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THE APPLICATION OF PIXE AND PIGE FOR THE STUDYING OF IMPURITIES DISTRIBUTION IN SPACE NEAR THE SEAM AT WELDING PRODUCTS OUT OF THE Zr1%Nb ALLOY

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In this work the nuclear-physics methods of analysis of the content of a matter based on the using of proton induced characteristic X-ray emission of the atoms and momentum γ-ray emission from nuclear reaction was applied to determine the gaseous impurities N, O, F and elements B, Ca, Ti, V, Cr, Fe, Ni, Cu, Nb, Mo, Cd, Sn, Hf, Pb, in zirconium alloys and to research the absorption of oxygen, nitrogen and fluorine by a matter of tubes made from alloy Zr1%Nb during the procedures of the fabricating of models of fuel assembly. There are a number of the factors, which affect negatively on material of shells and fuel assembly as hole at a technological process of manufacture fuel assembly for nuclear reactor VVER-1000. Such factors are the interstitial impurities (oxygen, nitrogen), hitting in metal during operations of hyper thermal processing, in particular, at welding details of fuel assembly. The gaseous impurities of atmosphere of the weld – nitrogen and oxygen inserted in a welding seam can degrade rust resistance of a seam and slash a plasticity of a material. A surface of manufactured fuel assembly or samples for researches can to be polluted by fluorine from pickling compositions at the stage of a chemical polish by an etching in fluorine inclusive solutions. Fluorine, as is known, is a fissile element lowering rust resistance and of details of ends of fuel assembly.

INTRODUCTION

Zirconium is one the based materials using in active zone of nuclear reactor. To add to handworks from zirconium demanded chemical, physical and mechanical characteristics it is necessary to clear of a starting material from a number of pollution and enter to the composition of zirconium alloys the certain elements in known content. The impurities containing in zirconium have sufficient difference in physical-chemical properties and content. Therefore an analytical arrangement is required including the possibility of determination of gas-making impurities C, N, O, F and elements Li, Be, B, Cl, Ca, Ti, V, Cr, Fe, Ni, Cu, Nb, Mo, Cd, Sn, Hf, Pb to manufacture the zirconium alloys using in nuclear energetic. The solving of such problem requires of the joint using of the complex of analytical methods with high sensitivity, expressivity, cheapness, ecological safety etc. In this work nuclear-physics methods of analysis of a matter using characteristic X-ray emission induced by accelerated protons (PIXE) and proton induced momentum γ-emission from nuclear reaction (PIGE) was applied to determine the content of elements with atomic number in range $20<Z<82$ and N, O, F in zirconium alloys.

1. EXPERIMENTAL ARRANGEMENT USED TO ANALYSES OF ELEMENTAL CONTENT OF ZIRCONIUM UNITS

In National Science Center Kharkov Institute of Physics and Technology was designed the small-sized analytical installation "Sokol" for the analysis of elemental content of a matter by nuclear-physical methods using accelerated charged particles [1]. This installation since 1983 was used for the analytical purposes. The installation consists of the electrostatic accelerator of a horizontal type with output equipments; experimental cameras for application of a set of nuclear-physical methods of the analysis; measuring - computing equipment permitting the automation of processing of outcomes of experiment. The accelerator has following parameters: energy of accelerated single-charged ions – 0.2…2 MeV; stability and energy homogeneity of ions - 0.04 … 0.07 %; a current of beam of ions on straight output - 50 μA; a current of beam of ions after the analyzer - 20 μA; accelerated ions - hydrogen and helium; resource of operation - 3000 hours annually.

The experimental cameras are installed on four channels. They allow to analyze the matter by PIGME, PIXE, using elastic backscattering at large angles (RBS), X-ray emission exited by particle induced X-ray emission (PXX); elastic recoils from nuclear reaction (ERD); the analysis by nuclear microbeam. This arrangement was used for the solving of a broad spectrum of the tasks: definition of element composition of matter (construction materials, materials of an electronics engineering, geologic samples, objects of an environment, medicine etc.); learning of allocation of impurities on a surface and in bulk of a sample with high space permission; learning of physical-chemical processes (corrosion, thermal and radiation-stimulate diffusion, ion implantation, ionic - plasma coating.

For execution of this work the camera using the complex of methods PIXE and PIGE was utilized. The target folder allows to dispose in the camera simultaneously up to 16 thick or thin targets. The camera was isolated from beam tube vacuum and adjusting equipment and was utilized as a Faraday cap for measurement of the charge of protons, which has landed on the target. To measure X-ray and γ-ray emission Si(Li) and Ge(Li) detectors were used. The

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Pb-Ta collimator of X-ray emission and set of absorbers were allocated before the face of Si (Li) detector.

1.1. SAMPLE PREPARATION

The demountable device was designed for learning absorption of gases from a welding atmosphere during argon-arc and helium-arc welding (Fig. 1). This devise permitted to produce welded samples for carrying out of the analysis. It allowed to butt-weld two nipples ∅ 9,15x7,72 mm at tight fit on hearts. The temperature regime of thermal investment at welding was alike to conditions of welding of nozzles of fuel assembly to the shell.

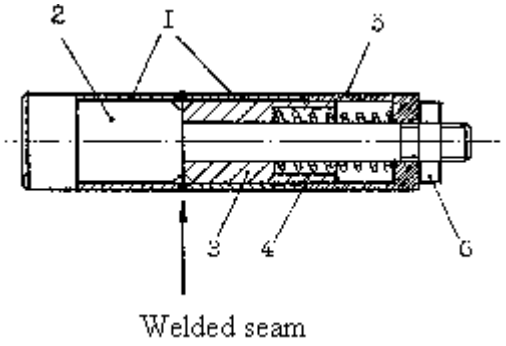

Fig. 1. The scheme of device for manufacture of samples of welded joints of tubes from alloy Zr1%Nb: 1 - welded nipples; 2 - end tube expanders; 3 - spigot expander; 4 - a pressing spring; 5 - pressing cap; 6 - nut

The welding was produced using improved installation of electric arc-welding of SA - 281 with application of the new system admission of gas and preparation of a welding atmosphere. Before the welding camera was pumped off up to pressure $5 \cdot 10^{-2}$ Pa and spacefilled by an argon or helium of given cleanness, then again pumped off and spacefilled by gas up to 0,14 MPa. The welding was made in argon atmosphere at current 22 A and in helium atmosphere at current 16 A. The welded nipples cut on formative line, unbent on slices, from which one produced disks for an exposure by a beam of protons from the accelerator. For learning a kinetics of an oxidizing the cutting samples was mechanically ground or chemically polished in fluorine compounds traditionally applied in surfacing of zirconium workpieces. At such processing on a surface of workpieces the difficultly deleted residual amounts of fluorine are saved which were determined in the given work. The two kind of welded samples were made. First was prepared using pure welded argon with impurities O_2 – 50 ppm, N_2 – 7 ppm, H_2O – 9 ppm. Second kind of samples was prepared using the same argon but after it purification in special patron/ The content of impurities were no more then 1 ppm O_2, N_2, H_2, CO_2 and H_2. The etching was produced in two solutions: 5% HF, 45% HNO3, rest water, and 10% HF, 30% HNO3, 30% H2SO4 and 30% of water. The series wash in distilled water and in special solutions was produced to delete of fluorine salts after an etching. The researches were fulfilled using two sorts of samples for comparison of tubes from experimental alloy Zr1%Nb and samples of standard nominal alloy E110 applied for shells of fuel assembly of nuclear reactor VVER-1000.

2. DETERMINATION OF ELEMENT COMPOSITION AND ALLOCATIONS OF IMPURITIES NEAR THE WELDING SEAM

For the analysis of element composition samples of interest the targets from zirconium alloys have used as disks with diameters 20 and thickness of 0.3 mm. The energy of protons was 1.6 MeV, current of a beam – 3 mA, the spectrums were measured up to a charge of protons fallen on the target 5000mC. The characteristic X-ray emission registered by Si (Li) detector with energy resolution 250 eV for a line 5.9 keV, which placed at 135° to a beam direction. The momentum γ-ray emission originating in nuclear reactions excited by accelerated protons registered by Ge(Li) detector with resolution 2.5 keV for a line 1332 keV placed at 45° to a direction of a beam. The irradiated targets were in vacuum inside the camera. X-ray emission reached Si(Li) detector after passing through a foil from aluminum by thickness 50 μm and diaphragm from a set of lead-tantalum foils with diameter of a hole of 0.3 mms, that has allowed to diminish loading a spectrometric tract of the Si(Li) detector and measure X-ray spectra simultaneously with spectra of γ-radiation. The sizes of a projection of a beam of protons on the target varied from 1 mm in diameter at scan of a surface of the target up to 15 mm.

To determine of contents of oxygen and fluorine the lines with energy 495 keV from reaction ^{16}O (p, γ)^{17}F and 6129 keV from reaction $^{19}F(p,\alpha\gamma)^{16}O$ were used. These lines registered by Ge(Li) detector simultaneously. For optimization of conditions of measurements the signal from the detector was divided into two channels: including a line with energy 495 keV and including all range of energies from 0 up to 8 MeV. It has allowed to improve energy resolution and to increase accuracy of determination of oxygen. On Fig. 2 are shown the parts of spectrum including lines used for the analysis O, N and F.

For determination of nitrogen a line 4439 keV from reaction $^{15}N(p,\alpha\gamma)^{12}C$ was used. The elements with atomic number in a range $20 < Z < 50$ were determined using X-ray emission of K – shell and contents of hafnium and lead were determined using X-ray emission of L-series [2].

The data obtained testify that the adding of oxygen into surface layers of zirconium units happens mainly during the welding. If the welding argon without padding clearing was used the content of oxygen in surface layer of metal was raised on 0.01…0.02 %. The using of the patron of special clearing allows to decrease the absorption of oxygen up to 0.01 %. An etching of the samples on depth up to 20 microns promotes the padding decrease of surface contamination by oxygen. The absorption of nitrogen during welding happens to a lesser degree, than oxygen.

There were a number of cases of absorption of nitrogen up to 0.002 % at welding without the clearing patron. It can be explain by the using of poor cleanness of gas.

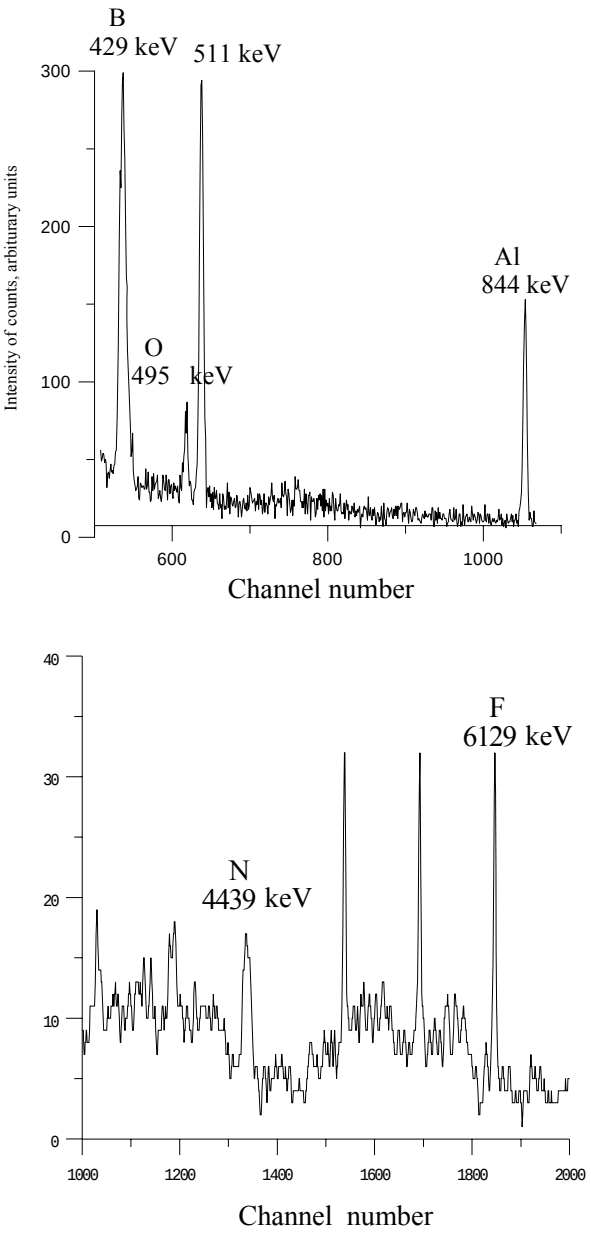

Fig. 2. Spectrum of γ-radiation of a sample of a zirconium alloy

The absorption of nitrogen did not exceed 0.001 % for the majority of measurements. If the patron of clearing and etching was used the absorption of nitrogen was less than 0.001 weight. %. This value is close to level of dispersion of concentration of nitrogen in initial state of alloy.

The application of sequentially connected patrons has reduced to twofold lowering of a level of surface contamination by oxygen and nitrogen of welding seam. After operations of an etching of a surface the concentrations of nitrogen and oxygen in surface layers have achieved basic values. The content of fluorine after the etching was raised beside nominal value. This enlargement makes at optimal time of an etching value in an interval of 0.001…0.002 %. This value on the sum with an original content of fluorine for depth of a stratum of alloys 1…2 microns gives less than 0.06…0.10 μg/cm^2. To research the distribution of light impurities near the welding seam the local analysis some samples was made. The diameter of proton beam was focused to 1mm and the scanning the sample across welding seam was carried out to determine the content of O, N, F using PIGME.

The scan was carried out at energy of a proton beam 1518 keV. Width of the welding seam was about 3 mm. The distribution of oxygen and nitrogen near the seam are shown in Fig. 3.

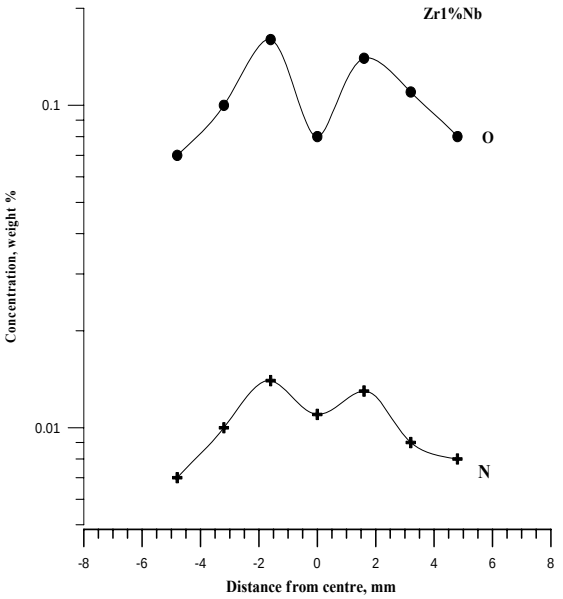

Fig. 3. The variation of content of oxygen and nitrogen inside and around welding seam. Helium-arc welding of two nipples from an alloy Zr1%Nb

The impurities concentrations have two maximum on the left and on the right side of center. With the increasing of distance from centre the concentration of both impurities descend reaching a reference value for the given sample of an alloy.

SUMMARY

As a result of the held researches it was be shown that using methods PIXE and PIGME it is possible to determine simultaneously the contents of nitrogen, oxygen, fluorine and elements with atomic numbers in a range $20 < Z < 82$ in samples of zirconium alloys. The information about of contents in a sample of elements at a level N - 0.006 weight. % with an error 16%, O - 0.10 weight. % with an error 16 %, F - 0.0005 weight.. % with an error 4%, Ca, Ti, V, Cr, Fe, Ni, Cu, Cd, Sn, Hf, Pb with an error 10…15%, Nb with an error 3…5 %, Zr with an error 0.1…0.2% can be received during 25…40 minutes.

It is shown that the using of electric arc installation with application of the padding clearing device of welding gas provides the obtaining of enough high cleanness of a welding seam on contents of oxygen. The quantity of absorbed oxygen in the field of a welding seam compounds a maximum 0.01% if a special clearing of welding gas used. An averaged padding absorption of nitrogen by surface layer in the field of a welding seam compounds values about 0.001 %. With improvement of cleanness of welding gas and control of its composition it is possible to provide complete cleanness of welding seam from impurities.

An absorption of fluorine by surface layers of fuel assembly tubes near of welding seam during of the welding and etching according to laboratory technology is not so many as 0.001…0.002 weight. % (0.06…0.10 μg/cm^2).

REFERENCES

1. A.D. Vergunov, Yu.Z. Levchenko, M.T. Novikov, V.M. Pistryak, V.E. Storizhko, S.Ya. Chekhanov // *Problems of atomic science and tecnology. Ser. "General and nuclear physics".* 1983, v. 3(24), p.13.

2. V.V. Levenets, A.O. Shchur, O.P. Omelnyk, V.A. Zaporozhchenko, I.A. Petelguzov**,** Simultaneous determination of oxygen, nitrogen, fluorine and metal impurities in zirconium by nuclear-physical methods // *Manuscripts of 14 International conferences on physics of radiation appearances and radiation technology. 12-17 of June 2000, Alushta, Ukraine.* Харьков, 2000.

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ПРИМЕНЕНИЕ ХРИ И МИЯР ДЛЯ ИССЛЕДОВАНИЯ РАСПРЕДЕЛЕНИЯ ЭЛЕМЕНТОВ В ОКОЛОШОВНОМ ПРОСТРАНСТВЕ В ТРУБАХ ИЗ Zr1%Nb

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Ядерно-физические методы анализа состава вещества применены для определения элементного состава изделий из циркониевых материалов, включая газообразующие примеси C, N, O, F, элементы B, Ca, Ti, V, Cr, Fe, Ni, Cu, Nb, Mo, Cd, Sn, Hf, Pb, и исследования поглощения материалом трубок из сплава Zr1%Nb кислорода, азота и фтора во время операций по изготовлению моделей твэлов. В технологическом процессе изготовления твэлов ВВЭР-1000 присутствует ряд факторов, воздействие которых на материал оболочки и на твэлы в целом может иметь негативные последствия. Такими факторами являются примеси внедрения (кислород, азот), попадающие в металл во время операций высокотемпературных обработок, в частности при сварке деталей твэлов. Внедренные в сварной шов газовые составляющие атмосферы сварки азот и кислород могут ухудшать коррозионную стойкость шва и снижать пластичность материала. На стадии химической полировки поверхности изготовленных твэлов или образцов для исследований путем травления в фторсодержащих растворах поверхность может загрязняться фтором из травильных составов. Фтор, как известно, является активным элементом, снижающим коррозионную стойкость оболочек и концевых деталей тепловыделяющих элементов.

ВИКОРИСТАННЯ ХРВ І МВЯР ДЛЯ ДОСЛІДЖЕННЯ РОЗПОДІЛУ ЕЛЕМЕНТІВ БІЛЯ СВАРНОГО ШВУ В ТРУБКАХ ІЗ Zr1%Nb

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Ядерно-фізичні методи аналізу складу речовини використані для визначення елементного складу виробів із цирконієвих матеріалів з включенням газових домішок C, N, O, F і елементів B, Ca, Ti, V, Cr, Fe, Ni, Cu, Nb, Mo, Cd, Sn, Hf, Pb, а також дослідження поглинання матеріалом трубок із сплаву Zr1%Nb кисню азоту і фтору при операціях по виготовленню моделей твелів. В технологічному процесі виготовлення твелів ВВЕР-1000 присутні фактори, вплив яких на матеріал оболонки і на твели в цілому можуть мати негативні наслідки. Такими факторами є домішки укорінення, що потрапляють в метал в наслідок високотемпературних обробок, зокрема при зварюванні деталей твелів. Укоріненні в зварний шов газові складові атмосфери зварки азот і кисень можуть погіршити корозійну стійкість шву і знизити пластичність матеріалу. На стадії хімічної поліровки поверхні твелів в розчинах, що вміщують фтор, можуть бути забруднення фтором, що також може знизити корозійну стійкість оболонок і кінцевих деталей твелів.