BASIC APPROACHES TO THE STUDY OF THE STRUCTURE AND PROPERTIES OF THIN OXIDE LAYERS ON THE EXAMPLE OF THE OXIDE FILMS OF ZIRCONIUM ALLOYS

ОСНОВНЫЕ ПОДХОДЫ К ИЗУЧЕНИЮ СТРУКТУРЫ И СВОЙСТВ ТОНКИХ ОКСИДНЫХ СЛОЕВ НА ПРИМЕРЕ ОКСИДНЫХ ПЛЕНОК ЦИРКОНИЕВЫХ СПЛАВОВ

Ph.D. Koteneva M.V., Dr. Sci. Nikulin S.A., Ph.D. Rozhnov A.B.
The National University of Science and Technology "MISIS", Leninsky pr. 4, Moscow, 119049, Russia
mariakt@yandex.ru

Abstract: *The structure and mechanical properties of the oxide films formed on zirconium alloys Zr - 1% Nb, Zr – 2,5% Nb upon autoclave tests at a temperature of 360°C and pressure of 18,6 MPa for 600 days were studied. Basic methodological approaches to the study of the structure and properties of thin oxide films were shown. The 10-15 μm thick oxide films of different structural types were shown to be formed on the specimens: the structures with predominately elongated grains and the layered structures. The structure of the oxide films subjected to loading determines both the crack formation stress and the character of fracture.*
KEY WORDS: *ZIRCONIUM ALLOYS, OXIDE FILMS, AUTOCLAVE TESTS, STRUCTURE AND FRACTURE OF THE OXIDE FILMS, COMPREHENSIVE ANALYSIS OF THE OXIDE FILMS*

1. Introduction

One of the reasons that limits reliability of structural elements of the nuclear reactor core is the uniform corrosion of zirconium alloys. The corrosion rate depends on the composition, structure and defectness of an oxide film. Currently, there are few published comprehensive studies of structure and mechanical properties of the oxide films obtained at different oxidation conditions. Modern research equipment allows us today to obtain new data on the structure and properties of oxide films to specify the mechanism of the process of uniform corrosion.

It was shown for Zircaloy alloys that the structure of oxide films of zirconium alloys is a mixture of elongated and equiaxial grains present in various proportions. Equiaxial grains are usually disposed between the elongated ones [1], the cracks are formed as a rule at their boundaries [2, 3, 4]. The structure changes depending on the stage of oxidation.

The object of this work was to develop the techniques and study the structure and mechanical properties of the oxide films formed on zirconium alloys Zr - 1% Nb, Zr – 2,5% Nb.

2. Experimental procedure

Studies were performed on tube specimens of zirconium alloys after testing in an autoclave under the following conditions: T = 360 ° C, P = 18,6 MPa, τ = 600 days. The microstructure was studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Method of focused ion beam (FIB) was used to prepare specimens for TEM [5]. The hardness of oxide films was measured at low loads by Oliver Far method.

Compression of tubular specimens with acoustic emission measurement was made to analyze the fracture kinetics of the oxide films [6]. The phase composition of the oxide films was studied by X-ray diffraction. Adhesive/cohesive strength was determined by scratching of the surface of the tube specimen.

3. Results and discussion

There are two morphological types of the grains of monoclinic zirconium dioxide modification are present in the structure of oxide films: equiaxed grains and elongated grains, which are clearly seen both in the bright- and dark-field image.

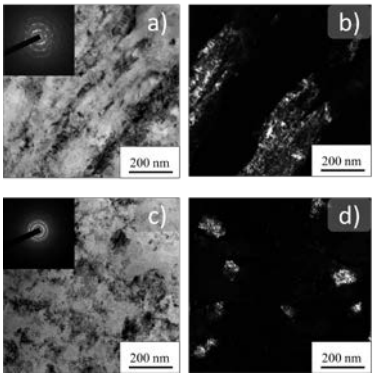

Fig. 1. *The microstructure of oxide films of zirconium alloys with elongated (a,b) and equiaxed (c,d) grains (bright-field (a,c) and dark-field (b,d) images).*

The oxide film structure with predominately elongated grains is characteristic of the specimens of Zr – 2,5% Nb. Layered structure of the films is characteristic of the specimens of Zr - 1% Nb.

SEM analysis of oxide films structure on the cross sections showed the chains (the layers) of microcracks parallel to the surface of oxide film.

The microhardness of zirconium oxide films of identical phase composition (monoclinic ZrO_2) does not differ significantly in different states and amounts to 20 GPa.

The fracture of oxide films with different structures may occur by the formation of transverse cracks or longitudinal cracks and flaking.

The implementation of a fracture mechanism of oxide films is determined by the structure (ratio and the location of elongated and equiaxed grains) and the initial defectiveness of the oxide film.

For the film structures with predominately elongated grains, the fracture occurs through the formation of transverse cracks developing across the whole film layer up to a base metal. In this case, the greatest values of fracture stress for the specimens subjected to loading are observed as compared to other states. The fracture of oxide films with layered structure proceeds by flaking. Flaking occurs at the interface between the layers of elongated grains and equiaxed.

4. Conclusion

The use of such techniques of structure and properties analysis allows to compare oxide films and determine their structure and fracture kinetics.

It was shown that oxidation of the zirconium alloys Zr - 1% Nb, Zr – 2,5% Nb in water results in the formation of oxide films with the structure of two types, characterized by different proportion of the elongated and equiaxed grains: the structures with predominately elongated grains and the layered structures.

Fracture of the oxide films different in structure occurs according to two alternative schemes: by the formation of transverse cracks or by the formation of longitudinal cracks and flaking.

The greatest fracture stress is characteristic of the films with elongated thin grain structure.

This work was funding from Russian Foundation for Basic Research (14-03-31422 мол_а).

4. Literature

[1] Weijia Gong, Hailong Zhang, Yi Qiao, Hang Tian, Xiaodong Ni, Zhongkui Li, Xitao Wang. Grain morphology and crystal structure of pre-transition oxides formed on Zircaloy-4//Corrosion Science.-2013. – Vol 74. – c. 323-331.

[2] Anada H., Takeda K. Microstructure of Oxides on Zircaloy-4, 1.0 Nb Zircaloy-4, and Zircaloy-2 Formed in 10.3-MPa Steam at 673 K //ASTM SPECIAL TECHNICAL PUBLICATION. – 1996. – Т. 1295. – С. 35-53

[3] Pecheur D. et al. Microstructure of oxide films formed during the waterside corrosion of the Zircaloy-4 cladding in lithiated environment //ASTM STP. – 1996. – Т. 1295. – С. 94-112.

[4] Yilmazbayhan A. et al. Transmission electron microscopy examination of oxide layers formed on Zr alloys //Journal of Nuclear Materials. – 2006. – Т. 349. – №. 3. – С. 265-281

[5] Giannuzzi L.A., Stevie F.A. Introdution to focused ion beams: instrumentation, theory, techniques and practice. – N.Y.: Springer, 2004. – 357 p.

[6] Nikulin S. A., Khanzhin V. G. Monitoring of materials, processes, and technologies by measuring acoustic emission //Metal science and heat treatment. – 1999. – Т. 41. – №. 4. – С. 174-181.