Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2022, **32**, 498–500

Mendeleev Communications

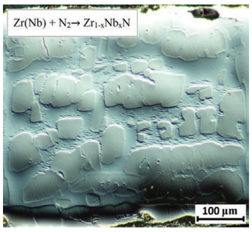
Compositional evolution of zirconium and niobium in the process of high-temperature nitridation of Zr–Nb alloys

Ivan A. Kovalev,*[a] German P. Kochanov,[a] Leonid O. L'vov,[a,b] Sergey V. Shevtsov,[a] Sergey V. Kannikin,[c] Alexey N. Sitnikov,[a] Svetlana S. Strel'nikova,[a] Andrey S. Chernyavskii[a] and Konstantin A. Solntsev[a]

[a] *A. A. Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences, 119991 Moscow, Russian Federation. E-mail: vankovalskij@mail.ru*
[b] *Department of Materials Science, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation*
[c] *Voronezh State University, 394018 Voronezh, Russian Federation*

DOI: 10.1016/j.mencom.2022.07.022

The mechanism of formation of zirconium nitride-based ceramics in the single-stage high-temperature nitridation of Zr–Nb alloys with different niobium contents (0.1–10 at%) in a wide temperature range was determined using an oxidative constructing approach. In the process of nitridation, the segregation of a metallic niobium phase occurred with the subsequent formation of NbN. This should be taken into account when producing new high-temperature materials with unique functional properties.



Formation of composite structures $Zr_{1-x}Nb_xN$–ZrN_{1-n}/β-Zr to Nb–$Zr_{1-x}Nb_xN$ imaged in transmitted DIC microscopy

Keywords: ceramic, zirconium nitride, niobium nitride, alloy nitridation, oxidative constructing.

Alloys based on solid solutions of niobium and zirconium are widely used as construction materials in the nuclear industry, mechanical engineering and medicine due to their high melting points, low reactivity, strength and biocompatibility.[1–5] Ceramics based on zirconium and niobium nitrides combines the properties of thermal barrier alloys and ceramic materials and expands the scope of chemically inert and radiation-resistant construction materials.[6] The development of nuclear technologies increasingly requires available special materials, such as fuel diluents based on binary ZrN–NbN nitrides and ceramic fuel based on uranium and plutonium nitrides in an inert nitride matrix.[7,8] The compaction of nitride powders seems to be a rather difficult process.[9] Therefore, the development of a single-stage synthesis of complex-shaped ceramics by complete nitriding of the required composition is an urgent scientific problem.[10] The investigation of the processes of nitriding solid solutions of zirconium and niobium will make it possible in the future to develop methods for the synthesis of nitride nuclear fuel.

Complex-shaped compact binary zirconium and niobium nitrides can be synthesized by the method of oxidative constructing of thin-walled ceramics *via* complete nitriding of a metal preform based on zirconium–niobium solid solutions of various compositions. This is a method that allows one to get a nitride product in the form of an initial preform from a metal or alloy.[11,12] Nitriding of Zr–Nb alloys is of interest as a method of hardening materials by saturating their surface with nitrogen.[13,14] Establishing the regularities and mechanisms of the formation of compact binary nitrides under the conditions of heterophase reactions expands the fundamental understanding of the formation of nitride, oxide, carbide and carbonitride ceramics.[15–17] This makes it possible to propose appropriate mathematical models, control the structure by directional crystallization with monitoring of the initial texture and grain structure of metal solid solutions and investigate the kinetics of nitride generation in the liquid phase and endotaxy.

In this work, we investigated the nitridation of Zr–Nb alloys and the formation of compact ceramics.[†] The synthesis temperatures were chosen in accordance with the Zr–Nb phase diagram[18] below and above the melting point of the alloys.[19] According to the results of X-ray diffraction (XRD) analysis,[‡] it was found that nitriding of individual metals at 1900 °C for 180 min leads to the formation of compact nitrides consisting of face-centered cubic (fcc) phases of ZrN (a = 4.5783 Å) and NbN (a = 4.3758 Å) [Figure 1(*a*), curve *3*]. The only phase of zirconium nitride was detected by XRD upon nitriding of binary alloys with a niobium content of up to 7.5% under the same conditions. For example, a nitrided Zr alloy with up to 5% Nb had an fcc lattice with a = 4.5731 Å [Figure 1(*a*), curve *1*]. The

---

[†] Zr–Nb alloy samples containing 0.1, 2.5, 5, 7.5 and 10 at% Nb were prepared in the form of a foil 60 mm long and 3 × 0.3 mm in cross section. Nitridation of pure Zr and Nb samples was carried out according to the original method of resistive heating in an atmosphere of high purity nitrogen (99.9999%) at temperatures of 1700 °C (below the melting point of the alloy[15]), 1900 °C (near the melting point of the alloy) and 2400 °C (above the melting point of the alloy) for 180 min. The reaction temperature was determined by a LumaSense IMPACT IS 50-LO optical pyrometer.

[‡] XRD analysis was carried out on a Shimadzu XRD-6000 vertical X-ray θ–2θ diffractometer with CuKα radiation.[20]

The microstructure of the surface and cross section of the ceramics was observed using a Carl Zeiss Zxio Observer 3 optical inverted microscope in polarization and differential interference relief contrast (DIC), as well as using a Carl Zeiss LEO 1420 scanning electron microscope equipped with an INCA Energy 300 device for energy-dispersive X-ray analysis (EDX).

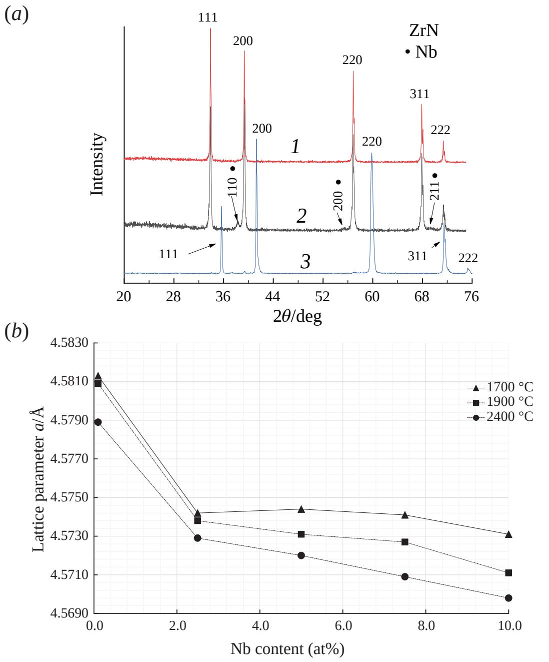


Figure 1 (*a*) XRD patterns of ceramic samples synthesized at 1900 °C from (*1*) the Zr–2.5% Nb alloy, (*2*) the Zr–7.5% Nb alloy and (*3*) pure Nb. (*b*) Changes in the crystal lattice parameter (confidence interval ±0.0005 Å) of the ZrN phase depending on the Nb content in the initial alloy and the synthesis temperature.

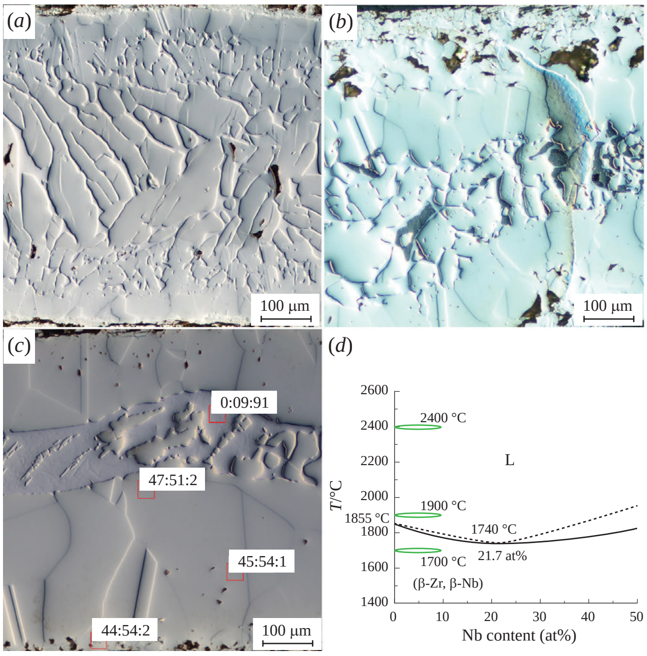


Figure 2 DIC microscopy images of the cross sections of ceramic samples synthesized from (*a*) the Zr–10% Nb alloy at 1700 °C, (*b*) the Zr–10% Nb alloy at 1900 °C and (*c*) the Zr–5% Nb alloy at 2400 °C. (*c*) Elemental composition (atomic N/Zr/Nb ratio) in different parts of the cross section of a ceramic sample. (*d*) Phase diagram of the Nb−Zr system.[18]

phase of metallic niobium was observed by XRD as a result of nitriding of alloys in which the niobium content exceeded 7.5% [Figure 1(*a*), curve *2*]. The XRD data indicate that, as the niobium concentration increases, the crystal lattice parameter of zirconium nitride decreases compared to pure ZrN [Figure 1(*b*)]. The microstructure of ceramics[‡] prepared at different temperatures has morphological differences consisting in a different distribution of phases of the niobium solid solution [Figure 2(*a*)–(*c*)]. The EDX analysis of the microstructure revealed an inhomogeneity in the distribution of elements in different parts of the cross section of the samples. Figure 2(*c*) shows the elemental composition across the cross section of a ceramic sample (for example, the atomic N/Zr/Nb ratio is 44 : 54 : 2).

Based on the experimental data, we proposed the following model for nitriding an alloy at temperatures below and above the melting point of the alloy. The interaction of the alloy with nitrogen below the melting temperature occurs in the process of nitride endotaxy relative to the α-solid nitrogen solution formed at the initial stage of high-temperature saturation of zirconium with nitrogen. Niobium, which has a lower chemical affinity for nitrogen, is released as a solid solution with a low content of zirconium. Metallic niobium reacts with nitrogen to form NbN, where zirconium is bound into nitride.

At a temperature above the melting point of the alloy, the liquid phase formed in the inner part of the sample is retained by a ceramic layer of refractory nitride, which appears when the temperature rises to the specified values. In this case, the growth of nitrides proceeds both by the chemoepitaxial mechanism on the inner surface of the ceramic layer and in the liquid phase.[21] Zirconium nitride with a content of up to 3 at% is formed at the initial stage in the entire temperature range studied. The unreacted niobium then segregates into an individual phase as a solid solution with zirconium having a cubic crystal lattice [Figure 1(*a*), curve *2*]. At temperatures below the melting point of the alloy, niobium metal is distributed throughout the bulk of the sample, with the exception of the surface layer [Figure 2(*a*)]. Nitriding of the alloy above the melting point of zirconium is accompanied by a gradual growth of a solid layer of zirconium nitride containing up to 3 at% Nb. The concentration of niobium in the remaining volume is constantly increasing due to the chemical reaction of zirconium. An increase in the concentration of niobium in the liquid phase leads to the formation of refractory solid solutions with a higher content of niobium, and a solid phase based on it appears in the volume of the sample. At a temperature of 1900 °C, a metal phase is formed in the internal volume of the ceramics [Figure 2(*b*)], and at 2400 °C, niobium is concentrated in the center of the ceramics, where the transition of zirconium from the alloy to the nitride occurs. It has been found that the limiting composition of the Nb-based solid solution is 5 at% [Figure 2(*c*)]. After that, niobium begins to react with nitrogen, forming a nitride of the composition NbN. According to the known data,[22,23] zirconium (ZrN) and niobium (NbN) mononitrides with fcc crystal lattice dissolve in each other unlimitedly. After completion of the high-temperature saturation of the sample with nitrogen, no traces of individual niobium nitride were found on the XRD patterns. It is noted that with an increase in the synthesis time, the crystal lattice parameter of zirconium nitride decreases to values corresponding to different compositions of solid solutions of niobium nitride in zirconium nitride.[24]

Thus, ceramics based on higher nitrides (ZrN–NbN) were synthesized by complete nitridation of zirconium alloys with different niobium content. At the first stage of high-temperature nitriding of Zr–Nb alloys, binary zirconium nitride is formed with a content of up to 3 at% niobium nitride. Subsequent nitriding of Zr–Nb solid solutions at temperatures below and above the melting point of the alloy leads to the formation of a metallic niobium phase. At temperatures below the melting point, the metal phase is distributed throughout the volume of the sample. At temperatures above the melting point, a refractory solid solution based on niobium with an admixture of zirconium is formed in the center of the sample. Upon completion of the nitridation, metallic niobium reacts with nitrogen to form the stoichiometric nitride NbN, which completely dissolves in the zirconium nitride matrix, reducing its crystal lattice parameter.

This work was supported by the Russian Science Foundation (grant no. 20-13-00392) and the A. A. Baikov Institute of Metallurgy and Materials Science, Russian Academy of Sciences.

References

1 V. I. Sokolenko, A. V. Mats and V. A. Mats, *Fiz. Tekh. Vys. Davlenii (High Pressure Phys. Technol.)*, 2013, **23** (2), 96 (in Russian).
2 Y. Zhao, H. Li and Y. Huang, *J. Alloys Compd*., 2021, **862**, 158029.
3 A. Y. Eroshenko, A. M. Mairambekova, Y. P. Sharkeev, Z. G. Kovalevskaya, M. A. Khimich and P. V. Uvarkin, *Letters on Materials*, 2017, **7**, 469.
4 A. G. Kononov, V. A. Kukareko, A. V. Belyi and Yu. P. Sharkeev, *Mekhanika Mashin, Mekhanizmov i Materialov (Mechanics of Machines, Mechanisms and Materials)*, 2013, no. 1, 47 (in Russian).
5 Y. Arai and K. Nakajima, *J. Nucl. Mater.*, 2000, **281**, 244.
6 M. Streit, F. Ingold, L. J. Gauckler and J.-P. Ottaviani, *J. Nucl. Sci. Technol*., 2002, **39** (sup3), 741.
7 T. Hollmer, *Diploma Thesis*, KTH Royal Institute of Technology, Stockholm, 2011.
8 K. Wheeler, P. Peralta, M. Parra, K. McClellan, J. Dunwoody and G. Egeland, *J. Nucl. Mater.*, 2007, **366**, 306.
9 I. N. Popescu and R. Vidu, *Sci. Bull. Valahia Univ.: Mater. Mech.*, 2018, **16**, 28.
10 A. S. Chernyavskii, *Inorg. Mater.*, 2019, **55**, 1303.
11 K. A. Solntsev, E. M. Shustorovich and Yu. A. Buslaev, *Dokl. Chem.*, 2001, **378**, 143 (*Dokl. Akad. Nauk*, 2001, **378**, 492).
12 K. A. Solntsev, E. M. Shustorovich, A. S. Chernyavskii and I. V. Dudenkov, *Dokl. Chem.*, 2002, **385**, 193 (*Dokl. Akad. Nauk*, 2002, **385**, 372).
13 Y. Liu, Y. Yang, D. Dong, J. Wang and L. Zhou, *Surf. Interfaces*, 2020, **20**, 100638.
14 A. V. Belyi, A. G. Kononov and V. A. Kukareko, in *Sovremennye methody i tekhnologii sozdaniya i obrabotki materialov (Modern Methods and Technologies for Creating and Processing Materials)*, ed. A. V. Belyi, PTI NAS of Belarus, Minsk, 2017, vol. 2, pp. 87–99 (in Russian).
15 V. Yu. Osipov, F. M. Shakhov, N. M. Romanov and K. Takai, *Mendeleev Commun*., 2021, **31**, 415.
16 A. A. Chernyshev, D. N. Lytkina, A. S. Buiakov, S. N. Kulkov and I. A. Kurzina, *Mendeleev Commun.*, 2021, **31**, 881.
17 G. P. Kochanov, A. N. Rogova, I. A. Kovalev, S. V. Shevtsov, A. I. Sitnikov, A. V. Kostyuchenko, S. N. Klimaev, A. A. Ashmarin, S. S. Strel’nikova, A. S. Chernyavskii and K. A. Solntsev, *Inorg. Mater*., 2021, **57**, 1077 (*Neorg. Mater.*, 2021, **57**, 1138).
18 J. P. Abriata and J. C. Bolcich, *Bull. Alloy Phase Diagrams*, 1982, **3**, 34.
19 S. V. Ushakov, A. Navrotsky, Q.-J. Hong and A. van de Walle, *Materials*, 2019, **12**, 2728.
20 *Powder Diffraction File Alphabetical Index: Inorganic Phases*, JCPDS, Swarthmore, PA, 1997.
21 S. V. Shevtsov, A. I. Ogarkov, I. A. Kovalev, K. B. Kuznetsov, A. A. Ashmarin, A. S. Chernyavskii and K. A. Solntsev, *Inorg. Mater*., 2016, **52**, 600 (*Neorg. Mater.*, 2016, **52**, 651).
22 P. Duwez and F. Odell, *J. Electrochem. Soc*., 1950, **97**, 299.
23 L. E. Toth, C. M. Yen, L. G. Rosner and D. E. Anderson, *J. Phys. Chem. Solids*, 1966, **27**, 1815.
24 K. B. Kuznetsov, K. A. Shashkeev, S. V. Shevtsov, A. I. Ogarkov, N. N. Tretyakov, M. P. Saprina, A. V. Kostyuchenko, A. S. Chernyavskii, V. M. Ievlev and K. A. Solntsev, *Inorg. Mater*., 2015, **51**, 820 (*Neorg. Mater.*, 2015, **51**, 893).

Received: 8th December 2021; Com. 21/6771