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In-situ XRD study at linear heating in vacuum of nanoscale multilayer Zr/Nb coatings

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Abstract. This work presents the results of thermal stability of nanoscale multilayer coatings based on Zr/Nb. In situ X-ray diffractometry was used for the studies. The thermal stability was investigated over a large temperature range from 100 to 900 °C. Because of the studies, it was revealed that when the temperature reached 440–480 °C, the coating delamination from the substrate occurred. This effect is due to the different thermal characteristics of the silicon substrate and the Zr/Nb coating. At temperatures of 100 and 300 °C, the layered structure of the coatings was preserved, which is confirmed by the data from optical emission spectrometry of glow discharge.

Keywords: nanoscale multilayer coating, Zr/Nb, in-situ X-ray diffraction, glow discharge optical emission spectrometry.

1. Introduction

Nuclear energy systems that are advanced and modern depend heavily on structural materials that can tolerate high radiation doses [1, 2]. Structural materials exposed to radiation generate a great deal of interstitial atoms and vacancies, which aggregate to create dislocation loops, stacking fault tetrahedra, or nanovoids. The formation of swelling, hardening, amorphization, and embrittlement is facilitated by these fault agglomerates and ultimately results in faster material deterioration under irradiation [3–5]. The systems with hexagonal-cubic (hcp/bcc and hcp/fcc) crystal lattices have the structural difference. Furthermore, because hcp/bcc systems have a high crystal lattice discrepancy, they have a great deal of potential for making composites that are resistant to radiation. According to recent research [6–11], the significant disparity enables the incoherent and semi-coherent interfaces of hcp/bcc systems to function as an efficient sink for radiation defects and a barrier to dislocation propagation during deformation. Different sink efficiencies are expected for incoherent and semi-coherent surfaces with unique crystallographic orientations, compositions, and structures. In particular, there is active research being done on Zr/Nb nanoscale multilayer coatings (NMCs) radiation resistance. Studies on the effects of Si^+ [10], C^+ [12], Cu^+ [13], He^+ [14] and H^+ [15] ions on NMC Zr/Nb irradiation reveal that these nanocomposites are also very radiation resistant.

However, there is not enough information about the structural stability of Zr/Nb NMCs at high temperatures. Irradiation with various ions can cause heating to high temperatures. Hence, the aim of this work is to investigate the thermal stability of Zr/Nb NMCs under linear heating in vacuum using in-situ X-ray diffractometry.

2. Materials and methods

Nanoscale multilayer coatings (NMCs) were deposited by magnetron sputtering, individual layer thickness was 100 nm, and total coating thickness was 1.1±0.2 µm.

An in-situ diffraction study was carried out using a high-temperature chamber HTK 2000N (Anton Paar, Austria) on a diffractometer XRD-7000S (Shimadzu, Japan). The samples were heated by resistive method; a platinum plate was used as a heater. The study was carried out under vacuum conditions 10^{-3} Pa. Heating was performed linearly up to 900 °C with a step of 20 °C. Imaging was performed in the range of 30.4–47.5° using a high-speed 1280-channel OneSight detector. The exposure time was 1 min.

Isochronous annealing under vacuum conditions of Zr/Nb NMCs with a thickness of individual layers of 100 nm was carried out for 1 h at temperatures of 100, 300, 600 and 900 °C in an induction furnace. The heating rate was 1 °C/min. 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 10–90°, scanning speed 5.0 deg/min. The distribution of elements before and after heating was analysed by glow discharge optical emission spectrometry (GD–OES) on a GD-Profiler 2 spectrometer (Horiba, Japan).

2. Results and discussions

An in situ diffraction study of Zr/Nb NMCs with an individual layer thickness of 100 nm showed that no intermetallic compounds or other crystalline phases are formed in the coating during linear heating in vacuum to a temperature of 900 °C. The diffraction reflections of Zr(002) and Nb(110) remain well distinguishable throughout the heating time, as shown in Fig. 1.

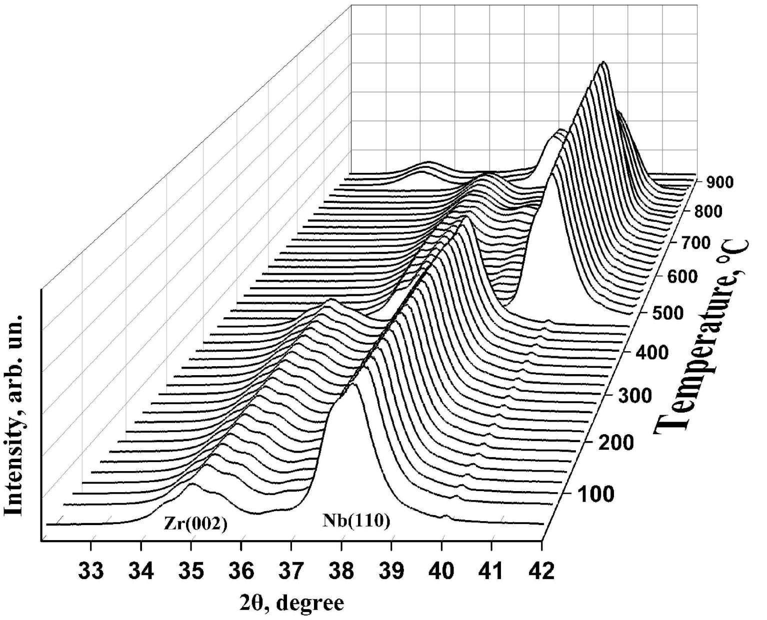

Fig. 1. Diffractogram of Zr/Nb NMC sample with individual layers thickness of 100 nm obtained by linear heating in vacuum.

However, during the heating process, in the temperature range of 440–480 °C, a simultaneous sharp shift of the diffraction reflections towards higher angles by more than 2° is observed. This shift is associated with delamination of the coatings from the substrate, which is confirmed by visual inspection. The effect of delamination at high-temperature exposure is related to the difference of thermal characteristics for all components (Zr, Nb, Si) of the coating-substrate system. Isochronous vacuum annealing in vacuum revealed that heating up to 100 °C in Zr/Nb NMCs is not accompanied by structural changes (Fig. 2).

Increasing the annealing temperature to 300 °C leads to a shift of the Nb(110) reflex towards larger angles, while the Zr(002) reflex shifts towards smaller angles, which may indicate stress relaxation in the Zr and Nb layers. When the temperature of 600 °C was reached, the presence of areas of delamination of the coating from the substrate was noted, which affects the shape of the reflexes. For the annealing temperature of 900 °C it was not possible to carry out a diffraction study due to the complete detachment of the coating from the substrate. According to GD–OES data, the distribution of elements in Zr/Nb100 NMCs after vacuum isochronous annealing up to 300 °C does not change significantly (Fig. 3 and 4). Annealing at temperatures above 600 °C leads to delamination of the coating from the substrate, which makes it impossible to analyses by the GD–OES method.

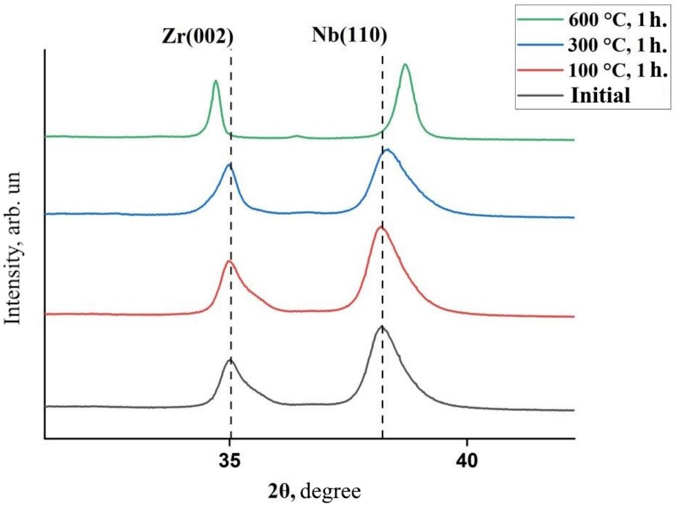

Fig. 2. Diffractograms of initial and annealed for 1 hour samples of Zr/Nb NMCs with thickness of individual layers 100 nm.

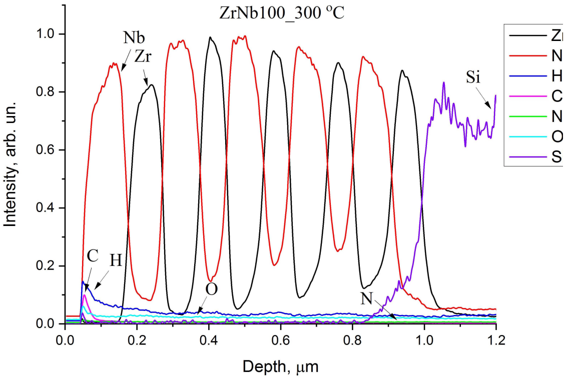

Fig. 3. Distribution of Zr/Nb NMC layers with individual layer thickness of 100 nm after isochronous annealing in vacuum for 1 hour at 300 °C.

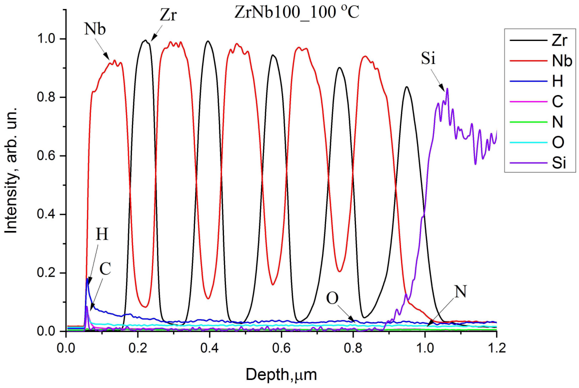

Fig. 4. Distribution of Zr/Nb NMC layers with individual layer thickness of 100 nm after isochronous annealing in vacuum for 1 hour at 100 °C.

4. Conclusion

The in-situ diffraction study showed the stability of the phase composition of Zr\Nb NMCs when heated up to 900 °C, no additional phases are detected. In the temperature range 440–480 °C, a simultaneous sharp shift (> 2°) of diffraction reflexes towards higher angles is observed due to the delamination of the coating from the substrate. Analysis of the results of X-ray diffraction analysis and GD–OES at isochronous vacuum annealing showed that heating up to 100 °C has no effect on the structure and composition of the coating, the layers are not mixed, and the value of microstresses is at the initial level. At increase of annealing temperature up to 300 °C there is a multidirectional shift of Nb(110) and Zr(002) reflexes that testify to the process of stress relaxation in monolayers. Increase of the annealing temperature up to 900 °C is accompanied by delamination of the coating from the substrate and destruction of the composite.

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5. References

[1] S.J. Zinkle and J.T. Busby, Structural materials for fission & fusion energy, *Materials Today*, vol. **12**(11), 12, 2009; doi: 10.1016/s1369-7021(09)70294-9

[2] G.R. Odette and D.T. Hoelzer, Irradiation-tolerant nanostructured ferritic alloys: Transforming helium from a liability to an asset, *JOM*, vol. **62**(9), 84, 2010; doi: 10.1007/s11837-010-0144-1

[3] M. Victoria, et al., The microstructure and associated tensile properties of irradiated fcc and bcc metals, *Journal of Nuclear Materials*, vol. **276**(1–3), 114, 2000; doi: 10.1016/s0022-3115(99)00203-2

[4] S.J. Zinkle and N.M. Ghoniem, Operating temperature windows for fusion reactor structural materials, *Fusion Engineering and Design*, vol. **51–52**, 55, 2000; doi: 10.1016/s0920-3796(00)00320-3

[5] J.F. Stubbins, Void swelling and radiation-induced phase transformation in high purity Fe-Ni-Cr alloys, *Journal of Nuclear Materials*, vol. **141–143**, 748, 1986; doi: 10.1016/0022-3115(86)90085-1

[6] F. Wang and H.R. Gong, First principles study of various Zr–H phases with low H concentrations, *International Journal of Hydrogen Energy*, vol. **37**(17), 12393, 2012; doi: 10.1016/j.ijhydene.2012.06.037

[7] D.C. Ford, L.D. Cooley, and D.N. Seidman, First-principles calculations of niobium hydride formation in superconducting radio-frequency cavities, *Superconductor Science and Technology*, vol. **26**(9), 095002, Jul. 2013; doi: 10.1088/0953-2048/26/9/095002

[8] H.S. Sen and T. Polcar, Vacancy-interface-helium interaction in Zr-Nb multi-layer system: A first-principles study, *Journal of Nuclear Materials*, vol. **518**, 11, 2019; doi: 10.1016/j.jnucmat.2019.02.030

[9] 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

[10] 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

[11] M.A. Monclús, M. Callisti, T. Polcar, L.W. Yang, J. Llorca, and J.M. Molina-Aldareguía, Selective oxidation-induced strengthening of Zr/Nb nanoscale multilayers, *Acta Materialia*, vol. **122**, 1, 2017; doi: 10.1016/j.actamat.2016.09.021

[12] M. Karlík, N. Daghbouj, J. Lorinčík, T. Polcar, M. Callisti, and V. Havránek, Ion implantation into ZrNb nanometric multilayers, *Acta Crystallographica Section A Foundations and Advances*, vol. **77**(a2), C839, 2021; doi: 10.1107/s0108767321088590

[13] N. Daghbouj, M. Callisti, H.S. Sen, M. Karlik, J. Čech, M. Vronka, V. Havránek, J. Čapek, P. Minárik, P. Bábor, and T. Polcar, Interphase boundary layer-dominated strain mechanisms in Cu+ implanted Zr-Nb nanoscale multilayers, *Acta Materialia*, vol. **202**, 317, 2021; doi: 10.1016/j.actamat.2020.10.072

[14] 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**(1), 193, 2023; doi: 10.3390/coatings13010193

[15] 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**(4), 535, 2020; doi: 10.3390/met10040535