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# CARBURIZING OF Zr-1Nb ALLOY IN A CARBON-CONTAINING GAS ENVIRONMENT: STRUCTURE AND PROPERTIES OF THE MODIFIED SURFACE LAYER

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This study investigates the effect of carbon saturation in a controlled gas environment on the structure and microhardness of the surface layers of Zr-1Nb alloy. Durometric, X-ray diffraction and metallographic analyses provide data necessary for quality control and prediction of the microhardness gradient. The results provide data for optimization processing parameters to achieve reliable surface hardening and ensure high operational characteristics.

## INTRODUCTION

The industrial development of zirconium alloys is closely associated with the growth of high-tech industries such as nuclear power, aerospace, and chemical engineering [1–5]. Zirconium-based alloys offer significant advantages over steel in aerospace, chemical, medical, and other applications. In particular, they are lighter, more corrosion-resistant, and possess high specific strength [6–9]. At the same time, several factors strongly influence the functional properties of zirconium-based alloys. One of the most important is their high reactivity with environmental elements – particularly oxygen, nitrogen, and carbon – which readily form solid solutions or compounds such as oxides, nitrides, and carbides [10–14].

The condition of the near-surface layer plays a key role in ensuring the long-term performance of products. For this reason, surface engineering has become an effective approach to broadening the functional properties of materials, with thermochemical treatment being one of the primary methods of surface modification [15–17]. Owing to zirconium's high affinity for interstitial elements (oxygen, nitrogen, carbon), thermochemical treatment (TCT) is considered an efficient means of tailoring the structure and properties of near-surface layers [18–20].

Thermochemical treatment, which produces hardened surface layers of controlled composition, has proven effective in improving the performance of titanium and its alloys [21, 22]. Since zirconium alloys share structural and property similarities with titanium alloys, studies on thin-walled zirconium specimens have likewise demonstrated enhanced fatigue life [23].

Nevertheless, there remains limited information on the effect of surface modification of zirconium alloys through diffusion saturation with interstitial elements from carbon-containing gaseous environments. This gap highlights the need for further investigation.

## MATERIALS, SAMPLES AND RESEARCH METHODS

The material used in this study was the Zr-1Nb alloy with the following composition: Zr – 98.97 wt.% and Nb – 1.03 wt.%. Diffusion saturation with carbon was performed using a vacuum annealing installation with a controlled gas environment, developed and manufactured at the Karpenko Physico-Mechanical Institute of the NAS of Ukraine. The saturating medium was a gas mixture of argon and propane, with a propane volume fraction of 16.7%. Saturation was carried out for 1 to 10 h at temperatures of 650, 750, and 850 °C.

The microstructure of the alloys after different TCT regimes was revealed by chemical etching with a reagent composed of 1 part HF, 1 part $H_2NO_3$, and 3 parts glycerol. For surface illumination, a reagent consisting of 5 ml HF and 95 ml $H_2NO_3$ was used.

The phase composition of the surface layers was determined by X-ray diffraction (XRD) analysis on a DRON-3.0 diffractometer using monochromatic CuKα radiation and Bragg-Brentano focusing geometry. Metallographic examinations of the samples before and after surface layer modification with interstitial elements were performed using optical microscopes ("Epiquant" and "Neophot-2").

The surface microhardness and its cross-distribution in the surface layer of samples were determined using a PMT-3M durometer with an indenter load of 0.49 N.

To measure the surface roughness, a measuring and computing complex was used: a standard profilometer model 176021, corresponding to type II, accuracy level 2 according to GOST 19300-86; a personal computer; a communication interface between the profilometer and the computer; a package of application programs.

## RESULTS AND DISCUSSION

Durometric and profilometric studies revealed the surface microhardness and roughness, and also thickness of the hardened near-surface layer of the Zr-1Nb alloy after carburizing (Table 1).

Table 1

Characteristics of the surface layer of carburized Zr-1Nb alloy samples

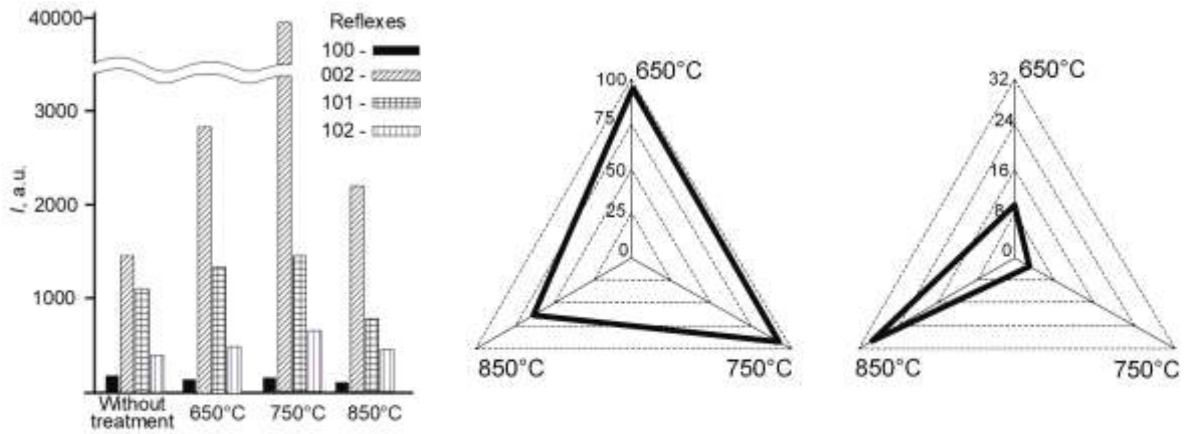
| Carburizing temperature *T*, °C | Surface microhardness $HV_{0.49}$ and roughness $R_a$, size of modified layer *l* | Duration of carburizing, h | | |
|---|---|---|---|---|
| | | 1 | 5 | 10 |
| 650 | $HV_{0.49}$ | 230±10 | 250±10 | 355±15 |
| | $R_a$, µm | 0.031 | 0.432 | 0.337 |
| | *l*, µm | – | – | 18...22 |
| 750 | $HV_{0.49}$ | 250±20 | 200±10 | 225±10 |
| | $R_a$, µm | 0.420 | 0.180 | 0.370 |
| | *l*, µm | – | – | 53...58 |
| 850 | $HV_{0.49}$ | 260±15 | 280±10 | 520±30 |
| | $R_a$, µm | 0.439 | 0.406 | 0.428 |
| | *l*, µm | – | – | 125...135 |

The results show that with increasing temperature and duration of treatment, the surface microhardness, roughness, and thickness of the modified layer all increase. This is explained by the higher reactivity and diffusion mobility of carbon in zirconium at elevated temperatures, as well as by the longer diffusion time, which expands the strengthened zone.

Table 2

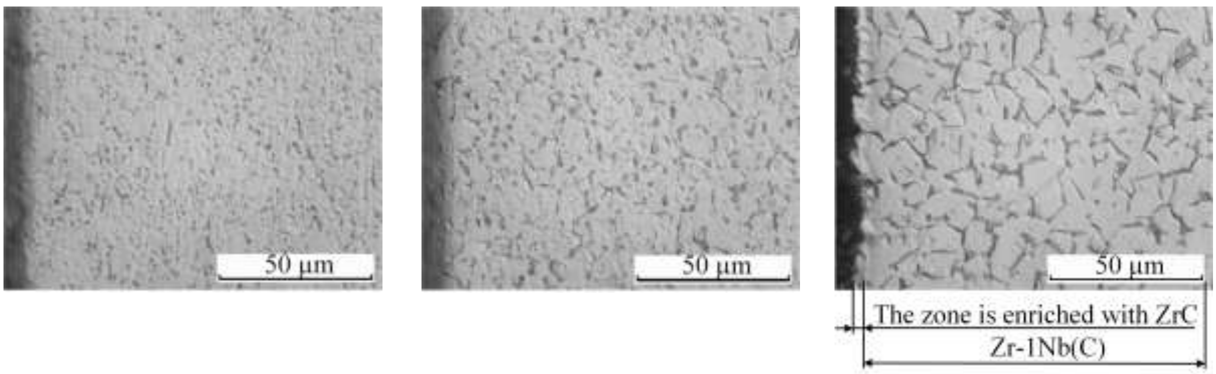
Crystal lattice parameters of Zr-1Nb alloy phases after carburizing for 10 h

| Treatment | Phases | | |
|---|---|---|---|
| | α-Zr | | ZrC |
| | *a*, nm | *c*, nm | *a*, nm |
| Etalon | 0.3203 | 0.5147 | 0.4693 |
| Without treatment | 0.3213 | 0.5126 | – |
| 650 °C | 0.3232 | 0.5149 | 0.4656 |
| 750 °C | 0.3230 | 0.5145 | – |
| 850 °C | 0.3230 | 0.5147 | 0.4671 |




*a* *b* *c*

*Fig. 1. Intensity and volume fraction of phases formed on the surface of Zr-1Nb alloy after carburizing under different regimes: a – reflection intensity of phase α-Zr; b – α-Zr volume fraction; c – ZrC volume fraction*




*a* *b* *c*

*Fig. 2. Microstructure of the Zr-1Nb near-surface layer after diffusion saturation with carbon at 650 (a); 750 (b), and 850 °C (c) for 10 h*

The lattice parameters of the phases formed on the alloy surface also changed after carburizing (Table 2).

XRD analysis (Fig. 1) (diffractograms were obtained from the surface of the samples) demonstrated that increasing the temperature and duration of carburizing decreased the intensity of α-Zr reflections, while simultaneously increasing the intensity of ZrC reflections. This trend is associated with the growth of the ZrC carbide layer, which enhances its shielding effect on the underlying α-Zr sublayer.

Microstructural analysis (Fig. 2) further confirmed these changes. With increasing temperature and duration of treatment, the ZrC carbide layer became more pronounced, while the α-Zr phase was progressively shielded.

## CONCLUSIONS

1. It was established that increasing the temperature and duration of diffusion saturation in a carbon-containing gas environment enhances the intensity of zirconium carbide reflections, which is explained by the growth of the ZrC carbide layer.

2. Carburizing at 650…850 °C for up to 10 h increases both the surface microhardness ($HV_{0.49}$) from 350 to 520 and the thickness of the modified layer (from 20 to 130 μm).

## REFERENCES


1. J.H. Schemel. *Zirconium Alloy Fuel Clad Tubing*: Engineering Guide, 1st Edition. Sandvik Special Metals Corporation. Washington, USA, 1989, 112 p.

2. Y.W. Chen, J. Moussi, J.L. Drury, and J.C. Wataha. Zirconia in biomedical applications // *Expert Review of Medical Devices*. 2016, v. 13(10), p. 945-963.

3. R.B. Adamson, P. Rudling. Properties of zirconium alloys and their applications in light water reactors (LWRs) // *Materials ageing and degradation in light water reactors* / Ed. K.L. Murty. Woodhead Publishing Ltd., 2013, p. 151-245.

4. A.S. Zaymovsky, A.V. Nikulina, N.G. Reshetnikov. *Zirconium alloys in nuclear technology*. M.: “Energoatomizdat”, 1994, 453 p.

5. W.T. Elwell, D.F. Wood. *Analysis of the New Metals Titanium, Zirconium, Hafnium, Niobium, Tantalum, Tungsten and Their Alloys.* Pergamon Press, 2014, 298 p.

6. R.B. Adamson and P. Rudling. Properties of zirconium alloys and their applications in light water reactors (LWRs) // *Materials Ageing and Degradation in Light Water Reactors*. 2013, p. 151-245.

7. R. Tewari, Karri Krishna V. Mani, S. Neogy, C. Lemaignan. Zirconium and its Alloys: Properties and Characteristics // *Comprehensive Nuclear Materials*. 2020, v. 7, p. 284-302; https://doi.org/10.1016/B978-0-08-056033-5.00015-X

8. W. Qin. Improvement and Application of Zirconium Alloys // *Metals.* 2018, v. 8, p. 794; doi:10.3390/met8100794

9, R.Q. Zhang, B.B. Jiang, C. Pang, X. Dai, Y.D. Sun, W. Liao, Q. Wang, C. Dong. New low-Sn Zr cladding alloys with excellent autoclave corrosion resistance and high strength // *Metals*. 2017, v. 7, p. 144.

10. J.L. Vandegrift, P.M. Price, J.-P. Stroud, C.J. Parga, I.J. Van Rooyen, B.J. Jaques, and D.P. Butt. Oxidation behavior of Zirconium, Zircaloy-3, Zircaloy-4, Zr-1Nb, and Zr-2.5Nb in air and oxygen // *Nuclear Materials and Energy*. 2019, v. 20, p. 100692.

11. V. Trush. Effect of oxidation and nitriding on the properties of zirconium alloys // *Eastern-European Journal of Enterprise Technologies.* 2017, N 2(11-86), p. 34-42;
https://doi.org/10.15587/1729-4061.2017.97446

12. V. Trush, P. Maruschak, M. Student, S. Lavrys, A. Luk’yanenko. Effect of heat treatment in oxygencontaining medium on fatigue life of zirconium alloy. Strojnícky časopis *// Journal of Mechanical Engineering*. 2022, v. 72, N 2, p. 211-218;
https://doi.org 10.2478/scjme-2022-0030

13. S. Lavrys, I. Pohrelyuk, O. Tkachuk, J. Padgurskas, V. Trush, and R. Proskurnyak. Comparison of friction behaviour of titanium grade 2 after non-contact boriding in oxygencontaining medium with gas nitriding // *Coatings*. 2023, v. 13, Article number 282; https://doi.org/10.3390/coatings13020282

14. G. Boureau, P. Gerdanian. High temperature thermodynamics of solutions of oxygen in zirconium and hafnium // *J. Phys. Chem. Solids*. 1984. v. 45, N 2, p. 141-145.

15. V.S. Trush, A.E. Stetsko, V.M. Korendiy, R.Ya. Predko, V.M. Fedirko, K.V. Trush, Ya.Ya. Sirak. Structure of the complex chromium-based coating formed on steel 45 // *Materials Science*. 2025, v. 61; https://doi.org/10.1007/s11003-025-00965-0

16. M. Király, Z. Hózer, M. Horváth, T. Novotny, E. Perez-Feró, N. Vér. Impact of thermal and chemical treatment on the mechanical properties of E110 and E110G cladding tubes // *Nuclear Engineering and Technology*. 2019, v. 51, issue 2, p. 518-525;
https://doi.org/10.1016/j.net.2018.11.002

17. N.A. Azarenkov, L.A. Bulavin, I.I. Zalyubovsky, V.G. Kirichenko, I.M. Neklyudov, B.A. Shilyaev. *Nuclear energy*. Chapter 2. *Nuclear power*: Textbook. V.N. Karazin KhNU, Kharkiv, 2012, 480 p.

18. V.S. Trush, N.N. Pylypenko, P.I. Stoev, V.M. Fedirko, M.A. Tikhonovsky, I.M. Pohrelyuk, A.G. Luk’yanenko, S.M. Lavrys, K.V. Trush, V.M. Korendiy, A.E. Stetsko, R.Ya. Predko, T.M. Kravchyshyn, Ya.Ya. Sirak. Effect of diffuse nitrogen saturation on the structure and microhardness of the surface layer of Zr-1Nb // *Problems of Atomic Science and Technology*. 2025, N 2, p. 27-31; https://doi.org /10.46813/2025-156-027

19. M. Reif, F. Scherm, M.C. Galetz, and U. Glatzel. An Enhanced Three-Step Oxidation Process to Improve Oxide Adhesion on Zirconium Alloys *// Oxidation of Metals*. 2014, v. 82(1-2), p. 99-112.

20. D. You, S. Ganorkar, M. Joo, D. Park, S. Kim, K. Kang, and D. Lee. Ab initio study of H, B, C, N, O, and self-interstitial atoms in hcp-Zr // *Journal of Alloys and Compounds*. 2019, v. 787, p. 631-637.

21. V.N. Fedirko, A.G. Luk’yanenko, V.S. Trush. Solid-Solution Hardening of the Surface Layer of Titanium Alloys. Part 1. Effect on Mechanical Properties // *Metal Science and Heat Treatment*. 2014, v. 56, issue 7, p. 368-373;

https://doi.org /10.1007/s11041-014-9764-3

22. R.V. Proskurnyak, O.V. Tkachuk, M.M. Student, J. Padgurskas. Structure and mechanical properties of hydroxyapatite coating deposited on nitrogen-modified titanium surface // *Materials Science*. 2025, v. 60(5), p. 634-639; https://doi.org/10.1007/s11003-025-00930-x

23. V.S. Trush, V.N. Voyevodin, P.I. Stoev, V.N. Fedirko, A.G. Luk'yanenko, V.A. Panov, M.A. Tikhonovsky. Properties of tubes from Zr-1% Nb alloy after thermochemical treatment and hydrogenation // *Problems of Atomic Science and Technology*. 2021, N 5(135), p. 84-87; https://doi.org /10.46813/2021-135-084

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## НАВУГЛЕЦЮВАННЯ СПЛАВУ Zr-1Nb У ВУГЛЕЦЕВМІСНОМУ ГАЗОВОМУ СЕРЕДОВИЩІ: СТРУКТУРА ТА ВЛАСТИВОСТІ МОДИФІКОВАНОГО ПОВЕРХНЕВОГО ШАРУ

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Наведено дані щодо впливу дифузійного навуглецювання на структуру, фазовий вміст та мікротвердість поверхневого шару сплаву Zr-1Nb. Показано, що з підвищенням температури та тривалості дифузійного насичення вуглецем інтенсивність рефлексів α-Zr зменшується, а інтенсивність рефлексів ZrC зростає. Таке явище пояснено збільшенням товщини шару карбіду ZrC, через що зростає його екранувальний ефект для підшару α-Zr. Показано вплив температурно-часових параметрів насичення на зміну товщини зміцненого шару та мікротвердість поверхні. Зроблено висновок, що застосування дифузійного насичення вуглецем з газового середовища є перспективним методом впливу на мікротвердість та структуру сплаву Zr-1Nb.