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Positron annihilation analysis of nanosized metal coatings Zr/Nb after He^+ ion irradiation

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Abstract. New technologies for obtaining structural materials resistant to hydrogen and radiation damage are pressing problems of materials science. Hydrogen damage and radiation degradation are important factors limiting the fatigue life of structural materials. One promising alternative in the development of radiation-hydrogen resistant materials with improved physical and mechanical properties is the application of nanoscale metal systems (NMS). The present work is devoted to the study of the defect structure of Zr/Nb NMS with a thickness of separate layers of Zr and Nb of 100±10 nm after irradiation by He^+ ions with doses from $3\cdot10^{16}$ ions/cm^2 to $3\cdot10^{17}$ ions/cm^2 using positron annihilation spectroscopy and XRD analysis.

Keywords: nanoscale multilayer system; Zr/Nb; He^+ ions irradiation; positron annihilation spectroscopy; XRD

1. Introduction

Over the past four decades, a tremendous amount of research has been devoted to the synthesis, characterization, and application of nanoscale materials. This is partly due to continuous scientific and technological advances, which have made it possible to develop materials at the atomic level of precision [1, 2]. Interest in materials synthesized at the nanoscale level remains relevant because nanoscale components typically result in unique physical and chemical properties [3, 4]. Currently, the synthesis and application of thin films is one of the broadest areas of research in materials science.

Most of the investigated nanoscale metal systems (NMSs) contain two different alternating metal layers. Such bimetallic structures are classified as coherent, semi-coherent, or incoherent systems depending on the interfaces formed between the two components [5–9]. In coherent systems (also called superlattices), the two metallic components have the same type of crystal structure and a small lattice mismatch (generally on the order of a few percent) [10, 11]. In semi-coherent systems, the crystal structure of the components is the same, but the lattice mismatch is larger [11]. Thus, misfit dislocations (disordered dislocations) are formed to compensate the mismatch. Misaligned systems are formed from materials with different crystal structures, which leads to greater lattice mismatch [12].

Positron annihilation spectroscopy (PAS) [7–9] is an excellent tool for characterizing defects formed in the crystal lattice of materials. The theory of positron annihilation in solids [13] is well developed, particularly for metals. Annihilation characteristics can be determined by first-principles calculations and compared directly with experimental ones. Consequently, in this study, the main method for controlling the defective structure of the material is the methods of positron annihilation spectroscopy.

2. Materials and methods

The preparation of samples of nanoscale metallic Zr/Nb NMSs layers was carried out by magnetron sputtering. The multilayer coatings were obtained on a specialized machine developed at the Weinberg Research Center, TPU (Tomsk, Russia). The monocrystalline silicon substrates with orientation (111) were fixed inside an experimental chamber with an axial rotation system. The residual pressure in the chamber was 0.002 Pa, and the coatings were applied in an Ar atmosphere at a working pressure of 0.3 Pa. Before coating, the substrates were cleaned with Ar ions for 30 min at 2.5 kV and 2.5 mA ion current. The total coating thickness for all samples was 1.1±0.1 μm [7–9].

The irradiation of Zr/Nb NMSs with helium ions with energy 25 keV was carried out using a plasma ion source with a non-pouring cathode "PION-1M". The ion current density during irradiation was 0.23 mA/cm^2 with a corresponding ion flux of $1.44 \cdot 10^{15}$ ions/cm^2·s. The irradiation time was chosen to provide a dose of $3 \cdot 10^{16}$ and $3 \cdot 10^{17}$ ions/cm^2. During irradiation, the temperature of the samples was monitored with a pyrometer and did not exceed 200 °C. The depth of helium implantation was determined from the simulation results in the SRIM-2013 software package. It was found that at the ion energy of 25 keV the Bragg peak falls at a depth of ~100 nm.

X-ray diffractometer XRD-7000S Shimadzu, Japan, using Bregg-Brentano geometry, angles 20–75°, scanning speed 5.0 deg/min [14].

The analysis of structural defects before and after helium ion irradiation was performed on a specialized SPONSOR (The Slow-Positron System of Rossendorf) HZDR (Dresden, Germany) using the Doppler annihilation line broadening analysis (DB) with variable energy positron beams with a 4 mm diameter monoenergetic positron beam. The range of energies of the implanted positrons was from 0.30 eV to 36 keV. Annihilation γ-rays were recorded with a particularly pure germanium (HpGe) detector with an energy resolution of 1.09±0.01 keV, interpolated along the 511 keV line. The resulting DB 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 the defects or their concentration. The W parameter is responsible for the chemical environment of the annihilation site. The dependence $S = f(W)$ was also analyzed, with the help of which it is possible to identify the type and number of defects of different kinds. Most applications of positron beams require knowledge of the implantation characteristics for an appropriate interpretation of the experimental data. It is generally recognized that the positron implantation profile for a monoenergetic positron beam in a semi-infinite solid can be expressed by the Gaussian derivative, which is described in general terms by the so-called Makhovian profile [15].

3. Result and discussion

3.1. SRIM Calculations

The SRIM-2013 [16] calculation of He^+ irradiation was performed on Zr/Nb NMSs with individual layer thicknesses of 100±10 nm and a total thickness of 1 μm (Fig.1). The simulation was carried out using ion distribution and a quick calculation of damage mode with perpendicular 25 keV He^+ beam, where the total number of incident particles was $5 \cdot 10^5$. According to [17] the threshold displacement energy was 40 eV for Zr and 78 eV for Nb.

The simulation shows that the chosen energy provided He^+ implantation with deposition peak at depth of approximately 100 nm below the surface of the coating According to the simulation results, fluence $3 \cdot 10^{16}$ ions/cm^2 corresponds to 0.6 displacements per atom and 0.053 at.% He concentration, fluence $3 \cdot 10^{17}$ ions/cm^2 corresponds to 6 displacements per atom and 0.526 at.% He concentration. Due to the difference in stopping power of Zr and Nb, there were dips and peaks on the graph that corresponded to Zr and Nb layers.

3.2. XRD Structure Analysis

The XRD study carried out for the initial and He-irradiated Zr/Nb NMSs showed that NMS have Zr (002) and Nb (110) orientation. In the case of Zr/Nb NMSs with an individual layer thickness of 100±10 nm (Fig.2), the diffraction peaks shift to a smaller angle 2θ (for Zr) and to a larger angle 2θ (for Nb) after irradiation, which indicates the formation of mechanical stresses in layers.

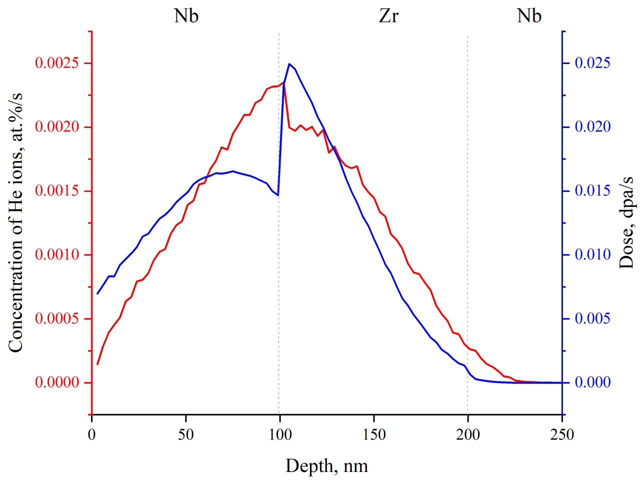

Fig.1. Displacement-per-atom rate (dpa/s) and He^+ implantion rate at 25 keV according to SRIM simulation for Zr/Nb NMS with an individual layer thickness of 100±10 nm.

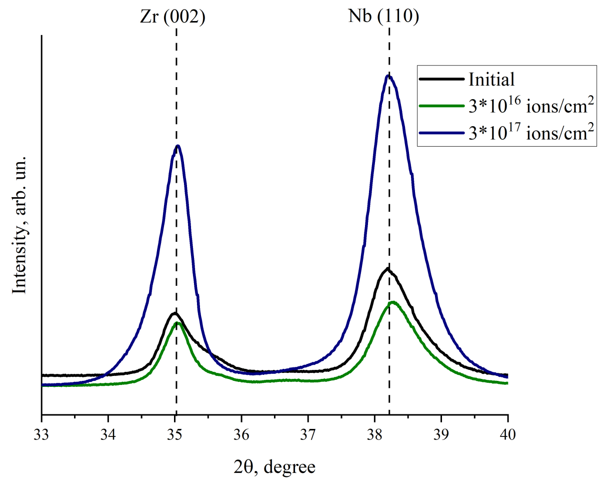

Fig.2. XRD patterns for the initial and He^+ ions-irradiated Zr/Nb MNS with an individual layer thickness of 100±10 nm.

3.3. Characteristics of positron annihilation in Zr/Nb MNSs after irradiation with He^+ ions

Fig.3, Fig.4 shows the dependence of the *S*, *W* parameter on the positron energy for Zr/Nb NMSs with an average layer thickness of 100±10 nm and an irradiation dose range from $3\cdot10^{16}$ to $3\cdot10^{17}$ ions/cm^2.

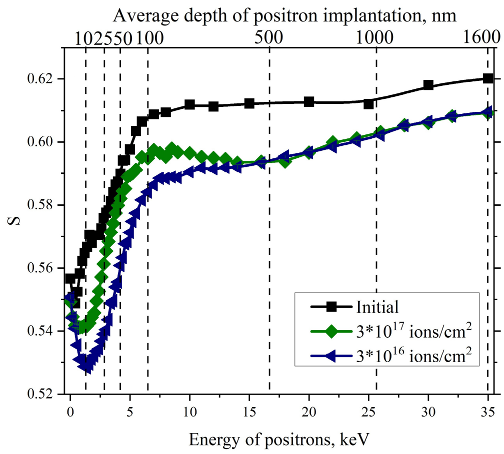

Fig.3. Dependence of the S parameter on the positron energy of the Zr/Nb NMSs with the thickness of individual layers of 100±10 nm and the range of irradiation doses from $3\cdot10^{16}$ to $3\cdot10^{17}$ ions/cm^2.

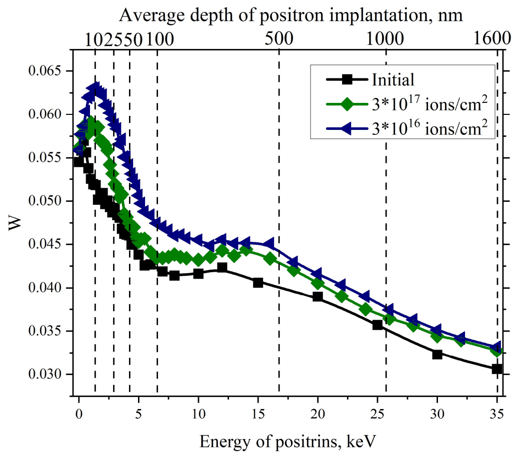

Fig.4. Dependence of the W parameter on the positron energy of the Zr/Nb NMSs with the thickness of individual layers of 100±10 nm and the range of irradiation doses from $3\cdot10^{16}$ to $3\cdot10^{17}$ ions/cm^2.

The irradiation by He^+ ions of NMSs Zr/Nb with the thickness of individual layers of 100±10 nm independently of the dose does not lead to an increase in the parameter S and a decrease in W relative to the initial value (Fig.3, Fig.4). This fact testifies to the absence of excessive accumulation of radiating defects, the profiles of these parameters distribution on depth do not differ essentially, probably, because of features of formation of similar helium-vacancy complexes in layer volume and near to interfaces. After 20 keV, the *S* parameter increases and the *W* parameter decreases, which indicates the predominant positron annihilation in the single-crystal silicon substrate. Fig.5 shows the dependence of the *S* parameter on the *W* parameter of a Zr/Nb NMSs with a thickness of individual layers of 100±10 nm and a range of irradiation doses from $3 \cdot 10^{16}$ to $3 \cdot 10^{17}$ ions/cm^2.

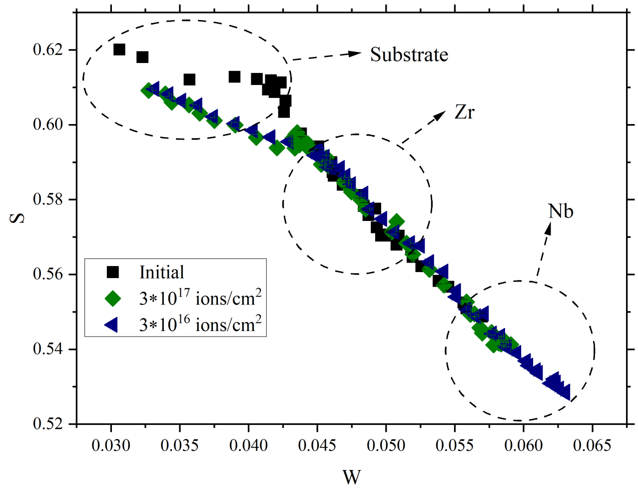

Fig.5. Plot of the dependence of the S parameter on the W parameter for Zr/Nb NMCs with an individual layer thickness of 100±10 nm and an irradiation dose range from $3 \cdot 10^{16}$ to $3 \cdot 10^{17}$ ions/cm^2.

As can be seen from Fig.5, the graph of the dependence $S = f(W)$ consists of 2 curves with different slope angles, this is due to the annihilation of positrons in the substrate, annihilating positrons in the substrate change the slope of the curve.

4. Conclusion

A layer-by-layer analysis of positron annihilation in Zr/Nb NMCs shows that increasing the irradiation dose by He^+ ions leads to the formation of stable radiation defects. Once the energy reaches 20 keV, the probability of positron annihilation in the monocrystalline silicon substrate increases. Based on SRIM modeling, there is no accumulation of defects in the Bragg peak region (100 nm) and no change in structure after irradiation, as demonstrated by XRD analysis

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