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**JOINT APPLICATION AES AND SIMS METHODS FOR HALF-  
QUANTITATIVE MEASUREMENTS OF AN ELEMENT COMPOSITION OF  
RUPTURE / INTERACTION SURFACE OF VARIOUS IRRADIATED  
MATERIALS**

**Yu.Goncharenko, L.Evseyev, V.Kazakov**

**State Scientific Centre**

**Research Institute of Atomic Reactors**

**Dimitrovgrad, Russia**

JOINT APPLICATION AES AND SIMS METHODS FOR HALF-QUANTITATIVE  
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**Yu.Goncharenko, L.Evseyev, V.Kazakov**

*State Scientific Centre of Russian Federation Research Institute of Atomic Reactors*

*433510, Dimitrovgrad, Ulyanovsk region, Russia*

*Tel.: (84235)32021, Fax: (84235)35648, e-mail: [fae@niiar.ru](mailto:fae@niiar.ru)*

The manufacture from zirconium alloys are widely used in nuclear engineering. Their operational reliability is determined by a state of a protective oxide film in many respects. Therefore permanent attention to investigate its state after neutron irradiation is quite clear, especially for real constructive elements. One of parameters determining the protective oxide film properties, is impurities distribution in the film.

At present large volume data on the physical-chemical oxide films properties, formed in different conditions on Zr-alloys specimens surface has accumulated. The most part of the facts comprises information about microstructure and physical properties of the oxide films, and the properties alteration under influence of different factors taking place during nuclear units operation [1]. There is much less information about possible element composition alteration in the transitional region between metal matrix and the oxide. At the same time, these changes can influence on the physical-chemical oxide films properties determine operational reliability of the elements from zirconium alloys eventually[2].

The examples of using of the surface analysis methods for investigation of elements distribution in similar structures are known [3, 4]. A number of methodical procedures for realization of such researches with using method of secondary ion spectrometry (SIMS) are described in paper [5]. They are method for three-dimensional elemental analysis for investigation of corrosion layers on irradiated zirconium alloys. However, as the carried out additional researches have shown, essential change and addition of the method are needed for study elemental composition of the oxide film and adjacent layers of metal to its.

As it is known, in SIMS method such sensitive method for removal a near-surface sample layers like ion etching is applied. The rate of ion etching  $Z$  is estimated under the known formula:

$$Z = \frac{M}{\rho \cdot N_A \cdot e} \cdot S \cdot j_p$$

where M - atomic mass of the target subjected to ion etching, ( $\rho$ - its density,  $N_A$  - Avogadro constant, e - electron charge,  $j_p$ - density of primary ion beam, S - output of atomization. Some coefficients in this formula may be change insignificantly, but the output of atomization S can be change rather essentially. This coefficient depends of the numerous factors, including energy and atomic mass of primary ions, the primary ion beam incidence angle, and the most main, composition and state of the investigated surface.

Presence of selective sputtering effect reduces considerably the ion etching advantages used for removal near-surface investigated samples layers if there are the heterogeneities in the layers or sites with strongly differing speed of ion etching. In particular, it took place in the work [5] at the transition from oxide film to metal matrix. In this report we suggest the original procedure for the elemental composition investigation of the thin regions located between the oxide film and the metal matrix in the irradiated samples from zirconium alloys.

The procedure takes into account the following items:

- a) Essentially larger ion sputtering rate of the metal matrix in comparison to oxide;
- b) Essentially larger homogeneity of the metal matrix in comparison to oxide;
- c) Absence of accumulation electrical charge effect on the investigated metal surface;
- d) Absence of complex rearrangement of the SIMS recording equipment necessity on the investigated metal surface;
- e) Possibility to use the electron probe analysis methods, similar SEM and AES, on the investigated metal surface.

This technique consists in preliminary removal of the metal matrix part, i.e. in metallographic microsection preparation, and subsequent ion etching of the sample with approach to regions located between metal matrixes and oxide from the metal side. Traditionally at similar researches deposits on the surface of fuel cladding are removed at first, then oxide layers and only after that a turn of an actually metal basis of fuel cladding is come [2, 3].

The sample scheme of preparation to investigation consists in flooding of the metal part of the zirconium fuel cladding segment to metallographic yoke in that way, that its internal side was directed to the grinding surface. The process following-on till we shall not receive suitable width of metallographic section, which depends on the researched fuel cladding diameter. So if the fuel cladding diameter is 9,1 mm, then a metallographic section width

should be equal about 2-3 mm. As it is easy to understand, in the result of such preliminary preparation we receive the sample which has the metal part thickness from zero (at the edges) up to about 250 microns in the sample middle (Fig. 1).

During investigation of such form sample we have an opportunity to register the distribution chosen elements profile by SIMS - spectrometer with using of the electronic diaphragm (fig. 2, top). It is periodically necessary to record these elements distribution maps on the investigated sample surface. For exception the edge effects the raster size for registration elements distribution maps should be choose slightly less, than one for mass-spectrum registration with using of the electronic diaphragm. As soon as any elements distribution differing from homogeneous will appear on the maps it is necessary to begin the layer-by-layer elements distribution maps registration to restore interesting their distribution profiles in future.

So far as planes of etching surface and interface between zirconium oxide and metal matrix are not parallel, therefore thin transitional layer between metal and oxide will be multifoldly passed in various points of the analyzed area at the sequential removal layers. As a result, we can accumulate the sufficient statistics and bring to light even insignificant changes which can take place in the intermediate layer (fig. 2, bottom).

After using of the ion etching we approached to the oxide matrix (on a part of a investigated area) and have an opportunity to stop etching and more carefully to study the investigated area in the scanning electron microscope to connect of some element composition changes with possible visual features: voids, cracks, precipitates, etc. (fig. 3). It is necessary to note, that the oxide component sputtering rate is much less than metal one. Moreover, the metal sprays very uniformly, and the moment of the transition from metal matrix to oxide can be easy determined in different points of the investigated area.

After inspection of the subjected ion etching surface, and for confirmation the detected element composition changes, we can insert the investigated sample to the AES vacuum chamber for precise investigation of element composition alteration in the transition region from metal to oxide.

As it is known, SIMS- and AES- methods are the surface analytical technique. Therefore it is expediently to trace the overpatching of pertaining to element composition in various points of a metal part of the etching surface by Auger-spectrometer with application its own ion guns. The layer-by-layer measurements are finished, as soon as the power shift of AES-peaks

is found out. This shift connected to the transition in oxide part of fuel cladding. In future the results received with three methods application (SIMS, SEM, AES) are confronted, compared and corrected. Such the experimental results correction received by any one method on the data of other methods desirable, and in a number cases necessary procedure during investigation of the chemical composition.

Suggested procedure for using SIMS- and AES-methods allow to receive a representation about distribution of various elements not only in the region between zirconium oxide and metal matrix of the irradiated fuel cladding, but they can be used for other similar researches of pertaining to element composition on the interface between dielectric films and metal matrix (coverings, deposits on the used elements of nuclear reactor). The addition of such investigations by more traditional methods for the element analysis like electron-probe microanalysis is quite possible too.

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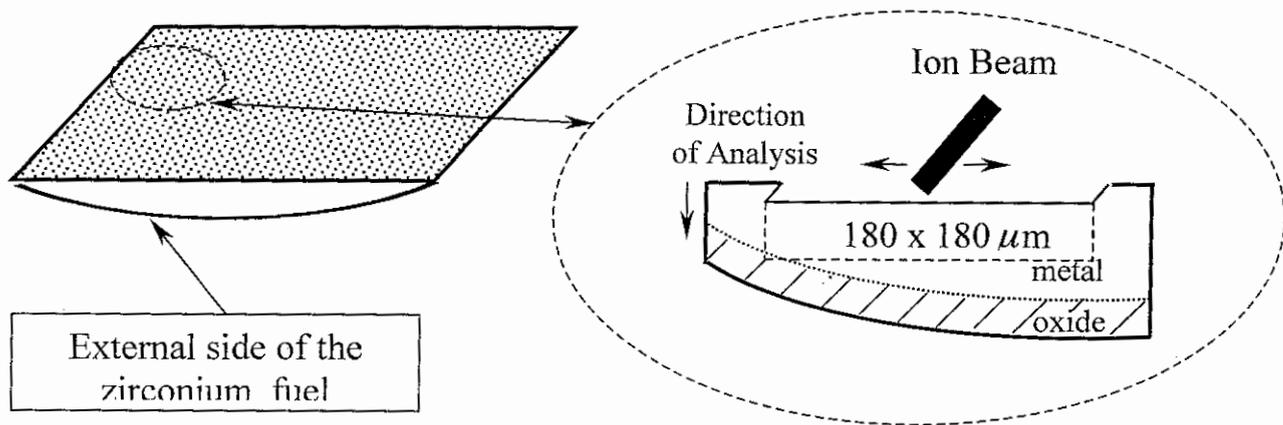


Fig.1 Scheme for realization layer-by-layer analysis by SIMS method.

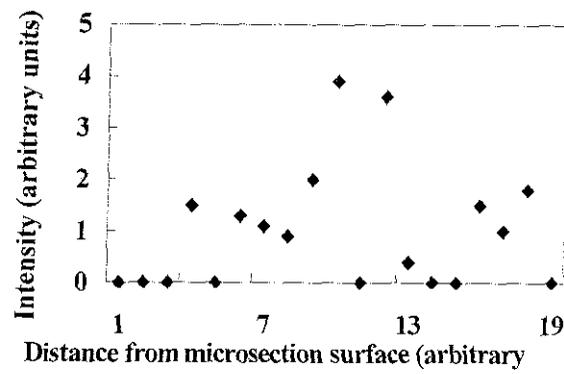
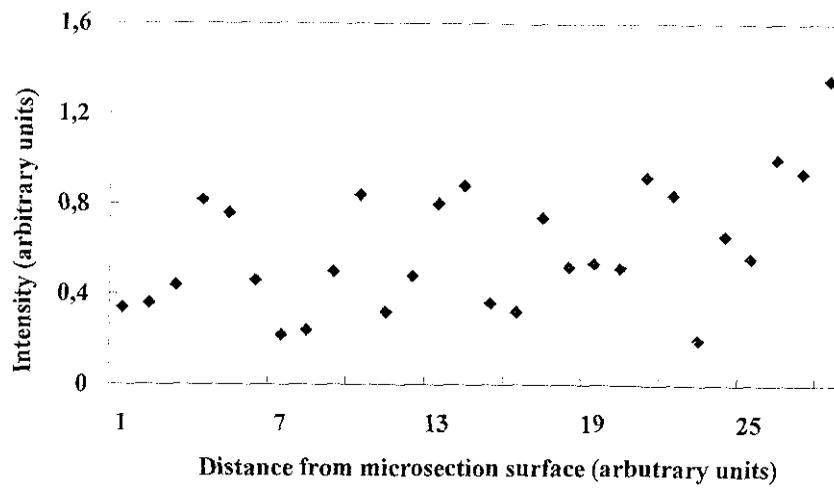


Fig. 2 Change of mass-peak  $^{93}\text{Nb}$  relative intensity at moving from the microsection surface (by 136 measurements in spectrum) - top. The relative intensity change of  $^{93}\text{Nb}$  mass-peak along depth in the transition from metal to oxide area (by 20 measurements in maps) - bottom.

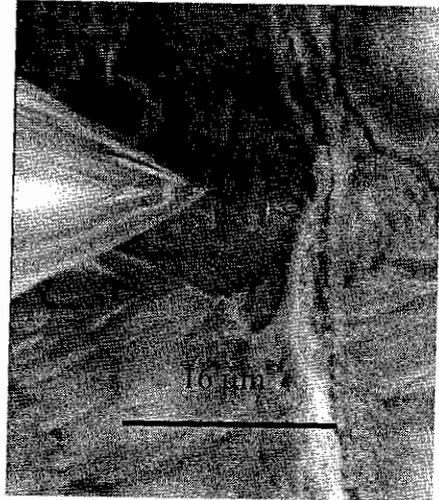
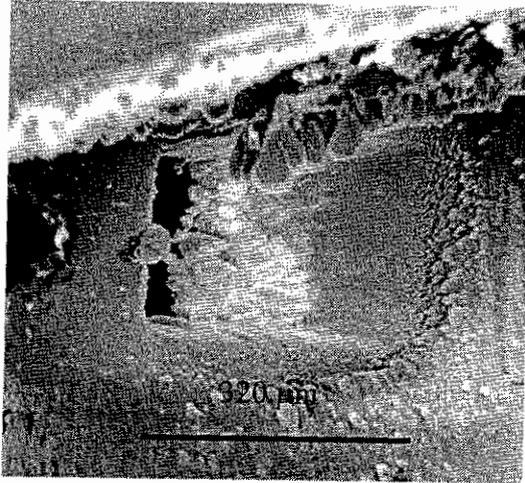


Fig. 3. The sample surface photomicrography after investigation in SIMS- spectrometer. Left - the all area exposed to ion etching. Right - transition from the fuel cladding metal part to the oxide.