



Synthesis and properties of multicomponent hydrides with high density

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Abstract

The results of research of interaction of hydrogen with alloys of Ti–V–M (M=Fe, Co, Ni), Ti–Ta; Zr–Ta; Ti–W; Ti–Ta–W; Zr–Sc; Hf–Sc systems are presented. The study of these materials was carried out in two directions aimed at an increase of hydride density preserving a high content of hydrogen in them and a decrease of synthesis parameters preserving high thermal stability of hydrides. The phase diagrams of the studied systems were obtained. © 1999 Published by Elsevier Science S.A. All rights reserved.

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1. Introduction

Metal hydrides are prospective materials for neutron radiation shielding. First of all this refers to hydrides of titanium, zirconium and hafnium which are described by high volumetric concentration of hydrogen. So, for example, the theoretical value of hydrogen atom number in 1 cm³ of titanium hydride (N_H) is 9.5×10^{22} , though in practice it does not exceed a magnitude of 8×10^{22} . For zirconium hydride $N_H = 7 \times 10^{22}$ [1]. The research of related materials was carried out in two directions aimed at an increase of hydride density preserving a high content of hydrogen in them and a decrease of synthesis parameters preserving high thermal stability of hydrides. The results of research of hydrogen interaction with alloys of Ti–V–M (M=Fe, Co, Ni), Ti–Ta; Zr–Ta; Ti–W; Ti–Ta–W; Zr–Sc; Hf–Sc systems are presented.

2. Experimental

The alloys were obtained by arc melting in a furnace with nonspendable tungsten electrode on a copper water-cooled hearth in a purified argon atmosphere at 2 atm pressure. X-ray analysis was performed in an X-ray spectrometer DRON-2 with Cu K α -radiation. The phase compositions of the obtained alloys agree with known phase diagrams of metallic systems Ti–V–Fe [2], Ti–V–Ni [3], Ti–V–Co [4], Ti–W [5], Ti–Ta–W [6], Zr–Sc [7], Hf–Sc [8]. The hydriding and DTA were carried out using standard Sieverts type apparatus. X-ray K-series emission

spectra of transition metals were obtained with spectrograph DRS-2M from quartz planes at fluorescent excitation of Cr-, Cu- and Au-anodes. X-ray L-series emission spectra for Ta, Zr, were obtained with a fluorescent ultralong-wave spectrometer 'Stearat'. X-ray L-series emission spectra for Ti were measured with a spectrometer-monochromator RSM-500. Element comparison of emission bands on a uniform energy scale was done using energy values of inner L $_{\alpha 1}$ and K $_{\alpha 1}$ lines as normalisation factors.

3. Results and discussion

3.1. Ti–V–M (M=Fe, Co, Ni) alloys

Compositions and some hydrogen absorption characteristics of the Ti–V–M (M=Fe, Co, Ni) β -alloys are presented in Table 1. All alloys needed a preliminary activation at 523 K and 50 atm. After such a treatment they absorbed hydrogen at room temperature and 10 atm hydrogen pressure. Visually the hydriding rate of the Ti–V–M alloys is higher than that of Ti–V alloys, suggesting that addition of iron, cobalt and nickel decrease the activation energy of the hydriding reaction.

All alloys form stable hydride phases with high hydrogen concentration. Minor addition of iron (2 at.%) to titanium–vanadium alloys leads to a more complete hydriding and the dependence of hydrogen concentration from Ti/V-ratio goes through a maximum in the range of 40 to 60 at.% of vanadium. Additions of cobalt and nickel slightly decreased the absorption capacity.

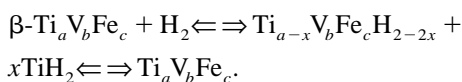
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Table 1
Characteristics of Ti–V–M alloys

No.	Alloy composition (at.%)					H/M	ρ_r (g/cm ³)	$N_H \times 10^{22}$ (at. H/cm ³)
	Ti	V	Fe	Co	Ni			
1	78	20	2			2.00	3.84	9.40
2	58	40	2			2.10	3.94	9.99
3	38	60	2			2.10	4.11	10.30
4	18	80	2			2.00	4.33	10.21
5	50	45	5			2.00	4.05	9.72
6	78	20		2		1.84	3.78	8.68
7	58	40		2		1.91	3.88	9.16
9	18	80		2		1.85	4.23	9.45
10	50	45		5		1.81	3.81	8.74
11	78	20			2	1.77	3.90	8.44
12	58	40			2	1.90	3.94	9.06
13	65	30			5	1.96	3.92	9.25
14	60	35			5	1.86	4.12	9.21
16	15	80			5	1.74	4.42	9.01

The decomposition of the hydride phase begins only at temperature higher than 470 K. The Ti–V–Fe phases with increasing vanadium concentration (up to 60 at.%) exhibit an endothermic effect of hydrogen desorption at ~890 K. At higher vanadium concentration decomposition comes to an end at temperature lower than 570 K. The intensity of the first ‘low-temperature’ effect and the amount of hydrogen evolving during the effect increase with increasing vanadium concentration.

The reabsorption after full hydrogen desorption for samples 2 and 3 (compositions as in Table 1) while cooling to room temperature showed that only half of the desorbed hydrogen is absorbed back (Table 2). According to the results of X-ray analysis the samples consisted of two phases with cell parameters very close to those of pure titanium dihydride and a bcc-hydride phase impoverished in titanium. This proves that the decomposition process of β -Ti–V–Fe hydrides passes through an intermediate stage of metal matrix destruction according to the reaction:



The fcc hydride phase exists only at maximum hydrogen content. The formation of titanium dihydride during decomposition is thermodynamically favourable compared to all possible intermediate products.

Table 2
Reabsorption characteristics of Ti–V–Fe alloys

Sample (as in Table 1)	Cell parameter (Å)	H/M	Hydride cell parameter (Å)	H/M after reabsorption	Cell parameters after reabsorption (Å)
2	3.171	2.1	fcc – 4.381	1.4	fcc – 4.424 bcc – 3.057
3	3.130	2.1	fcc – 4.337	0.9	fcc – 4.397 bcc – 3.154

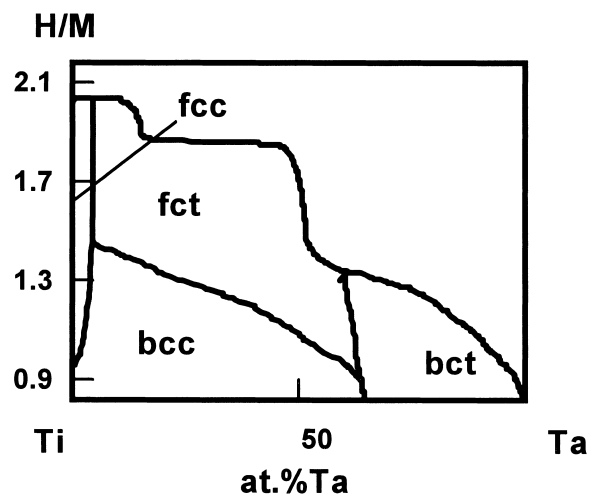


Fig. 1. Phase diagrams of the Ti–Ta–H system.

3.2. Ti–Ta–W alloys

All alloys of the Ti–Ta system, representing a continuous solid solution, contrary to pure metals, react with hydrogen with a high rate at $P < 30$ atm and $T \sim 500$ –550 forming two types of hydrides: fct TiH_2 -type structure ($\text{Ta} < 55$ at.%) and bct TaH -type structure ($\text{Ta} > 55$ at.%) (Fig. 1). According to DTA and calorimetric data the formation and decomposition of fct-type hydrides pass through the stage of formation of bct-type phase, i.e. with ordered location of hydrogen atoms in the metal cell. Fig. 2 shows that the differential enthalpy of hydriding dependence on hydrogen concentration exhibits two regions. The first region corresponds to the formation of the monohydride bct-phase, and the second to dihydride fct-phase. Bct-hydrides, like $\text{TaH}_{0.8}$, decompose in one stage at 750–850 K. The integral hydriding enthalpy values for pure tantalum, $\text{Ta}_{0.5}\text{Ti}_{0.5}$ and $\text{Ta}_{0.4}\text{Ti}_{0.6}$, presented in Table 3, confirm the additive character of formation enthalpies of hydrides of metals and alloys.

The investigation of the electronic energy spectrum of the valence zone of $\text{Ti}_{1-x}\text{Ta}_x$ showed that for all studied hydrides d- and p-electrons of titanium take part in the metal–hydrogen bonding. The shape of the TiK_{β_5} -band drastically changes for hydride compared to that of alloy (Figs. 3–5). The substitution of 50% of titanium atoms for tantalum does not lead to considerable change in the

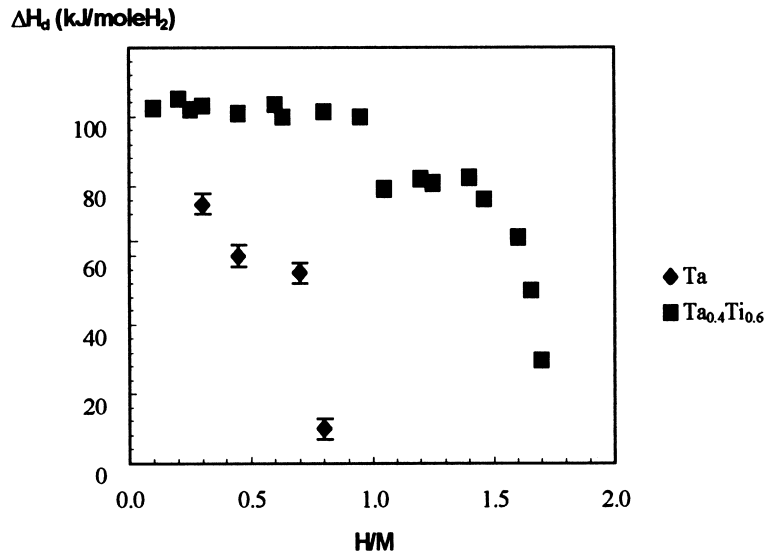


Fig. 2. Hydriding differential enthalpy vs. composition of the hydride for pure Ta and Ta_{0.4}Ti_{0.6}.

Table 3
Thermodynamic parameters for Ti–Ta–H₂ system

Composition	H/M range	T (K)	\Delta H , (kJ/mol H ₂)
Ta	0–0.8	312	70.2±0.9 (integral)
Ta _{0.5} Ti _{0.5}	0–1.6	300	98.4±1.8 (integral)
	0–1.7	385	107.4±0.7 (integral)
Ta _{0.4} Ti _{0.6}	0–1.0	385	103.6±1.0 (α→β)
	1–1.4	385	82.4±1.3 (β→γ)

electronic energy spectrum. For these hydrides in the long-wave slope there is a maximum several times bigger than the maximum of the TiK_{β5}-band. So, some peculiar rearrangement of p-electron density from metal–metal to metal–hydrogen bonds takes place. For bct-hydrides this rearrangement is much less pronounced.

β-Alloys of the titanium–tungsten system interact with hydrogen at 523 K and P = 30–40 atm without preliminary activation. The alloys with tungsten content less than 20 at.% form fct TiH₂-type hydrides. The increase of tungsten

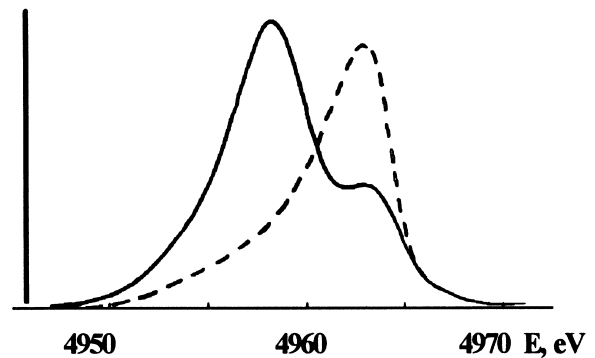


Fig. 4. TiK_{β5}-band of Ti_{0.5}Ta_{0.5}H_{1.8} (full line) and in starting alloy (dashed line).

content to 25 at.% leads to a separation of excess tungsten as a phase while hydriding. The decomposition of fct Ti–W-hydrides is a rather complicated process, described by the equation:

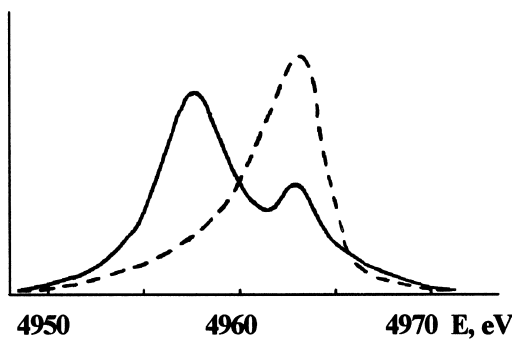


Fig. 3. TiK_{β5}-band of Ti_{0.3}Ta_{0.7}H_{1.3} (full line) and in starting alloy (dashed line).

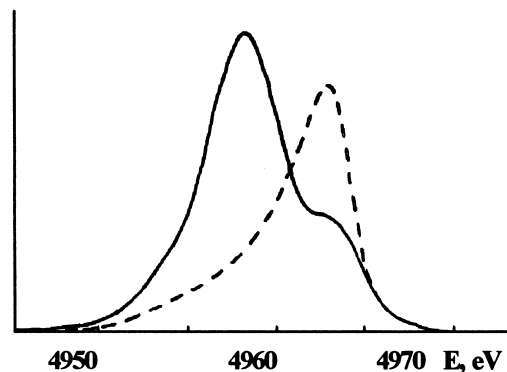
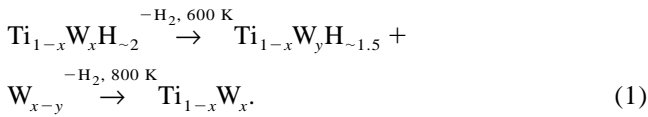


Fig. 5. TiK_{β5}-band of Ti_{0.7}Ta_{0.3}H_{1.0} (full line) and in starting alloy (dashed line).



β -Alloys of the titanium–tantalum–tungsten system interact with hydrogen at ambient temperature and $P=20$ atm after a short induction period. The alloys with constant tungsten concentration (12 at.%) and also $\text{Ti}_{0.1}\text{Ta}_{0.8}\text{W}_{0.1}$ and $\text{Ti}_{0.1}\text{Ta}_{0.7}\text{W}_{0.2}$ were studied. X-ray analysis showed that at tantalum content lower than 45 at.% hydrogen absorption results in a formation of fct TiH_2 -type hydrides and at a content higher than 65 at.% it results in bct TaH -type hydrides (Fig. 6). Similar to the Ti–Ta– H_2 system, bct-hydrides decompose in one stage with re-formation of initial metal structure. Fct-hydrides, like hydrides of the Ti–W– H_2 system, decompose in two stages similar to Eq. (1). The dependencies of roentgen density (ρ_{H}) and N_{H} on hydride composition are presented in Figs. 7–9.

3.3. Zr–Ta, Zr–Sc, Hf–Sc alloys

Zr–Ta alloys with tantalum content 50–90 at.% absorb hydrogen at room temperature, the other only at 573–623 K. We could not manage to synthesise the hydrides with a broad homogeneity region. The zirconium-rich alloys form hydrides with fct ZrH_2 -type structure and tantalum-rich alloys form bct TaH -based hydrides. Two-phase alloys form two hydrides with fct- and bct-structure.

Phase diagrams of Zr–Sc and Hf–Sc systems consist of continuous solid solutions. The alloys can be divided into two groups related to their interaction with hydrogen. The first group – alloys with zirconium content up to 50% –

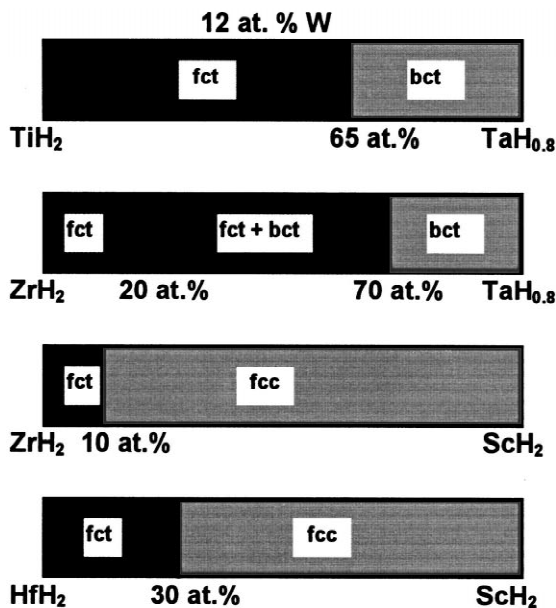


Fig. 6. Phase diagrams of investigated systems.

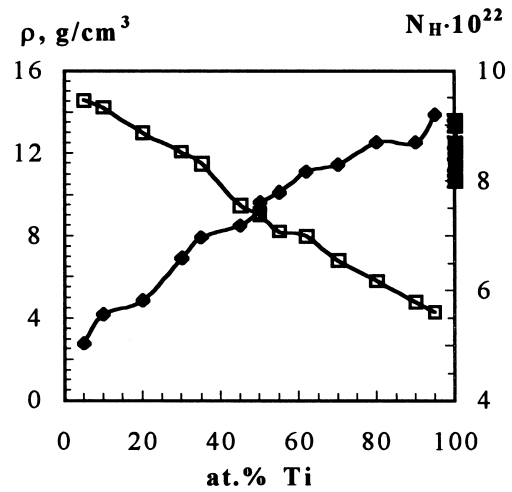


Fig. 7. N_{H} (♦) and ρ_{H} (□) values for hydrides of Ti–Ta alloys.

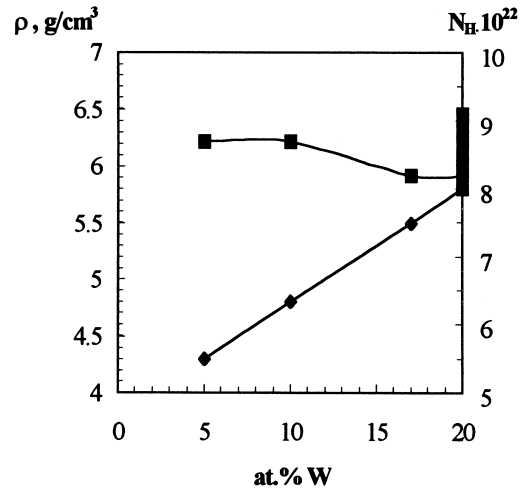


Fig. 8. N_{H} (■) and ρ_{H} (♦) values for hydrides of Ti–W alloys.

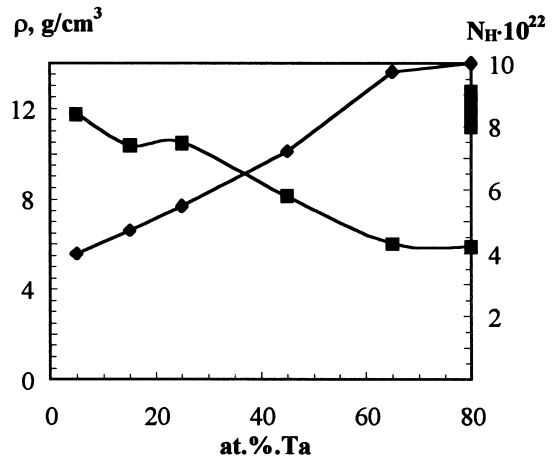


Fig. 9. N_{H} (■) and ρ_{H} (♦) values for hydrides of Ti–Ta–W (12 at.%) alloys.

react with hydrogen at room temperature and pressure of 5–15 atm. Alloys with zirconium content more than 50% react with hydrogen at 523–573 K practically without induction period. The behaviour of the Hf–Sc alloy is similar. Microscopic study showed that in this case also the reaction with hydrogen starts on the alloy grain boundaries, along which hydrogen enters into the bulk volume. Further hydriding is connected with the formation of hydride phase grains in the sample volume leading to its crushing.

Synthesised Zr–Sc- and Hf–Sc-hydrides do not decompose while heating up to 1073 K, which agrees with the high thermostability of binary hydrides of zirconium, hafnium and scandium. All hydrides forming in the Zr–Sc–H₂ system except Zr_{0.9}Sc_{0.1}H₂ have an fcc structure (Fig. 6). Similar to zirconium dihydride with maximum hydrogen content, Zr_{0.9}Sc_{0.1}H₂, has a tetragonal structure. It should be noted that the region of the fct-phase in Hf–Sc–H₂ system is much broader than that in the zirconium system and makes up ~30%.

4. Conclusions

The investigation of hydrogen interaction with alloys of Ti–Ta; Zr–Ta; Ti–W; Ti–Ta–W; Zr–Sc; Hf–Sc systems and β -alloys of Ti–V–M (M=Fe, Co, Ni) systems was carried out for the first time using X-ray and DTA methods. The peculiarities of hydride formation were studied and phase diagrams of investigated systems were

proposed. The results of the present work show that the density of Ti-containing materials can be increased by 1.5 to 2 times, while preserving high hydrogen density in the volume unit. Taking into account the above mentioned data on conditions of alloy interaction with hydrogen, it is possible to conclude that multicomponent hydrides are rather prospective for neutron radiation shielding.

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