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Oxidation of Zirconium after Argon Ion Irradiation

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An oxidation of the near surface layers of pure zirconium samples resulting from ion irradiation in residual gas atmosphere of vacuum chamber was observed in the work. The irradiation was performed with 100 keV Ar^+ ions at fluence of 1×10^{17} cm^{-2}, temperature of the samples did not exceed 150 °C. An element analysis of the modified layers was carried out using Rutherford (RBS) and Resonant Elastic (ResBS) Backscattering Spectrometry of ^4He ions (resonance in $^{16}O(^4He,^4He)^{16}O$ scattering at about 3.045 MeV). A stoichiometric composition of the surface oxide film was found out related to ZrO_2. The films were colored in violet. A thickness of the oxide layer was measured to be about 660 nm, which is by about an order of magnitude greater than a value of the calculated projected range of Ar ions in Zr ($Rp = 69.3$ nm, SRIM2008 code). It is supposed that the oxidation has a linear (or destructive) character. The obtained results allow us to propose an alternative mechanism of the enhanced anticorrosion resistance of U, Zr, and its alloys after irradiation with He, Ar, Kr, Xe ions experimentally observed in the literature previously. A possible mechanism of the fast oxygen diffusion and formation of an extensive oxide layer was discussed.

Keywords: Zirconium, Ion irradiation, Oxidation, Projected range.

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1. INTRODUCTION

The problem of study of the radiation-induced oxygen diffusion and oxidation of pure metals (Ti, Zr, etc.) and their alloys at elevated temperatures are currently very relevant from the point of view of both the fundamental and applied research [1-7]. Thus, the authors of [2, 3] studied the influence of the specific nuclear and electron bremsstrahlung loss at energy of Ar^+ ions in the range of 1-9 MeV on the surface oxidation of pure metals (Ti, Zr) at elevated temperatures in the residual gas atmosphere of the vacuum chamber. In particular, it is established that ballistic collisions at great depths make a definite contribution to oxidation of Ti surface when irradiated by Ar ions with the maximum effect at the energy of about 3 MeV.

The authors of [4] studied the radiation-induced surface oxidation of thin iron films under their irradiation by fast heavy ions in the energy range of some MeV/amu in the working vacuum. Two different surface oxidation processes were found near the boundary value of the electron-ion loss, at which track formation occurs. It is established that values of the effective diffusion coefficients of oxygen in iron 100-1000 times exceed the values for the case of thermally activated oxygen diffusion in iron melts. The authors notice that additional experimental and theoretical works are necessary for determination of the exact oxidation and diffusion mechanisms.

The authors of [7] observed a corrosion inhibition of pure Zr and its alloys with Nb after irradiation of the surface by He^+ and Ar^+ ions with the energy of 150 keV at room temperature. Corrosion tests were performed in distillation water at the temperature of 300 °C. The greatest effect was observed under irradiation with argon ions at the radiation dose of 1×10^{16} cm^{-2}. The authors of the work [6] observed a corrosion inhibition of uranium and Zr + 1 % Nb alloy after irradiation with Ar^+ ions with the energies in the range of 5-25 keV at elevated temperatures. Dependence of the corrosion resistance (CR) on the ion irradiation dose at elevated pressures and temperatures in distillation water had an extreme character. All other things being equal, irradiation with Xe^+ and Kr^+ ions did not significantly influence the CR change. Formation of a protective oxide film as far back as at the stage of ion implantation at different doses can be one of the possible causes of the increase in the CR of pure zirconium and other materials discovered in the works [6, 7] after irradiation with argon ions.

The primary goal of the present work was to study the possible influence of irradiation with argon atoms of the samples of pure zirconium on the formation of an oxide film on the surface in the working vacuum.

2. EXPERIMENTAL RESULTS

Samples of pure zirconium (Zr) were investigated. The samples were cut from a bar of vacuum remelting of the diameter of about 20 mm and thickness of about 3 mm and ground to a high finish. Implantation of the singly-charged argon ions (Ar^+) was carried out on the modernized high-current industrial implanter “Vesuvius” of the Institute of Applied Physics of NAS of Ukraine at the ion energy of 100 keV and current density on the sample surface of about 4 μA/cm^2. Argon ion fluence was approximately equal to 1×10^{17} cm^{-2}. Temperature of the samples did not exceed 150 °C. Irradiated samples were placed in the receiving chamber of the implanter with the residual vacuum of about 3×10^{-4} Pa. For the analysis of the elemental composition of the samples we used methods of the Rutherford (RBS) and resonant elastic (ResBS) backscattering of helium ions (resonance in the $^{16}O(^4He,^4He)^{16}O$ scattering at the energy of 3.045 MeV) realized in the group EG-5 of the Frank Laboratory of Neutron Physics in the Joint Institute for Nuclear Research (FLNP JINR). Color of the surface of the initial samples and coatings formed after irradiation was evaluated visually.

In Fig. 1 we show the backscattering energy spectra of helium-4 ions with different initial energies of about 3.045 MeV obtained from the samples of irradiated zirconium. An analyzing beam was incident at an angle of 10° to the normal to the samples surface. Backscattered particles were detected at the scattering angle of 170°. Standard detector and equipment were used for spectral detection. Spectra processing was performed by SIMNRA and DVBS programs which allow to extract from the spectra concentration of one or another element and its occurrence depth in the matrix.

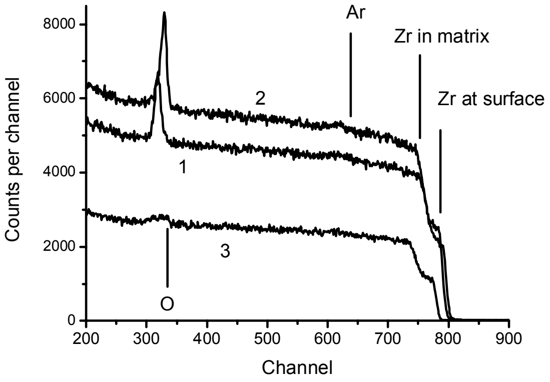

Fig. 1 – RBS and ResBS spectra of helium ions from the zirconium sample irradiated by argon ions. Energy of the primary analyzing beam of helium-4 ions was equal to: 1 –3.067; 2 – 3.045; 3 – 3.022 MeV. Vertical lines denote the kinematic boundaries of the partial spectra of different elements

As seen from the spectra, a substantial "feeding" of the signal from Zr in the form of two stairs near 800 channel is observed. Peaks near 350 channel are conditioned by the resonance yield of alpha-particles (Fig. 1) backscattered by nuclei of oxygen-16 distributed in the formed oxide film. The spectrum measured at the energy of 3.022 MeV (Fig. 1) shows that widths of the partial spectra from oxygen and zirconium-deficient layer are approximately equal that directly implies the formation of a thin oxide film. Thickness of this film was found to be equal to 1300×10^{15} atm/cm^2 within an accuracy of about 4 %. We will take the film thickness to be equal to 5.85 g/cm^3 (density of ZrO_2 monoclinic modification with the following lattice parameters: $a = 0.5169$ nm; $b = 0.5232$ nm; $c = 0.5141$ nm; beta = 80.75°). Based on these assumptions, the linear film thickness is estimated of about 660 nm.

Joint processing of the RBS and ResBS spectra allowed to establish that film stoichiometry is close to ZrO_2 with an accuracy of about 5 %. On top of that, the film was colored in violet that, in particular, is also typical for fianite single-crystals (ZrO_2). The obtained data indicates that a thin titanium dioxide film is formed on the surface of the samples.

3. CALCULATION OF THE PROJECTED RANGES AND DISTRIBUTION OF ION VACANCIES IN A TARGET

Projected range of argon ions and distribution of vacancies over depth of zirconium samples were evaluated using the SRIM2008 program [8].

Distributions of ranges of argon ions and vacancies generated by irradiation in zirconium matrix calculated using the SRIM2008 program are illustrated in Fig. 2 and Fig. 3, respectively.

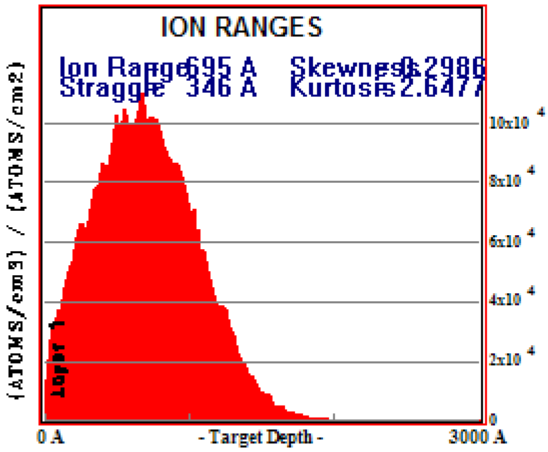

Fig. 2 – Distribution of the ranges of argon ions with the initial energy of 100 keV at normal incidence on the zirconium target

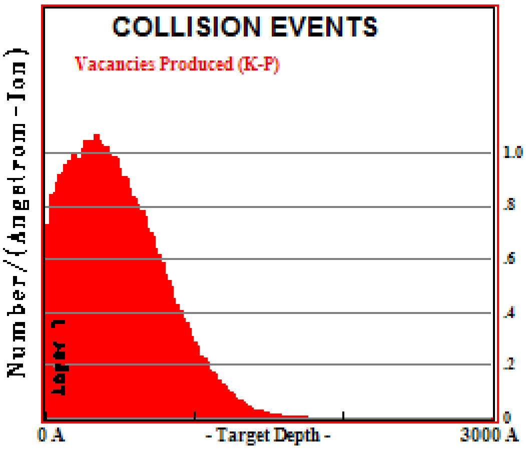

Fig. 3 – Distribution of the vacancies generated by 100 keV argon ions over the depth of zirconium matrix

Comparing the values of the calculated range of argon ions and distribution depth of vacancies generated by irradiation (SRIM2008) in the Zr matrix with the thickness of an oxide film formed on the surface (from Fig. 1), it is established that real film thickness almost one order of magnitude higher than the value of the projected range (the more so the distribution depth of vacancies generated by irradiation). We are not aware of any published work, in which one would observe oxidation of the surface of pure Zr irradiated by Ar ions on such significant depths in the working vacuum.

4. DISCUSSION OF THE RESULTS

We will resort to the analysis of data from the literature for understanding the Zr surface oxidation mechanism discovered in the present work.

Thus, the authors of [9] investigated the defect-formation processes and the nonstoichiometry change in the oxide films on pure Zr and Zr + 2.5 % Nb alloy during thermal oxidation in air at the temperature of 875 °C. Connection between these processes and corrosion behavior of metals on the stage of parabolic protective oxidation and during the transition to the linear destructive one is established. The ways to extend in time the stage of protective oxidation and the initiating factors of destructive oxidation are studied. Shown, that it is possible to extend the stage of protective oxidation of zirconium and alloy by maintaining an oxygen deficient environment in an oxide film in its modification by lithium ions. Plastic strain (5-10 %) reduces the stage of protective oxidation of Zr + 2.5 % Nb alloy.

Taking into account the results of [9], it is possible to draw the following analogies with the observations in our experiment. Stoichiometry of the oxide and its violet color points to the destructive oxidation in our case. Protective films are usually nonstoichiometric and of a dark color – dark protective oxide with broken stoichiometry towards oxygen deficiency. Such an oxide is transformed into the stoichiometric light peeling oxide not able to protect the metal.

What is interesting, in our case lateral surfaces of Zr samples, which were not subjected to mechanical polishing and ion implantation, and also the initial polished surface had a dark color typical for protective films. The latter observations are an indirect argument in favor of the below proposed scenario of the formation of a stoichiometric oxide film. One more possible reason of the destructive oxidation of the surface can be formation of a strained (cold-worked) surface layer after mechanical polishing of the initial zirconium sample, as well as the formation of shock waves during implantation, which, in turn, can induce a cold plastic strain of the near-surface matrix layers modified by ion irradiation.

The authors of [6] associate the effect of irradiation with argon ions at elevated temperatures on the increase in the corrosion resistance of uranium and zirconium alloy with the formation of blisters on the irradiated surface and their dissection during prolonged ion bombardment. Meanwhile, our data show that formation of a sufficiently extended layer of zirconium dioxide is possible under irradiation with argon ions in the residual gas atmosphere of the vacuum chamber.

It should again be noted that formation of oxide layers on the surface of pure metals and thin metal films in the working vacuum was also observed in [1-4]. Irradiation parameters varied in a wide range, for example, both on the type of ions used for irradiation and on the irradiation energy in the range from a hundred of keV, units of MeV to hundreds of MeV. The general laws, at which formation of such films is observed, have not been established yet because of a limited number of works well-known in the literature.

It can be assumed that in this work the oxide film is formed rather quickly on the surface of Zr at the initial stage of ion irradiation due to the protective parabolic oxidation. Residual atmosphere of the vacuum chamber, most probably, serves as the oxygen source. Preferential sputtering of O atoms from this film during long-term irradiation can also promote the formation in its composition of oxygen-deficient, more plastic zirconium dioxide, as it is established, for example, in [9]. In its turn, also according to the results of [9], oxygen deficiency in the film extends the stage of protective oxidation of Zr and its alloys. At the growth of the film thickness with increasing implantation dose and achievement of some critical value, there can occur, for example, film cracking and further linear (destructive) oxidation of Zr surface.

In favor of the above described scenario of oxidation one can also adduce the data of [7], where pure Zr and its alloys were irradiated with Ar ions with irradiation parameters and conditions of the receiving chamber residual vacuum close in value to those in this work. The maximum effect in [7] was observed at irradiation dose of 1×10^{16} cm^{-2}, at that a sharp increase and decay of the effect of CR enhancement occurs in the vicinity of this dose. A slow insignificant decrease in the effect with increasing dose up to 3×10^{17} cm^{-2} is also a remarkable fact. One more result of [7] does not contradict our data. Namely, the maximum effect of CR enhancement was observed for the case of irradiation with Ar, but not He ions.

The authors of [6] do not give exact quantitative data on the irradiation doses of uranium samples with Ar^+, Xe^+, Kr^+ ions with energies in the range of 5-25 keV at elevated temperatures. The maximum effect of corrosion rate reduction (2.5 times) was observed for the energy of Ar^+ ions of 25 keV. Dependence of the CR on the irradiation dose was similar to that revealed in [7]. All other things being equal, irradiation with Xe^+ and Kr^+ ions did not significantly influence the CR change. The authors explain the extreme dependence of the CR by the appearance on irradiated surface of blisters and surface destruction due to long-term bombardment with argon ions and dissection of gas bubbles earlier formed under the surface. But the proposed mechanism cannot explain the absence of the extreme dependence for the case of irradiation of U with Xe^+ and Kr^+ ions.

According to the data of this work and [9], it is possible to propose another feasible mechanism of CR enhancement of U, Zr and its alloys and other effects revealed in [6, 7]. The extreme dependence of the effect of CR enhancement after irradiation with He^+ and Ar^+ ions and absence of such dependence for the cases of irradiation with Xe^+ and Kr^+ ions can be explained by the fast formation of a thin protective oxide film on the surface of a metal or alloy on the initial stage of irradiation in vacuum. In the case of use of Xe^+ and Kr^+ ions at irradiation, such a film has no time to be formed, for example, because of higher values of the ion sputtering coefficients of the surface. Decrease in the CR effect with increasing dose can be explained by the subsequent destructive oxidation described above.

An additional experiment with exposure of the samples in the residual atmosphere of $^{18}O_2$ at different values of the dose and irradiation temperature with determination of the energies of diffusion activation and oxide films growth would help to clarify the exact oxidation mechanism of pure zirconium irradiated with argon ions.

5. CONCLUSIONS

Thus, oxidation of the surface layers of zirconium at significant depths (about 0.7 μm) after irradiation with argon ions with the energy of 100 keV (calculation range of argon ions in zirconium is ≈ 0.07 μm) in the working vacuum is revealed in this work. The measured stoichiometric composition of the formed coating and its color do not contradict the conclusion that zirconium dioxide (ZrO_2) is formed on the surface. Review of the literature taking into account the data of the present work shows that it is possible to implement two different oxidation mechanisms, namely, parabolic (protective) and linear (destructive) at the stage of ion irradiation in vacuum. Additional experiments are required to clarify the exact mechanism of oxygen diffusion and surface oxidation of pure zirconium under irradiation with heavy ions with different energies and doses at elevated temperatures in the residual gas atmosphere of O-18. The obtained data can be directly used in technologies of CR enhancement of the products of Zr, Ti and their alloys in various fields of science and engineering.

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