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Hydrogen-Sorption Properties of the Alloy $\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$ Based on the Laves Phase (Type C14)

V. A. Dekhtyarenko

*G. V. Kurdyumov Institute for Metal Physics, N.A.S. of Ukraine,
36 Academician Vernadsky Blvd.,
UA-03142 Kyiv, Ukraine*

Microstructure and phase composition of the cast $\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$ alloy as well as the phase composition of hydrogenation and dehydrogenation products are investigated using the methods of x-ray phase analysis and scanning electron microscopy. As established, due to the partial replacement of manganese with cobalt, it is not possible to expand the area of existence of the Laves phase (type C14), since, in the phase composition of the studied alloy, a second intermetallic phase based on the Zr_2Co compound is formed. As determined, the change in the phase composition of the alloy does not affect significantly the kinetics of hydrogen absorption and desorption at the first sorption–desorption cycle. As established, the formed intermetallide based on the Zr_2Co compound interacts actively with hydrogen at room temperature and a hydrogen pressure of 0.23 MPa. As shown, the process of hydrogen release begins with the start of heating; at a temperature of 430°C, a reversible capacity of 95% is achieved.

Key words: Laves phase (type C14), intermetallic Zr_2Co , hydrogenation, dehydrogenation, hydrogen capacity.

Методами рентгенівської фазової аналізи та сканувальної електронної мікроскопії досліджено мікроструктуру та фазовий склад литого ступу $\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$, а також фазовий склад продуктів гідрування та

Corresponding author: Volodymyr Anatoliyovych Dekhtyarenko
E-mail: devova@i.ua

*G. V. Kurdyumov Institute for Metal Physics, NAS of Ukraine,
36 Academician Vernadsky Blvd.,
UA-03142 Kyiv, Ukraine*

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дегідрування. Встановлено, що завдяки частковій заміні Мангану на Кобальт не вдалося розширити область існування Лавесової фази типу C14, оскільки у фазовому складі досліджуваного ступу утворилася друга фаза — інтерметалід на основі сполуки Zr_2Co . Визначено, що зміна фазового складу ступу істотно не впливає на кінетику процесів поглинання та виділення Гідрогену у першому циклі сорбція–десорбція. Встановлено, що утворений інтерметалід на основі сполуки Zr_2Co активно взаємодіє з Гідрогеном за кімнатної температури та тиску Гідрогену у 0,23 МПа. Показано, що процес виділення Гідрогену розпочинається з початком нагріву; за температури у 430°C досягається реверсивна місткість на рівні 95%.

Ключові слова: Лавесова фаза типу C14, інтерметалід Zr_2Co , гідрування, дегідрування, воднева місткість.

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1. INTRODUCTION

Among the existing variety of materials for hydrogen batteries developed today, a special place is occupied by intermetallics of type AB_2 [1–6]. This is due to the fact that, unlike type AB_5 ($LaNi_5$), they have a higher hydrogen capacity, and compared to type AB ($TiFe$), the activation process is facilitated [5]. The main representative of AB_2 type intermetallic is $TiMn_2$ compound (Laves phase (type C14)) [7, 8]. Intermetallic $TiMn_2$ occupies a special place among analogues in its class ($ZrCo_2$ and ZrV_2) [9]. Since it is easily activated at room temperature and a pressure of 3.2 MPa [10], it releases all the absorbed hydrogen when heated to a temperature of 400°C [11], has a significant hydrogen capacity of $\cong 1.0$ H/Me [12, 13], a large homogeneity region of 11 at.% [14] and low specific gravity [5].

Despite all the mentioned advantages of the $TiMn_2$ binary intermetallic, currently, when creating materials for hydrogen batteries, more complex alloying systems are used [15–18].

The authors of [19] suggested partial substitution of titanium for zirconium in $TiMn_2$ intermetallic compound (as component A).

It was shown in [20] that due to the partial replacement of titanium for zirconium, it was possible to expand the area of existence of the Laves phase to 54.4 at.% Mn, and this, in turn, made it possible to increase the hydrogen capacity to H/Me $\cong 1.2$ and decrease the hydrogenation pressure from 3.2 MPa to 0.6 MPa. The authors showed that this improvement in hydrogen-sorption properties occurs because zirconium has a higher affinity for hydrogen than titanium. The paper [20] proved the positive effect of doping and deviation from the stoichiometric composition of AB_2 on the hydrogen-sorption properties of alloys based on intermetallic AB_2 . However, the conducted research was done only for the partial replacement of titanium with zirconium,

which in the AB_2 type intermetallic is component A . That is why the authors [15, 17, 21] proposed to carry out a partial replacement of component B (that is, to replace manganese, which does not interact with hydrogen, by vanadium, which is able to interact).

This idea was developed in works [17, 22]. Using the example of the $(\text{Ti}_{0.34}\text{Zr}_{0.66})\text{Mn}_{1.1}\text{V}_{0.1}$ alloy, the effect of partial replacement of component B (manganese with vanadium) on the hydrogen sorption properties of intermetallic type AB_2 was investigated [22]. Referring to literature data [17, 21], the authors [22] note that the partial replacement of manganese with vanadium allows lowering the homogeneity region to 49 at.% Mn. The interaction of this alloy with hydrogen took place at room temperature at a high speed, while it was possible to reach the value of the amount of absorbed hydrogen at the level of $\text{H}/\text{Me} \cong 1.3$. The authors explain the improvement of the hydrogen-sorption properties of the investigated alloy by a significant expansion of the homogeneity region.

From literature data, it was found [23, 24] that chromium is also able to effectively influence the kinetics of hydrogen sorption-desorption processes, as well as the hydrogen capacity of alloys based on the TiMn_2 intermetallic. In works [25, 26], it was proved that additional doping of the alloy $(\text{Ti}_{0.34}\text{Zr}_{0.66})\text{Mn}_{1.1}\text{V}_{0.1}$ with chromium (the investigated composition $(\text{Ti}_{0.34}\text{Zr}_{0.66})\text{Mn}_{0.96}\text{V}_{0.12}\text{Cr}_{0.12}$) allows decrease the hydrogenation pressure from 0.6 to 0.23 MPa, and increase the hydrogen capacity to $\text{H}/\text{Me} \cong 1.38$.

The authors of Refs. [25, 26] claim that the increase in hydrogen capacity to the specified level is a consequence of reducing the amount of manganese to 44 at.%.

However, the ever-increasing requirements for the hydrogen battery [27–29] (time of operation on one charge) require further improvement of the developed material $(\text{Ti}_{0.34}\text{Zr}_{0.66})\text{Mn}_{0.96}\text{V}_{0.12}\text{Cr}_{0.12}$, that is, the search for elements for additional alloying. Based on certain literary data [30], it was established that cobalt is a promising element for additional alloying. The choice of cobalt as an alloying element is related to the fact that it is able to form a chemical compound with hydrogen, as well as to dissolve in Laves phases [31].

The aim of the present study establishes the effect of the expansion of the homogeneity region of the Laves phase (type C14) below 44 at.% Mn, due to partial replacement by cobalt, on its hydrogen-absorption properties. The alloy $\text{Ti}_{15.4}\text{Zr}_{30.2}\text{Mn}_{44}\text{V}_{5.4}\text{Cr}_5$ (formula composition $(\text{Ti}_{0.34}\text{Zr}_{0.66})\text{Mn}_{0.96}\text{V}_{0.12}\text{Cr}_{0.12}$) was chosen for the investigated, the hydrogen sorption-properties of which were described in detail in [25, 26], in which partial substitution was carried out manganese, by 5.5 at.% cobalt (as in previous experiments [22, 25]). In the investigation, the effect of doping with cobalt was considered only at the first cycle of hydrogen sorption-desorption.

2. EXPERIMENTAL/THEORETICAL DETAILS

An alloy weighing up to 1 kg was obtained by the method of induction melting in an argon atmosphere using open crucibles with Al_2O_3 . Titanium sponge (TG-110), iodide Zr (99.975), electrolytic Mn (99.9), electrolytic V (99.5), electrolytic Cr (99.5) and electrolytic Co (99.5) were used as starting components. To obtain the alloy, a previously developed technological scheme was used, which is described in detail in the paper [32]. It should be noted that during the preparation of the charge additional were added, 4% wt. of manganese compared to the nominal composition, since in [17], when studying the hydrogen sorption properties of the $\text{Ti}_{0.9}\text{Zr}_{0.1}\text{Mn}_{1.2}\text{V}_{0.1}$ alloy, the authors proved that exactly this amount of manganese is lost due to evaporation during the preparation of the alloy.

The phase composition and lattice parameters of the alloy were determined by x-ray phase analysis at a DRON-3M diffractometer.

Metallographic examinations were performed at a scanning electron microscope VEGA3 TESCAN equipped with EDX detector XFlash610M (Bruker).

For the study of hydrogen absorption properties, a bulk cast alloy was used. The interaction of the alloy with hydrogen was studied by the Sieverts' method at an IVGM-2M unit [33] at room temperature and a pressure of 0.23 MPa. The hydrogen desorption process was also investigated on IVGM-2M equipment at an initial pressure of 0.0002 MPa. The amount of absorbed hydrogen was determined by weighing with an accuracy of $1.5 \cdot 10^{-5}$ g and calculation of changing the pressure in a closed volume.

3. RESULTS AND DISCUSSION

3.1. Phase Composition and Microstructure

Since all components of the melt, especially titanium, zirconium, and chromium, could react relatively easily with the crucible material, it was important to establish, whether an interaction between the melt and the crucible material had occurred. Since it is well known that aluminium has a negative effect on the hydrogen-sorption properties of titanium and alloys based on it [34], the chemical composition of the molten alloy was determined using EDAX energy dispersive analysis (Table 1). It was established that aluminium in the ingot is present in a small amount, from which it can be concluded that there was no significant interaction between the crucible material and the melt.

As can be seen from the presented chemical composition data, the obtained alloy had a slightly increased manganese concentration, and all other elements within the measurement error of ± 0.3 at.% coincided.

TABLE 1. The composition of the obtained alloy.

Composition	Elements, at. %						
	Ti	Zr	Mn	V	Cr	Co	Al
Initial materials	15.5	30	38	5.5	5.5	5.5	–
Alloy	15.34	29.68	38.58	5.22	5.42	5.65	0.11

ed with the nominal composition. The increased final concentration of manganese is due to the fact that the total amount in the charge (partial replacement by chromium and cobalt) was significantly less compared to the alloy, for which the calculations were made [17]. That is why, despite the fact that an ingot weighing up to 1 kg was obtained in an open crucible, the manganese burnout turned out to be somewhat less than predicted one.

The phase composition of the $\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$ alloy at issue was determined using x-ray phase analysis (Table 2, Fig. 1, *a*). It was established that the investigated alloy was multiphase, a hexagonal Laves phase (*C14* type) of space group $P6_3/mmc$ (structural type MgZn_2) was found in the structure. In addition, the presence of a second phase was established, which was identified as an intermetallic based on a Zr_2Co compound with a face-centred cubic lattice of the space group $Fd\bar{3}m$ (structural type Ti_2Ni).

To determine correctly the changes occurring in the unit cell of the Laves phase when doping with cobalt, based on the data of x-ray phase analysis and presented in works [35, 36], the volume of the unit cell and the radius of the tetrahedral internode were calculated. Because it was proved in Ref. [36] that, regardless of the type of crystal lattice of the Laves phase, it is the tetrahedral internodes, which are the sites of hydrogen localization during dissolution. The authors of [35, 36] showed that the radius of the tetrahedral internode is calculated from the approximation of ‘hard spheres’ using the expressions $R_s(C14) = 0.074475a$, $R_s(C15) = 0.052662a$ (where a is crystal lattice parameter). The calculation was made exclusively for one type of internodes A_2B_2 . Since, the authors of [35, 36] proved that hydrogen, when dissolved in the crystal lattice of the Laves phase, occupies only them. It was determined that the volume of the unit cell is 182.42 \AA^3 , while the radius of the tetrahedral internode is 0.3753 \AA , for the original alloy $\text{Ti}_{15.4}\text{Zr}_{30.2}\text{Mn}_{44}\text{V}_{5.4}\text{Cr}_5$ [25, 26] 185.52 \AA^3 and 0.3778 \AA , respectively. Their comparison indicates a significant decrease, which may further negatively affect the amount of absorbed hydrogen, as it was shown earlier [5].

TABLE 2. The results of x-ray phase analysis.

Alloys	Parameters of crystalline lattice of phases ± 0.0009 nm					
	Initial		Hydrogenated		Dehydrogenated	
	λ -C14	New	λ -C14	New	λ -C14	New
$\text{Ti}_{15.4}\text{Zr}_{30.2}\text{Mn}_{44}\text{V}_{5.4}\text{Cr}_5$ [25, 26]	$a = 0.5073$ $c = 0.8334$	—	$a = 0.5489$ $c = 0.9017$	—	$a = 0.5074$ $c = 0.8335$	—
$\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$	$a = 0.5040$ $c = 0.8302$	$a = 1.1907$	$a = 0.5469$ $c = 0.8917$	$a = 1.2455$	$a = 0.5058$ $c = 0.8291$	$a = 1.1936$

With the use of scanning electron microscopy, it was confirmed the data obtained by the x-ray phase analysis method, regarding the fact that two phases are observed in the structure of the investigated alloy $\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$ (Fig. 2, *b*), while in the original alloy [25, 26], only one (Fig. 2, *a*).

Since a second phase of intermetallic based on Zr_2Co is formed in the structure of the investigated $\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$ alloy, it is important to determine the chemical composition of the coexisting phases. This will make it possible to establish, how the cobalt introduced

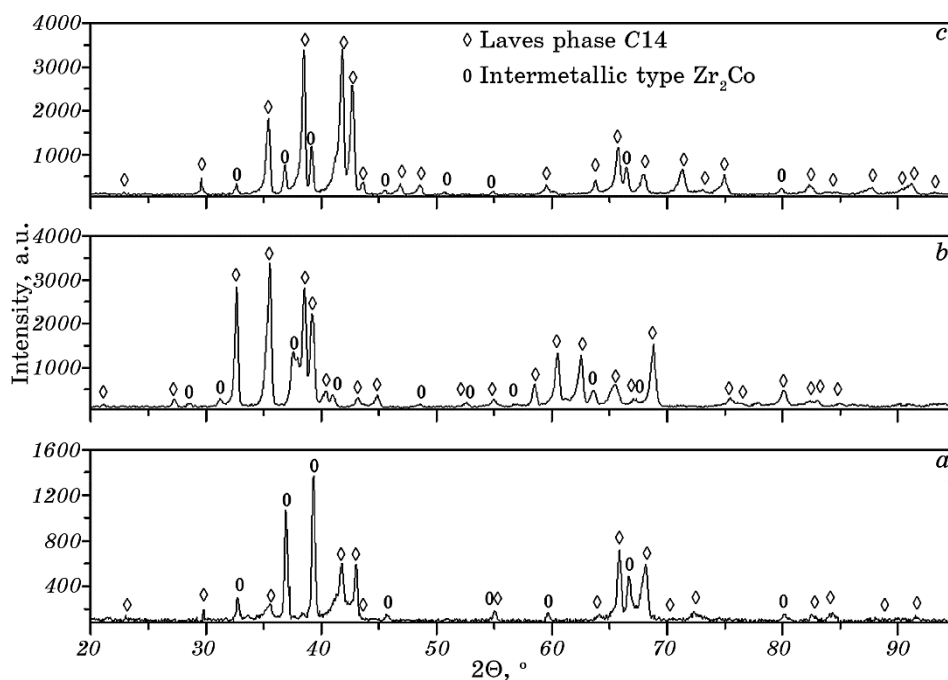


Fig. 1. X-ray diffraction pattern of alloy $\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$: cast state (*a*), hydrogenated (*b*), after dehydrogenated (*c*).

into the alloy is distributed. With the use of EDAX energy-dispersive analysis, it was established that the dark-coloured phase (Fig. 2, *b*) had a composition of 9.71Ti–26.76Zr–45.25Mn–6.26V–7.95Cr–4.08Co (at.%) (with composition formula $(\text{Ti}_{0.27}\text{Zr}_{0.73})\text{Mn}_{1.24}\text{V}_{0.17}\text{Cr}_{0.22}\text{Co}_{0.11}$) based on the amount of manganese; it can be stated that these are Laves phase crystals. The light-coloured crystals had a composition of 17.54Ti–41.09Zr–28.93Mn–3.66V–3.25Cr–5.53Co (at.%). From the obtained data, it can be seen that only part of the cobalt introduced into the original $\text{Ti}_{15.4}\text{Zr}_{30.2}\text{Mn}_{44}\text{V}_{5.4}\text{Cr}_5$ alloy [25, 26] dissolved in the Laves phase. Most of the cobalt having combined with other components of the alloy form an intermetallic compound based on Zr_2Co .

Based on the obtained chemical composition of Laves phase crystals, for the studied alloy $\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$, it is possible to explain the decrease in the volume of the unit cell and the radius of the tetrahedral internode in comparison with the original alloy [25, 26]. Corresponding changes are primarily associated with a decrease in their chemical composition, the concentration of titanium (atomic radius 0.147 nm) and zirconium (0.160 nm), which have a significantly larger atomic radius compared to all other alloy components [37]. Secondly, according to literature data [38], partial replacement of manganese with cobalt also leads to corresponding changes.

It is also important that, according to JCPDS data (International Centre for Diffraction Data), the binary intermetallic of the stoichiometric composition Zr_2Co has the unit cell parameter $a = 1.2551$ nm,



Fig. 2. The microstructure of the cast alloy: $\text{Ti}_{15.4}\text{Zr}_{30.2}\text{Mn}_{44}\text{V}_{5.4}\text{Cr}_5$ [25, 26] (*a*), $\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$ (*b*).

while the one calculated for the formed intermetallic (Table 2) is significantly smaller. This is due to the fact that a large part of zirconium (25.61 at.%) in the formed intermetallic is replaced by other components (primarily titanium). In comparison with zirconium, the other components of the investigated $\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$ alloy have a smaller atomic radius ranging from 8 to 22% [37]. This fact clearly demonstrates the significant influence the size of the atom of the element used for doping has on the parameters of the unit cell of the formed compound.

In addition, the ratio of the number of coexisting phases was determined in the work using the ImageJ program (distributed without license restrictions as public domain). This will make it possible to establish, how the presence of the second phase affects the main hydrogen sorption characteristics of the original alloy $\text{Ti}_{15.4}\text{Zr}_{30.2}\text{Mn}_{44}\text{V}_{5.4}\text{Cr}_5$ [25, 26]. Since coexisting phases can significantly differ in terms of hydrogenation–dehydrogenation and hydrogen capacity, it was established that the volume fraction of the Laves phase (type C14) for the investigated alloy is 82.6% (dark crystals), and the intermetallic based on Zr_2Co is 17.4%, respectively.

In Ref. [31], the influence of cobalt doping on the phase composition of the alloy $\text{Zr}(\text{Mn}_{1-x}\text{Co}_x)_2$ ($x = 0, 0.2, 0.3$ and 0.4) with the Laves phase (type C14) structure was investigated. The authors experimentally proved that within the indicated limits of alloying, the alloy retained its original structure, but at the same time, the crystal lattice parameters of the Laves phase gradually decreased. Based on the data presented in [39], the authors claim that the corresponding decrease in parameters occurred as expected. However, as it was established in this investigation, alloying of the $\text{Ti}_{15.4}\text{Zr}_{30.2}\text{Mn}_{44}\text{V}_{5.4}\text{Cr}_5$ alloy with cobalt in the amount of 5.5 at.% leads to the formation of the second phase of the intermetallic based on Zr_2Co . The specified differences in the effect of cobalt on the phase composition of the alloy were considered in the literature [31] and this investigation is related to significantly different stoichiometry. The authors of Ref. [31] considered alloys, which had a stoichiometric composition of AB_2 , while, in this investigation, an alloy with a non-stoichiometric composition of $AB_{1.2}$ was considered. Based on the determined chemical composition of Laves phase crystals for the investigated $\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$ alloy and literature data [32, 40], it can be stated that the area of homogeneity Laves phase (type C14) cannot be expanded below 44 at.% Mn, with this manufacturing method alloy, fails.

3.2. Kinetics of Hydrogen Sorption–Desorption

According to literature data [25, 26], the process of active absorption of hydrogen by the original $\text{Ti}_{15.4}\text{Zr}_{30.2}\text{Mn}_{44}\text{V}_{5.4}\text{Cr}_5$ alloy began ten

minutes (incubation period) after contact with the hydrogen environment (hydrogen pressure of 0.23 MPa, room temperature) and continued five minutes (Fig. 3, *a*), while the hydrogen capacity was reached at the level of 2.05% wt. ($\text{H}/\text{Me} \cong 1.34$). Further exposure for 60 minutes, with the same hydrogenation parameters, led to a slight increase in the amount of absorbed hydrogen by 2.08% wt. ($\text{H}/\text{Me} \cong 1.36$). Increasing the exposure time to 24 hours did not lead to an increase in the amount of absorbed hydrogen.

The process of hydrogen saturation of the investigated alloy $\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$ was carried out at the same hydrogenation parameters as for the original alloy, for the possibility of correct comparison of hydrogen-sorption properties. It was established that the process of active absorption of hydrogen by the investigated alloy began from the first second of contact with the hydrogen environment (there is no incubation period) (Fig. 3, *a*). The investigated alloy in the first 6 minutes, from contact with a hydrogen environment, absorbs the main part of the sorbed hydrogen 1.61% wt. ($\text{H}/\text{Me} \cong 1.05$) (unlike the original alloy). Increasing the exposure time to 35 minutes, with the same hydrogenation parameters, it possible to increase the amount of absorbed hydrogen to 1.86% wt. ($\text{H}/\text{Me} \cong 1.22$). Further exposure for 48 hours did not lead to recovery of the hydrogen absorption process.

A certain decrease in the total amount of hydrogen absorbed by the studied $\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$ alloy compared to the original alloy may be due to the simultaneous action of several factors. First, with a significant change in the chemical composition of Laves phase crystals. In their chemical composition, the amount of manganese (which

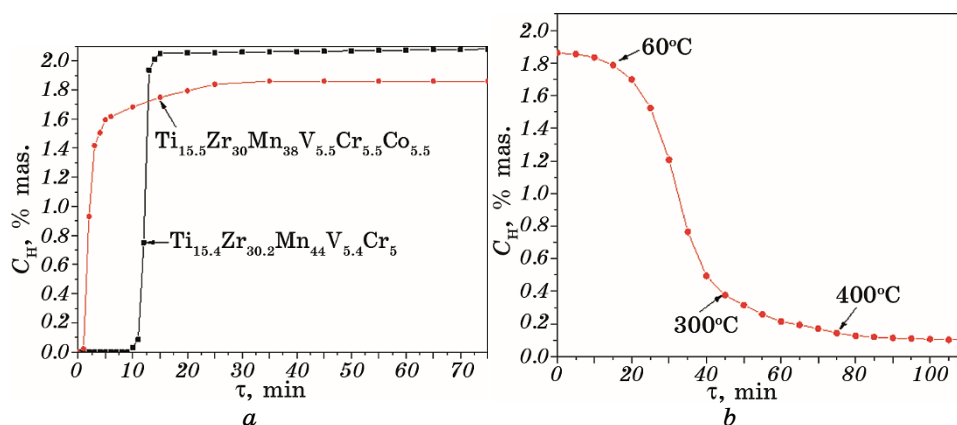


Fig. 3. Change in hydrogen capacity over time during for investigated alloy $\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$ in the process: hydrogenation (*a*), dehydrogenation (*b*).

does not interact with hydrogen) has increased, due to the decrease in the amount of titanium and zirconium (which have a high hydrogen capacity). The obtained result, regarding the fact that the decrease in the amount of titanium and zirconium in the composition of the Laves phase leads to a decrease in the total amount of absorbed hydrogen, correlates well with the data presented in works [5, 10]. In addition, there was also a decrease in the volume of its unit cell and the radius of the tetrahedral internode, which was mentioned above. Secondly, due to the formation of the second phase of intermetallic based on Zr_2Co .

Figure 3, *a* show that the process of hydrogen absorption by the investigated $Ti_{15.5}Zr_{30}Mn_{38}V_{5.5}Cr_{5.5}Co_{5.5}$ alloy is slightly different from the original one. In the original alloy $Ti_{15.4}Zr_{30.2}Mn_{44}V_{5.4}Cr_5$ [25, 26], almost all hydrogen is absorbed in five minutes; however, this indicates that the entire volume of the material absorbs hydrogen simultaneously; whereas, in the investigated alloy, the absorption process occurs in two stages (Fig. 3, *a*), which differ in absorption speed.

At the first stage, the time interval from the start of absorption to the achievement of a hydrogen capacity of 1.61% wt., hydrogen saturation of the Laves phase occurs, most likely, and the absorption rate is 0.268% wt./min (this assumption is made based on the volume fraction of each of the phases and the amount of absorbed hydrogen). Due to the high rate of the hydrogen absorption process and the room temperature of hydrogenation, the monolithic sample is destroyed into a powder state [41], and as a result, surfaces free from oxide films are formed.

At the second stage, thanks to the already formed surface free from the oxide film, saturation of the second phase, an intermetallic based on Zr_2Co , occurs. At the same time, the reaction rate decreases by several orders of magnitude.

The x-ray phase analysis method confirmed (Fig. 1, *b*, Table 2) the assumptions made regarding the fact that both phases can be saturated with hydrogen at the specified hydrogenation parameters. The resulting hydrogenation product consists of a hydride based on the Laves phase, as well as a hydride based on a new phase. This shows, however, that, during hydrogenation, there is no formation of new or dissolution of already existing phases. The obtained data coincide with the literature [42] in that during hydrogenation there are no changes in the structure of the metal matrix of the Laves phase (type C14), but it is only accompanied by an isotropic increase in the volume of the unit cell by 20%.

The process of desorption of hydrogen from the hydrogenation products obtained when the investigated $Ti_{15.5}Zr_{30}Mn_{38}V_{5.5}Cr_{5.5}Co_{5.5}$ alloy was saturated with hydrogen was carried out at an initial pressure of 0.0002 MPa. At a heating rate of 3°C/min, active hydrogen release begins with the start of heating (Fig. 3, *b*), and the process takes place

in four stages. The first stage, from the start of heating to a temperature of 60°C , the release process occurs relatively slowly at a rate of 0.0045% wt./min, while only 3% of absorbed hydrogen is released. Starting from a temperature of 60°C , the rate of hydrogen release increases to a value of $\cong 0.047\%$ wt./min, and up to a temperature of 300°C , it is possible to release 80% of the total amount of absorbed hydrogen. Above 300°C , the release rate decreases to 0.0077% wt./min, and up to a temperature of 400°C , it is possible to increase the amount of released hydrogen to 92%. When heated to a temperature of $\approx 430^\circ\text{C}$, it was possible to desorb about 95% of the total amount of absorbed hydrogen.

Using the x-ray phase analysis method, it was established that after the desorption process, two phases remained present in the structure of the investigated alloys (Table 2, Fig. 1, *c*). The obtained data made it possible to state that, during desorption of hydrogen from the formed hydrides, there are no changes in the phase composition of the investigated alloy. When comparing the crystal lattice parameters of the phases for the investigated alloy in the cast state, after hydrogenation and partial desorption of hydrogen (Table 2), it was established that residual hydrogen is found in both phases, but with a preference towards the Laves phase.

A comparison of the data obtained in this study and those in the literature [31, 40] regarding the effect of cobalt doping on the hydrogen-sorption properties of alloys based on the Laves phase (type C14) made it possible to note an important regularity. The introduction of cobalt into alloys based on the Laves phase (type C14) of non-stoichiometric composition should be in such an amount that does not lead to a change in the phase composition of the original alloy and as a result of a change in hydrogen-absorption properties.

4. CONCLUSIONS

1. It was shown on the example of the alloy $\text{Ti}_{15.5}\text{Zr}_{30}\text{Mn}_{38}\text{V}_{5.5}\text{Cr}_{5.5}\text{Co}_{5.5}$ at issue that it was not possible to expand the homogeneity of the Laves phase below 44 at.% Mn, with the considered method of obtaining the alloy.
2. Doping with cobalt did not significantly affect the processes of hydrogen sorption–desorption by the original alloy, but led to a certain decrease in the hydrogen capacity. The specified changes occurred due to a change in the phase composition and a decrease in the number of atoms active in relation to hydrogen (titanium, zirconium) in the unit cell of the Laves phase (type C14).

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