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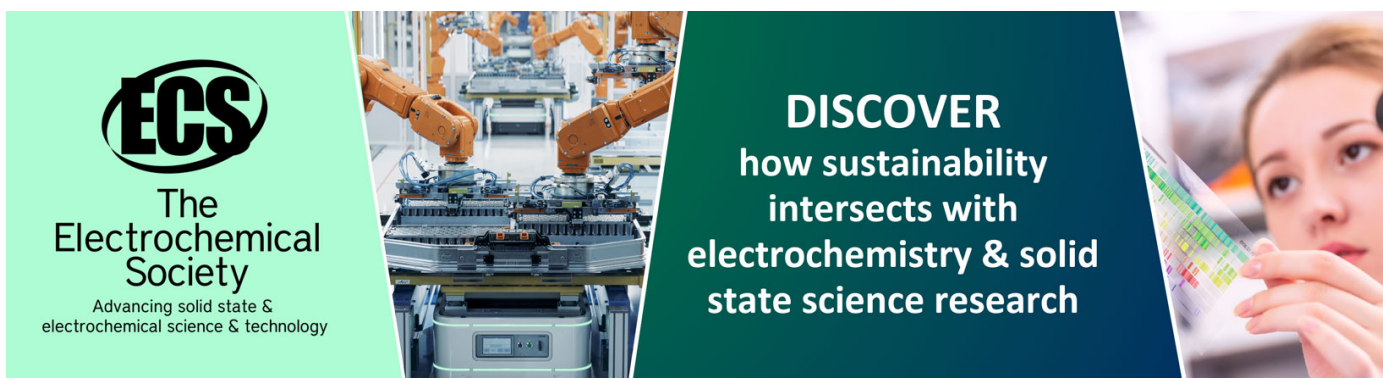
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Nondestructive diagnostics of surface layers elements content for cylindrical shape material objects

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Abstract. The methodics background for the nondestructive element concentration diagnostics of cylindric shape material objects surface layer is developed. The diagnostics is produced without objects form-factor distortion on base of ion beams and X-ray analytical methods. The depth element concentration distribution determination found on the ion beams Rutherford backscattering data and results of X-ray fluorescence testing in conditions of TXRF modified measurements. Possibilities of the elaborated analytical conception are illustrated by experimental data obtained at study of element content in surface layer of the nuclear heat release cell shell.

1. Introduction

The element diagnostics of material objects surface layers and thin films coatings can be executed by wide set of analytical methods [1–6]. The methods choice is usually defined by problem peculiarities, unsociable level of element, structure and phase analysis accuracy and expected depth of the object surface layer. In similar investigations, the material element diagnostic procedure has the most important significance owing to the structure and phase material features are directly depended on the elements constitution. Moreover, the element diagnostics takes on additional significance when the material object is characterized by visible heterogeneity.

Important factor of any analytical technology is the degree of its destructivity, and the destructivity in studied object can be appeared both in process of the diagnostic procedure and during of the preparation stage. It is well known that the ion beam analytical technology [7] and X-ray fluorescence analysis carried out in conditions of total external reflection [6] are very beautiful element diagnostic technologies, which do not lead to atomic redistribution in studied volume during of the testing process. Therefore, these methods combined application for effective element analysis of thin surface layers and coatings was represented as the more rationalistic approach and was realized in practice.

2. Technological peculiarities of measurement and preparing

RBS and PIXE measurements and TXRF spectrometry were executed by use the vacuum chamber of Sokol-3 ion beam analytical complex and the HZG-4 digital horizontal precision X-ray goniometer.



Schemes of this experimental setup are presented in figure 1. RBS and PIXE chamber is equipped by scattering ions detectors, X-ray register, vacuum goniometer and total charger integrator. TXRF spectrometer consists of X-ray generator with focus F, X-ray beam former, goniometric microtable for studied target, aligning system and X-ray fluorescence yield register. Main task of RBS material investigation is the determination of depth element concentration distribution [7]. Helium ion beam scattering allows to fix the depth element concentration profiles with depth resolution near 10 nm. In case of the hydrogen ion beam scattering the depth resolution aggravates up to 50 nm. Measurements with use the RBS method are characterized by absence of the standard and etalon specimens necessary use. The method demonstrates multielementness and is able to fix all elements apart from hydrogen atoms. But the hydrogen atoms concentration can be determined by the nuclear recoil method application [8]. RBS spectrometry is characterized by an insufficient analytical sensitiveness. Detection limits of different elements are usually near 0.1 % at. However, this experimental shortage is balanced out by possibilities of the proton (particle) induced X-ray emission spectrometry (PIXE) [9]. This method is distinguished by very low element detection limits ($\sim 10^{-7}$ % at.). PIXE bears some similarity to the fluorescence yield excited by electron beam. However, the proton beams energy absorption by material is characterized by small values of the bremsstrahlung photon intensity yield. So, PIXE measurements are distinguished by very low of the background level. A PIXE measurement in the standard geometry [9] allows to analyze the volume element concentration of studied material. At the same time, it is possible to modify the PIXE spectrometry for element diagnostics of thin surface layer of studied object [10] by including into the PIXE experimental scheme the planar X-ray waveguide-resonator (PXWR) [11]. Unlike RBS measurements, PIXE spectrometry are the semi-quantitative method both in own main and modified configurations because of this measurement technology is not free from the matrix effect [12]. Some discomfort of RBS and PIXE measurement technologies application is connected with necessary of the work in vacuum conditions and to have high-energy ion beam source.

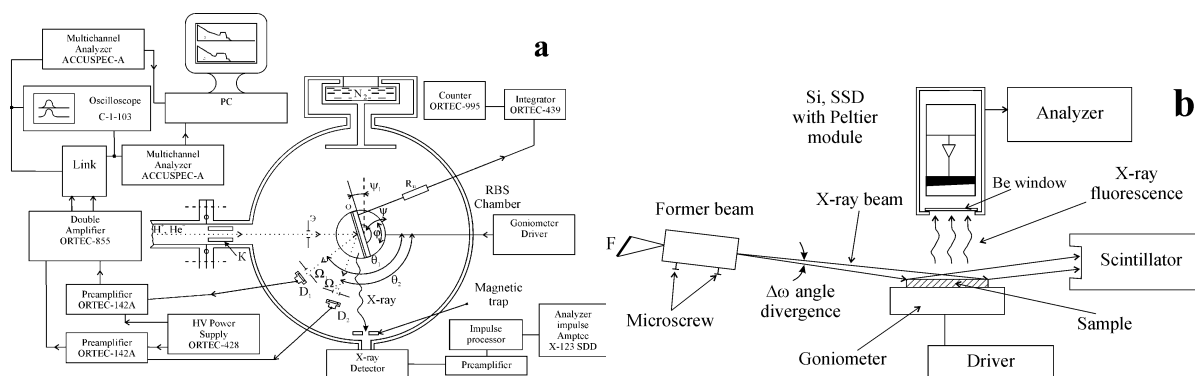


Figure 1. Schemes of RBS and PIXE vacuum chamber (a) and experimental setup for TXRF standard and specific measurements (b).

TXRF measurements are not demanded vacuum conditions and oriented on application of X-ray source as stimulus of the X-ray characteristic radiation yield. It is shown in figure 1 by its focus position (F). TXRF investigations are carried out at the exciting beam incidence on studied sample at angles, which do not exceed the critical angle of exciting beam radiation for studied material ($\theta \leq 0.1^\circ$). The exciting beam must have the thread form with minimum width and angular divergence. The exciting beam former realizes these conditions. Best characteristics of TXRF analysis were achieved at use of PXWR as the former for TXRF spectrometry [13]. Thin surface layer of studied specimen forms X-ray characteristic fluorescence yield with thickness near 10 nm. In the result of this, the background intensity in the registering spectrum shows sharp decreasing, and element detection limits reduce up to $(1-2) \cdot 10^{-6}$ % at. Moreover, TXRF measurements are free from the matrix factor, and X-ray fluorescence lines intensity can be used for direct determination of elements concentration in samples.

The experimental data correctness depends not only on the element diagnostic methods rational choice. It is very important peculiarities of the measurement procedure and preparation features. For example, it is well known that the deformation of material sample leads to redistribution of elements and defects in the studied objects. Therefore, it is very important to elaborate the preparation and measurement procedures ensuring the studied object form-factor conservation. This approach has a particular value for elaboration of the surface layer modified technique for units destined to work in hard conditions of radiation and aggressive influence. The cylinder shell of fuel rods destined to water-water nuclear reactors is the bright example of similar units [14].

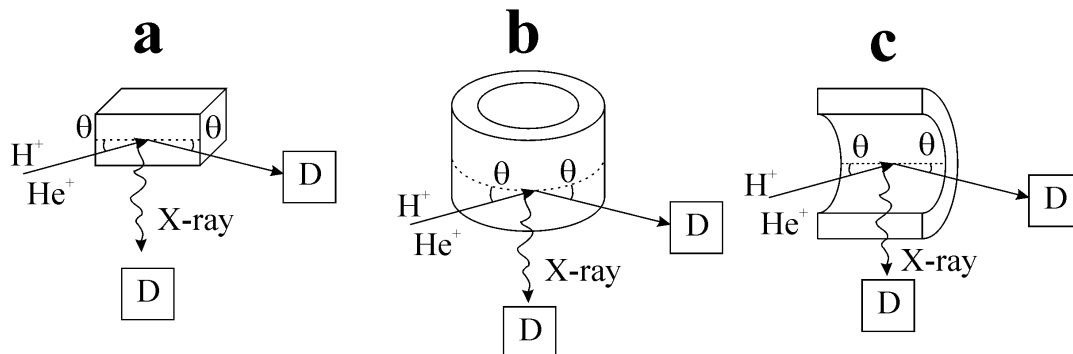


Figure 2. Schemes of RBS and PIXE measurements execution in standard experimental geometry (a) and in conditions of an external surface (b) and an internal surface (c) study of the cylinder shell.

Ion beam analysis of materials supposes that the studied object has the planar outline (figure 2a). At the same time, the fuel rod shell is characterized by other form. But the ion beam spot on the studied object has diameter near 1 mm, and the ion beam scattering geometry was not differed from the planar one for shell external surface layer (figure 2b). The scattering planar geometry will be realized for case of the internal surface layer study after the shell longitudinal section (figure 2c). The presented preparation procedure guarantees the material deformation absence and allows to evaluate the shell surfaces state both pre- and post- modification treatment. Figure 3 demonstrates RBS and PIXE spectra obtained in the testing result of fuel rod shell external surface layer both pre- and post-modification by the vacuum deposition of Cr atoms.

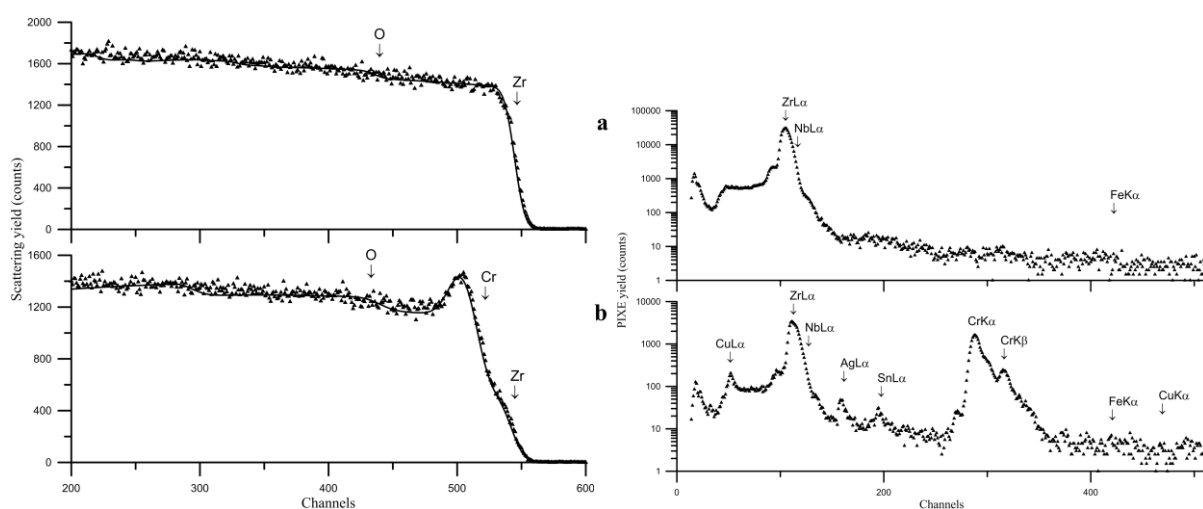


Figure 3. RBS and PIXE spectra obtained for the external surface of fuel rod shell pre- (a) and post- (b) modification by Cr atoms vacuum deposition.

3. Instrumental study of the fuel rod shell modification

The fuel rod shell is built on base of zirconium with small niobium concentration (~1 % at.). RBS spectrum approximation of the initial shell external surface showed that the material contains oxygen atom in quantity near 3 % at. PIXE of this material demonstrates availability of Fe atoms trace concentration. After modification, one can see some changes in RBS and PIXE spectra outline. Approximation of the Rutherford backscattering spectrum presented in the figure 3b obtained for the modified shell showed that on its external surface the specific layer appeared. Its thickness is equal 5.7 μm . The layer is characterized by some oxygen atoms concentration (up to 10 % at.) and evident content of hydrogen and structure vacancies. Cr atoms concentration is characterized by maximum on the shell surface and decreases as a depth increasing. PIXE spectrum showed that the surface layer after modification demonstrates a great quantity of Zr and Cr atoms and small content of Nb, Fe, Cu, Ag and Sn atoms. Next studied step was connected with comparison investigation of initial and modified shells by TXRF methods. Results of these investigation presented in figure 4 showed that the Nb atoms concentration in nonmodified shell is 1.25 % at. Total impurity concentration (Fe, Co, Ni, Cu, Zn) is not exceeded $2 \cdot 10^{-2}$ % at. ArK α line presence in the spectra shows that the measurements are carried out in air medium. The shell modification led to appearing the CrK $\alpha\beta$ high intensity duplet and some lines of doping atoms (Fe, Cu) and impurity atoms (Ca, Ti, Zn, Ga). Spectrum approximation obtained for modified sample allowed to affirm that the very thin surface layer with thickness near 10 nm is characterized by ZrCr₂ compound appearing. Moreover, this layer contains visible quantity of Cu (~4 % at.) and Fe (~4 % at.) atoms.

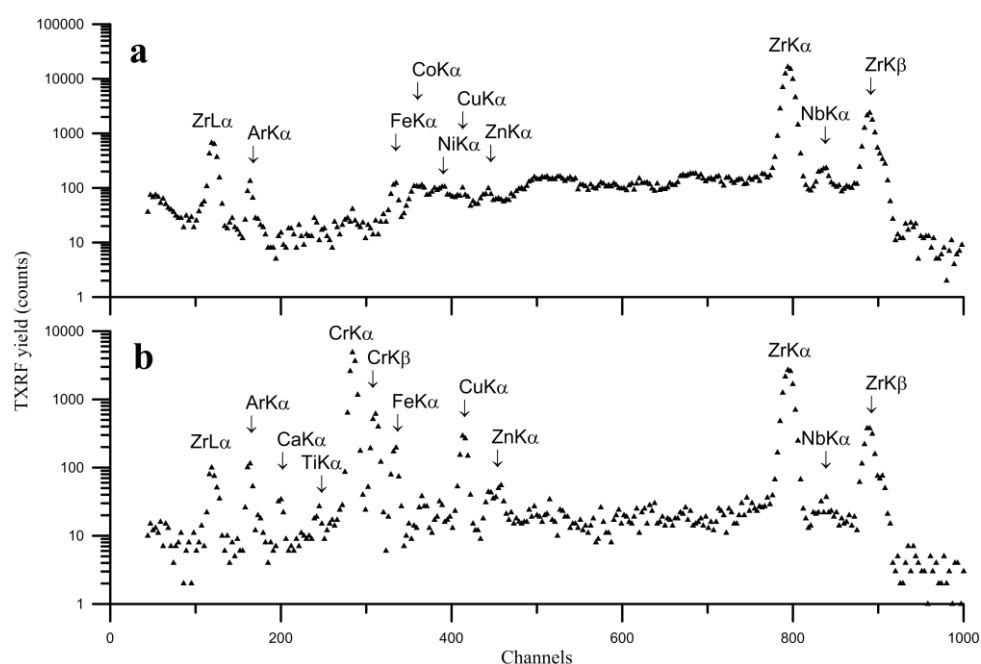


Figure 4. TXRF spectra obtained for the external surface layer of fuel rod shell for initial state (a) and after the Cr deposition modification (b).

RBS investigations allowed to determinate the total thickness of modified layer $t = 5.7 \mu\text{m}$ but low resolution of the spectrum did not present possibilities to receive the depth element distribution in the layer. TXRF measurements showed that the surface sublayer with thickness near 10 nm has ZrCr₂ composition. For the better understanding of the modification peculiarities we elaborated specific procedure for determination of the depth element distribution in all modified layer. The procedure bears similarities to TXRF method but allows to registrate the X-ray characteristic radiation yield from the material layer with thickness is defined by degree of exciting beam damping by the cylinder shell.

The measurement scheme is shown in figure 5a. The exciting beam was formed by the double slit-cut former with width of slit-cuts $s = 6 \mu\text{m}$ and distance between them 100 mm [15]. The angular divergence of the beam was not exceeded 0.03° . Similar structure with $l = 30 \text{ mm}$ was placed before the X-ray fluorescence register. Angular divergence of the exciting beam allowed to test of the shell external surface layer on depth $15 \mu\text{m}$. Experimental X-ray fluorescence spectra obtained in result of the elaborated procedure application allowed to receive the dependence diagram of $\text{CrK}\alpha$, $\text{ZrK}\alpha$, $\text{CuK}\alpha$ and $\text{FeK}\alpha$ fluorescence intensity yields on the exciting beam depth penetration (figure 5b). As the addition information, the Figure shows the calculated dependence of $\text{ZrCr}_2/\alpha\text{-Zr}$ phase's relation on the depth penetration. It is notice that the last dependence has the quality character owing to the fluorescence experimental data is not free from matrix effect and real fluorescence intensity must be corrected by taking into account of previous sublayers yield.

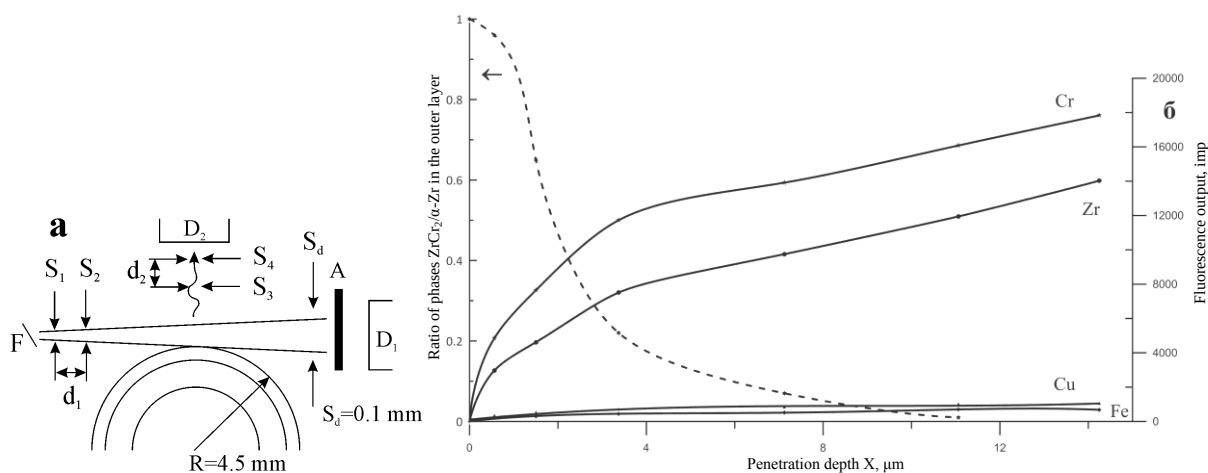


Figure 5. Scheme of X-ray characteristic radiation yield registration (a) and experimental functions of $\text{ZrCr}_2/\alpha\text{-Zr}$ phase relation and Cr, Zr, Fe and Cu X-ray line intensities dependences on the external layer depth for modified shell (b).

4. Discussion and conclusion

Obtained experimental data are the beautiful background for interpretation of the Cr atoms modified procedure deposited on the shell external surface. It is known that $\alpha\text{-Zr}$ solid solution with Cr atoms is limited by volume is near 0.5 % at. After deposition on the surface owing to the bulk and grain boundary diffusion Cr atoms penetrate into the volume of shell. However, owing to the diffusion flux is smaller as the atoms depositing flow the ZrCr_2 compound can appear on the surface. In conditions of the stationary deposition regime and some temperature of the shell we can receive parallel process of Cr atom diffusion into the shell volume and growth of the compound phase. Time process and the regime variation allow to select conditions for preparation of the best external protective layer on the fuel rod shell. Nevertheless, it is a need to take into account that the presented model has simplistic character. The model does not include into discussion of doping atoms presence and some concentration of oxygen atoms and possible existence of hydrogen atoms and vacancies. Total picture of the fuel rod shell modification by Cr atom deposition will be described by other publication.

The main task of the work was short description of original procedure of quality testing the depth element profile of cylinder samples external surface without its form-factor variation. RBS method is oriented on similar investigations. However, in some cases the Rutherford backscattering data is characterized by insufficient resolution and small testing depth. New procedure is designed to complement possibilities of RBS and TXRF material diagnostics.

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