doi: 10.56761/EFRE2024.R2-O-034403

Effect of proton irradiation on the defect structure of Zr and Nb monolayer coating

A.D. Lomygin[1,], R.S. Laptev[1], D.G. Krotkevich[1]*

[1]*National research Tomsk polytechnic university, Tomsk, Russia*
[*]*lomyginanton141@gmail.com*

Abstract. This work is devoted to the influence of proton irradiation on the structural-phase state, element distribution and defect structure of Zr and Nb monolayer coatings. By controlling these changes in monolayer coatings, it will be possible to predict the behaviour of nanoscale multilayer coatings based on these materials. As a result, it was shown that Nb returns to the initial structural-phase state upon proton irradiation. However, Zr starts to degrade at the maximum irradiation dose, which is confirmed by X-ray structural analysis and positron spectroscopy. Optical emission spectrometry of glow discharge showed a complete agreement between the proton implantation depth and SRIM calculations.

Keywords: monolayer coatings, zirconium, niobium, X-ray diffraction, glow discharge optical emission spectrometry, positron annihilation spectroscopy, Doppler broadening spectroscopy.

1. Introduction

One of the promising directions in the creation of materials with enhanced qualities that can withstand radiation and hydrogen is the development of nanoscale multilayer coatings, or NMCs [1, 2]. By generating distinct particular dimension flaws for sink generation and boosting diffusion mobility, NMCs can withstand high radiation levels. Over the past ten years, there has been a lot of research done on radiation-induced defects and the corresponding changes in the mechanical and physical characteristics of NMCs [3, 4]. Because vacancy-type defects and interstitial atoms can recombine at the interfaces, NMCs with various crystalline structures are thought to be prospective materials with strong radiation resistance [5, 6]. This means that radiation-tolerant nanoscale multilayer coatings (NMCs) can be made by alternating metallic multilayers with distinct crystal structures (BCC, FCC, and HCP) [7, 8].

The increased radiation resistance of NMCs is due to the presence of incoherent or semi-coherent interfaces. These interfaces are formed when applying multilayer coatings with metals having different crystal structures. One of the promising interfaces is the Zr/Nb system of NMCs. In previous studies, excellent resistance to proton irradiation was shown [8–10]. However, it is not sufficiently clear why these NMCs have low susceptibility to proton irradiation. Consequently, the aim of this work is to investigate the structural phase state, layer distribution and defect structure of Zr and Nb monolayer coatings after proton irradiation.

2. Materials and methods

The coatings were deposited by magnetron sputtering of Zr (99.99% purity) and Nb (99.99% purity) targets on a substrate of monocrystalline Si (100). The total thickness of the obtained coatings was 1±0.1 μm.

Proton irradiation was carried out at the electrostatic accelerator ESG-2.5 located at the TPU (Tomsk, Russia) with a proton beam with a diameter of 5 mm and energy of 1750 keV. The energy stabilization error was 0.02 %. An aluminum absorber was used to provide the projective span, the thickness of which was determined using the SRIM-2013 software package. Modelling was carried out for monolayer Zr and Nb coatings mentioned above. The total number of incident particles was $5 \cdot 10^5$, the proton beam with an energy of 1720 keV was directed perpendicularly to the surface through an aluminium absorber with a thickness of 33 μm. According to SRIM, the specified parameters of proton irradiation allow obtaining a Bragg peak with a maximum in the region of ~ 85±30 nm. Thus, irradiation at the above parameters will allow us to study the influence of all possible interfaces on the accumulation of defects under radiation exposure, while the fraction of

embedded ions in the first layers increases significantly, which will allow them to be probed more effectively by positrons at the same depth resolution. Based on the irradiation parameters, the doses were: $3.4 \cdot 10^{15}$ (small dose), $8.6 \cdot 10^{15}$ (average dose), $3.4 \cdot 10^{16}$ (large dose) ions/cm^2.

The structural changes because of annealing were also monitored by diffraction method on a XRD-7000S diffractometer (Shimadzu, Japan) using Bragg-Brentano geometry, investigated angles 20–75°, scanning speed 5.0 deg/min. The distribution of elements before and after proton irradiation was analysed by glow discharge optical emission spectrometry (GD–OES) on a GD-Profiler 2 spectrometer (Horiba, Japan).

Structural defects before and after proton irradiation were analyzed using the Doppler broadening spectroscopy (DBS) method with variable energy positron beams at the Dzhelepov Laboratory of Nuclear Problems (Joint Institute for Nuclear Research, Dubna, Russia). A monoenergetic positron beam with a diameter of 5 mm and an intensity of 10^6 e^+/s was used. The energy range of implanted positrons was from 0.1 keV to 30 keV. The annihilation γ-radiation was recorded by a detector based on an extremely pure germanium (EPG) model GEM25P4-70 (AMETEK ORTEC, USA) with an energy resolution of 1.20 keV, interpolated along the 511 keV line. The resulting DBS spectra were analyzed by determining the S and W parameters using SP-11 software. The S parameter is defined as the ratio of the area under the central part of the 511 keV line to the total area of this peak. It characterizes the annihilation of positron-electron pairs with low momentum, occurring mainly in open volume defects in the crystal structure. A higher value of this parameter reflects an increase in the free volume due to an increase in the size of defects or their concentration. The parameter W is responsible for the chemical environment of the annihilation site.

3. Results and discussions

Figs. 1 and 2 show diffractograms for monolayer coatings of Zr and Nb, before and after proton irradiation. After proton irradiation no formation of new phases was detected, the presence of crystalline structure is preserved.

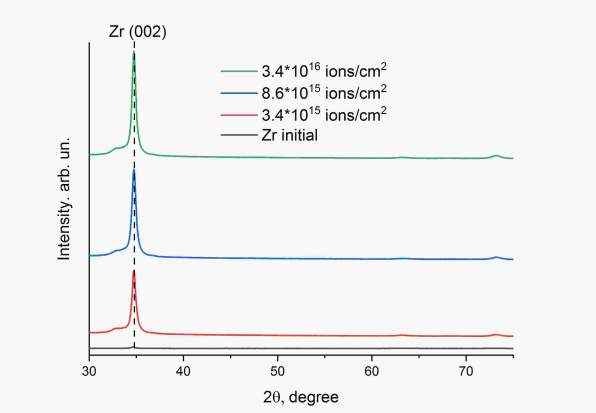

Fig. 1. Diffractograms of Zr monolayer coating irradiated by protons with different dose.

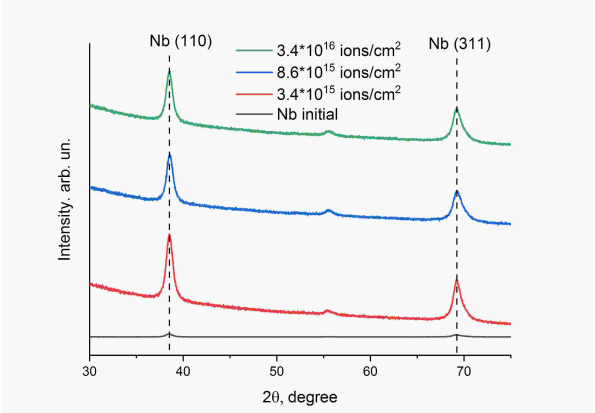

Fig. 2. Diffractograms of Nb monolayer coating irradiated by protons with different dose.

Figs. 3 and 4 show the corresponding changes in the interplanar distance and FWHM values. It can be noted that under large dose irradiation ($3.4 \cdot 10^{16}$ ions/cm^2), niobium relaxes and the interplanar spacing and FWHM values return to the initial values. However, in the Zr monolayer coating, a small decrease in the interplanar distance and FWHM values is noticeable, which is associated with an increase in the level of microstresses in the coating.

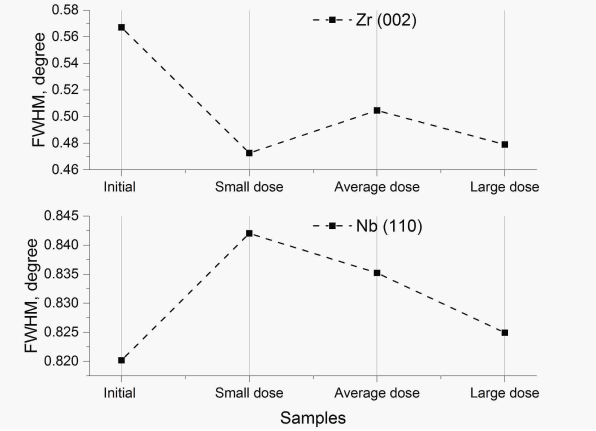

Fig 3. Plots of FWHM value.

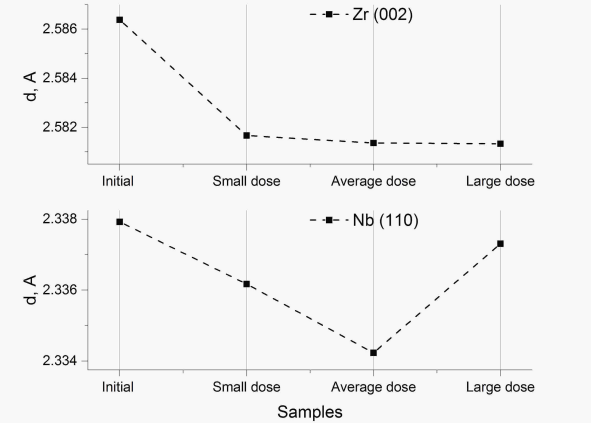

Fig. 4. Plots of interplanar spacing.

Figs. 5 and 6 show the element distribution profiles for the initial monolayer Zr and Nb coatings, respectively. As can be seen from the element distribution profiles, there are no impurities in the coatings

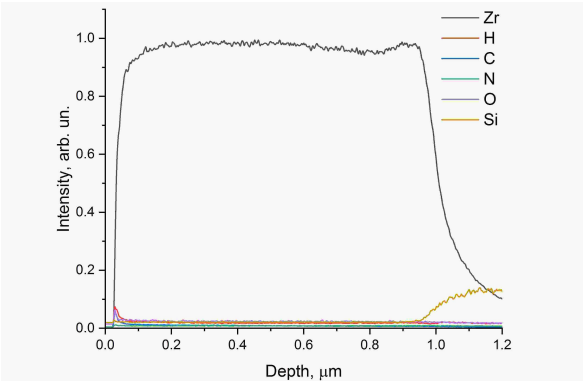

Fig. 5. Depth distribution of elements for the initial monolayer Zr coating.

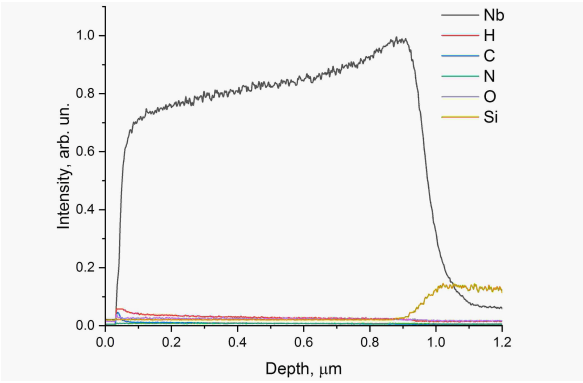

Fig. 6. Depth distribution of elements for the initial monolayer Nb coating.

Figs. 7 and 8 show the elemental distribution profiles for irradiated Zr and Nb monolayer coatings with a dose of $3.4 \cdot 10^{16}$ ions/cm^2. The hydrogen distribution profile in Zr and Nb coatings corresponds to SRIM calculations. A peak of hydrogen luminescence intensity in the near-surface region ~ 50–100 nm is observed.

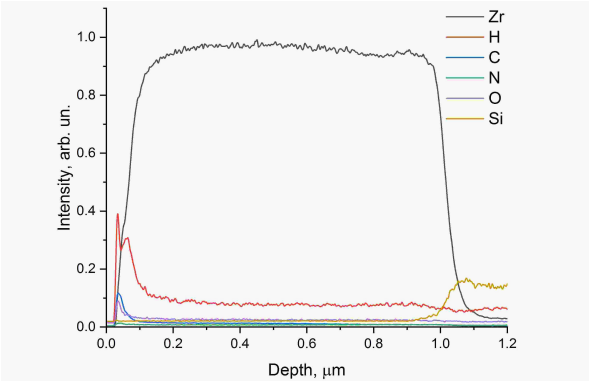

Fig 7. Depth distribution of elements for monolayer Zr coating irradiated by protons with dose $3.4 \cdot 10^{16}$ ions/cm^2.

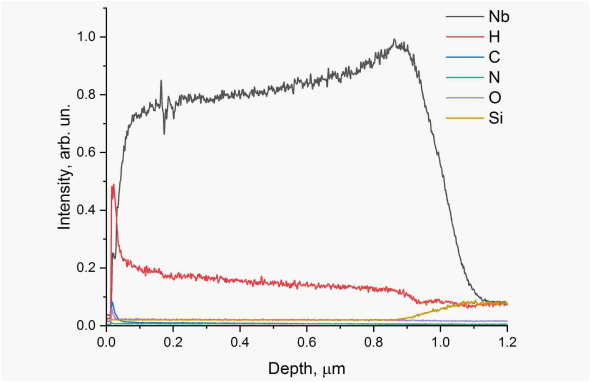

Fig. 8. Depth distribution of elements for monolayer Nb coating irradiated by protons with dose $3.4 \cdot 10^{16}$ ions/cm^2.

Figs. 9 and 10 show plots of dependence of *S* parameter on positron energy for monolayer coatings of Zr and Nb, respectively. The *S* parameter of the Zr monolayer at high dose rose above the initial value, which indicates the accumulation of defects above the initial level; at low dose irradiation, a decrease in the *S* parameter below the initial level is observed, which is due to irradiation annealing. No such tendency is observed for proton irradiation of Nb monolayer coatings. When the irradiation dose is increased, a decrease of the *S* parameter below the initial level is observed.

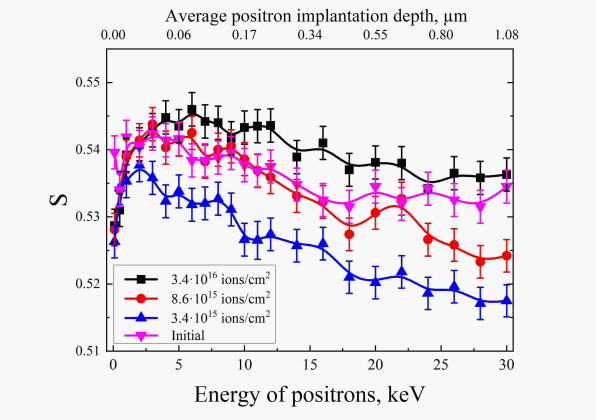

Fig. 9. Graph of the dependence of the *S*-parameter on the positron energy for a monolayer of Zr.

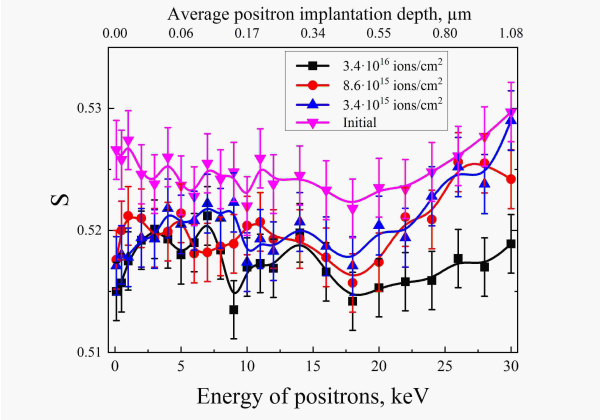

Fig. 10. Graph of the dependence of the *S*-parameter on the positron energy for a monolayer of Nb.

Figs. 11 and 12 show the S=f(W) dependence for monolayer coatings of Zr and Nb, respectively. From the curves of S=f(W) dependence one can conclude that only one type of defects prevails.

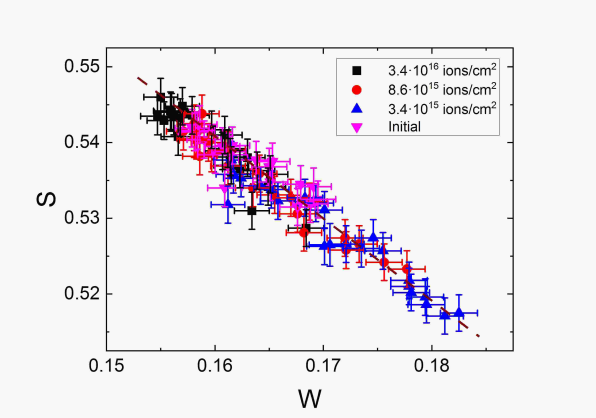

Fig 11. Graph of dependence $S = f(W)$ for monolayer Zr coating.

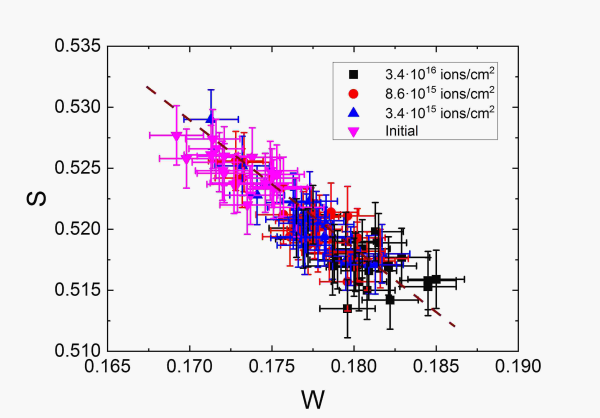

Fig. 12. Graph of dependence $S = f(W)$ for monolayer Nb coating.

4. Conclusions

The results of this work revealed that Nb is more prone to relax under proton irradiation than Zr. This effect is probably due to the presence of the Nb BCC structure, which has many more slip planes than the HCP structure of Zr. By analyzing the elemental distribution profile, it was obtained that hydrogen is located in the surface region of ~ 50-100 nm, which is in agreement with SRIM calculations. X-ray diffraction analysis shows that the FWHM value and interplanar spacing of Nb coating returns to the initial value at high dose. In Zr monolayer coating, a decrease in FWHM value and interplanar distance is observed, which is due to the increase in microstresses.

Acknowledgements

The work was funded by the Russian Science Foundation, research project No. 20-79-10343.

5. References

[1] N. Daghbouj, H. S. Sen, M. Callisti, M. Vronka, M. Karlik, J. Duchoň, J. Čech, V. Havránek, and T. Polcar, Revealing Nanoscale Strain Mechanisms in Ion-Irradiated Multilayers, *SSRN Electronic Journal*, 2021, doi: 10.2139/ssrn.3931600

[2] H. Li, D. Ma, H. Wang, D. Yun, Z. Hao, J. Deng, R. Zhang, and Z. Li, Microstructure and oxidation behavior of CrCN/TiSiCN nano-multilayer coatings on Zircaloy in high-temperature steam, Corrosion Science, vol. **211**, 110883, 2023, doi: 10.1016/j.corsci.2022.110883

[3] M. Callisti, S. Lozano-Perez, and T. Polcar, Structural and mechanical properties of γ-irradiated Zr/Nb multilayer nanocomposites, *Materials Letters*, vol. **163**, 138, 2016, doi: 10.1016/j.matlet.2015.10.057

[4] M. Callisti, M. Karlik, and T. Polcar, Competing mechanisms on the strength of ion-irradiated Zr/Nb nanoscale multilayers: Interface strength versus radiation hardening, *Scripta Materialia*, vol. **152**, 31, 2018, doi: 10.1016/j.scriptamat.2018.03.039

[5] B. Ham and X. Zhang, High strength Mg/Nb nanolayer composites, *Materials Science and Engineering: A*, vol. **528**, 2028, 2011, doi: 10.1016/j.msea.2010.10.101

[6] G. H. Yang, B. Zhao, Y. Gao, and F. Pan, Investigation of nanoindentation on Co/Mo multilayers by the continuous stiffness measurement technique, *Surface and Coatings Technology*, vol. **191**, 127, 2005, doi: 10.1016/j.surfcoat.2004.02.006

[7] R. Laptev, E. Stepanova, N. Pushilina, E. Kashkarov, D. Krotkevich, A. Lomygin, A. Sidorin, O. Orlov, and V. Uglov, The Microstructure of Zr/Nb Nanoscale Multilayer Coatings Irradiated with Helium Ions, *Coatings*, vol. **13**, 193, 2023, doi: 10.3390/coatings13010193

[8] R. Laptev, A. Lomygin, D. Krotkevich, M. Syrtanov, E. Kashkarov, Y. Bordulev, K. Siemek, and A. Kobets, Effect of Proton Irradiation on the Defect Evolution of Zr/Nb Nanoscale Multilayers, *Metals*, vol. **10**, 535, 2020, doi: 10.3390/met10040535

[9] R. Laptev, E. Stepanova, N. Pushilina, L. Svyatkin, D. Krotkevich, A. Lomygin, S. Ognev, K. Siemek, A. Doroshkevich, and V. Uglov, Distribution of Hydrogen and Defects in the Zr/Nb Nanoscale Multilayer Coatings after Proton Irradiation, *Materials*, vol. **15**, 3332, 2022, doi: 10.3390/ma15093332

[10] R. Laptev, L. Svyatkin, D. Krotkevich, E. Stepanova, N. Pushilina, A. Lomygin, S. Ognev, K. Siemek, and V. Uglov, First-Principles Calculations and Experimental Study of H^+-Irradiated Zr/Nb Nanoscale Multilayer System, *Metals*, vol. **11**, 627, 2021, doi: 10.3390/met11040627