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ACCUMULATION OF RADIATION DAMAGE IN ZIRCONIUM ALLOYS Zr-1 AND Zr-4 UNDER IRRADIATION WITH 300 keV HEAVY IONS

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Experiments were carried out to induce radiation defects in zirconium alloys for fuel elements Zr-1 and Zr-4 using accelerated heavy ion beams. The required irradiation dose was delivered using 300 keV Fe^{2+} and Zr^{2+} ions with an ion implanter in the Institute of Applied Physics of the National Academy of Sciences of Ukraine. These ion types were selected as the most relevant for the irradiation of structural materials due to their elemental composition. The results were analyzed using the PIXE method to assess the elemental concentration profiles in the surface layer of the alloys, and by TEM microscopy to study the effects of irradiation at doses of 5, 50, and 100 dpa at different substrate heating temperatures of 250, 350, and 500 °C.

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INTRODUCTION

The development and investigation of new structural materials for the fabrication of nuclear reactor components is currently one of the most pressing challenges in the field of nuclear technology. The production of metal alloys capable of withstanding high-energy neutron irradiation over decades also presents a significant challenge for solid-state physics and materials science. For instance, active research is now being conducted on novel high-entropy alloys (HEAs), which have already demonstrated promising performance compared to conventional austenitic stainless steels [1].

Materials used in nuclear installations, particularly those located in the reactor core region, are continuously exposed to intense neutron fluxes, which induce a variety of destructive processes. Radiation damage in an alloy depends on the energy of the incident particles bombarding its surface and is generally characterized by the following stages:

- The incident particle interacts with the atoms of the crystal lattice, transferring a portion of its kinetic energy;
- If the transferred energy exceeds ~ 2.5 E_d, where E_d is the atomic binding energy within the crystal lattice (E_d = 40 eV for Fe, Zr, and Cr), the atom is displaced from its original position [2];
- If the irradiation energy is even higher, the primary knock-on atom may additionally initiate the displacement of other atoms, resulting in the formation of a displacement cascade.

As a result of this process, groups of Frenkel-type point defects are formed in the material, consisting of vacancies and interstitial atoms, as well as clusters of such defects, as discussed in this study [3].

In a nuclear reactor, irradiation is caused by neutrons with a broad energy spectrum. High-energy neutrons make the main contribution to the formation of radiation-induced defects, while thermal neutrons (E_n < 0.5 eV) trigger transmutation reactions, leading to the formation of hydrogen and helium atoms. The presence of these elements in alloys causes significant alterations in the initial properties of steels, provoking such detrimental processes as loss of ductility, embrittlement, and swelling.

The study of destructive changes in various alloys can be conducted not only via neutron irradiation in a nuclear reactor. It is much more cost-effective, faster, and safer to perform such investigations using particle accelerators with intense heavy ion beams. This approach offers significant advantages:

- The dose accumulation rate under heavy ion irradiation is approximately 10^5 higher than under neutron irradiation, as the cross-sections of ion interactions with the atoms of the crystal lattice are orders of magnitude greater compared to those of neutrons [4];
- The irradiated samples do not exhibit residual radioactivity, making them safe to handle;
- Irradiation using an ion implanter or particle accelerator can be precisely controlled, allowing adjustment of operational parameters to meet the specific requirements of the experiment.

Given the aforementioned, it should be noted that the generation of radiation defects through heavy ion irradiation is a widely accepted and actively practiced method worldwide.

1. SIMULATION AND EVALUATION OF IRRADIATION PARAMETERS

As part of the presented work, a series of irradiations was conducted on samples of the structural material zirconium, represented in two alloy variants: Zr-1 and Zr-4. Zr-1 (Zircaloy-1) and Zr-4 (Zircaloy-4) are widely known materials used in nuclear energy, primarily for the fabrication of fuel elements (fuel rods). They differ in their elemental composition and, consequently, in several important properties [5], as shown in Table 1.

Table 1
Elemental composition and properties
of Zr-1 and Zr-4 alloys

Parameter	Zr-1	Zr-4
Amount of impurities of other elements, %	Sn - ~2.5	Sn - 1.2…1.7 Fe - 0.18…0.24 Cr - 0.07…0.13
Density, g/cm^3	6.50	6.55
Thermal conductivity, W/(m·K)	16.0	16.5
Corrosion rate (for water, 360 °C), μm/year	~ 10…30	~ 1…5
Hydrogen accumulation rate on the surface, μg/(dm²·h)	~ 5…10	~ 1…3
Tensile Strength, MPa	~480…520	~ 550…610

Currently, Zircaloy-4 is the most actively used material for the production of fuel elements, as it offers several advantages, such as high corrosion resistance when operated in water-cooled nuclear reactors. The alloy is used by well-known global corporations such as Westinghouse, Framatome, and others.

The Institute of Applied Physics (IAP) has an ion implanter with a maximum particle acceleration energy of up to 150 keV. Therefore, the use of doubly charged ions Fe^{2+} and Zr^{2+} for the experiment provides the opportunity to irradiate prepared samples with particles having an energy of 300 keV.

Irradiation doses of 5, 50, and 100 dpa were chosen. During the irradiation, the samples were also heated to temperatures of 250, 350, and 500°C. The heating was necessary to simulate the real conditions in reactors, where the temperature of the coolant and the contacting structural components reaches 280…320 °C, depending on the reactor type and model.

The estimation of the time required to accumulate the specified doses was performed using the SRIM software. This program is designed for calculating the interaction of charged particles with materials and is widely used in radiation materials science.

The relationship between the ion flux and the dpa value on the sample can be estimated using the following expression [6]:

$$dpa = \sigma_D \varphi t, \quad (1)$$

where σ_D – the displacement damage cross-section; φt – the irradiation flux, which is evaluated as the product of t – the irradiation time, and the ion beam current density.

The reaction cross-section σ_D can be estimated as:

$$\sigma_D \approx 0{,}4\,\frac{S_n}{E_d}, \quad (2)$$

where S_n – nuclear stopping cross-section; E_d – displacement threshold energy.

The values E_d of threshold displacement energies for atoms to be displaced from their positions in the crystal lattice can be taken from experimentally verified data provided by the American Society for Testing and Materials (ASTM) [7]. The nuclear stopping cross-section S_n depends on the initial ion energy and can be estimated by the following expression:

$$S_n = \left(\frac{dE}{dx}\right)_n / n, \quad (3)$$

where $\left(\frac{dE}{dx}\right)$ – energy losses during interactions with target atoms; n – atom density in the target.

As a result, using the specified values, the following approximate irradiation parameters were obtained for zirconium targets irradiated with Fe^{2+} and Zr^{2+} ions at 300 keV energy and beam current density on the target of approximately 2…3 μA/cm^2, as shown in Table 2.

Table 2
Simulation results in SRIM

Particle	Fe^{2+}	Zr^{2+}
Projected ion range, Å	1506	961
Sputtering yield	2.54	4.07
Dose rate, dpa/s	0.014…0.02	0.03…0.05
Ion fluence for 100 dpa, 10^{16} cm^{-2}	4.5	2.1
Time required to reach 100 dpa, h	1.2…2	0.55…0.9

Using the "quick calculation of damage" mode of the SRIM software, graphical profiles of ion implantation depth and generated vacancies were obtained. The simulation results shown in Fig. 1 demonstrate that the majority of ions with an energy of 300 keV penetrate into zirconium samples to a depth of up to 4000 Å for Fe^{2+} ions and up to 2500 Å for Zr^{2+} ions. In both cases, the maximum of the vacancy distribution is observed at a depth smaller than that of the implanted ions.

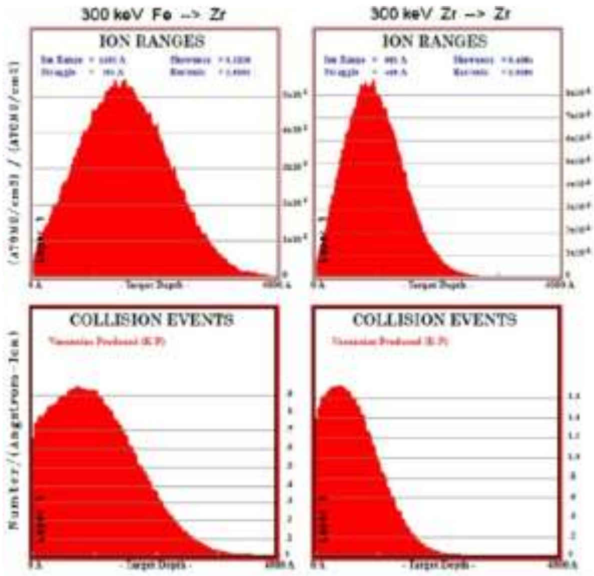


Fig. 1. Screenshot of the SRIM software showing the simulation results of ion depth distribution and vacancy formation under irradiation with Fe^{2+} and Zr^{2+} ions at 300 keV energy

Additionally, based on the results of the work, a clear graph was created showing the dependence of the irradiation dose (dpa) on the irradiation time and the beam current density on the target, which is continuously monitored during the experiment in automatic mode and displayed on a PC screen using custom software developed at the IAP. The result is presented in Fig. 2.

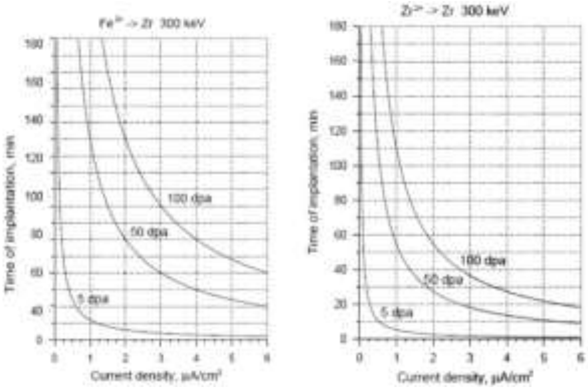


Fig. 2. Graphs of the irradiation dose dependence on time and beam current density on the target

2. IRRADIATION OF ZIRCONIUM SAMPLES AT THE IAP IMPLANTER AND RESULTS

Based on the data obtained from simulations and theoretical calculations, a series of irradiations of zirconium samples was carried out, with details presented in Table 3. To generate iron and zirconium ions, an ion source developed at IAP and described in detail in [8] was used, along with an ion implanter built at IAP on the basis of the industrial installation "Vezuviy-5".

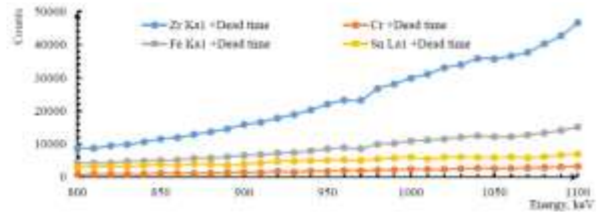
In general, ions are extracted from the source with an initial energy of 20 keV. Then, using a magnetic sector separator, the beam is bent, and the desired ion fraction is selected based on the mass-to-charge ratio (M/Z). After the bend, the beam is accelerated by a voltage up to 150 kV. Given that beams of doubly charged Fe and Zr ions were selected for irradiation, their energy at the target reached 300 keV.

Table 3
Irradiation parameters of Zr-1 and Zr-4 samples with a 300 keV heavy ion beam

Ions	Dose, dpa	T, °C	Ions	Dose, dpa	T, °C
Fe^{2+}	5	250	Zr^{2+}	5	250
Fe^{2+}		350	Zr^{2+}		350
Fe^{2+}		500	Zr^{2+}		500
Fe^{2+}	50	250	Zr^{2+}	50	250
Fe^{2+}		350	Zr^{2+}		350
Fe^{2+}		500	Zr^{2+}		500
Fe^{2+}	100	250	Zr^{2+}	100	250
Fe^{2+}		350	Zr^{2+}		350
Fe^{2+}		500	Zr^{2+}		500

To perform non-destructive analysis of the obtained samples and obtain elemental concentration profiles in the surface layers of the material, the Particle Induced X-ray Emission (PIXE) method was used. This method is suitable for detecting heavy elements in the samples, offering high sensitivity. The measured elemental concentrations allow for further assessment of radiation-induced segregation in the studied alloys. The work was carried out using the existing electrostatic ion accelerator for H and He ions at the IAP, with an energy of 2.0 MeV, and a high-resolution magnetic spectrometer with a chamber equipped with a modern AMPTEK XR-100SSD X-ray detector.

Figs. 3, 4 clearly show the increase in iron concentration after zirconium irradiation with Fe^{2+} ions, with samples of both alloys, Zr-1 and Zr-4, being taken as examples. The effect becomes more pronounced as the irradiation dose increases.



a

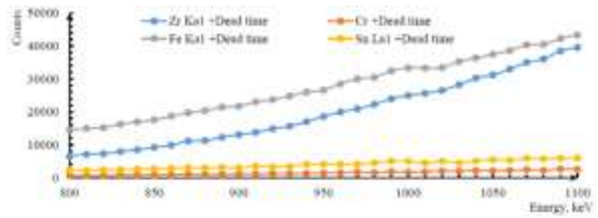


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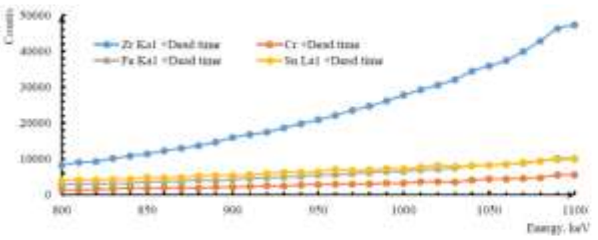
Fig. 3. Elemental composition analysis of Zr-1 samples irradiated with Fe^{2+} ions with a dose of:
a – 5 dpa; b – 100 dpa

With stable concentrations of the main alloy components (Zr, Cr), the Fe signal level significantly increases as the irradiation dose increases from 5 to 100 dpa. A similar situation occurs in the case of the Zr-4 alloy as well.



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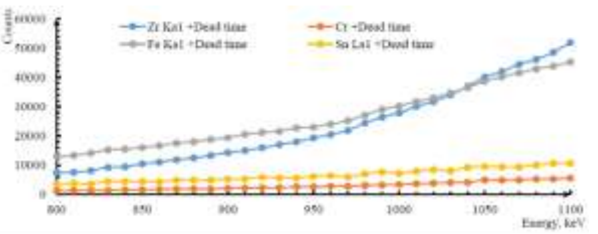

b

Fig. 4. Elemental composition analysis of Zr-4 samples irradiated with Fe^{2+} ions with a dose of:
a – 5 dpa; b – 100 dpa

It can be stated that the task of irradiating the samples using the IAP ion source with doses of 5, 50, and 100 dpa has been successfully completed, and the results of the PIXE method can be used for further study of changes in the Zr-1 and Zr-4 alloys.

Additionally, investigations were conducted using a TEM microscope on both non-irradiated samples and those irradiated with Fe^{2+} and Zr^{2+} ions at an energy of 300 keV. Since the structures of the Zr-1 and Zr-4 alloys are nearly identical, Figs. 5, 6 present the results obtained from studying Zr-4.

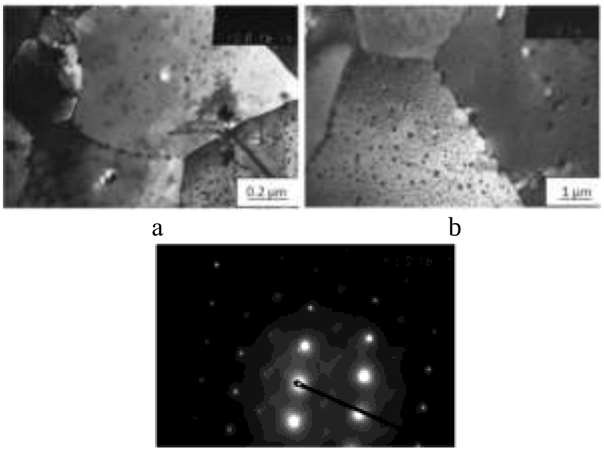

Fig. 5. Structure and microdiffraction of a non-irradiated Zr-4 alloy sample: a – grain structure of the alloy, b – BF image, c – micro-electron diffraction pattern along the [031] α-Zr zone axis and reflections from the intermetallic phase lattice

Fig. 6 demonstrates the changes that occurred after irradiation, with similar effects observed even at minimal irradiation doses of just 0.5 dpa and a heating temperature of 250 °C.

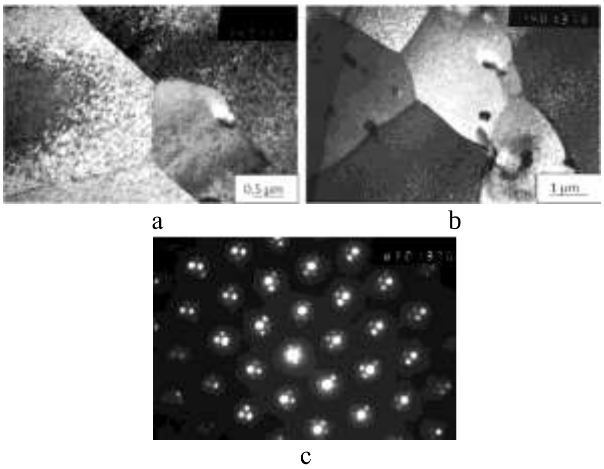

Fig. 6. Structure and microdiffraction of the irradiated Zr-4 alloy sample: a – grain structure of the alloy; b – BF image; c – electron microdiffraction pattern with zone axis [001]-αZr

The investigation of the irradiated samples shows that various radiation-induced defects form within their structure, with a defect density reaching up to 10^{11} cm^{-2}. The difference between the irradiation results for the Zr-1 and Zr-4 alloys lies in the fact that, in the case of Zr-4, satellite reflections are observed near the matrix reflections in the electron diffraction pattern. Their presence is typically explained by the phenomenon of double diffraction, occurring due to the presence of a second phase in the thin foil during foil or film preparation. Similar phenomena have previously been observed in zirconium alloys and were associated with the formation of a so-called secondary phase [9].

It was also noted that during irradiation of zirconium samples at minimal doses of 0.5…5 dpa and at a heating temperature of 250 °C, the intermetallic phases in the material structure almost completely disappear, which may result from their dissolution or dispersion. This dissolution effect has also been observed in other studies [10].

CONCLUSIONS

This work presents the results of irradiation of zirconium samples of two alloy types, Zr-1 and Zr-4, with Fe^{2+} and Zr^{2+} ions at an energy of 300 keV.

Using simulations performed in the SRIM program, the necessary irradiation parameters were evaluated, and the time required to achieve the selected doses was determined based on the beam current density on the irradiated target, where this parameter is continuously monitored during operation via a custom-developed PC software.

A series of zirconium samples was irradiated with doses of 5, 50, and 100 dpa, while maintaining the sample temperatures at 250, 350, and 500 °C. For this purpose, a metal and gas ion source developed at IAP was used.

Some of the samples were analyzed using the PIXE method, and elemental concentration profiles within the structure of the zirconium alloys were obtained. A significant increase in the concentration of the irradiating element was observed in the irradiated samples compared to the original ones, with the effect becoming much more pronounced as the irradiation dose increased from 5 to 100 dpa.

The analysis of both pristine and irradiated samples using a TEM microscope clearly demonstrated the formation of a large number of various defects within the material structure, with a defect density of approximately 10^{11} cm^{-2}. The obtained DF and BF images show that the defects are uniformly distributed along different crystallographic directions. It was observed that even minimal irradiation doses up to 5 dpa, combined with sample heating to 250 °C, lead to the disappearance of most intermetallic phases in the material, likely as a result of their dissolution.

The irradiation of a large set of zirconium samples under different conditions provides broad opportunities for further study of the radiation-induced defects and the changes in material properties caused by such exposure.

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НАПРАЦЮВАННЯ РАДІАЦІЙНИХ ПОШКОДЖЕНЬ У ЦИРКОНІЄВИХ СПЛАВАХ Zr-1 ТА Zr-4 ОПРОМІНЕННЯМ ВАЖКИМИ ІОНАМИ З ЕНЕРГІЄЮ 300 кеВ

В.А. Батурін, О.Ю. Роєнко, С.О. Єрьомін, П.О. Литвинов, О.Ю. Карпенко, В.М. Білик, М.І. Даниленко

Виконано експерименти по напрацюванню радіаційних дефектів у цирконієвих сплавах для тепловиділяючих елементів Zr-1 та Zr-4 з використанням пучків прискорених важких іонів. Набір необхідної дози опромінення проводився іонами заліза Fe^{2+} та цирконію Zr^{2+} з енергіями 300 кеВ на іонному імплантері в ІПФ НАН України. Даний сорт іонів вибраний як найбільш затребуваний для опромінення конструкційних матеріалів у силу їх компонентного складу. Результати було досліджено за допомогою методу PIXE для оцінки профілів концентрації елементів у поверхневому шарі сплавів та на ТЕМ-мікроскопі для вивчення наслідків опромінення дозами 5, 50, 100 ЗНА при різних температурах нагріву підкладки – до 250, 350 та 500 °С.