Physico-chemical fundamentals for high-temperature single-stage synthesis of compact ceramics based on zirconium nitride

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Abstract. The process of complete nitridization of zirconium tape samples in a nitrogen atmosphere at temperatures below and above the peritectic temperature has been implemented. Using the high resolution TEM method, it was found that the intragranular structure of the nitride is characterized by a high dislocation density \(5 \times 10^{11} \text{ cm}^{-2}\). The hardness of the synthesized samples of ceramics corresponds to the hardness of single-crystal samples. Irradiation with high-energy xenon ions and gamma-irradiation does not lead to a change in the grain structure of ceramics.

1. Introduction

Due to thermal, chemical and radiation resistance and record indicators of mechanical and electrophysical properties, titanium subgroup metal nitrides have found application in various branches of technology: thin-film diffusion barriers in microelectronics [1-3], protective and strengthening coatings [4], functional ceramics and structural ceramics for nuclear power engineering [5-7]. Depending on the purpose of nitride ceramics, various methods are used to obtain thin-film structures and hardening coatings using various physical and chemical deposition methods (gas-phase processes, vacuum and plasma technologies, etc.), as well as the creation of bulk products by compacting the respective powders. The previously proposed approach to the synthesis of oxide ceramics [8], successfully solving the problem of creating thin-walled ceramic products of complex shape, was implemented for compact samples of titanium, zirconium and hafnium nitrides with a volume of \(~ 100 \text{ mm}^3\).

According to the Zr – N system state diagram, the width of the homogeneity region of the ZrN phase is 34 – 50 at. % \((9.5 – 13.3 \text{ wt. %})\) For nitrogen. It should be expected that the resulting nitride may be characterized by a variable composition, which should affect the mechanical and electrophysical properties of the material. The mechanism and kinetics of the process under consideration, as well as the features of the structure and properties of the ceramics produced, have not been fully studied.
The purpose of this work is to characterize the structure and substructure, assess the hardness, electrical conductivity and radiation resistance of ZrN synthesized in the process of high-temperature nitriding of zirconium foil, as well as to establish the mechanism and kinetic regularities of the process.

2. Materials and techniques
To compare possible structural-phase changes occurring in the material before and after the temperature of the peritectic reaction (1 880 °C), the nitridization of samples 60 mm long and 3.0 x 0.5 mm in cross section made from zirconium foil was performed by heating electric current at 1 500, 1 800, 1 965 and 2 400 °C. The duration of the process for each temperature was 4, 6, 11, 21, 30, 40, 50 and 60 minutes.

The kinetics of zirconium saturation with nitrogen was experimentally determined by the weight gain of the sample. In the process of heating at each temperature, the change in the electrical resistance of the sample was evaluated.

The study of the phase composition, structure and morphology of the free surface was performed by X-ray diffractometry (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Raman spectroscopy.

The mechanical properties of ceramics were investigated by the method of measuring nanoindentation. The atomic force microscopy (AFM) method was used to determine the surface roughness of ceramics in scanning areas of 1 × 1 μm², which approximately corresponds to the indenter footprint. The average roughness of such portions of the surface of the ZrN ceramics is determined in the range of 7–10 nm, which allows the use of a nanoindentation method.

The samples were irradiated with 24Xe ions with an energy of 167 MeV to a fluence of 5.3 x 10¹⁴ cm⁻² at a temperature of 20–25 °C; total exposure time 10 days. The irradiation of the samples was performed on the ITs-100 accelerator. The use of xenon ions with a given energy, which are not radioactive, imitates fragments of uranium fission.

For certification of samples of compact ceramics based on zirconium nitride, gamma irradiation of 60Co radionuclide was carried out.

3. Results and its discussion
The diffractograms characterizing the initial structure of the zirconium foil and the initial stage of nitridation are shown in Fig. 1. It follows from them that even at 1 500 °C (diffractogram 2) a thin nitride layer is formed, under which the phase of a solid solution of nitrogen in zirconium appears. At a temperature of 1 800 °C (diffractogram 3) (near the temperature of the peritectic reaction), the thickness of the nitride layer increases and, as a result, the phase of the solid solution is extremely weak. As the temperature increases to 2 400 °C (diffractogram 4), a nitride layer with a thickness of up to 60 μm is formed, which is formed by large crystallites (Fig. 2). According to the nature of the split within the layer, the size of the crystallites is commensurate with its thickness. The surface of the central part of the transverse cleavage differs from the cleaved surface of the outer layer by its morphology and smaller grain size. Qualitative assessment of the presence of elements in the composition of the material indicates the presence of nitrogen throughout the thickness of the sample (table 1). Thus, already in 4 minutes, nitridation at a temperature of 2 400 °C nitrogen penetrates to the entire depth. One should expect the formation of nitrides of equiatomic composition on the surface of the material, and in the inner part - the nitride phase with a nitrogen deficiency and a solid solution of nitrogen in zirconium. As the synthesis time increases, the outer nitride layer grows. The diffraction pattern of the surface of the transverse cleavage of the sample confirms the expected composition of the resulting composite, which affects the nature of the cleavage surface. Diffractogram-identified solid solutions of nitrogen in zirconium are located in the central part of the sample, while nitride is
the outer layer. For temperatures of 1500 and 1800 °C and short times for the nitridation process, the crystal lattice parameter is overestimated compared to the values for the powder patterns of the ZrN composition, which indicates the formation of nitride with a nitrogen deficiency. The different ratios of the diffraction peaks intensity, characteristic for the entire studied group of samples, are a consequence of the coarse-grained structure of the metal billet, which has undergone recrystallization upon reaching the regime temperature. Up to the melting point of the metal within the grains, the polymorphic transition of the hcp metal structure in the bcc creates the conditions for single-directional chemoepitaxy of cubic nitride. The formation of the nitride phase can be considered as a solid phase endotoxia process of zirconium nitride relative to the matrix (a solid solution of nitrogen in the α-Zr limit composition). The crystal lattice of the new phase at the interface with the source metal undergoes tensile stresses (a necessary condition for epitaxy with a relatively large size mismatch of the crystal lattices). In accordance with the principle of parallelism of close-packed planes and dense directions of cutting phases, one would expect an orientation relation:

\[(\bar{1}1\bar{1}), [\bar{1}0\bar{1}] \text{ZrN} \parallel (000\bar{1}), [2\bar{1}0\bar{1}] \alpha\text{-Zr}\] (1)

But the growth direction <111> is unfavorable for a material with a NaCl type crystal lattice. With a dimensional discrepancy of about 0.005 in both cases, in dense directions, relations (2) and (3) are likely:

\[(00\bar{1}), [\bar{1}0\bar{1}] \text{ZrN} \parallel (000\bar{1}), [2\bar{1}0\bar{1}] \alpha\text{-Zr}\] (2)
\[(\bar{1}0\bar{1}), [\bar{1}0\bar{1}] \text{ZrN} \parallel (000\bar{1}), [2\bar{1}0\bar{1}] \alpha\text{-Zr}\] (3)

On diffractograms of samples obtained within 60 minutes. at 1500 and 2400 °C, all diffraction peaks belong to zirconium nitride. When comparing the intensities of the main reflections on the obtained diffraction patterns with the reference one for the statistical ZrN polycrystal, the manifestation of a strongly pronounced texture <110> for 1500 °C and <311> for 2400 °C, respectively, was established.

In fig. 3 shows the dependences characterizing the change in the mass of the sample in the process of nitridation at different temperatures. It is established that the saturation of zirconium with nitrogen is characterized by two stages: the first is described by an exponential law, the second is well approximated by a linear dependence. The transition point of the exponential to the linear stage, depending on the synthesis temperature, corresponds to 40, 35, 30 and 18 minutes. for 1 500, 1 800, 1 965 and 2 400 °C, respectively. At the point of transition from the exponential stage to the linear fraction of absorbed nitrogen from ZrN contained in the equiatomic composition, the values are 0.24, 0.36, 0.39, and 0.63 for 1 500, 1 800, 1 965, and 2 400 °C, respectively. The calculation in Arrhenius coordinates for the exponential segment gives the value of the effective activation energy of 22.8 kJ/mol, and for the linear one – 37.4 kJ/mol. It has been established that with increasing temperature, the limiting amount of nitrogen absorbed increases. The minimum temperature, above which the saturation of zirconium with nitrogen is described by an exponential law, is ~ 900 °C.

The SEM images of the outer surface and the surface of the transverse cleavage show that the open pores with faceting corresponding to the faces of the crystal lattice are characteristic of the first. For example, for a surface close to (001), a section close to a rectangular (Fig. 4a). On the transverse section, internal pores are also revealed. The internal pores of the near-surface zone are clearly visible on TEM images of the cross sections of the samples (Fig. 4b). They have a clear cut corresponding to all planes with small indices, but mainly (001) and (110), and also according to (111) and (111). Electron diffraction pattern and bending extinction contours confirm the single-orientation chemoepitaxy of nitride within large grains.
In fig. 4c shows a TEM image with a resolution of the planes (111), (111) and (002) of the <110> zone of the ZrN crystal lattice. A large dislocation density is characteristic of the resulting crystalline nitride. Based on the scale of the image, it is 5·10¹¹ cm⁻¹. The following areas with dislocations are distinguished by the circles: 1 and 3 with the Burgers vector \( \mathbf{b} = \frac{1}{2} [101] \) and \( \mathbf{b} = \frac{1}{2} [011] \).

The fact that two dislocations of a different sign (2) did not annihilate at the synthesis temperature testifies to the extremely low plasticity of ZrN. The force of interaction of two dislocations of different sign, calculated per unit length by the formula

\[
F = \frac{b^2}{2r} \ast E
\]

where \( E \) – Young's modulus, \( r = 4d_a \) – elastic distance ( \( d_a = \frac{a}{\sqrt{3}} \)), is 43.6 N/m (\( \mathbf{b} = \frac{a}{\sqrt{2}} \cdot 3.2296 \) Å).

In the process of high-temperature nitridization of zirconium, a compact heterophase structure is formed with a pronounced difference in the grain structure of the layers (Fig. 2). The ratio of the volumes of these phases depends on the temperature and time of the process. The general pattern of structural transformations is the formation of the initial stage of the surface layer of ZrN and a solid solution of nitrogen in zirconium in the bulk of the sample. With an increase in the duration of the process, along with the near-surface layer of zirconium nitride, a second layer is formed, which differs substantially from the first one in grain size. In this case, respectively, there is a decrease in the layer of solid solution. At 1500 °C for 21 min. and at 2400 °C for 16 min. the formation of zirconium nitride is completed and a two-layer nitride heterostructure is formed. For 1500 °C with nitridization within 60 minutes two-layer structure is preserved. When this occurs, an increase in the thickness of the surface layer without a significant change in the grain structure and recrystallization of the inner nitride layer. For 2400 °C nitridation for 60 min. leads to the formation of a homogeneous nitride structure. The observed texture formation of the nitride layer is in good agreement with the texture of the initial zirconium samples, and is a consequence of the endotaxia process of ZrN relative to the solid solution of nitrogen in \( \alpha \)-Zr. The peculiarity of the grain structure of nitride can be explained by the fact that three-way endotaxion in equivalent orientational ratios contributes to the nucleation of the initial surface layer of nitride with a more dispersed grain structure than that of the original metal. It should be borne in mind that the formation of a dispersed structure of zirconium nitride is promoted by its nucleation in the process of reaching the operating temperature, as well as a more defective structure of the surface layer of the initial metal. Upon reaching the temperature of 1500 °C, the recrystallization process (\( T > 1/3T_{SL} \)) proceeds in the starting metal, and the formation of nitride occurs already within larger grains of a solid solution of nitrogen in \( \alpha \)-Zr, which contributes to the formation of a coarse-grained structure of the inner layer of nitride. With an increase in the duration of heating, recrystallization and selective growth of grains of preferential orientation <110> in the surface layer of nitride occur.

The deformation of indentation is of an elastic-plastic nature. The change in the hardness of the sample cross section (2400 °C, 4 min.) When passing through the ZrN - solid solution interface from 26-36 GPa within the ZrN layer to 4.0-4.5 GPa within the internal region of the solid solution confirms what was said above about the formation during nitridation in the high temperature region of the heterogeneous structure of the samples. Thus, the possibility of forming a composite structure formed by a hard shell (ZrN) and a relatively viscous core (solid solutions for introducing nitrogen
into zirconium) is shown, which is also reflected on the surface of the transverse split of the sample (Fig. 2).

The phase composition of compact samples after irradiation with high-energy xenon ions practically does not change, the lattice parameter is preserved. The study of the morphology of the free surface and the surface of the transverse cleavage of the samples before and after their irradiation with the SEM method shows approximately the same pore density for the initial and irradiated samples. The pore size characteristic of irradiated ZrN is larger than that of the unirradiated sample. This can be explained by the fact that vacancies resulting from irradiation diffuse to the existing pores, and the formation of new pores practically does not occur. In the near-surface region, grain boundaries and dislocation rows forming sub-grain boundaries are revealed. According to the high-resolution TEM, no noticeable changes occur in the dislocation substructure of the irradiated samples. The density of intragranular dislocations of the order of $10^{11}$ cm$^{-2}$ is preserved. Along with the dislocations in the irradiated samples, local stresses are detected within the limits of the sections commensurate with the lattice parameter. The nature of microdiffraction patterns and bending extinction contours indicate the preservation of the microcrystalline grain structure. The Raman spectra characterizing the samples before and after their irradiation contain modes corresponding to vibrations of cubic zirconium nitride. The decrease in the intensity of the bands is due to point defects and their complexes formed in the elastic scattering channel. The analysis of the spectra indicates that the amorphization of ceramics does not occur during the irradiation process.

Gamma irradiation of a $^{60}$Co radionuclide of compact samples based on zirconium nitride does not lead to a change in the phase composition; the lattice parameter of nitrides does not change.

Table 1. Elemental composition according to X-ray spectral analysis of the cleaved surface of the sample shown in Fig. 2 (synthesis temperature 2400 °C, synthesis time 4 minutes).

| Point | Zr, at. % | N, at. % | Detection error of Zr, % | Detection error of N, % |
|-------|-----------|----------|--------------------------|------------------------|
| 1     | 33.42     | 64.53    | 1.65                     | 23.55                  |
| 2     | 38.33     | 61.5     | 1.33                     | 16.31                  |
| 3     | 39.62     | 51.44    | 1.35                     | 17.99                  |
| 4     | 38.79     | 61.21    | 1.68                     | 24.54                  |
| 5     | 39        | 49.59    | 1.37                     | 19.05                  |
| 6     | 41.79     | 50.55    | 1.4                      | 21.63                  |

Summarizing the results of the study presented in the work, one can make a number of assumptions about the possible mechanism of the nitridization process of zirconium foil. In accordance with the state diagram, when the temperature rapidly reaches a temperature above 2000 °C, we should expect a peritectic reaction and the formation of a liquid solution phase with ZrN inclusions. Therefore, in the synthesis of nitride under the conditions described above, at the initial stage up to the temperature of the peritectic reaction, oriented growth of ceramics occurs via a chemoepitixial mechanism on the
surface of zirconium grains due to diffusion of nitrogen through the resulting nitride layer. At the next stage of the synthesis, when the process temperature exceeds the melting point of the metal, the formation of nitride by the mechanism described above is impossible due to the melting of the crystalline structure of zirconium. At the same time, the formation of nitride proceeds both in the zirconium melt and on the surface of the formed outer layer of nitride, again by the chemoepitaxial mechanism. Apparently, under the considered conditions, the growth of the outer layer occurs due to epitaxial deposition of zirconium nitride from the melt of the central part of the sample, as well as chemoepitaxial growth due to the liquid phase containing solid solutions of nitrogen in zirconium.

Figure 1. Diffractograms of the sample surface: 1 — initial zirconium foil; 2 — 1 500 °С, 4 min; 3 — 1 800 °С, 4 min; 4 — 2 400 °С, 4 min

Figure 2. Image of the cross-split of zirconium nitride, synthesized at a temperature of 2400 °С for 4 minutes.

Figure 3. Dependences of the preform mass on the time of nitridation of zirconium at different temperatures: line - calculation, points - experiment.
Figure 4. SEM image of the ZrN ceramic surface (a); TEM image and microelectron diffraction pattern of a thin transverse slice of the surface region of ZrN ceramics synthesized at 2400°C for 60 minutes. (b); TEM image of the planes (002), (1 1 1) n (1 1 1) (zone axis <110>) (c).

4. Conclusions
Thus, the process of complete nitridization of zirconium tape samples in a nitrogen atmosphere at temperatures below and above the peritectic temperature is realized. The possibility of synthesis in a single-stage technological process of compact ceramics of a given form based on zirconium nitride or composites is experimentally shown: solid solution (core) - nitride (shell); zirconium - solid solution - nitride.

The general pattern of nitridation kinetics is the two-stage nature of the process: in the first stage it is approximated exponentially by the dependence of the mass gain on time (with the formation of a solid solution and the nitride phase), in the second - by a linear dependence (nitride saturation with nitrogen).
In the temperature range above the peritectic temperature, as a result of complete nitriding, a layered microstructure of nitride is formed: the outer layer (shell) is formed by crystallites of several tens of microns in size, the inner layer with a smaller grain size of nitride (core). The features of the grain substructure reflect two stages of nitride formation: the first is the process of solid-phase endotaxia within large grains of metal, which is manifested in the inheritance by nitride of the texture of the initial metal samples; on the second, the process of autoepitaxy of the nitride from the liquid solid solution phase is implemented, and there is also a multiple unoriented nucleation of the nitride phase when the corresponding nitrogen concentration is reached (more than 30%).

Using the high resolution TEM method, it was found that the intragranular structure of the nitride is characterized by a high dislocation density ($5 \times 10^{11} \text{ cm}^{-2}$). Despite the high temperatures of the nitriding process, polygonization does not occur; “dislocation nanostructuring” is preserved in the volume of crystallites, detected under conditions of amplitude (deformation) contrast.

The hardness of the synthesized samples of ceramics corresponds to the hardness of single-crystal samples.

Irradiation with high-energy xenon ions and gamma-irradiation does not lead to a change in the grain structure of ceramics.

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