

## CRYSTAL-LATTICE DEFECTS

PACS numbers: 61.66.Dk, 61.72.S-, 64.75.-g, 68.43.Mn, 68.43.Nr, 88.30.R-

### Alloy Based on Intermetallic (Ti, Zr)(V, Mn, Cr)<sub>2-x</sub> Obtained Using Titanium Sponge for Hydrogen Sorption

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The microstructure and phase composition of a cast Ti<sub>15.4</sub>Zr<sub>30.2</sub>Mn<sub>44</sub>V<sub>5.4</sub>Cr<sub>5</sub> alloy obtained using titanium sponge, as well as the phase composition of hydrogenation product, are investigated by scanning electron microscopy and X-ray phase analysis. As found, the complete replacement of expensive iodide titanium with a relatively cheap titanium sponge does not affect the structure and phase composition of the alloy. As shown, the saturation of the alloy with hydrogen occurs at room temperature and pressure of hydrogen of 0.21 MPa in a short time up to a capacity of 2.12% mass.

**Key words:** Laves phase, titanium sponge, hydrogenation, dehydrogenation, hydrogen capacity.

Методами сканувальної електронної мікроскопії та рентгенівського фазового аналізу досліджено мікроструктуру і фазовий склад литого сплаву Ti<sub>15,4</sub>Zr<sub>30,2</sub>Mn<sub>44</sub>V<sub>5,4</sub>Cr<sub>5</sub>, отриманого з використанням титанової губки, а також фазовий склад продукту гідрування. Встановлено, що повна заміна коштовного титану йодидного на відносно дешеву титанову губку не впливає на структуру та фазовий склад сплаву. Показано, що насичення сплаву воднем відбувається за кімнатної температури та тиску водню 0,21 МПа за короткий час до ємності 2,12% мас.

**Ключові слова:** фаза Лавеса, титанова губка, гідрування, дегідрування, воднева ємність.

Методами сканирующей электронной микроскопии и рентгеновского фа-

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Citation: V. A. Dekhtyarenko, Alloy Based on Intermetallic (Ti, Zr)(V, Mn, Cr)<sub>2-x</sub> Obtained Using Titanium Sponge for Hydrogen Sorption, *Metallofiz. Noveishie Tekhnol.*, 41, No. 10: 1283–1290 (2019), DOI: [10.15407/mfint.41.10.1283](https://doi.org/10.15407/mfint.41.10.1283).

зового анализа исследованы микроструктура и фазовый состав литого сплава  $\text{Ti}_{15,4}\text{Zr}_{30,2}\text{Mn}_{44}\text{V}_{5,4}\text{Cr}_5$ , полученного с использованием титановой губки, а также фазовый состав продукта гидрирования. Установлено, что полная замена дорогого титана йодидного на сравнительно дешёвую титановую губку не влияет на структуру и фазовый состав сплава. Показано, что насыщение сплава водородом происходит при комнатной температуре и давлении водорода 0,21 МПа за короткий промежуток времени до ёмкости 2,12% масс.

**Ключевые слова:** фаза Лавеса, титановая губка, гидрирование, дегидрирование, водородная ёмкость.

*(Received May 5, 2019; in final version, August 16, 2019)*

## 1. INTRODUCTION

At present, due to the rapid development of hydrogen energy and the active use of hydrogen in the automotive industry, the search for new materials for its safe storage and transportation in a bound state (as hydrides) is promising [1]. Particular attention is paid to the alloys based on the Laves phase  $\text{TiMn}_2$  as they have a fairly high sorption capacity  $\text{H}/\text{Me} \approx 1$  [2] and are easily activated [3].

It was shown in [4] that partial replacement in the Laves phase  $\text{TiMn}_2$  of titanium by zirconium and manganese by vanadium allows to increase the amount of absorbed hydrogen and improve the sorption kinetics; however, the thermal stability of the resulting hydride increases. The authors have shown that an increase in hydrogen capacity occurs due to the redistribution of hydrogen atoms in the tetrahedral voids. Also, the authors found that an increase in the thermal stability of the resulting hydride is explained by the fact that titanium atoms occupy vacant positions of manganese atoms. The raw components used to obtain the alloy had purity at least 99.9%.

The authors of [5] investigated the hydrogen-adsorption properties of the alloy  $\text{Ti}_{0.72}\text{Zr}_{0.28}\text{Mn}_{1.6}\text{V}_{0.4}$  obtained by induction smelting and mechanical alloying. It was shown that, regardless of the method of obtaining, the alloy had two-phase structure comprised of Laves phase and bcc-solid solution; however, the hydrogen capacity significantly differed: for the alloy obtained by the casting method it was up to 2% mass, whereas after mechanical alloying it was only 1.2% mass. Elementary powders with size of 60  $\mu\text{m}$  and purity of 99.9% were used to obtain the alloy, irrespective of the manufacturing method.

In the work [6], the possibility of  $(\text{Ti}_{0.85}\text{Zr}_{0.15})_{1.05}\text{Mn}_{1.2}\text{Cr}_{0.6}\text{V}_{0.1}\text{M}_{0.1}$  alloy (where  $\text{M} = \text{Ni}, \text{Fe}, \text{Cu}$ ) using as a material for hydrogen storage was shown. It was found that this alloy is a single-phase one with the Laves phase, and the maximum hydrogen capacity can be achieved only in one cycle of sorption-desorption. It was also shown that replacing manga-

nese by Ni, Fe or Cu in the given range leads to an improvement in the processes of sorption and desorption of hydrogen, as well as to increase in hydrogen capacity. The authors used components with a purity of at least 99.5 % to produce the alloy.

The authors of [7] studied the hydrogen-adsorption properties of  $\text{Ti}_{1.02}\text{Cr}_{1.1}\text{Mn}_{0.3}\text{Fe}_{0.6}$  alloy with RE additions (RE – La, Ce, Ho), which is used as a material for hydrogen storage. It was shown that in the initial state the alloy had single-phase structure of the Laves phase, and after adding RE a second phase, an oxide based on RE appeared. The addition of RE leads to an increase in the size of the primitive cell, and, consequently, to an increase in the amount of hydrogen absorbed and to the improvement of the sorption and desorption processes. The authors claim that after adding RE the alloys are able to absorb hydrogen at room temperature and pressure of hydrogen 34–43 MPa to a capacity of 1.715% mass. The raw components used to obtain the alloy had purity at least 99%.

Previously, we have shown [8] the prospect of using as a material for safe storage and transport of hydrogen in a bound state the alloy  $\text{Ti}_{15.4}\text{Zr}_{30.2}\text{Mn}_{44}\text{V}_{5.4}\text{Cr}_5$  based on intermetallic  $(\text{Ti}, \text{Zr})(\text{V}, \text{Mn}, \text{Cr})_{2-x}$ . This alloy has rather high for its class hydrogen capacity of 2% mass and the maximum rate of hydrogen desorption is reached at 115°C. Like most other researchers, to obtain the alloy we used high-purity (expensive) components: iodide titanium and zirconium, as well as electrolytic vanadium, manganese and chromium, which significantly increased the cost of the hydride.

The purpose of the present work was to assess the possibility of reducing the cost of the resulting hydride by replacing the high-purity components by cheaper ones. For this goal, previously investigated [8] alloy  $\text{Ti}_{15.4}\text{Zr}_{30.2}\text{Mn}_{44}\text{V}_{5.4}\text{Cr}_5$  was melted, wherein iodide titanium (\$70 for 1 kg) was replaced by cheap grades of titanium sponge (TG-110, TG-130, TG-TV, \$10 for 1 kg).

## 2. MATERIALS AND METHODS

The alloy was produced by electric arc melting in a laboratory furnace with a non-expendable tungsten electrode in an atmosphere of purified argon. Titanium sponge, iodide Zr (99.975), electrolytic Mn (99.9), electrolytic V (99.5), electrolytic Cr (99.5) were used as starting components. The deviation of the chemical composition of the alloy from the nominal was determined by fluorescence X-ray spectral analysis (VPA-30). It coincided with the nominal one within the measurement error (0.03%).

Metallographic studies were performed using a scanning electron microscope VEGA3TESCAN.

The phase composition and parameters of crystalline lattices were

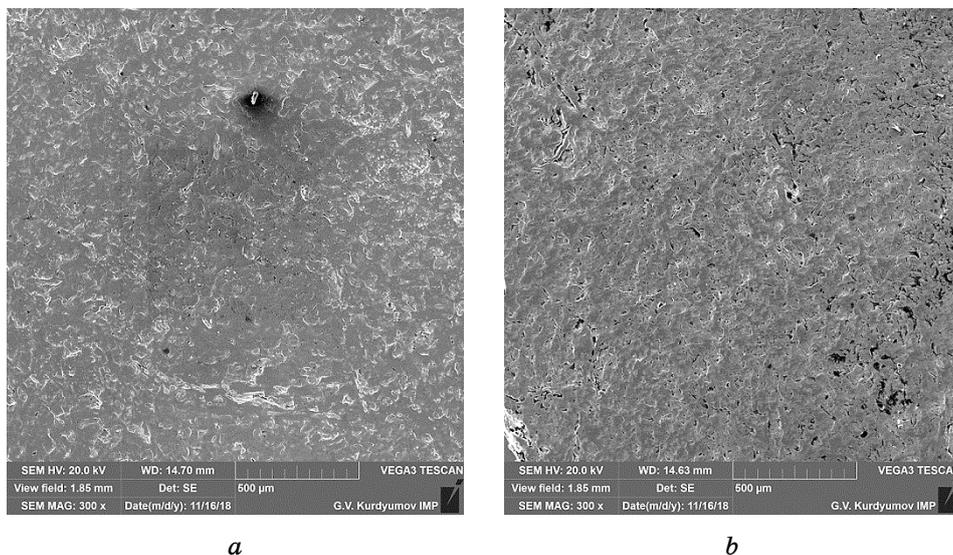
determined by X-ray phase analysis at a DRON-3M diffractometer.

For the study of hydrogen adsorption properties, cast alloy was used in a monolithic state. The interaction of the alloy with hydrogen was studied by the Sievert's method at unit IVGM-2M [9] at room temperature and pressure of 0.21 MPa. The amount of absorbed hydrogen was determined by weighing with an accuracy of  $1.5 \cdot 10^{-5}$  g and calculated by changing the pressure in a closed volume. The studies on the desorption of hydrogen were carried out on an automated dilatometric complex (ADC) with a mass spectrometer [10].

### 3. RESULTS AND DISCUSSION

Scanning electron microscopy showed that the complete replacement of iodide titanium by titanium sponge did not affect the structure of the alloy (Fig. 1). As in earlier work [8], the structure of the alloy comprised of coarse crystals of the intermetallic  $(\text{Ti}, \text{Zr})(\text{V}, \text{Mn}, \text{Cr})_{2-x}$  (Laves phase) with faceted shape, with inclusions of b.c.c.-solid solution inside.

The presence of intermetallic  $(\text{Ti}, \text{Zr})(\text{V}, \text{Mn}, \text{Cr})_{2-x}$  and traces of bcc-solid solution was confirmed by the X-ray phase analysis method, which indicated the stability of the phase composition of the alloy (Table 1). As expected, two intermetallics  $(\text{Ti}, \text{Zr})(\text{V}, \text{Mn}, \text{Cr})_{2-x}$  with different crystalline lattices (hexagonal C14 and cubic C15, Table 1) were



**Fig. 1.** The microstructure of the cast alloys  $\text{Ti}_{15.4}\text{Zr}_{30.2}\text{Mn}_{44}\text{V}_{5.4}\text{Cr}_5$ : *a*—iodide titanium, *b*—titanium sponge.

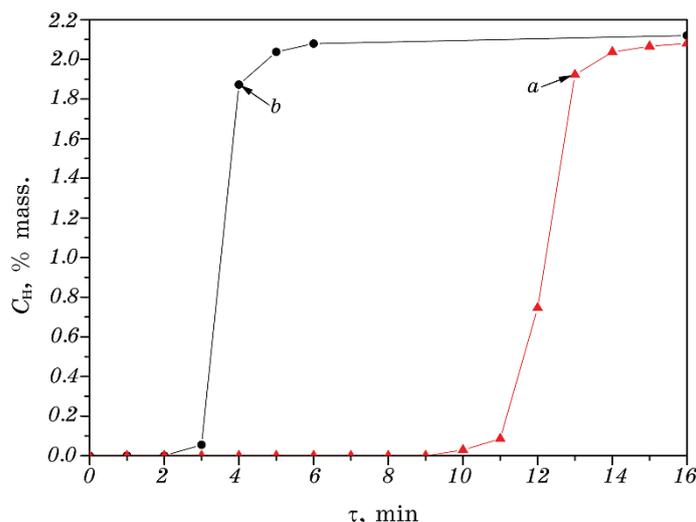
**TABLE 1.** The results of X-ray phase analysis of the initial and hydrogenated alloys.

Alloy $\text{Ti}_{15.4}\text{Zr}_{30.2}\text{Mn}_{44}\text{V}_{5.4}\text{Cr}_5$	Parameters of crystalline lattice of phases $\pm 0.0002$ (nm)			
	Initial		Hydrogenated	
	C14	C15	C14	C15
Iodide Titanium [8]	$a = 0.5093$ $c = 0.8367$	$a = 0.7203$	$a = 0,5491$ $c = 0,9019$	$a = 0.7665$
Titanium sponge	$a = 0.5073$ $c = 0.8334$	$a = 0.7188$	$a = 0,5489$ $c = 0,9017$	$a = 0.7776$

present in the alloy. The presence of intermetallic compound (Ti, Zr)(V, Mn, Cr)<sub>2-x</sub> with a cubic lattice can be explained basing on the phase diagram of the Zr–Cr system [11]. In accordance with this diagram, a Laves phase with a hexagonal lattice, which exists up to a temperature of 1550°C, is formed from the liquid, and below there is a phase transformation during which a Laves phase with a cubic lattice is formed, which exists in equilibrium conditions at room temperature.

The process of interaction of the alloy with hydrogen was studied under the same hydrogenation parameters as for the alloy previously investigated (room temperature, pressure of hydrogen 0.21 MPa). The process of active absorption of hydrogen by the alloy obtained from titanium sponge started after two minutes (incubation period) of contact with the hydrogen-containing medium and lasted for five minutes, wherein the hydrogen capacity of 2.12% mass was achieved, and for the alloy obtained from iodide titanium it was 2.08% mass (Fig. 2). Subsequent exposure for 30 minutes did not result in renewal of the hydrogen absorption. When saturated with hydrogen, regardless of the initial state of titanium, the destruction of solid samples to the state of powder occurred. This occurred due to the high rate of hydrogenation at room temperature, so there was not enough time for relaxation of the stresses that arose upon hydrogen dissolving. Analysis of the obtained hydride showed that after the first hydrogenation, the size of powder particles varied from 1 to 100  $\mu\text{m}$ , while the largest amount of powder obtained had a size of 22  $\mu\text{m}$ .

According to the data of the X-ray phase analysis, hydrogenation of the alloy obtained from titanium in different starting conditions resulted in the formation of hydrides based on the original phases (Table 1, Fig. 3). As expected, during hydrogenation there was no change in the structure of the metal matrix, but only an isotropic increase in the volume of the primitive cell by 20% occurred, and the data obtained coincide with the results of [12]. Comparing the parameters of the crystalline lattice of the phases after hydrogenation (Table 1), it can be



**Fig. 2.** Change of the concentration of hydrogen over time upon the first hydrogenation of the alloy: *a*—iodide titanium, *b*—titanium sponge.

suggested that the hydrogen capacity of the alloy obtained from titanium sponge increased due to the Laves phase of the C15 type.

According to the data presented in [13] for alloys with chromium, the process of decomposition of the obtained hydrides can be carried out without heating, at room temperature. It can be assumed that the difference between the parameters of the lattices of the C15-type Laves phase in the alloys after hydrogenation is explained by the different amounts of desorbed hydrogen at room temperature and atmospheric pressure.

The process of hydrogen release at an initial pressure of  $4 \cdot 10^{-3}$  Pa from hydrogenation products obtained by saturation of the alloy with hydrogen, regardless of the initial state of titanium, started at room temperature, while it is possible to remove no more than 4% of the absorbed hydrogen. The renewal of the process of hydrogen release by alloys was possible only under heating (Fig. 4), and the maximum rate of hydrogen release was achieved at a temperature of 115–120°C, where in full desorption occurred at 300–320°C.

After the sorption-desorption cycle, the alloy, irrespective of the initial state of titanium, had an activated surface, and therefore, the subsequent sorption of hydrogen occurred at room temperature and the same pressure (0.21 MPa) starting from the first seconds of contact with the hydrogen-containing medium. The reduction of the incubation period after the sorption-desorption cycle from minutes to seconds can be explained by the following factors. Firstly, the destruction of the monolithic sample to the state of the powder occurred, at the ex-

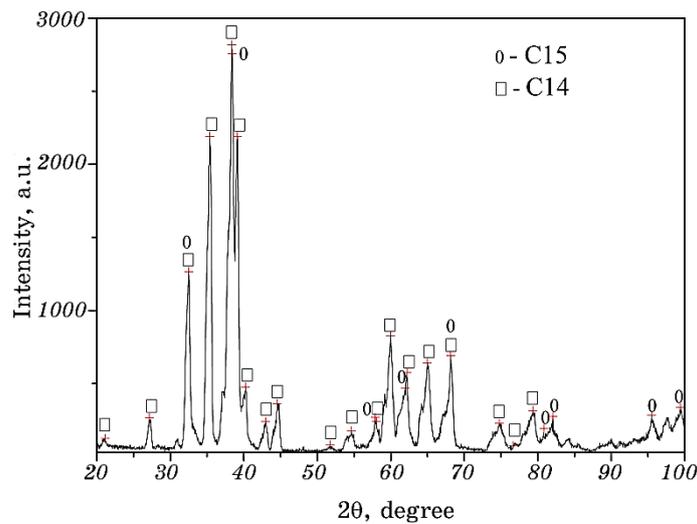


Fig. 3. Hydrogenated alloy diffraction pattern.

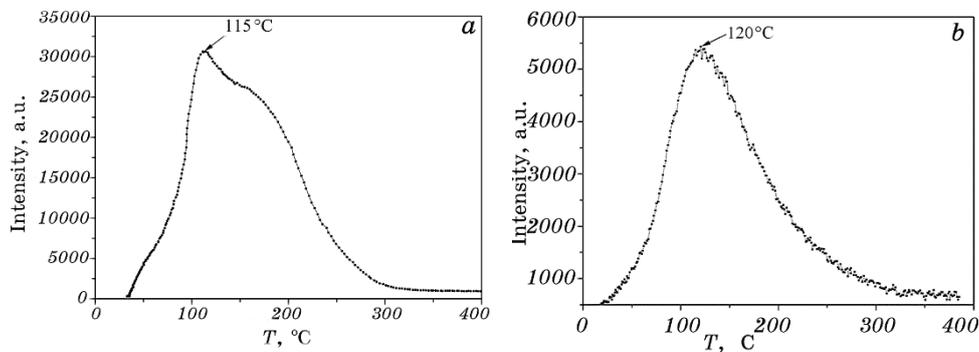


Fig. 4. Dependence of the intensity of hydrogen release from temperature: *a*—iodide titanium, *b*—titanium sponge.

pense of which the reaction surface for the dissociation of hydrogen molecule increased, and secondly, the decrease in the concentration of oxygen on the surface of the particles as a result of its interaction with released atomized hydrogen.

#### 4. CONCLUSION

The complete replacement of titanium iodide by sponge does not affect the structure, phase composition and hydrogen sorption-desorption properties of  $\text{Ti}_{15.4}\text{Zr}_{30.2}\text{Mn}_{44}\text{V}_{5.4}\text{Cr}_5$  alloy.

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