation of the crystallite size and lattice strains was performed by using a „single-line“ method with the Pearson VII approximation of the profiles' shape [2].

Experimental conditions

An ω - goniometer SIEMENS with Cr K α radiation was used to measure diffraction patterns. In oxide layers of the samples investigated the measurements were performed on the {10-4} planes with $2\theta_{tab} = 119.5^\circ$ for CrK α radiation. In metal substrates the measurements were performed on the {112} planes for which $2\theta_{tab} = 113.5^\circ$ for the CrK α radiation. Four partially overlapping diffraction lines were recorded within the 2θ 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 2θ , integral breadth W_{int} , integral intensity I_{int} . The same procedure was applied on standard samples of both the alloys under investigation.

RESULTS AND DISCUSSION

The kinetics of oxidation of the alloys under investigation are depicted in Fig.1A.

The experimental values of the integral intensity of the oxide diffraction line (10-4) vs. oxide thickness are plotted in Fig.1B. Assuming that the reflective layer is of isotropic character we can calculate the hypothetical intensity of the selected diffraction line depending on the thickness of the layer. The calculated values of I are also plots in Fig.1B.

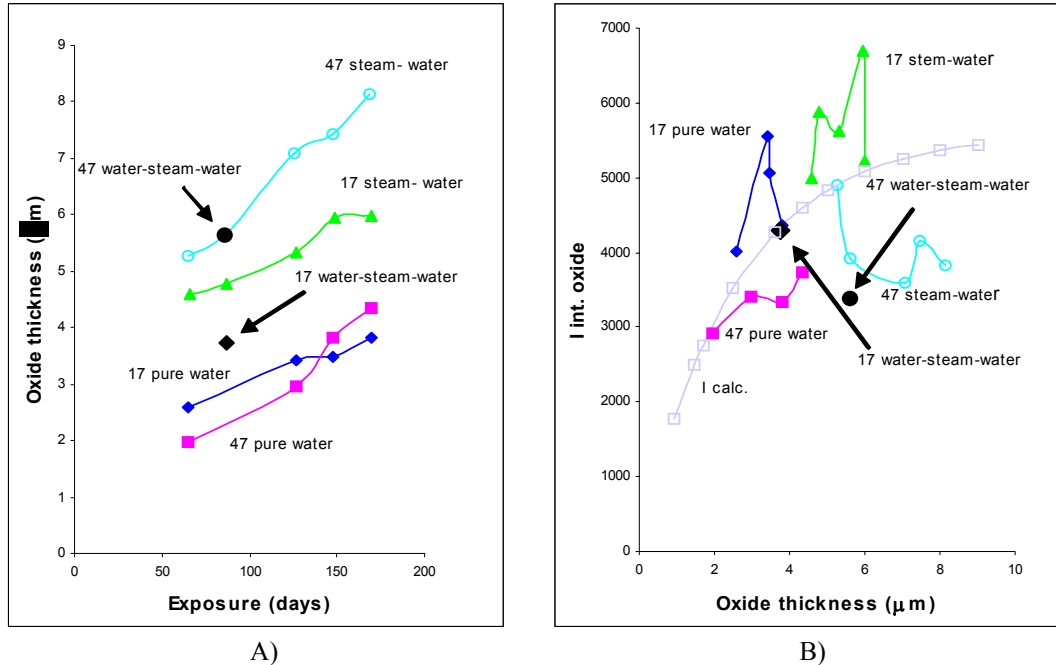
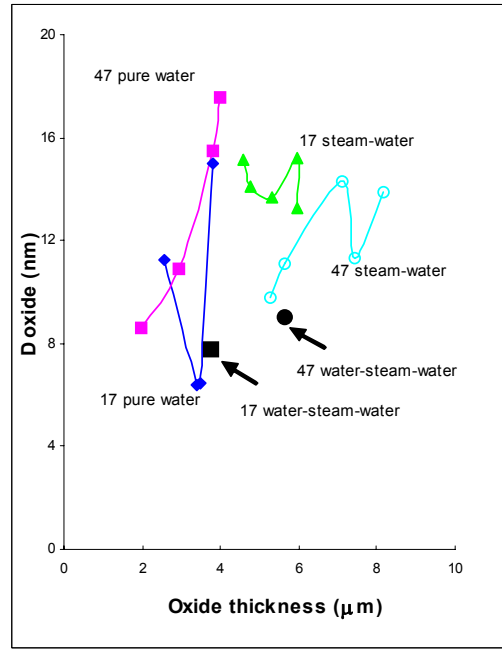
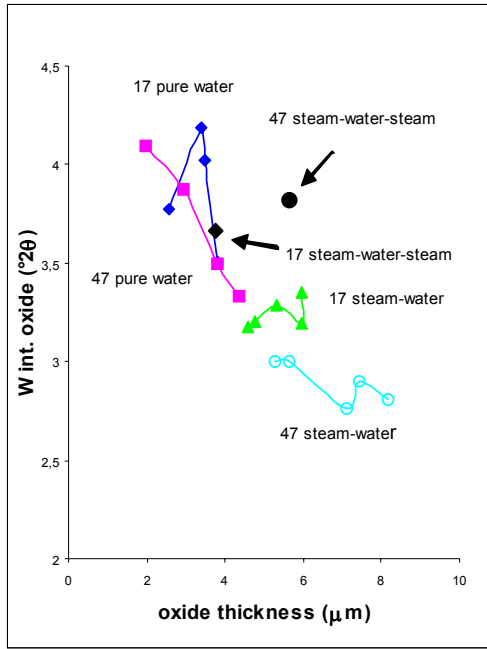


Fig.1 A - corrosion kinetics of Zr1Nb alloy (denoted 17) and Zry-4 S alloy (denoted 47) under different conditions. B – integral intensity I of the oxide diffraction line (10-4) vs. oxide thickness of samples investigated. The hypothetical course of diffracted intensity I_{calc} vs. oxide thickness is also shown

As it followed from the experimental values of I_{int} , the texture in oxide layers strongly varied in quantity at almost each exposure. This phenomenon has been established in the earlier research which was concerned with the short-time oxidation of Zr1Nb alloy under temperature transient conditions. Consequently the plots of W_{int} (Fig.2A), D (Fig.2B) and ϵ vs oxide thickness have had quite inhomogeneous character. Similarly inhomogeneous courses can be observed for these quantities in textured layers of metal underlying of Zr1Nb alloy.

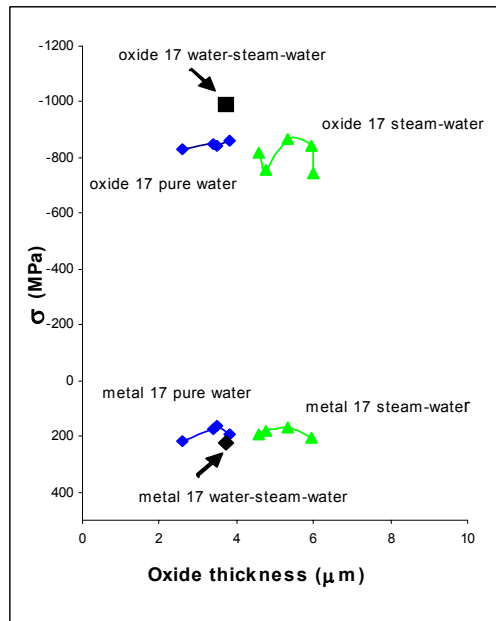
The results of residual stresses σ determination in oxide layers and metal underlying are given in Fig.3A (for Zr1Nb alloy) and Fig.3B (for Zry-4 S alloy). It can be seen that the distribution of stresses in a metal/oxid system as a whole has a similar character to the distribution reported recently [3], i.e., there exist high compressive stresses up to -1 GPa in the oxide layer and tensile stresses up to 220 MPa in the metal underlying. Therefore, the behavior of the two alloys oxidized under transient conditions can be qualitatively examined using average values of oxide thickness T_{ox} , stresses σ , and integral breadth W_{int} . These values for oxide layers including crystallite size D and lattice strains ϵ are given in Table 1 and for metal underlying in Table 2.



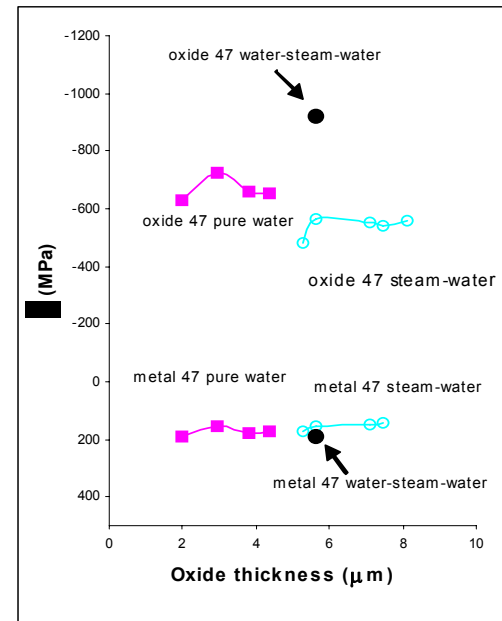
A)

B)

Fig.2 A – integral breadth W of the oxide diffraction line (10-4) vs. oxide thickness of samples investigated. B – crystallite size D vs. oxide thickness in oxide layers of samples investigated.



A)



B)

Fig.3 Stresses σ vs. oxide thickness in oxide layers and metal underlying of samples investigated. A – Zr1Nb alloy (denoted 17), B – Zry-4 S alloy (denoted 47)

It follows from the data tabulated that:

- oxidation of both the alloys under transient conditions leads to a rapid increase in weight gain (or T_{ox}). The largest increase in T_{ox} occurs for Zry-4 S alloy,
- macroscopic stresses in oxide layers of Zry-4S alloy are significantly lower than those of Zr1Nb oxide layers in all the cases of oxidation. The greatest stresses in the oxide layers of both the alloys occur for oxidation in water + steam + water,
- smaller values of W_{int} occur during oxidation in steam + water for both the alloys,
- an unambiguous conclusion from D and ε average values cannot be made, probably because of high quantitative variability of texture of the oxide layers,
- if we suppose that oxidation is controlled by diffusion of oxygen via oxide grain boundaries and pores, there may be another easy paths (or another mechanism) in the case of temperature transient oxidation.

Average values of oxide thickness T_{ox} , macroscopic stresses σ , integral breadth W_{int} , crystallite size D and lattice strains ε determined for oxide layers of the alloys under investigation

Table 1

alloy	oxidation conditions	$T_{ox}(\mu\text{m})$	$\sigma(\text{MPa})$	$W_{int}(2\theta)$	$D(\text{nm})$	ε
Zr1Nb	pure water 360 °C	3.33	-846	3.87	10	0.0037
	steam 500 °C + water 360 °C	5,32	-806	3.26	14	0.0049
	wt. 360 °C + st. 500 °C + wt. 360°C	3.74	-993	3.89	8	0.0033
Zry-4S	pure water 360 °C	3.27	-668	3.70	13	0.0046
	steam 500 °C + water 360 °C	6.71	-539	2.90	12	0.0034
	wt. 360 °C + st. 500 °C + wt. 360°C	5.63	-923	3.82	9	0.0043

Average values of oxide thickness T_{ox} , macroscopic stresses σ , integral breadth W_{int} , crystallite size D and lattice strains ε determined for metal layers of the alloys under investigation

Table 2

alloy	oxidation conditions	$T_{ox}(\mu\text{m})$	$\sigma(\text{MPa})$	$W_{int}(2\theta)$	$D(\text{nm})$	ε
Zr1Nb	pure water 360 °C	3.33	187	0,58	168	0,0014
	steam 500 °C + water 360 °C	5,32	180	0,68	175	0,0022
	wt. 360 °C + st. 500 °C + wt. 360°C	3.74	220	0,46	222	0,0011
Zry-4S	pure water 360 °C	3.27	165	0,92	189	0,0017
	steam 500 °C + water 360 °C	6.71	155	0,54	268	0,0014
	wt. 360 °C + st. 500 °C + wt. 360°C	5.63	194	0,89	82	0,0021

CONCLUSIONS

- all the given results are in good agreement with the habitual conception of mechanical behavior of the oxide/metal system as a whole
- the distribution of stresses in oxide/metal system has the similar character as those being reported recently [3], i.e. high compressive stresses up to -1 GPa in oxide layer and tensile stresses up to 220 MPa in metal underlying exist
- both the small crystallite size D and large strains ε in oxide as compared with these in metal demonstrate the high level of plastic deformation of oxide layers in comparison with metal near oxide/metal interface
- residual stresses can be considered as a reliable XRD characteristic of different behavior of the alloys under investigation.

This research has been supported by MSM 684077002.

REFERENCES

- [1] KRAUS, I., TROFIMOV, V.V.: *Rentgenová tenzometrie*. Academia Praha, 1988, 247 pp.
- [2] De KEIJSER, Th. H. et al.: *The determination of crystallite-size and lattice-strain parameters in conjunction with the profile-refinement method.....* In: J.Appl.Cryst., 1983, 16, p. 309-316, ISSN 0021-8898
- [3] VRTÍLKOVÁ, V., JAROŠ, J., GOSMANOVÁ, G., KRÝSA, J., MATĚJKA, P., BELOVSKÝ, L.: *Properties of corrosion layers grown on Zr-based alloys*. In: Proceedengs of 10th Intern. Conf. on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors, August 5 to 9 2001, NACE Intern., Houston Texas, 2002, CD ROM (PDF 0018), 10 pp
- [4] GOSMANOVÁ, G, KRAUS, I., GANEV, N., VRTÍLKOVÁ, V.: *X-ray diffraction analysis of Zr-based alloys oxidized in water and lithiated water at 360 °C*. In: Proceedings of SPIE. SPIE, Washington, 2004, vol. 5400, s. 204-208. ISBN 0-8194-5323-4
- [5] GOSMANOVÁ, G., KRAUS, I., GANEV, N., VRTÍLKOVÁ, V.: *X-ray diffraction study of Zr-based alloys oxidized in steam at 1000 °C*. In: Proceedings of . METAL 2005. 14th Intern. Metallurgical & Materials Conf. [CD-ROM]. Ostrava: Tanger, 2005, PDF 44, pp. 5. ISBN 80-86840-13-1
- [6] GOSMANOVÁ, G., KRAUS, I., VRTÍLKOVÁ, V.: *X-ray diffraction analysis of Zr-based alloys oxidized under temperature transient conditions*. In: Proceedings of Workshop 2006. Prague, CTU, 2006, vol.10 part A, p. 386-387, ISBN 80-01-03439-9.