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INFLUENCE OF HYDRATION ON THE CHARACTERISTICS OF ZIRCONIUM ALLOYS OXIDE LAYERS

VLIV HYDRATACE NA VLASTNOSTI OXIDICKÝCH VRSTEV ZIRKONIOVÝCH SLITIN

Abstract

The aim of the present study was to find out the influence of hydration on the properties of oxide layers arising on zirconium alloys during high temperature oxidation in VVER water environment. The residual stresses σ, crystallite size D and micro strains ε were examined by means of XRD. The microhardness HVM was determined as well. It has been shown that the characteristics of hydrated layers are different from those of dehydrated oxide.

Abstrakt

Cílem studia bylo zjištění vlivu hydratace na vlastnosti oxidických vrstev vznikajících na slitinách Zr po vysokoteplotní oxidaci v korozním prostředí VVER. Rentgenovou difrakční metodou byly stanoveny zbytková napětí σ, velikost krystalitů D a mikrodeformace ε pro dva typy oxidu po korozní expozici: dehydratovaném na vzduchu a nepřetržitě udržovaném ve vodním prostředí. Dále na hydratovaných a dehydratovaných vrstvách oxidu byla změřena mikrotvrdost HVM. Bylo ukázáno, že sledované charakteristiky jsou pro zkoumané typy oxidu odlišné.

1 INTRODUCTION

Zirconium alloys are currently used in nuclear power engineering as fuel cladding materials in nuclear reactors. The description and understanding of their corrosion behavior 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.

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The aim of the present study was to find out the influence of hydration on the properties of oxide layers arising on zirconium alloys during high temperature oxidation in VVER water environment. The residual stresses σ, crystallite size D and micro strains ε were examined by means of XRD. The microhardness HVM of the oxide layers was determined at the Institute of Rock Structure and Mechanics of the ASCR.

2 EXPERIMENTAL

The tubular samples of Zr1Nb and Zry4 W alloys were oxidized for various exposures at 360°C in pressurized VVER imitating water. Two types of samples were investigated. The so-called "dry" samples were dehydrated on air after corrosion expositions and "wet" samples were permanently kept in water after each one corrosion exposition. A hydrated layer is formed in the oxide of wet samples. It can be interpreted as a compact system of amorphous gel-like formations and crystalline oxide. Since X-rays cannot detect the amorphous gel, the XRD obtained characteristics are related only to the crystalline part of the hydrated layer whereas the microhardness HVM is related to hydrated layer as whole.

2.1 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 σ were calculated using appropriate macroscopic Young's module. Evaluation of the crystallite size D and microstrains ε 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 and microstrains ε.

2.2 Measurement conditions

A D8 Discover powder diffractometer with CoKα radiation was used to measure diffraction patterns. In oxide layers of the samples investigated, the measurements were performed on {10-4} planes with 2θ = 85.2° for CoKα radiation. The appropriate effective X-ray penetration depth $T_e^{(10-4)}$ = 3.68 μm. The fitting procedure had to be used to obtain the accurate profile characteristics such as peak position 2θ 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 15% of the calculated stress values; the error in crystallite size evaluation was about 20% of the calculated values. The Vickers microhardness was measured by using Amplival microscope with dry objective at 25x magnification. Measurements were performed in 24 sites on the surface of oxidized samples (the parts of claddings) and expressed as HVM 100p.

3 RESULTS AND DISCUSSION

The results of experiment are given in tables 1 - 4.

It follows from data tabulated that:

- The values of the compressive macroscopic stresses σ in the crystalline part of hydrated layers increase in comparison with those of dry samples. The effect is systematic even if the values dσ D-W often inhere within the error range. This effect can be caused by the increase of the hydrated layer volume provided that there is a mechanical stability in the compact oxide/metal system. The values of difference dσ D-W are larger for thin hydrated layers of Zr1Nb alloy then those for Zry4 W alloy.

- Both the values of crystallite size D and microstrains ε in the crystalline part of hydrated layers decrease in comparison with those of dry samples in most cases of investigation. This effect can be probably caused by dissolution of the mosaic block boundaries.
- The values of the microhardness HVM 100p are systematically lower for hydrated layers in comparison with those for dehydrated layers. Thus, the plasticity of hydrated layers increases. The values of differences dHVM relating to the appropriate exposures are larger for Zr1Nb alloy hydrated layers in comparison with Zry4 W alloy. Therefore the higher plasticity of the Zr1Nb hydrated layers can be expected compared with those for Zry4 W alloy.

Tab. 1 Specification of samples and XRD obtained characteristics σ, D, ε for oxide layers of Zr1Nb alloy. dσ D-W is the difference between the values of stresses for dry and wet samples

Sample	Condition	Exp. days	Tox, μm	σ, MPa	$|\Delta\sigma|$	dσ D-W	D, nm	ε
1136153	dry	7	0.84	-945	88	159	20	0.0069
1136153	wet	7		-1103	98		15	0.0062
1136348	dry	7	2.15	-661	110	144	41	0.0071
1136349	wet	7		-805	76		34	0.0075
1136350	dry	21	2.13	-885	63	67	18	0.0084
1136351	wet	21		-952	103		14	0.0079
1136017	dry	1997	30	-55	76	56	18	0.0055
1136008	wet	1997	30	-111	96		16	0.0044

Tab. 2 Specification of samples and XRD obtained characteristics σ, D, ε for oxide layers of Zry4 W alloy. dσ D-W is the difference between the values of stresses for dry and wet samples

Sample	Condition	Exp. days	Tox, μm	σ, MPa	$|\Delta\sigma|$	dσ D-W	D, nm	ε
3136162	dry	7	0.96	-1082	74	124	21	0.0082
3136162	wet	7		-1206	87		12	0.0077
3136348	dry	7	2.65	-596	100	75	44	0.0068
3136349	wet	7		-671	118		29	0.0065
3136350	dry	21	2.57	989	58	59	19	0.0086
3136351	wet	21		-1048	62		17	0.0081
3136020	dry	1997	52	-112	97	88	16	0.0047
3136006	wet	1997	50	-200	76		15	0.0038

Tab. 3 Specification of samples and values of HVM 100 p for oxide layers of Zr1Nb alloy. dHVM is the difference between the values of HVM for dry and wet samples

Sample	Condition	Exp. days	Tox, μm	HVM, MPa	d HVM
1136153	dry	7	0.84	1206	637
1136153	wet	7		569	
1136348	dry	7	2.15	1422	412
1136349	wet	7		1010	
1136350	dry	21	2.13	1236	304
1136351	wet	21		932	
1136017	dry	1997	30	3501	2344
1136008	wet	1997	30	1157	

Tab. 4 Specification of samples and values of HVM 100 p for oxide layers of Zry4 W alloy. dHVM is the difference between the values of HVM for dry and wet samples

Sample	Condition	Exp. days	Tox, μm	HVM, MPa	d HVM
3136162	dry	7	0.96	1236	98
3136162	wet	7		1138	
3136348	dry	7	2.65	1481	333
3136349	wet	7		1147	
3136350	dry	21	2.57	1285	196
3136351	wet	21		1089	
3136020	dry	1997	52	1648	843
3136006	wet	1997	50	804	

This study refers to recent research [3, 4].

4 CONCLUSIONS

- The comparative study of zirconium oxide layers was performed to find out the influence of the water environment on their properties,

- it has been shown that XRD obtained characteristics as well as the mechanical properties of hydrated layers are different from those of dehydrated oxide layers for both the alloys under investigation,

- the higher plasticity was observed for Zr1Nb alloy hydrated oxide layers compared with those of Zry4 W alloy.

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