

CRYSTAL-LATTICE DEFECTS

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Hydrogen Sorption Properties of $\text{Ti}_{0.475}\text{Zr}_{0.3}\text{Mn}_{0.225}$ Eutectic Alloy Alloyed with 2 at.% and 5 at.% of Vanadium

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Sorption properties and kinetic parameters of hydrogenating and dehydrogenating processes of $\text{Ti}_{0.475}\text{Zr}_{0.3}\text{Mn}_{0.225}$ eutectic alloy, in which partial substitution of each of its component with 2% and 5% of vanadium is performed, are investigated by Sieverts' method. As determined, the introduction of vanadium within the specified limits results in decrease of the temperature of the start of intensive hydrogen absorption, decrease of the duration of hydrogenating process, and also in substantial increase of sorption capacity (up to 2.85% wt.). As shown, the alloys, which are subjected to the sorption-desorption cycling, possess as much activated surface that behave themselves with regard to hydrogen similar to intermetallic compounds and can absorb hydrogen at the room temperature and the pressure of 0.23 MPa from the first seconds of the contact of the specimen with the hydrogen-containing medium with the average rate of $(2-4)\cdot 10^{-3}$ wt.%/s.

Сивертсовою методою досліджено сорбційні властивості і кінетичні параметри процесів гідрування і дегідрування виливаного евтектичного стопу $\text{Ti}_{0.475}\text{Zr}_{0.3}\text{Mn}_{0.225}$, в якому було виконано часткову заміну кожного з його компонентів на 2% і 5% Ванадію. Встановлено, що введення Ванадію в зазначених межах приводить до зниження температури початку інтенсивного вбирання Гідрогену, зменшення тривалости процесу гідрування, а також до істотного збільшення сорбційної місткості (до 2,85% мас.). Показано, що стопи, які пройшли циклування сорбція-десорбція, мають настільки активовану поверхню, що ведуть себе щодо водню неначе інтерметаліди і здатні вбирати Гідроген за кімнатної температури і тиску у 0,23 МПа з перших секунд контакту зразка з водневим середовищем із середньою швидкістю у $(2-4)\cdot 10^{-3}$ мас.%/с.

Методом Сиверта исследованы сорбционные свойства и кинетические параметры процессов гидрирования и дегидрирования литого эвтектического сплава $\text{Ti}_{45,5}\text{Zr}_{30}\text{Mn}_{22,5}$, в котором была произведена частичная замена каждого из его компонентов на 2% и 5% ванадия. Установлено, что

введение ванадия в указанных пределах приводит к понижению температуры начала интенсивного поглощения водорода, снижению продолжительности процесса гидрирования, а также к существенному увеличению сорбционной ёмкости (до 2,85% масс.). Показано, что сплавы, прошедшие циклирование сорбция–десорбция, обладают настолько активированной поверхностью, что ведут себя по отношению к водороду подобно интерметаллидам и способны поглощать водород при комнатной температуре и давлении 0,23 МПа с первых секунд контакта образца с водородосодержащей средой со средней скоростью $(2-4) \cdot 10^{-3}$ масс.% /с.

Key words: hydrogenating, dehydrogenating, hydrogen capacity, eutectic alloys, intermetallide, solid solution.

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1. INTRODUCTION

Modern investigations allow one to select quite certain materials with the prescribed properties, such as the temperature and pressure of formation and decomposition of hydrides, thermodynamic and kinetic characteristics of the hydride formation processes [1]. Currently, both LaNi_5 and the alloys based on it are such the most required compounds. However, the heavy weight of this class of materials makes problematic the issue of their use at development of automobile power sources. In connection with this, the search of new effective metal compositions for hydrogen accumulators, which use the elements lighter than REM, acquires a special applicability. AB_2 intermetallic systems with Laves' phase structure possess higher potential for changing of AB_2 compounds in the capacity of hydrogen absorptive materials. For example, Ti–Zr–Mn compounds absorb significant amount of hydrogen ($\cong 1.8-2.0\%$ wt.) without the preliminary heat treatment [2, 3]. Maximal sorption capacity is inherent to the alloys, which are located on the lower boundary of homogeneity range. For this reason, optimal relationship of titanium and zirconium, as well as minimal content of manganese in the intermetallic, makes possible to obtain the absorption capacity of 2.28% wt. [6].

For TiMn_2 intermetallic compounds, introduction of vanadium results in the substantial increase of the nonstoichiometry range from $\text{AB}_{1.4}$ to $\text{AB}_{2.8}$ for Ti–V–Mn system and from $\text{AB}_{1.2}$ to $\text{AB}_{3.5}$ for (Ti, Zr)–V–Mn system as contrasted with $(\text{AB}_{1.5}-\text{AB}_{2.1})$ binary system [2]. The results of Ref. [7] demonstrate that hydrogenating rate of (Ti, Zr)–V–Mn exceeds the hydrogenating rate of LaNi_5 by 20–50%.

Enhancement of the parameters listed above is possible not only due to the account of alloying or optimization of the alloy mixture ratio. Using of eutectic Ti–Zr–Mn-system-based alloys in the capacity of hydrogen accumulators also results in substantial increase of sorption

capacity and enhancement of kinetic parameters of hydrogenating and dehydrogenating processes due to combination of advantages of each phase [8, 9]. These alloys typically consist of b.c.c. solid solution β (Ti, Zr, Mn) with high hydrogen capacity and Laves phases $(\text{Ti, Zr})\text{Mn}_{2-x}$ with operation temperatures acceptable for exploitation and easiness of the surface activation.

Manufacturing four-component eutectic (Ti, Zr)–(Mn, V), one can expect the substantial increase of their sorption capacity and enhancement of the kinetic parameters of hydrogenating and dehydrogenating processes.

2. MATERIALS AND METHODS OF INVESTIGATION

Alloys are produced in a laboratory electric arc furnace with permanent tungsten electrode on cooled copper furnace hearth by the way of six-fold remelting in the atmosphere of the purified argon, using iodine titanium with a purity of 99.95%, iodine zirconium with the purity of 99.975%, electrolytic vanadium—99.9%, and electrolytic manganese—99.99% as primary components. Chemical composition of alloys is determined by fluorescent X-ray analysis using VRA-40 spectrometer. Coincidence with nominal composition is within an error of measurement ($\pm 0.03\%$).

Phase composition and lattice parameters are determined by the X-ray phase analysis method using DRON-3M diffractometer with GUR-8 standard goniometer in FeK_α radiation by the way of photography of both plane monolithic and powder specimens. Lines of diffractograms are identified using JCPDS (International Center for Diffraction Data) database.

Interaction of alloys and hydrogen is studied by Sieverts' method in IVGM-2M installation [10] in the heating mode with the rate of $\cong 4^\circ\text{C}/\text{min}$ within the temperature range from room temperature to 500°C and under isobaric-isothermal conditions under the pressure of $\cong 0.6$ MPa. Hydrogen purified by sorption is introduced at room temperature, when pressure in working reactor of the installation reaches the value of $1.33 \cdot 10^{-6}$ MPa. During the hydrogenating process, the time dependences $P_{\text{H}_2}(\tau)$, $T(\tau)$ are registered and all other parameters are calculated proceeding from them. Amount of the absorbed hydrogen is determined by weighing with the accuracy of $1.5 \cdot 10^{-5}$ g and is calculated by the pressure change in the closed space.

Desorption of hydrogen from hydrogenation products is investigated using automated dilatometric complex (ADC) designed at the G. V. Kurdyumov Institute for Metal Physics of N.A.S.U. for investigation of physical processes, which proceed during the heating of powder compacts [11].

The 47.5 Ti–30 Zr–22.5 Mn eutectic alloy is chosen as a based one

(hereinafter alloy compositions are presented in at.%). Alloying principle consists in partial substitution of each from its components by 2% and 5% of vanadium (see Table 1).

3. RESULTS AND DISCUSSION

Information concerning the impact of V on the structure and phase composition of 47.5 Ti–30 Zr–22.5 Mn eutectic alloy is presented in Ref. [12]. Partial substitution of 2% and 5% of zirconium and 2% of titanium by vanadium does not result in the structure change. The substitution of 5% of Ti, as well as the substitution of 2% and 5% of manganese by vanadium results in appearance of primary crystals of a solid solution. In all cases, alloying results in the increase of the volume part of the β -phase and is accompanied by the distribution of vanadium between β -solid solution and intermetallide with the advantage of the last one. In such a case, the Mn content in λ -phase decreases and the boundary of homogeneity range shifts toward the solid solution.

In the case of investigation of the sorption properties of specified alloys, the possibility of their hydrogenating at room temperature, as well as in the case of the initial 47.5 Ti–30 Zr–22.5 Mn eutectics is supposed. Alloys are held in the hydrogen atmosphere at the pressure of 0.6 MPa during 24 hours. The specified hydrogenation mode does not lead to the activation of specimens' surface. Obviously, some critical volume fraction of intermetallide on the surface of the specimen is necessary to initiate the process of the active hydrogen absorption at room temperature. The change of the ratio of phases' fractions due to the vanadium alloying renders impossible the process of hydrogenation at the specified parameters.

Intensive hydrogen absorption is detected during the heating process and under conditions of isobaric and isothermal holding of alloys at temperatures of $\cong 500^\circ\text{C}$ and the same pressure.

As in the case of the bearing 47.5 Ti–30 Zr–22.5 Mn eutectic alloy,

TABLE 1. Nominal composition of alloys.

Designation		Alloy composition, at. %			
		Ti	Zr	Mn	V
V \rightarrow Mn	V \rightarrow Mn – 2	47.5	30	20.5	2
	V \rightarrow Mn – 5	47.5	30	17.5	5
V \rightarrow Zr	V \rightarrow Zr – 2	47.5	28	22.5	2
	V \rightarrow Zr – 5	47.5	25	22.5	5
V \rightarrow Ti	V \rightarrow Ti – 2	45.5	30	22.5	2
	V \rightarrow Ti – 5	42.5	30	22.5	5

the process of doped alloys hydrogenation proceeds in two stages, rates of which differ by order of magnitude ($(2-3) \cdot 10^{-4}$ wt. % /s for the first and $(5-7) \cdot 10^{-3}$ wt. % /s for the second stage) (see Fig. 1, *a*). Duration of the first stage at which drastic increase of the hydrogenating rate occurs as well as the amount of absorbed hydrogen are in the direct dependence on the ratio of fractions of phases presented in the alloys.

Temperatures of the start of the intensive absorption, amount of occluded hydrogen at the temperature of isothermal holding and at room temperature, as well as the duration of the hydrogenating process are determined from the kinetic dependences (see Fig. 1, *b* and Table 2).

It is established that alloying with vanadium results in the decrease of the temperature of intensive absorption start (see Table 2) (for the initial alloy it is 540°C [8]). During avalanche-type absorption (the second stage), the drastic increase of the reactor temperature by 1012°C per one gram of the formed hydride is detected, *i.e.*, the absorption process proceeds with heat release. Duration of the hydrogenation process τ_{hyd} increases from 10–15 min for the alloys with vanadium content of 2% to 40–50 min for alloys with vanadium content of 5%.

Taking into account the temperature of the start of the active absorption and the rate of hydrogen adsorption on both stages, one can state that the hydration process begins from the solid solution β (Ti, Zr, Mn, V) [13], and cracks formation, which accompanies this process in material with the surface free of an oxide film, facilitates the process of the intermetallide activation and promotes its lightning-like saturation. Typical deviation of the dependence of change of pressure on temperature during cooling from the linear law, inherent to all alloys, attests to renewal of hydrogenating process with decrease of temperature to $250-300^\circ\text{C}$.

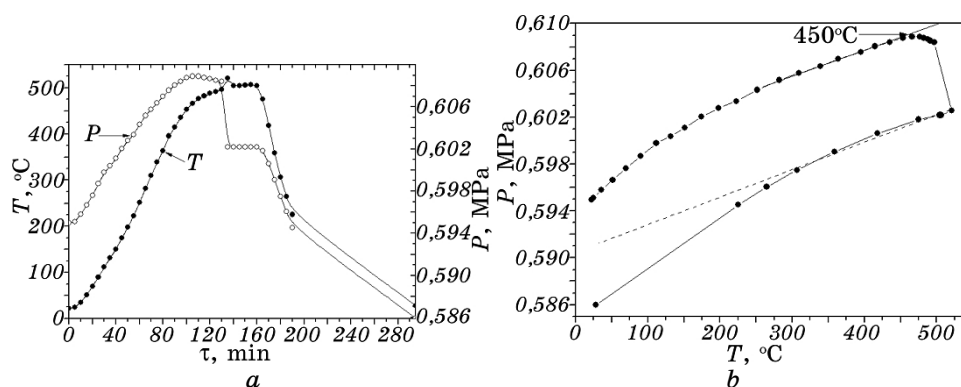


Fig. 1. Changes in temperature and pressure of hydrogen with time (*a*) and dependence of pressure (MPa) on temperature (*b*) at hydrogenation of 47.5 Ti–30 Zr–17.5 Mn–5 V alloy.

TABLE 2. Kinetic parameters of the process of alloys hydrogenation.

Alloy	$T_{\text{abs}}, ^\circ\text{C}$	$\tau_{\text{hyd}}, \text{min}$	Hydrogen concentration $C_{\text{H}}, \text{wt.}\%$		H/Me	$(\text{H}/\text{Me})_{\lambda}$	$(\text{H}/\text{Me})_{\delta+\epsilon}$
			at $T_{\text{room}}, P_{\text{hyd}}$	at $T_{\text{room}}, P_{\text{atm}}$			
V → Mn – 2	495	10	2.68	2.71	1.72	1.45	1.97
V → Mn – 5	450	40	2.81	2.85	1.81	1.43	2.16
V → Zr – 2	395	15	2.62	2.66	1.67	1.41	1.97
V → Zr – 5	490	45	2.48	2.66	1.64	1.34	1.91
V → Ti – 2	490	15	2.36	2.58	1.58	1.41	1.91
V → Ti – 5	335	55	2.58	2.62	1.67	1.39	1.98

Using X-ray phase analysis, it is established that the end product of hydrogenation of all alloys consists of hydrides, which are formed on the base of initial phases only:

- δ -hydride based on $(\text{Ti}, \text{Zr}, \text{V}, \text{Mn})\text{H}_{2-x}$ solid solution with face centered cubic arrangement of CaF_2 -type;
- ϵ -hydride based on $(\text{Ti}, \text{Zr}, \text{V}, \text{Mn})\text{H}_{2-x}$ solid solution with tetragonal arrangement of ThH_2 -type;
- λ -hydride based on $(\text{Ti}, \text{Zr})(\text{V}, \text{Mn})_{2-x}\text{H}_{1+x}$ Laves phase with crystalline structure of MgZn_2 -type.

Lattice parameters of products of alloys hydrogenation are presented in Table 3.

These results demonstrate that decomposition of phases during hydrogenation of the specified alloys does not take place.

It is assumed that the presence of two hydrides based on β -solid solution with cubic and tetragonal lattices is connected with impossibility of achievement of maximal hydrogen capacity of alloys under the specified modes of hydrogenation. This fact allows using not only alloying, but also optimization of parameters of hydrogenation processes of produced alloys for the increase of sorption capacity.

For separate estimations of the hydrogen capacity of β -solid solution and Laves phase, the ratio of their molar fractions by Rietveld refinement is performed. As far as phase decomposition does not take place at hydrogenation, it should come as no surprise that ratio of molar fractions of hydrides, produced based on each of phases, remains equal to the relationship of molar fractions in initial conditions.

Amount of hydrogen in the hydride based on the Laves phase is calculated in accordance with [14], hereunder the increase of the lattice cell volume comprises $2.9 \cdot 10^{-3} \text{ nm}^3$ per unit of H/M , where M is a number of metal atoms in the lattice cell (Pearson's symbol for the structure of the MgZn_2 type— $hP12$ type). Measured increment of the

TABLE 3. Results of X-ray phase analysis of the products of alloys hydrogenation.

Alloy	Lattice parameters a (and c), ± 0.0009 nm							
	Initial phases		Hydrogenated			Dehydrogenated		
	λ -phase	β -phase	λ -hydride	δ -hydride	ε -hydride	λ -phase	β -phase	α -phase
V \rightarrow Mn - 2	0.5195 (0.8430)	0.3347	0.5587 (0.9177)	0.4467	0.4553 (0.4700)	0.5189 (0.8523)	0.3380	0.3000 (0.4774)
V \rightarrow Mn - 5	0.5186 (0.8428)	0.3334	0.5574 (0.9155)	0.4438	0.4538 (0.4685)	0.5176 (0.8503)	0.3367	0.2985 (0.4750)
V \rightarrow Zr - 2	0.5199 (0.8449)	0.3362	0.5572 (0.9152)	0.4438	0.4534 (0.4681)	0.5187 (0.8520)	0.3382	0.2997 (0.4769)
V \rightarrow Zr - 5	0.5190 (0.8442)	0.3356	0.5548 (0.9113)	0.4420	0.4523 (0.4669)	0.5175 (0.8501)	0.3367	0.2965 (0.4718)
V \rightarrow Ti - 2	0.5203 (0.8439)	0.3375	0.5598 (0.9192)	0.4597	0.4534 (0.4680)	0.5203 (0.8546)	0.3386	0.2970 (0.4726)
V \rightarrow Ti - 5	0.5200 (0.8430)	0.3373	0.5569 (0.9148)	0.4433	0.4539 (0.4686)	0.5191 (0.8527)	0.3381	0.2985 (0.4750)

lattice cell of the Laves phase per one metallic atom provides the possibility to estimate the sorption capacity of intermetallide, and the rest of the adsorbed hydrogen to charge to contribution of δ - and ε -hydrides based on the solid solution (see Table 2).

The obtained data point at the fact that alloying with vanadium results in the substantial increase of the sorption capacity and enhancement of kinetic and thermodynamic parameters of hydrating processes due to combination of each phase advantages. It is specifically typical to the alloys, in which hydride-nonforming Mn is substituted with the hydride-forming V. In this case, the titanium-based solid solution absorbs hydrogen with the kinetics, similar to the kinetics of the hydrogen sorption by intermetallide and reaches the high level of hydrogen capacity for the short time. This feature is conditioned by the high surface area of the interphase boundaries, which is typical for the eutectic structures, across which the diffusion coefficient is approximately 10^3 times higher than that in the bulk. In addition, high rate of hydrogen absorption is in a greater part caused by the crystal b.c.c. structure of β -phase, in which the hydrogen diffusion coefficient is almost three orders of magnitude higher than hydrogen diffusion coefficient in α -phase with h.c.p. lattice [15].

Hydride formation process proceeds in the form of an avalanche also due to the brittleness of the Laves phase, resulting in quick cleaving of

the forming hydride and formation of the clean surfaces, ready for the hydrogen sorption.

Mass-spectrometric investigations of the products of hydrogenation of the vanadium-doped alloys shows that the release of hydrogen at the initial pressure in the chamber of $4 \cdot 10^{-3}$ Pa begins at the temperature of $\approx (55 \pm 5)^\circ\text{C}$ (see Fig. 2). It is lower by 25°C than that of non-doped eutectic alloy.

Integration of the surface area under each of peaks shows that in the temperature range from 200°C to 300°C under the specified technological conditions $\approx 50\%$ of the absorbed hydrogen precipitate from 47.5 Ti–30 Zr–17.5 Mn–5 V alloy. Taking into account that $\approx 34\%$ falls to the share of intermetallide, the first peak with the maximum at the temperature of 265°C may be interpreted as simultaneous release of hydrogen from the intermetallide-based hydride [6] and ϵ -hydride based on β -solid solution during its decomposition until δ -hydride. Proceeding from the data of Ref. [16], the peak at the temperature of 390°C corresponds to the δ -hydride decomposition. At the temperature of 500°C , the process of release of hydrogen terminates. Comparison of the lattice parameters of the initial, hydrogenated, and dehydrogenated alloys testifies to practically 100% reverse capacity of alloys (see Table 2).

Data of experiments on investigation of the influence of the sorption–desorption–sorption cycling on kinetic and sorption properties shows that the alloys of the specified group possess as much activated surface that the hydration begins at room temperature and the pressure of 0.23 MPa from the first seconds of contact of the specimen with

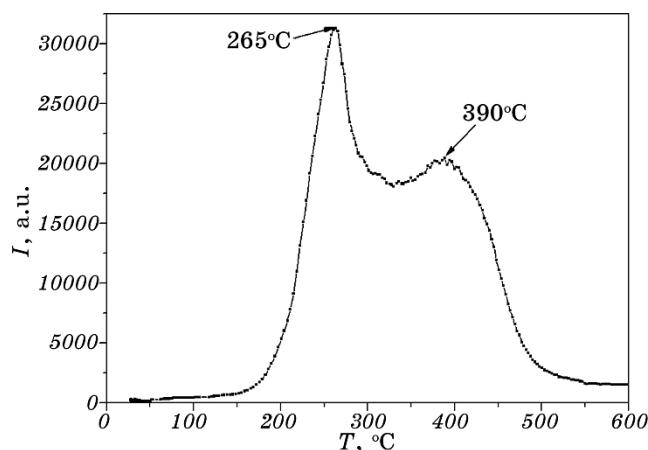


Fig. 2. Change of the intensity of the hydrogen release (in arbitrary units) during the heating of hydrogenating products of 47.5 Ti–30 Zr–17.5 Mn–5 V alloy.

hydrogen containing medium with an average rate of $(2-4)\cdot 10^{-3}$ wt. % /s.

Such an enhancement of the kinetic parameters can be explained by the dispergation of the specimen during the sorption–desorption cycle as well as by the decrease of the oxygen concentration on the surface and in a bulk of particles because of its interaction with the releasing atomic hydrogen. Hydrating temperature during the second cycle points at the fact that in this case the absorption begins from intermetallide [6].

Kinetic parameters of sorption and desorption as well as sorption capacity of alloys in succeeding cycles do not practically change. Insignificant increase of the hydrogen adsorption rate is connected with the increase of the reaction surface, caused by the disintegration of the particles.

4. CONCLUSIONS

1. Partial substitution of the alloy components by vanadium results in the substantial increase of the sorption capacity and the enhancement of kinetic and thermodynamic parameters of the processes of hydrogenation. In this case, the titanium-based solid solution absorbs the hydrogen with kinetics, similar to the kinetics of the sorption of the hydrogen by the intermetallide and reaches the high level of the hydrogen capacity during the short time.

2. Hydrogenation of the alloys activated by the sorption–desorption cycle takes place at room temperature and significantly lower pressure of 0.23 MPa. In this case, the sorption capacity remains unchanged, and time during which it reaches its maximal value decreases significantly.

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