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Evolution of Phase Composition and Microstructure upon Synthesis of Zr–Sn Alloy from Zirconium Hydride and Tin Powders

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Microstructure and density evolution as well as thermal effects are investigated upon synthesis of Zr–1.5% Sn alloy from powder blends of zirconium-hydride and tin particles. Melting of tin particles at the initial stage of heating results in increased porosity, but does not accelerate chemical homogenization of powder system. Formation of solid intermetallics is accelerated at increased temperatures of 550–800°C due to hydrogen desorption and activation of zirconium matrix. Solid-state homogenization and sintering processes at higher temperatures produce homogeneous tin solution in zirconium. Particle sizes, temperature and time of sintering provide formation of low-porous (with relative density of more than 97%) chemically and microstructurally homogeneous material. Mechanical properties of fabricated alloy are at the level of properties of corresponding material produced with conventional ingot technology.

Досліджено еволюцію мікроструктури, густини та термічні ефекти в ході формування сплаву Zr–1.5% Sn з порошкових сумішей частинок гідриду Цирконію та цини. Нагрівання частинок цини на початкових стадіях нагрівання збільшує пористість у порошковій системі, не завдавши помітного розвитку хемічної гомогенізації, але за підвищення температури до 550–800°C прискорюється процес формування твердих інтерметалідних фаз, в тому числі завдяки десорбції Гідрогену з гідриду й активації цирконійової матриці. За високих температур гомогенізація та спікання частинок відбуваються твердофазним шляхом з формуванням однорідного твердого розчину Стануму в цирконії. Використані в роботі розміри порошкових частинок та температурно-часові параметри нагрівання уможливають одержати малопоруватий (з відносною густиною більше 97%)

хемічно й мікроструктурно однорідний сплав з механічними характеристиками на рівні характеристик даного матеріалу, одержаного методом лиття та гарячого деформування.

Исследована эволюция микроструктуры, плотности и термические эффекты в процессе формирования сплава Zr–1.5% Sn из порошковых смесей частиц гидрида циркония и олова. Плавление частиц олова на начальных стадиях нагрева увеличивает пористость в порошковой системе, не приводя к заметному развитию химической гомогенизации, но при повышении температуры до 550–800°C ускоряется процесс формирования твёрдых интерметаллидных фаз, в том числе благодаря десорбции водорода из гидрида и активации циркониевой матрицы. При высоких температурах гомогенизация и спекание частиц происходит твердофазным путём с формированием однородного твёрдого раствора олова в цирконии. Используемые в работе размеры порошковых частиц и температурно-временные параметры нагрева позволяют получить малопористый (с относительной плотностью более 97%) химически и микроструктурно однородный сплав с механическими характеристиками на уровне характеристик данного материала, полученного методом литья и горячей деформации.

Key words: microstructure, mechanical properties, chemical homogenization, zirconium hydride, tin.

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1. INTRODUCTION

Due to corrosion resistance and small cross-section of thermal-neutron capture, zirconium is extensively used in the nuclear reactor structures. Particularly, fuel element cans of thermal neutron reactor cores [1] are fabricated of zirconium–tin alloys (with tin content about 1.2–1.7 wt.%). Conventional fabrication of these alloys includes very complex ingot technologies and hot working of ingots, while their subsequent machining results to appreciable percentage of material loss as the scraps. The obtaining of alloys from powder materials serves as an alternative and a relatively technologically simple method. This allows us not only to avoid a number of problems associated with melting of alloys, *viz.* uncontrolled grain growth, appearance of the segregation of alloying elements, but also to reduce significantly metal loss in obtaining of products several times reducing their cost. Production of zirconium alloys with necessary physical-mechanical characteristics via the synthesis of heterogeneous systems of powder particles of zirconium and alloying elements is interesting from material science and practical point of view. It was recently shown that this method of synthesis of titanium and zirconium alloys [2, 3] results to their desired characteristics due to replacement of the powders of appropriate met-

als by the powders of their hydrides. Hydrogen in a specified method is a temporary alloying element activating sintering of particles and chemical homogenization of powder systems when they are heated, which improves characteristics of synthesized alloys.

Synthesis of zirconium alloys occurs at a temperature above the 1000°C in a single-phase β -region [3]. According to the state diagram [4] (see Fig. 1), during the formation of Zr–Sn alloys from the powders of these elements, a liquid Sn phase appears at the initial stages of heating and chemical homogenization of powder system, while the complete synthesis of these alloys with a relatively small tin content occurs in a solid-phase way. It is well known that the appearance of liquid phases during sintering of different powder systems can lead to both significant pore formation (e.g., in Ti–Al [5] and Ti–Fe [6] systems) and, *vice versa*, accelerated sintering (e.g., in W–Cu, W–Ni, and Cu–Sn systems [7]) with a reduced volume fraction of pores.

The goal of this work is to study synthesis of Zr–1.5% Sn alloy from the heterogeneous powder blends of zirconium hydride and tin, to ascertain peculiarities of microstructure evolution of such systems when liquid phase appears, and to determine the potential of forming chemically- and microstructurally homogeneous alloy with low volume frac-

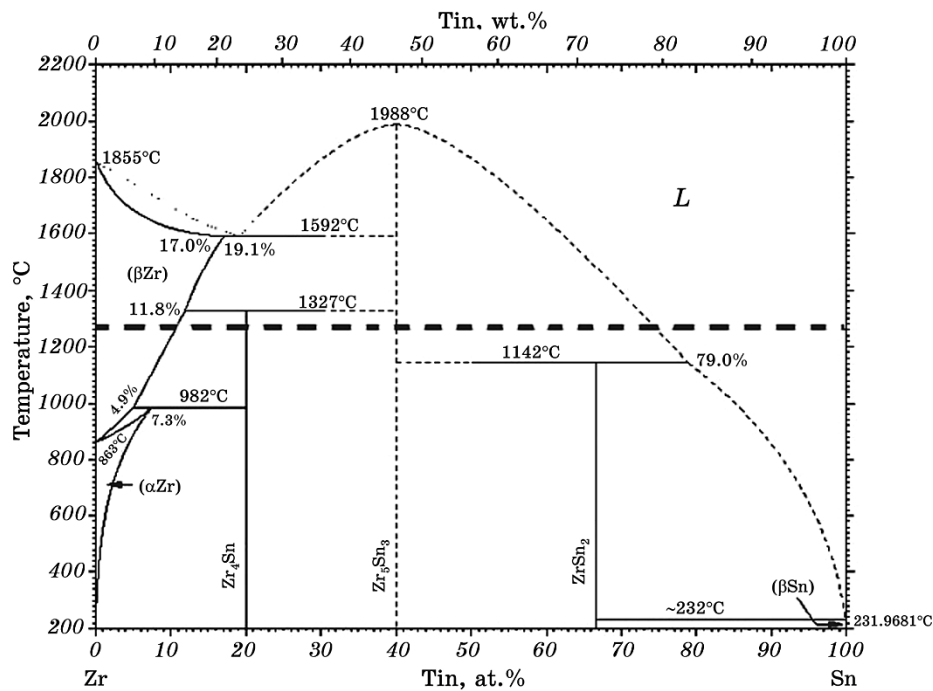


Fig. 1. State diagram of Zr–Sn system [4]. Heavy dashed line (at 1250°C) denotes the synthesis temperature of alloy at issue.

tion of pores and appropriate mechanical characteristics.

2. EXPERIMENTAL METHODS

The Zr–1.5 wt.% Sn alloy was prepared of the mixture with appropriate proportion of powder particles of zirconium hydride ZrH_2 and tin. In this work, we used the sieved fraction of hydride zirconium particles smaller than 100 μm while their average size was 56 μm , and tin particles smaller than 200 μm while their average size was 138 μm . The powder blend was pressed at a room temperature and pressure of 640 MPa in the cylindrical (with 10 mm of both diameter and height) and rectangular ($65 \times 10 \times 10 \text{ mm}^3$) samples, which then were heated up to 1250°C in a vacuum furnace ($\cong 10^{-3} \text{ Pa}$) with 10°C/min heating rate with further isothermal annealing during four hours for simultaneous dehydrogenation and formation of a bulky homogeneous alloy. For a step-by-step study of the phase and structural transformations during the hydrogen desorption and transformation of the powder blend into alloy, except of $ZrH_2 + 1.5\% \text{ Sn}$ composition, in some cases we also used a model blend of the powders with higher tin content, $ZrH_2 + 10\% \text{ Sn}$. The heating up to 320, 550, 800, and 1250°C at a rate of 10°C/min was followed by cooling in the furnace without isothermal annealing. Phase composition of the material was determined by the X-ray diffraction analysis using the CuK_α radiation. The differential scanning calorimetry method was used to establish general course of the phase transformations and thermal effects during the synthesis of alloy, for which we heated the powder blend $ZrH_2 + 10\% \text{ Sn}$ and hydride zirconium powder in an inert gas with the rate of 10°C/min up to 1250°C. The structure of material was investigated by the optic and scanning electron microscopy methods. The change in density of Zr–1.5% Sn samples at different heating stages was determined by the hydrostatic method. Mechanical characteristics of the synthesized Zr–1.5% Sn alloy were determined via tensile testing and measuring Vickers hardness. Oxygen content in the synthesized alloy was determined using the gas analyser ELTRA OH900.

3. RESULTS AND DISCUSSION

Applying the differential scanning calorimetry method, we determined the main temperature effects of the phase transformations occurring during the heating of $ZrH_2 + 10\% \text{ Sn}$ model blend (curve 1 in Fig. 2). Comparing this curve with the curve of heating for similar conditions of zirconium hydride powder (curve 2 in Fig. 2), we reveal that the first endothermic effect at 231°C is associated with melting of tin particles, and the following effects within the range of 390–800°C

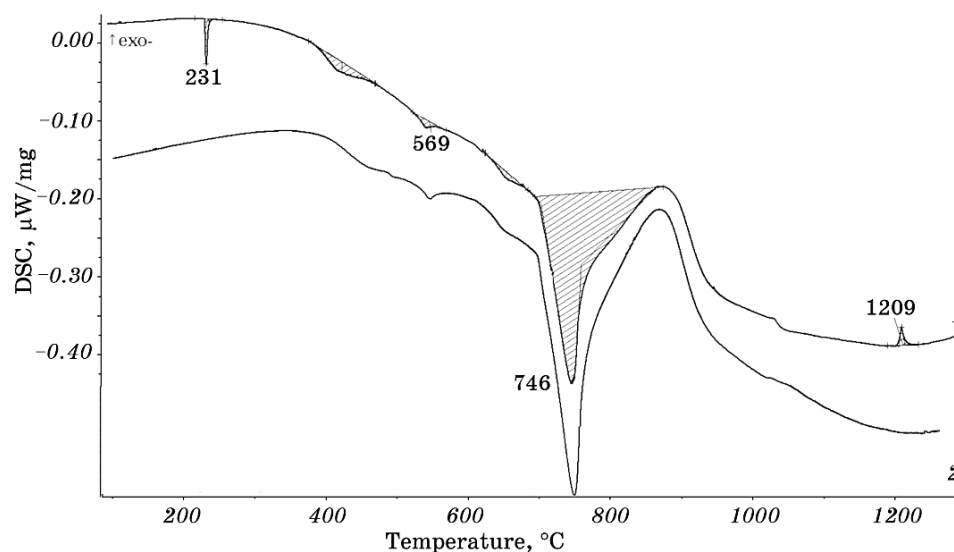


Fig. 2. Calorimetric curves of the heating of zirconium hydride and 10% of Sn powder (1), and zirconium hydride powder (2).

are resulted of hydrogen desorption from zirconium hydride and formation of zirconium dehydrated particles. Generally, calorimetric curve of the studied powder blend in the 300–1200°C temperature range practically coincides with the curve of heating of zirconium hydride powder (curve 2 in Fig. 2) without any appreciable effects dealing with the presence of tin and its possible reaction with zirconium matrix. The presence of tin results to the appearance of relatively weak exothermic peak only at 1209°C.

The microstructure evolution at a heating of the gathered powder blends is shown in Fig. 3. Tin particles located in hydride matrix are irregular in shape. Cleavage of powder compacts occurs mainly over the brittle hydride particles, which have low strength, therefore a relatively small number of tin particles is observed on the fractured surface (Fig. 3, *a*). Microstructure evolution appears already at a melting temperature of the tin. In the samples, cooled from 320°C, tin particles change their shape into spherical one (Fig. 3, *b*). Such shape of the particles indicates that at a heating temperature tin was in a melt state with spherical shape due to the surface tension, but appearance of liquid phase does not lead to the instantaneous reaction of tin with hydride particles. The gradual chemical homogenization of the system begins with the formation of tin liquid phase and occurs, however, rather slowly: X-ray microspectrum analysis data show that crystallized spherical tin droplet contains 4% of zirconium (Fig. 3, *b*), while hydride particles around it contain 1% of tin.

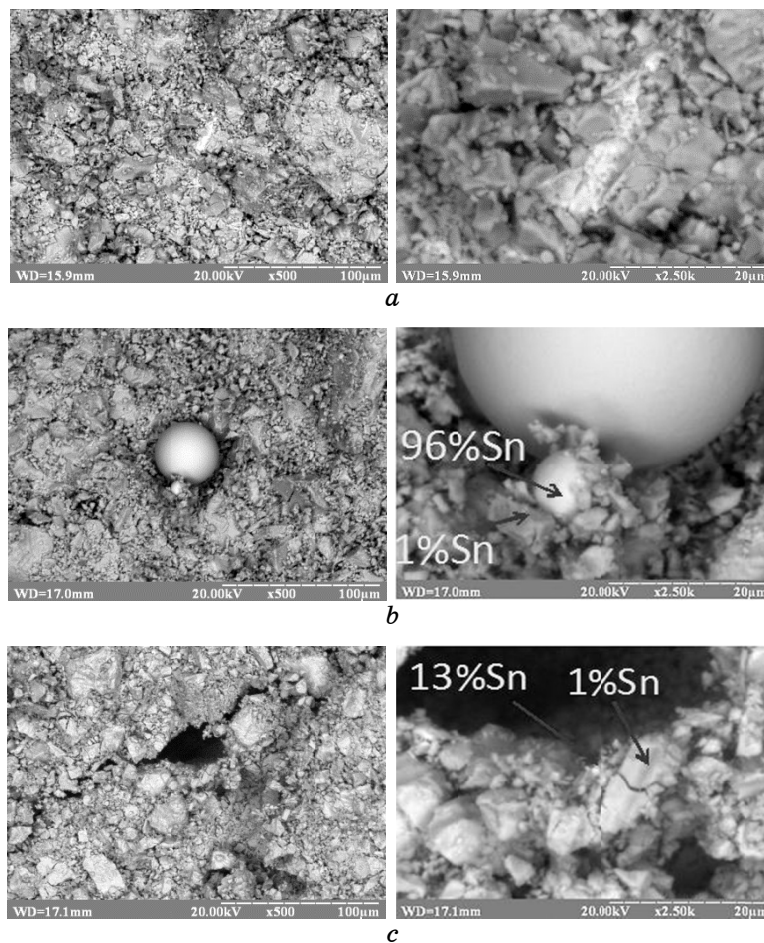


Fig. 3. Microstructure evolution of the system of zirconium hydride and tin particles (with composition corresponding to Zr–1.5% Sn alloy) during heating from the room temperature (*a*) to 320°C (*b*) and 800°C (*c*). Arrows denote local tin content.

These results agree with data of Ref. [8], where liquid tin phase can partly exist at 300°C during 48 hours while it is heated in contact with zirconium. According to Ref. [8], such temperature–time regimes result to the weak tendency for small Sn droplets to move to lower part of the pressed samples under the action of gravitational forces. However, in our study, a relatively rapid heating and, therefore, limited time for tin to exist as the droplets, did not result to the appearance of significant heterogeneity in the distribution of droplets over the samples volume.

At further temperature increasing, two processes occur simultane-

ously: desorption of hydrogen from hydride matrix (above the temperature of $\approx 390^\circ\text{C}$), which leads to $\text{ZrH}_2 \rightarrow \text{Zr}$ transformation, and redistribution of tin in the matrix with contribution of the liquid phase.

Tin droplets gradually react with zirconium matrix. We did not observe the crystallized spherical Sn droplets in the microstructure of the samples cooled from 550°C and 800°C (Fig. 3, c); instead of them voids with Sn-enriched surfaces were seen (e.g., 13% in Fig. 3, c). The X-ray analysis also confirmed the absence of pure tin after heating to 550°C (Fig. 4, a), while ZrSn_2 phase appeared, which coexists with hydride (δ -phase) and small amount of α -zirconium formed due to desorption of hydrogen from hydride. During heating to 800°C , the most active stage of hydrogen desorption occurs, and hydride is totally transformed into the α -phase of zirconium (Fig. 4, b). At the same time, the amount of Sn-enriched ZrSn_2 -phase significantly decreases, which can be caused by further tin spreading into the zirconium matrix and the formation of regions with lower local concentration of Sn.

Thus, the transition of Sn into the liquid state during heating provides its gradual reaction with zirconium matrix already at the relatively low temperatures (up to 550°C) with the formation of solid phases. As follows from Ref. [8], ZrSn_2 is the first phase forming at a contact of liquid tin and zirconium that occurs in a wide temperature range from 300 to 700°C and, in contrast to our data, requires long-term exposures. For instance, an isothermal exposure at 500°C during 1 hour is not sufficient for disappearance of pure tin [8]. In our case, the effect of accelerated disappearance of tin with the formation of ZrSn_2 -phase can be explained by the high defectiveness of dehydrogenated zirconium matrix [9] that contributes to the development of interdiffusion. Hydrogen desorption, being completed at 800 – 850°C ,

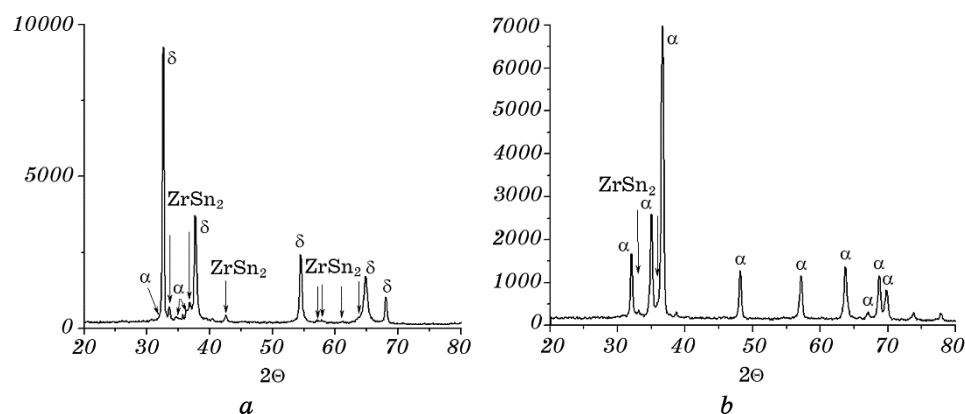


Fig. 4. The X-ray diffraction peaks for Zr–10% Sn sample after heating up to 550°C (a) and 800°C (b).

forms activated zirconium matrix that significantly accelerates sintering of zirconium particles and diffusion of tin into them with development of homogenization of the system.

According to the state diagram [4], intermetallic $ZrSn_2$ -phase exists up to $1142^\circ C$. Next stage of chemical homogenization of the system consists in the dissolution of $ZrSn_2$ and formation of intermetallic Zr_5Sn_3 -phase [8], and this process can be a solid-phase one during the long-term exposures below the specified temperature. In our experiments on the X-ray analysis for Zr–10% Sn samples heated to $800^\circ C$, the clear presence of Zr_5Sn_3 -phase was not revealed along with diffraction peaks of α -zirconium and $ZrSn_2$, which is caused by the short time of high temperatures subjected to the material. At a continuous heating in our case, the remains of the untransformed $ZrSn_2$ -phase have to be melting above the $1142^\circ C$. Therefore, one can explain an appearance of exothermal peak at $1209^\circ C$ (curve 1 in Fig. 2) by the accelerated chemical homogenization and formation of phases with lower tin content due to two reasons: first, activation of solid-phase diffusion at the increased temperatures, and, second, melting of the remains of $ZrSn_2$ -phase. The relatively weak endothermic melting effect in this case is suppressed by the exothermic effect of the formation of new phases, therefore it is not observed on calorimetric curves. According to the thermodynamic calculations [10] of energy effect of formation of intermetallic phases in Zr–Sn system, the strongest exothermic effect takes place for the formation of Zr_5Sn_3 phase. This effect exceeds the effects of the formation of Zr_4Sn and $ZrSn_2$ phase approximately by 3 and 3.5 times, respectively. Therefore, exothermic effect at $1209^\circ C$ can be associated with the formation of Zr_5Sn_3 phase, first, and, probably, Zr_4Sn one.

Increase in temperature up to $1250^\circ C$ leads to rapid tin spreading over all matrix and disappearance of the regions with high concentration gradient of this element, although some heterogeneity in a distribution remains. The concentration of tin in the sample cooled after the heating to $1250^\circ C$ is 1–2%. The total chemical homogeneity of the material can be reached relatively fast at the isothermal exposure at $1250^\circ C$.

The density increase of the samples at a heating is represented in Fig. 5. Note that, against the background of a general increase in density of the samples with increasing temperature, the density decreases at $800^\circ C$. During the heating in the range of 300 – $550^\circ C$, a certain decrease in density is typical for compressed powder systems based on the zirconium hydride particles [3]. For a relatively weak traction between zirconium hydride particles, the elastic energy accumulated in them relaxes, and hydride particles demonstrate microcracks being generated in the samples. This slightly increases volume of the compressed system, decreasing the density. In addition, the voids, being generated

on the same places occupied by the tin particles, also contribute to density decreasing for the samples heated to 800°C (Fig. 3, c). The hydrogen desorption is the most intensive within the 600–800°C. During this process, the particles decrease their volume, while sintering, being in progress at high temperature, leads to disappearance of voids between the particles, therefore the density rapidly increases. After 4-hour isothermal exposure at 1250°C, volume fraction of the pores significantly decreases, while massive chemically and microstructurally homogeneous Zr–1.5% Sn alloy is generated (Fig. 6). However, some rather large pores remain in the synthesized alloy and substitute voids appearing on the places of tin particles during the temperature increasing. The sizes of the largest pores are comparable with the sizes of initial tin particles (Fig. 6). Additional experiments confirmed that using of small tin particles allows decreasing of the volume and sizes of residual pores hereby approximating experimental density of the synthesized alloy to theoretical value, which is necessary condition to reach high mechanical characteristics. The sizes of tin particles used in the present work ($d_{\text{aver}} = 138 \mu\text{m}$) gave density of the synthesized alloy: 6.37 g/cm^3 —97.3% of theoretical value.

X-ray phase analysis indicates that alloy synthesized at 1250°C during four hours is a single-phase α (h.c.p.) solid solution of tin in zirconium. Such state practically corresponds to composition of Zr–1.5% Sn on the state diagram, while intermetallic Zr_4Sn -phase is not observed on the X-ray pattern.

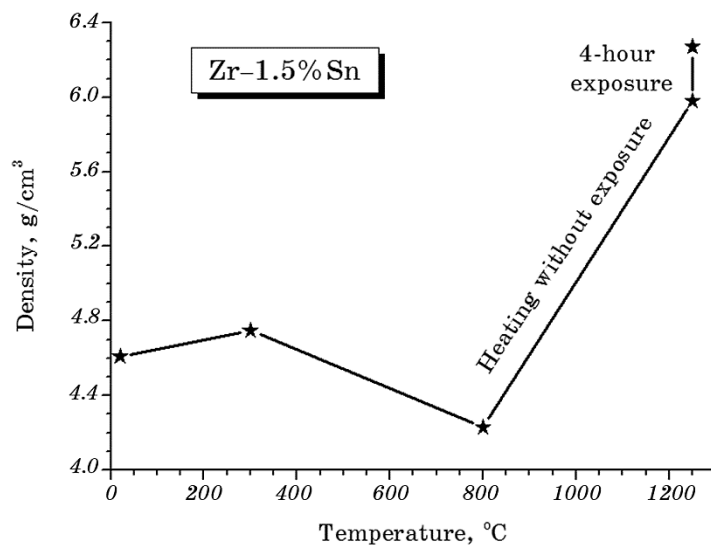


Fig. 5. Density evolution for samples during continuous heating up to 1250°C and four-hour isothermal exposure at this temperature.

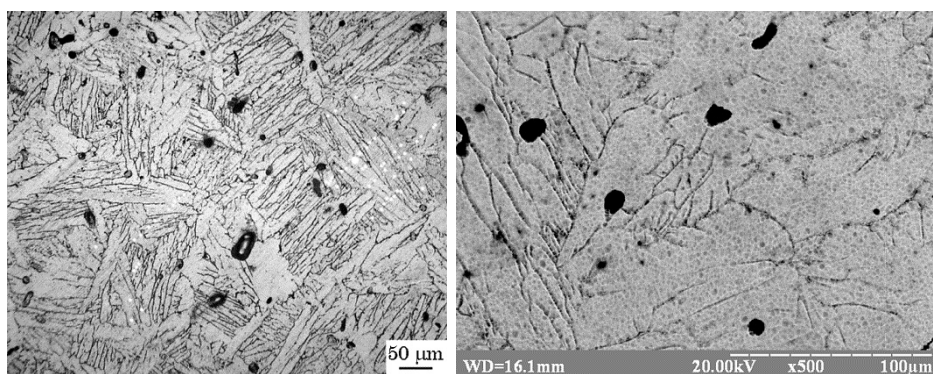


Fig. 6. Microstructure of Zr–1.5% Sn alloy synthesized at 1250°C during four hours.

TABLE. Characteristics of Zr–1.5% Sn alloy obtained in this work as compared with material obtained by a tradition method.

Method of obtaining	Density, g/cm ³	$\sigma_{0.2}$, MPa	σ_B , MPa	δ , %
Traditional technology [11, 12]	6.55	353	541	23.5
		430	520	–
Synthesized from ZrH ₂ powder	6.37 (97.3%)	475	561	12–13

Hardness of synthesized alloy is $H_V = (181.3 \pm 13.7) \text{ kg/mm}^2$. Mechanical properties of the alloy after the tensile test are presented in Table, where the data are also compared with literature ones [11, 12] on the properties of this material obtained by a traditional method of casting and hot working. Generally, the data presented in the literature differ widely due to different content of impurities, structure, and methods of the treatment of this alloy. At the same time, we can assert that characteristics of the strength and plasticity of alloy at issue are up to the corresponding characteristics that can be achieved by a traditional production method. Thus, the alloy synthesized from powders is a prospective for a practical use.

4. CONCLUSIONS

- (i) The Zr–1.5% Sn alloy was synthesized from a two-component zirconium hydride and tin powder blend. We used the size parameters of powder particles and temperature-time conditions of the synthesis allowing obtaining homogeneous alloy with density close to theoretical value.
- (ii) There are two simultaneous processes during the heating: hydrogen

desorption from the hydrogenated zirconium matrix and its reaction with melted tin. Sn totally reacts at the stage of heating to 550°C forming ZrSn₂-phase.

(iii) The melting of tin particles at early heating stages results in formation of pores that substitute tin droplets in hydride matrix. Decrease in size of tin particles enables decreasing sizes and total volume of residual pores in the synthesized alloy and makes closer its experimental density to theoretical value.

(iv) The Zr–1.5% Sn alloy synthesized by the presented method demonstrates the complex of tensile properties comparable with those a traditionally obtained material possesses. This confirms practical importance of the method applied in the paper.

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