UDC 669.296

# MICROSTRUCTURE AND CHARACTERISTICS OF Zr-1%Nb ALLOY, WHICH WAS SYNTHESIZED FROM HETEROGENEOUS POWDER MIXTURE

***O.M. Ivasishin[1], V.M. Voyevodin[2,3], P.E. Markovsky[1], M.M. Pylypenko[2], D.G. Savvakin[1], S.D. Lavrinenko[2,3], O.P. Karasevska[1]***

***[1]G.V. Kurdyumov Institute for Metal Physics of the NAS of Ukraine, Kiev, Ukraine;***
***[2]National Science Center "Kharkov Institute of Physics and Technology", Kharkov, Ukraine;***
***[3]V.N. Karazin Kharkov National University, Kharkov, Ukraine***
***E-mail: pmark@imp.kiev.ua***

Results of investigation of the alloy Zr-1%Nb, obtained by powder technology comprising a operations of pressing and sintering niobium and zirconium hydrides are presented. It is shown that the obtained alloy has a sufficient complex of mechanical characteristics, which is comparable to complex of the properties of the alloy produced by the conventional and more sophisticated technology.

## INTRODUCTION

An extremely important task for Ukraine is to create a complete production cycle of products from zirconium alloys for nuclear power needs on the basis of domestic raw materials. In the nuclear power industry for the production of different designs, and above all, for the cladding of fuel elements the most widely use alloy Zr-1(wt.%) Nb [1]. Products from this alloy are traditionally produced by vacuum melting technology, followed by a multi-step hot and cold plastic deformation of the bars, with the intermediate and final machining and heat treatment [2]. Unavoidable temperature differences in the various layers of the workpiece during hot rolling, as well as inhomogeneity plastic flow, including during cold deformation, will be promote the development of fibrewise texture and structural inhomogeneity, reducing the stability properties of the final product. Given the significant loss of metal during the obtaining of products using this technology and heterogeneity of their structural and textural characteristics, as well as high cost, both the zirconium, and the whole processing chain, of great interest is the development of new and more efficient methods for the obtaining of the alloy and its products by powder technology. For example, the synthesis of the alloy by pressing and sintering of solid heterogeneous mixtures of zirconium-based powder and alloying powder of niobium will greatly simplify and reduce the cost of the technology, and avoiding repeated remelting and multistage deformation of ingots. Except forming of structurally homogeneous and less texturing alloy (due to the lower total deformation degree) during sintering of powder mixtures can obtain preform whose shape is sufficiently similar to the shape of the final articles, thus reusable reducing loss of metal during subsequent machining.

On the other hand, during the solid-phase sintering heterogeneous mixtures residual pores remaining in the sintered material may adversely affect the complex of the mechanical characteristics, then often requiring additional hot deformation of the synthesized alloy to reduce porosity and improve the complex of properties. It has previously been shown that effective method of reducing the porosity of constructional titanium and zirconium alloys directly during sintering is replacement of the starting powder of titanium and zirconium on powders their hydrides [3–5]. Hydrogen acting as a temporary alloying element to these metals, and completely ever leaving the material during the vacuum sintering, activates the sintering process the powder particles. Using this hydride approach allows to obtain the necessary mechanical properties of sintered titanium alloys without additional hot deformation. However, the potential of hydride approach for obtaining industrial zirconium-based alloys, especially Zr-1%Nb, not yet been studied at the moment.

The aim of this work was to obtain an alloy Zr-1% Nb, by two simple technological operations – pressing and sintering a powder mixture of zirconium and niobium hydride, and assess the potential of this method for producing the alloy to achieve the required mechanical properties directly during sintering and using additional hot deformation of the resulting material.

## MATERIALS AND METHODS OF RESEARCH

Powders of zirconium hydride (particle size less than 100 microns) and niobium (size less than 63 microns) used to obtain the alloy. Zirconium hydride was obtained by hydrogenation of iodide zirconium rods in the laboratory of the Institute for Metal Physics of the NAS of Ukraine up to the hydrogen concentration of 1.9 wt.% followed by grinding to a powder required dispersion. The powders were mixed in the necessary proportions to obtain Zr-1%Nb and compacted at room temperature under pressure 640 MPa in press form to get samples with size 10x10x100 mm. Pressed samples were heated in a vacuum furnace to 1300 °C at initial vacuum of $10^{-3}$ Pa, during 4 hours followed cooling of furnace to room temperature. During this temperature cycle the processes of hydrogen desorption from zirconium hydride to form a zirconium matrix, particle sintering and chemical homogenization of the system were simultaneous and a massive homogeneous alloy was obtained (Fig. 1).

Additional hot deformation of the part of the obtained material was performed by rolling the samples in the round roll at 800...850 °C to form rods with a diameter of 8 mm (Fig. 2), whereupon a portion of the deformed specimens were annealed in a resistance furnace at 750 °C for 1 hours to relieve residual stresses and to obtain equilibrium state. From rectangular sintered samples, rolled samples and rolled and annealed rods were machined cylindrical specimens for mechanical tensile tests (see Fig. 2).

The density of the samples was determined by the method of hydrostatic weighing, the microstructure was investigated by optical microscopy, fractures after the tensile tests – scanning electron microscopy; phase composition and crystallographic texture – X-ray method using diffractometers the company “Stadi" and “Rigaku" (diffractometer “Ultima"). The oxygen content in the final material was determined by gas analyzer ELTRA OH900.

Mechanical tensile tests were performed at room temperature on Instron 3377 Installation according to standard ASTM-E8-79a on samples with dimensions of the working parts – 4 mm in diameter and 25 mm in length.

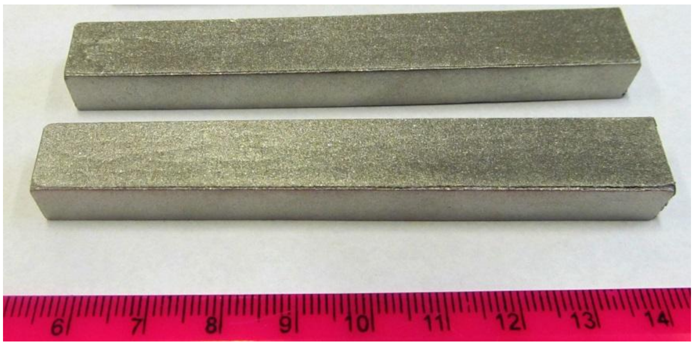
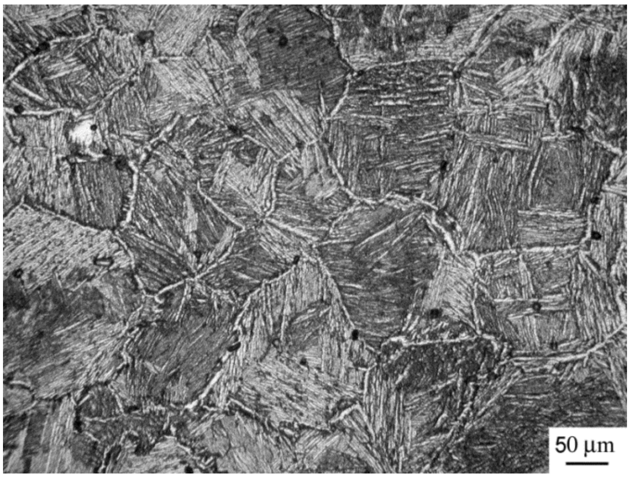


*Fig. 1. Samples of the sintered Zr-1%Nb alloy*

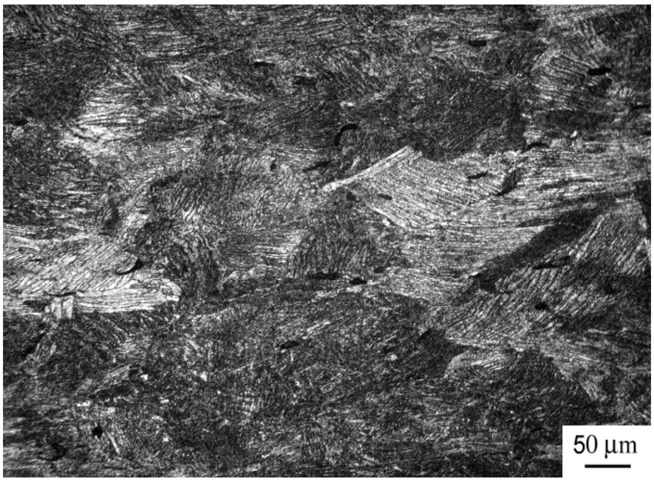
*Fig. 2. Rods Zr-1% Nb alloy, obtained by rolling, and the sample was machined from a rod for mechanical tests*

## RESULTS AND DISCUSSION

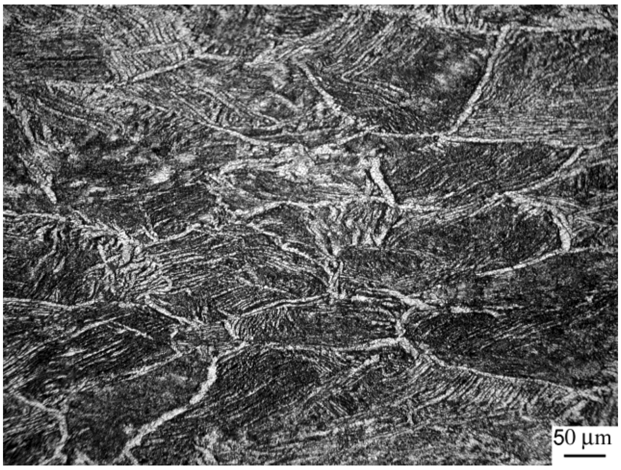
The microstructure of the synthesized alloy in the state after the sintering is shown in Fig. 3a. Used temperature-time regime ensures achievement of full microstructural uniformity of material with an average grain size of about 150 microns. According to the phase diagram of Zr-Nb and data on the phase composition of the cast alloy Zr-1Nb [1] at a given concentration of niobium in the material, apart from the main phase α-hcp of solid solution of niobium zirconium, there may be a small amount of β-phase with a high content of niobium. In our case, the presence of interlayers of the second phase in a microstructure to detect visually very difficult (see Fig. 3,a), while the X-ray analysis has revealed exclusively α-phase (Fig. 4). It should be noted that hydrogen is removed almost completely from the zirconium during the process of high temperature treatment; hydride phase is not detected or on radiographs or in the microstructure of the synthesized alloy. The characteristic feature of the alloy is that it contains the separate residual pores by size of 10...15 microns (see Fig. 3,a). Density of the material is 6.41 $g/cm^3$ and a total pores volume is about 2% (by microstructure studies). This relatively low percentage of the residual pores and their small size, as in the case of the synthesis of titanium alloys [3, 4], is explained by the positive influence of hydrogen on the activation of the diffusion process during the sintering [5].




*a*




*b*




*c*

*Fig. 3. The microstructure of the Zr-1Nb alloy in a state after: sintering (a), rolling (b) and aging (c)*

The thermomechanical treatment was applied to test the potential of improve of complex of the mechanical properties by reducing the porosity and the transformation of the initial coarse-grained and coarsely lamellar microstructure (see Fig. 3,a). Hot plastic deformation led to a marked change in the microstructure (see Fig. 3,b) when compared with the initial synthesized state, that was showed not only in increasing the density of the alloy with 6.41 to 6.51 g/cm$^3$ (porosity decreased), but formation a bit elongated in the direction of deformation of the grains (see Fig. 3,b). It should be noted that despite the fact that some pores are still observed in the microstructure, the density of deformed material has been even higher than the theoretical density of the alloy obtained by the conventional casting techniques (6.45 g/cm$^3$). This fact can be explained by the presence of the specific complex of impurities in the powder material, whereby the density in the absence of pores will be even higher. Increase dispersity of intragranular plates can be associated with a relatively high cooling rate from deformation temperatures. In the plane perpendicular to the flow axis of material on "θ–2θ" radiograph (Fig. 4) the ratio of the areas under base line (0002) and pyramidal (10–11) changed from 0.196 to the state after sintering (curve 1) to 0.256 after subsequent deformation (curve 2), which indicates a change in crystallographic texture. Additional heat treatment (annealing) is mainly contributed to the removal of stresses arising during deformation, while the grain structure, texture and density of the alloy not changed, and a coarsening of intragranular plates is explained by by slow cooling from the annealing temperature (see Fig. 3,c).

As might be expected, the Zr-1Nb alloy after sintering characterized by chaotic texture (Fig. 5,a). Follow the hot plastic deformation led to the formation of relatively weak basic-prismatic type of texture (see Fig. 5,b), indicating a preferential slip during hot deformation on planes ({10-11}, {11-21}) [6]. Separately it should be emphasized that the application of the proposed technology allows to reduce considerably the total plastic deformation, and therefore – to significantly reduce the sharpness of ultimate crystallographic texture of the product, as a result, provide greater isotropy of its properties.

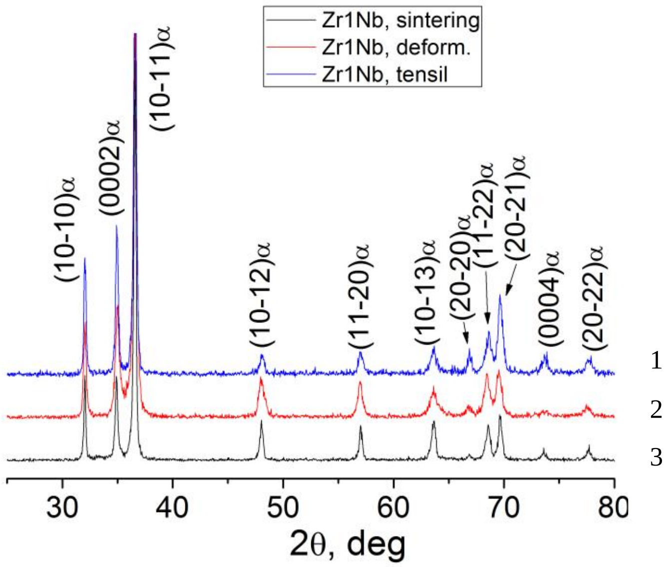
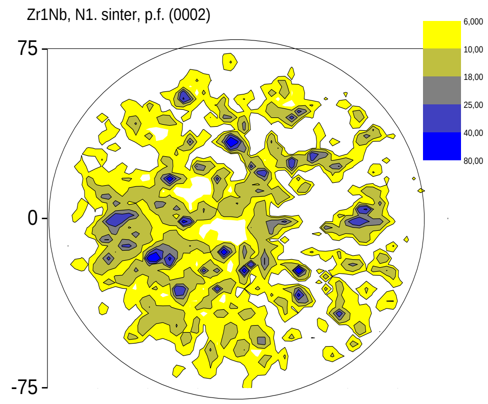
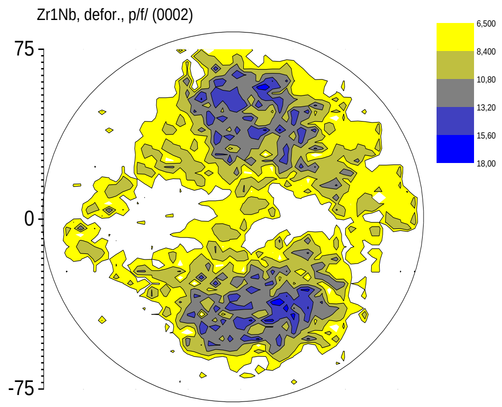


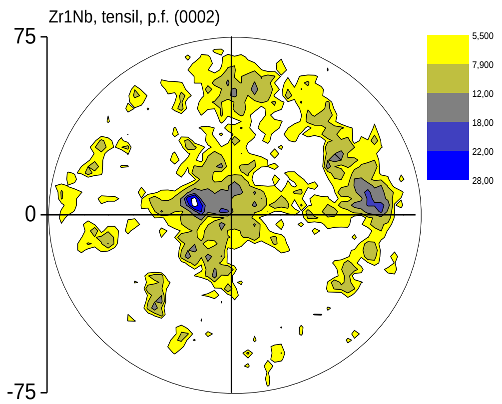

*Fig. 4. Radiographs of the Zr-1Nb alloy in states after: sintering (1), deformation (2) and after tensile test (3)*




*a*




*b*




*c*

*Fig. 5. Partial (0...75°) pole (0002) α figures alloy Zr-1Nb in states: after the synthesis (a) hot plastic deformation (rolling) (b), the texture of synthesized and rolled alloy on the surface of destroyed the sample after tensile test (c)*

Fig. 6 shows the dependences of the broadening of diffraction lines (FWHM) of the alloy Zr-1Nb after sintering and deformation, analysis of which leads to the conclusion about the nature of the causes of such broadening. The figure shows that the dependence of FWHM on angle θ for the synthesized alloy close to the dependence $\cos\theta^{-1}$ - f(θ), that according to [7, 8] corresponds to the effect on it of the size factor of coherent scattering regions (CSR). It also indicates the formation in the cooling process of the synthesis temperature CSR of certain size [7, 8]. Calculation using the program "Ultima IV" showed that as a result of sintering size CSR was $\sim 400$ Å, whereas after rolling it dropped to $\sim 200$ Å. In addition, hot deformation (rolling) has led to the fact that the broadening of the diffraction lines are not proportional $\cos\theta^{-1}$, and is proportional tgθ, that according to [9] indicates the formation of microstresses in the material, i.e. second kind of defects – dislocations, etc.

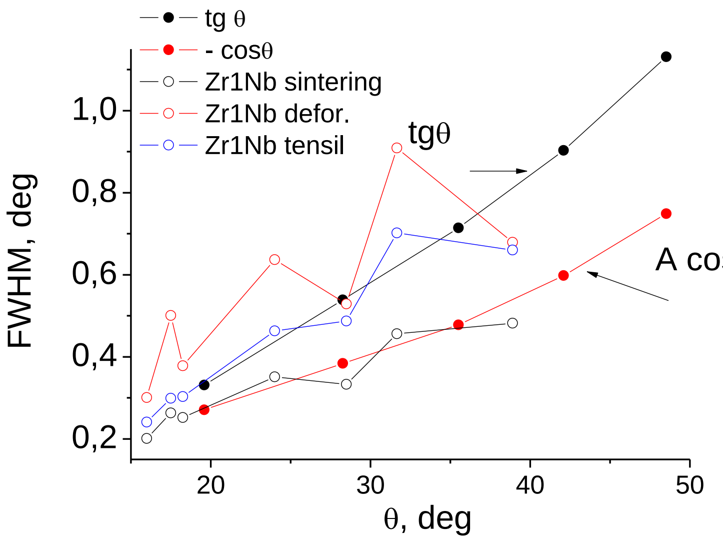


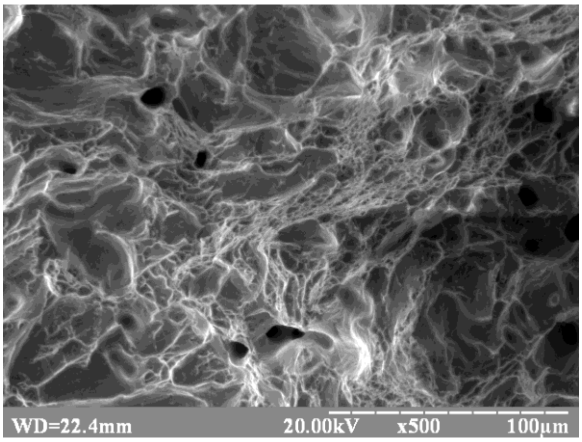

*Fig. 6. The dependence of the broadening of the diffraction lines of α-phase (FWHM) on the angle of reflection θ*

Results of mechanical tests are summarized in the table. Even after synthesizing the of Zr-1Nb alloy (Table, N 1) has a strength of almost at 40% higher in comparison with material prepared by the conventional technology, but the such characteristics of plasticity as relative elongation remains at the same level (compare with N 4 in Table). Sufficiently high strength of obtained alloy is explained by increased contents of oxygen, which increased to 6 times as compared with the oxygen content in the initial iodide zirconium, i. e. increases up to 0.25...0.30%. Furthermore, it is obvious that even the presence of 2% pores in the alloy has not been much negative impact on the mechanical characteristics of the material. A significant decreasing the relative contraction can explain by the presence of a small amount of residual pores that are clearly visible on the fracture surface (Fig. 7,a).

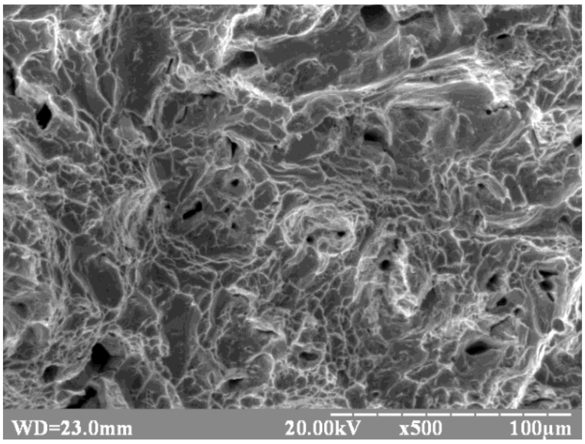
The density and mechanical properties of the Zr-1Nb alloy after different treatments compared with the properties of the alloy produced by the conventional technology

| N | The type of treatment | $\sigma_{0.2}$, MPa | $\sigma_B$, MPa | $\delta_{equil.}$, % | $\delta_{gen.}$, % | Ψ, % | Density, g/cm$^3$ |
|---|---|---|---|---|---|---|---|
| 1 | Synthesized | 605 | 663 | 8.4 | 18.5 | 28.5 | 6.41 |
| 2 | Synthesized and deformed | 765 | 822 | 3.6 | 11.3 | 33.8 | 6.51 |
| 3 | Synthesized. deformed and annealed | 576 | 698 | 10.6 | 22.3 | 40.2 | 6.51 |
| 4 | Cast and the deformed [2] | 365 | 477 | 6.8 | 19.6 | 47.4 | 6.45 |

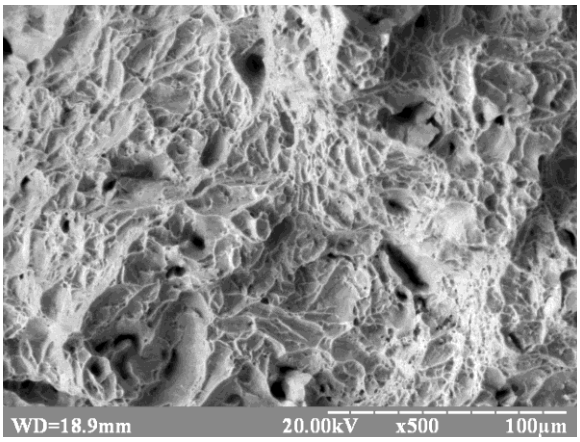
Hot deformation resulted in a significant change in the mechanical properties of the alloy, which was manifested in a marked increase in strength and necking, with a decrease in elongation (see Table, N 2), indicating a significant localization of plastic deformation under uniaxial tensile specimens. It is obvious that this increase in the strength is primarily the result of increasing dispersibility of intragrain microstructure during rolling and its defectiveness (hardening), and second – reducing the porosity in cross-sectional transverse of the tensile strength. At the same time, it is obvious that the appearance of the texture in the deformed state impact on the anisotropy of mechanical properties, the consequence of which is to localize the deformation. Also, due to the localization of plastic deformation in the place of fracture appreciably manifest the process of increasing the already existing pores and generation of new, which leads to the visual growth of porosity on the fracture surface in comparison with the synthesized condition (see Fig. 7,b). However, as in the case of testing of the sintered alloy, the fracture is viscous, as evidenced by relief of pits (see Fig. 7,a and b), and dimensions of pits are slightly smaller for the deformed alloy , what can be associated with relative grinding of plates α-phase in the microstructure (see Fig. 3,a and b).




*a*




*b*




*c*

*Fig. 7. The surface of fracture of the Zr-1Nb alloy samples after the tensile test in conditions after: sintering (a), rolling (b), and final annealing (c)*

The final annealing of the alloy does not have a significant effect either on the microstructure or crystallographic texture, but leads to a relaxation of accumulated stress in the rolling process, resulting in reduced strength characteristics, and increased ductility (elongation and relative contraction) (see Table, N 3). From a comparison of the levels of strength and ductility in this case and the relevant characteristics of synthesized condition (see Table, N 1) can estimate the contribution the reduction of porosity to the improvement in mechanical properties. Character of the fracture surface of the samples after sintering, deformation and annealing remain the same – a viscous, with a small pits relief (see Fig. 7,c), probably due to the dispersion of α-phase plates (see Fig. 3,b).

Fracture surface of sintered and deformed specimen after the tensile test were subjected to additional studies. The crystallographic texture and "θ–2θ" radiograph obtained with the fracture surface of the specimens after tension test are shown in Fig. 5 and in Fig. 4 (curve 3). From a comparison of textures (see Fig. 5) it can be concluded that plastic flow during uniaxial stretching leads to a significant change of orientation α-phase due to activation of the some slip planes in the zone of plastic metal flow. The ratio of the area under the base (0002) and pyramid (10-11) lines (see Fig. 4, curves 2 and 3) has been changed from 0.256 after rolling to 0.33 after stretching, which reflects the change in the textural condition, albeit without forming sharp texture highs. Fig. 8 illustrates the displacement of reflection angles δ2θ with respect to its equilibrium position for the Zr-1%Nb alloy samples after synthesis and subsequent rolling and samples after a uniaxial tensile test.

Reducing the angle of reflection (negative values of δ2θ) correspond to an increase in the interplanar distances; increasing (positive values of δ2θ) – a decrease in the interplanar distances. In the first case, the increase (growth interplanar distance) corresponds to the stretching of the lattice, in the second – its compression. As shown Fig. 8 can be seen that for displacement to both cases has place a difference to the sign of displacement of the diffraction lines. In other words, there is various change of interplanar distances, it shows heterogeneity of deformation as during rolling and then during tensile along different crystallographic directions in the samples, i. e., the existence of advantageous (limited number) slip systems. The deformation of the crystal lattice in both cases is heterogeneous; however, nonuniformity in uniaxial tension is less pronounced, and because in this case for all the values (*hkl*) displacement of reflection angles are observed in the direction of their increase, though not proportional to the angle 2θ.

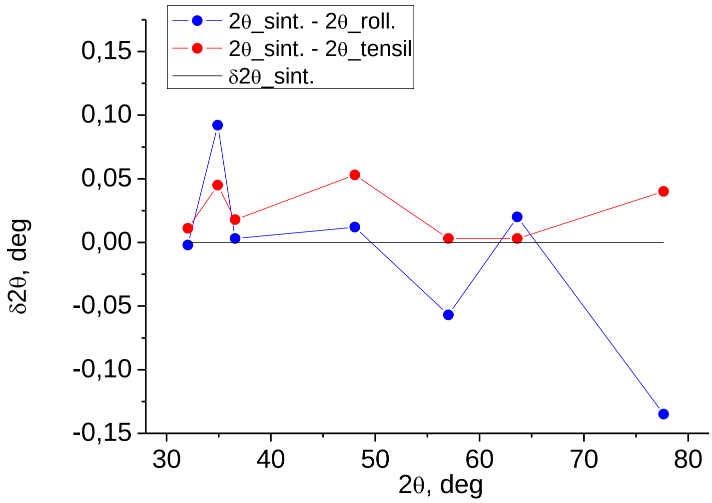



*Fig. 8. The displacement of diffraction reflections of angles $\delta 2\theta$ alloy Zr-1Nb: after rolling (blue line) and after tensile (red line)*

## CONCLUSIONS

From the analysis the obtained results it can be concluded that the alloy Zr-1Nb, produced using powder technology comprising only operations by pressing and sintering zirconium hydride powder and the niobium has the complex of sufficient mechanical properties which is comparable with the properties of the alloy produced by more complicated conventional techniques: vacuum melting and hot deformation. Structural state which formed at the same time is characterized by a homogeneous chaotic texture with a small value of CSR, which allows to assume the possibility of preserve the structural parameters of the model samples in subsequent real products, i. e., eliminate the inevitable differences of structure formation in the laboratory and industrial conditions.

Depending on the application of additional technological operations and hot deformation and annealing the complex of properties of the synthesized alloy can vary within wide limits, leading to a level of the material properties above same obtained with the traditional way. Feasibility of these additional technological operations determined by the conditions of application of the alloy and the requirements for its operational characteristics.

Taking into account that an alloy Zr-1Nb, obtained by powder technology differs from the conventional cast material containing the specific impurities, primarily increased oxygen content (up to 0.3% in this case), in the future, more research is needed directed to study the possible influence of oxygen and other impurities on the operational characteristics of the material, as well as improvement of technology to reduce the amount of undesirable impurities.

The work was performed within project P.4.6 the framework of a comprehensive program of science research NAS of Ukraine "The problem of resource and safety of structures, facilities and machines" ("Resource").

## REFERENCES

1. С.Ю. Заводчиков, Л.В. Зуев, В.А. Котрехов. *Металловедческие вопросы производства изделий из сплавов циркония*. М.: «Наука», 2012, 254 с.
2. В.М. Ажажа, О.М. Ивасишин, И.Н. Бутенко, П.Е. Марковский, Ю.В. Матвийчук, А.В. Теруков. Влияние режимов термомеханической обработки на структуру, кристаллографическую текстуру и механические свойства сплава Zr-1%Nb // *ВАНТ. Серия «Вакуум, чистые материалы, сверхпроводники»*. 2009, №6, с. 194-201.
3. О.М. Ивасишин, Д.Г. Саввакин, К.А. Бондарева и др. Производство титановых сплавов и деталей экономичным методом порошковой металлургии для широкомасштабного промышленного применения // *Наука та інновації*. 2005, №2, с. 45-57.
4. О.М. Ивасишин, Д.Г. Саввакин, Н.М. Гуменяк. Дегидрирование порошкового гидрида титана и его роль в активации спекания // *Металлофизика и новейшие технологии*. 2011, т. 33, №7, с. 899-917.
5. Д.Г. Саввакин, Н.М. Гуменяк. Синтез сплавов на основе бинарной системы цирконий-титан с использованием диспергированного гидрида циркония // *Металлофизика и новейшие технологии*. 2013, т. 35, №3, с. 349-358.
6. K. Linga Murty, I. Charit. Texture development and anisotropic deformation of zircaloys // *Progress in Nuclear Energy*. 2006, N 48, p. 325-359.
7. Я.С. Уманский, Ю.А. Скаков, А.Н. Иванов, Л.Н. Расторгуев. *Кристаллография, рентгенография и электронная микроскопия*. М.: «Металлургия», 1982, 632 с.
8. С.С. Горелик, Ю.А. Скаков, Л.Н. Расторгуев. *Рентгенографический и электронно-оптический анализ*. М.: МИСиС, 1994, 328 с.
9. М.А. Кривоглаз. *Дифракция рентгеновских лучей и нейтронов в неидеальных кристаллах*. Київ: «Наукова думка», 1983, 408 с.

*Article received 18.12.2014*

## МИКРОСТРУКТУРА И ХАРАКТЕРИСТИКИ СПЛАВА Zr-1%Nb, СИНТЕЗИРОВАННОГО ИЗ ГЕТЕРОГЕННЫХ ПОРОШКОВЫХ СМЕСЕЙ

***О.М. Ивасишин, В.Н. Воеводин, П.Е. Марковский, Н.Н. Пилипенко, Д.Г. Саввакин, С.Д. Лавриненко, О.П. Карасевская***

Приведены результаты исследования сплава Zr-1%Nb, полученного с применением порошковой технологии, включающей операции прессования и спекания гидрида циркония и ниобия. Показано, что полученный сплав обладает достаточным комплексом механических характеристик, который сравним с комплексом свойств соответствующего сплава, изготовленного по более сложной традиционной технологии.

## МІКРОСТРУКТУРА І ХАРАКТЕРИСТИКИ СПЛАВУ Zr-1%Nb, СИНТЕЗОВАНОГО З ГЕТЕРОГЕННИХ ПОРОШКОВИХ СУМІШЕЙ

***О.М. Івасішин, В.М. Воєводін, П.Є. Марковський, М.М. Пилипенко, Д.Г. Саввакін, С.Д. Лавриненко, О.П. Карасєвська***

Наведено результати дослідження сплаву Zr-1%Nb, отриманого із застосуванням порошкової технології, що включає операції пресування і спікання гідриду цирконію та ніобію. Показано, що отриманий сплав має достатній комплекс механічних характеристик, який можна порівняти з комплексом властивостей відповідного сплаву, виготовленого за більш складною традиційною технологією.