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Formation of alloys in Ti–V system in hydride cycle and synthesis of their hydrides in self-propagating high-temperature synthesis regime

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ABSTRACT

In the present work, the possibility of formation of titanium and vanadium based alloys of BCC structure using hydride cycle was investigated. The mechanism of formation of alloys in Ti–V system from the powders of hydrides TiH_2 and $VH_{0.9}$ (or of V) by compaction followed by dehydrogenation was studied. Then, the interaction of the synthesized alloys with hydrogen in combustion regime (self-propagating high-temperature synthesis, SHS) resulting in hydrides of these alloys was investigated. DTA and DSC analyses of some alloys and their hydrides were performed and their thermal characteristics were measured.

1. Introduction

At the laboratory of high-temperature synthesis of A.B. Nalbandyan Institute of Chemical Physics of Armenian NAS a powerful method "hydride cycle" for alloys and hydrides formation had been developed [1–3]. This method could be used for obtaining a wide range of alloys of transition metals and their hydrides. The main advantages of the "hydride cycle" method are: low power input, high productivity, waste-less process; high quality alloys and intermetallides of given composition yielding; not expensive source materials using – cheap SHS hydrides made from sponge, chips, etc. The alloys formed at rather low temperature (700–1000 °C), and short exposition (<30 min). More than 50 alloys are prepared in the systems: Ti–Zr, Ti–Hf, Zr–Hf, Ti–Nb, Zr–Nb, Zr–V, Ti–V–Cr, Ti–Zr–Hf, Zr–Ni, Zr–Co, Ti–Ni, Ti–Co, Ti–Al, etc.

The "hydride cycle" in association with SHS (self-propagating high-temperature synthesis) is a successful way for creation of alloys of given physical and chemical characteristics. In 1975, we predicted and realized for the first time SHS processes in Me–H systems [4–6]. The investigation of combustion processes in Me–H system has shown that SHS regime is a perspective direction for synthesis of hydrides of transition metals and alloys. More than 200 binary and complex hydrides of transition metals and alloys (carbohydrides, hydridonitrydes, hydrides of intermetallics) were synthesized; scientific bases of SHS processes proceeding in different condense systems in hydrogen environment were developed. The essence of SHS technique consists in usage of heat of exothermal reaction, proceeding after local instantaneous initiation of reaction in thin layer of non-heated mixture metal–nonmetal [3]. High temperature developed in the combustion front passes through a material in account of heat-transfer from layer to layer. Process proceeds without external power input, only in account of heat of chemical reaction.

It has been shown that some BCC alloys in Ti–V system have enhanced high sorption–desorption characteristics due to their special crystal structure, and are suitable as materials for hydrogen storage, as well as catalysts for other metal hydrides (for example, Mg and its alloys) [7–9].

In the present work, the possibility of formation of titanium and vanadium based alloys of BCC structure using hydride cycle was investigated. The mechanism of formation of alloys in Ti–V system from the powders of hydrides TiH_2 and $VH_{0.9}$ (or of V) by compaction followed by dehydrogenation was studied. Then, the interaction of the synthesized alloys with hydrogen in combustion regime SHS resulting in hydrides of these alloys [4–6] was investigated.

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Table 1
Phase composition, crystal structure and lattice parameters of the alloys and their hydrides synthesized in the present work. The hydrogen content of the hydrides is indicated in the units of the H/Me atomic ratio and in weight per cents.

Alloys and hydrides	Crystal phases	Crystal lattice parameters, Å	Crystal lattice parameters, Å (calculated)*	H/Me	H, wt.%
TiH_2	FCC	a = 4.44	–	2	4.01
Ti (α)	HCP	a = 2.944; c = 4.688	–	–	–
Ti (β)	BCC	a = 3.282	–	–	–
$Ti_{0.8}V_{0.2}$	BCC (57%)	a = 2.979 c = 4.726	–	–	–
	HCP (43%)	a = 3.223			
$Ti_{0.7}V_{0.3}$	BCC (77%)	a = 3.225;	a = 3.224;	–	–
	HCP (23%)	a = 2.96; c = 4.76			
$Ti_{0.7}V_{0.3}H_{1.9}$	FCC	a = 4.397	–	1.9	3.7
$Ti_{0.6}V_{0.4}$	BCC (81%)	a = 3.205	a = 3.198;	–	–
	HCP (19%)	a = 2.97; c = 4.775			
$Ti_{0.6}V_{0.4}H_{1.9}$	FCC	a = 4.384	–	1.9	3.73
$Ti_{0.5}V_{0.5}$	BCC (83%)	a = 3.173	a = 3.168	–	–
	HCP (17%)	a = 2.968; c = 4.775			
$Ti_{0.5}V_{0.5}H_{1.88}$	FCC	a = 4.371		1.88	3.63
$V_{0.6}$ $Ti_{0.4}$	BCC (86%)	a = 3.152	a = 3.139	–	–
	HCP (14%)	a = 2.97; c = 4.775			
$V_{0.6}$ $Ti_{0.4}H_{1.8}$	FCC	a = 4.389		1.8	3.5
$V_{0.8}Ti_{0.2}$	BCC (88%)	a = 3.063	a = 3.086	–	–
	HCP (12%)	a = 2.958; c = 4.728			
$V_{0.8}Ti_{0.2}H_{1.7}$	FCC	a = 4.281		1.7	3.3
$V_{0.9}$ $Ti_{0.1}$	BCC (93%)	a = 3.042	a = 3.056	–	–
	HCP (7%)	traces			
$V_{0.9}Ti_{0.1}H_{1.9}$	FCC	a = 4.277		1.9	3.65
$VH_{0.9}$	BCT	a = 3.31; c = 3.366		0.9	1.7
V	BCC	a = 3.022	–	–	–

* Parameters of crystal lattices of alloys are calculated on Vegard curve using Ti(β) and V parameters.

2. Materials and methods

A special installation has been designed and prepared, consisting of a quartz reactor, a furnace, and devices for controlling the vacuum and temperature in the reactor during dehydrogenation of compact sample and formation of alloy.

The source hydrides (TiH_2 and $VH_{0.9}$) were synthesized in SHS regime in reactors of constant pressure.

The full hydride cycle included:

- The SHS synthesis of titanium hydride was implemented in hermetic reactor under pressure 3–5 bar, and of vanadium hydride – at 10 bar. The temperature of exothermal reaction reached 400–800 °C.
- Grinding and mixing the powders of hydrides;
- Compacting this mixture at different pressures;
- Dehydrogenation of compacted sample 1000 °C for 30 min. The hydrogen removing did not loosen the sample; moreover, sintering of powders occurred. The process went on up to complete disappearance of hydride.
- Synthesis of hydrides of the formed alloys by SHS method was implemented under hydrogen pressure up to 5–10 bar, at $T_{comb.}$ = 307–565 °C.

The certification of samples has been performed at all stages of full cycle using the following analyses: chemical (pyrolysis method), differential-thermal (Derivatograph Q-1500), X-ray (DRON-0.5 and "Siemens D-500" – ISSP RAS, Chernogolovka), differential scanning calorimeter DSC Q10P V9.9.

3. Results and discussion

In the present work, the experiments were carried out using the earlier developed standard scheme [1–3]. Preliminary, TiH_2 and $VH_{0.9}$ hydrides were synthesized in SHS regime, crushed, mixed, and compacted under pressure. Dehydrogenation at 1000 °C provided the active dissociation of hydrides according reaction:

$$xTiH_2 + (1-x)VH_{0.9} \rightarrow Ti_xV_{1-x} + H_2 \uparrow$$

$$\text{or} \quad xTiH_2 + (1-x)V \rightarrow Ti_xV_{1-x} + H_2 \uparrow$$

It was shown that the chemical peculiarities and ratio of initial components, phase transformations during dehydrogenation, etc. influenced on the alloys formation in Ti–V system. In Table 1, the characteristics of formed alloys and their hydrides are listed.

The data of X-ray analysis shown that during dehydrogenation, an alloy was formed in accordance with the composition of initial charge. For example: $0.6TiH_2 + 0.4VH_{0.9} \rightarrow Ti_{0.6}V_{0.4}$

The alloy formed in $0.8TiH_2 + 0.2VH_{0.9}$ composition contained two solid solutions: the main based on α-Ti and the second – on vanadium (~10%, BCC-phase). The other compositions form the alloys containing mainly BCC phase and ~20–25% of HCP phase (I_{bcc}/I_{α} = 3.2–4.2).

As soon as all the obtained alloys contained two solid solutions, to reveal the real composition of each phase we constructed Vegard's curve based on the parameters of β-Ti (*a* = 3.028 A) and BCC-V (*a* = 3.028 A). Parameters of BCC phase, calculated from diffraction patterns are close to the parameters of BCC phase, determined from Vegard's curve (Table 1). Hence, we can conclude that a real composition of each phase of alloy coincides with the given initial composition and is identical for both phases (BCC and HCP).

The density of Ti–V based alloys received in hydride cycle was close to the theoretical.

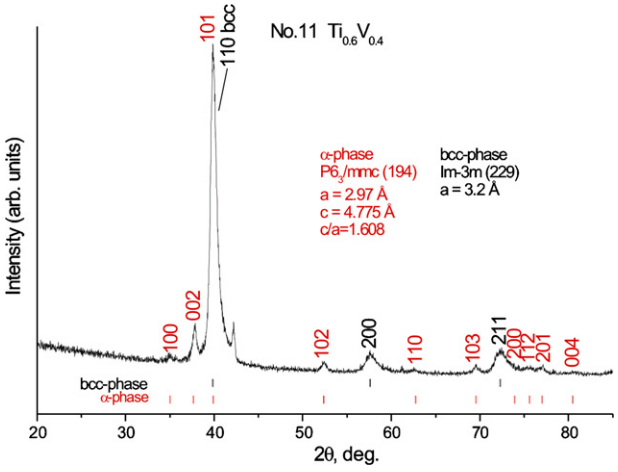

Fig. 1. The X-ray pattern of $Ti_{0.6}V_{0.4}$ alloy.

Table 2
Temperatures of thermal effects in the course of heating the alloys and hydrides from the second column. T(Ar) – DSC measurements at 1 bar of Ar; T(H_2) – DSC at 2 bar of H_2; T(DTA) – DTA measurements, endo-effects. *T* (comb) is the combustion temperature at SHS under ≤10 bar of hydrogen, exo-effects.

	Compounds	*T*(Ar), °C	*T*(H_2), °C	*T*(comb), °C	*H*, wt. %	*T*(DTA), °C
1	$Ti_{0.1}V_{0.9}$	–	364.64	307	–	–
1a	$Ti_{0.1}V_{0.9}H_{1.9}$	324.22 389.72	293.08 291.7	–	3.62	300340
2	$Ti_{0.2}V_{0.8}$	–	344.01	470	–	–
2a	$Ti_{0.2}V_{0.8}H_{1.88}$	365	366	–	3.6	300
3	$Ti_{0.6}V_{0.4}$	–	379.49	565	–	–
3a	$Ti_{0.6}V_{0.4}H_{1.9}$	439.7	443.9	–	3.78	360
4	$Ti_{0.7}V_{0.34}$	–	440.27	565	–	–
4a	$Ti_{0.7}V_{0.3}H_{1.9}$	424.72	435.74	–	3.78	360

In Figs. 1 and 2, the X-ray pictures of $Ti_{0.6}V_{04}$ alloy and of its hydride, respectively, are presented. The identification of these pictures shown that along with the basic BCC phase there is some amount of α-phase also.

These alloys interacted with hydrogen in SHS regime at pressure ≤10 bar. This interaction led to the formation of hydrides of alloys with rather high hydrogen content. In Table 1 the characteristics of the hydrides of formed alloys are presented also.

The multiple repetition of cycle "SHS-hydrogenation of alloy – dehydrogenation of alloy hydride", demonstrated the reversibility of process: $Ti_xV_{1-x} + H_2 \rightarrow Ti_xV_{1-x}H_{1.8-1.9}$. According to DTA analysis, the temperature of decomposition was within 300–400 °C depending on the ratio of metals in alloy.

DSC analyses of some alloys and their hydrides were performed. The thermal effects of interaction of Ti–V based alloys with hydrogen as well as of decomposition of obtained hydrides have been studied. Scanning was performed in the temperature range 40–500 °C in hydrogen (2 bar) or argon (1 bar) environment. In Fig. 3, DSC curve of $Ti_{0.2}V_{0.8}$ alloy is presented.

In Fig. 4, PCT curve for interaction with hydrogen of $Ti_{0.2}V_{0.8}$ alloy at $T = 400$ °C and $P_H = 1000$ abs (kPa), i.e. 10 bar, is presented. As it is seen, PCT data confirm the formation of hydride of $Ti_{0.2}V_{0.8}H_{0.578}$ composition (H_2 content = 1.136 wt%) at the indicated experimental conditions.

In work [10] pressure-composition isotherms were measured for the $Ti_{0.2}V_{0.8}$–H_2 and $Ti_{0.4}V_{0.6}$–H_2 systems at temperatures between 80 and 150 °C and pressures below 100 kgf cm^{-2} (100 atm or 98 bar). The conditions of PCT implementation in our work differ from those in the cited work. Therefore, we cannot compare our PCT results with the results obtained by Ono and coworkers. The data on DSC и PCT study are preliminary. They must to be continued in future.

The data for alloys and their hydrides presented in Table 2 allow comparing the maximal temperatures of formation and decomposition of hydrides of alloys at application of SHS, DSC and DTA methods. Here only the temperatures of thermal effects at DSC study of alloys and their hydrides in argon and hydrogen environment are presented. For comparison, there are shown also the temperatures of combustion at SHS (T_{comb}), and of endo-effects at DTA analysis. Let's note that while all these measurements are realized at conditions characteristic for the given method, the defined temperatures of endo- and exo-effects are rather close.

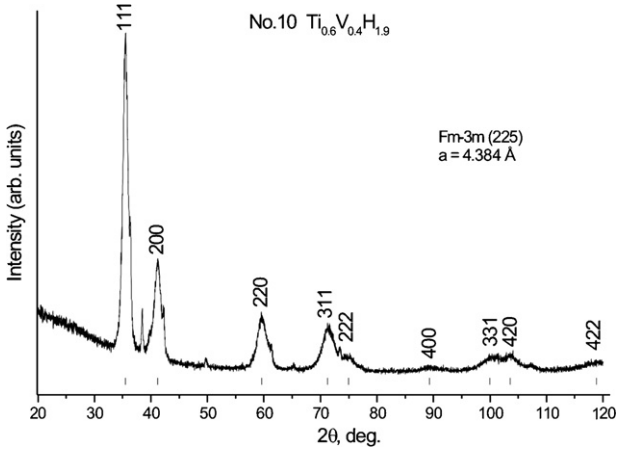

Fig. 2. The X-ray pattern of $Ti_{0.6}V_{0.4}H_{1.9}$ hydride.

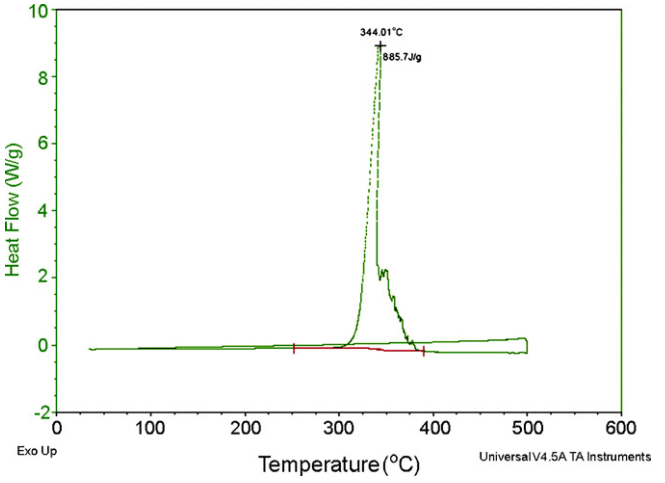

Fig. 3. DSC curve measured on heating the $Ti_{0.2}V_{0.8}$ alloy in hydrogen from 40 to 500 °C.

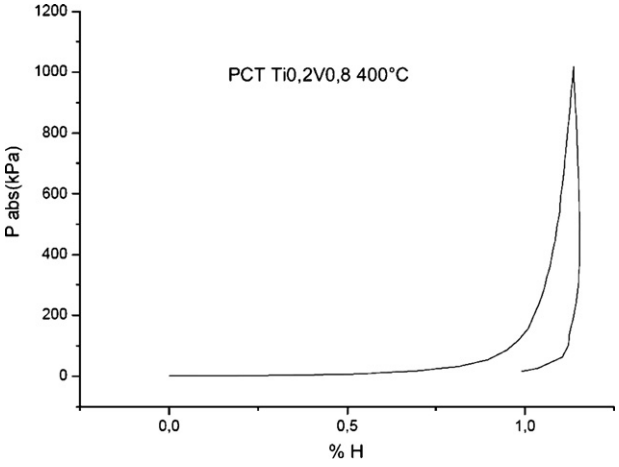

Fig. 4. PCT curve illustrating the interaction of the $Ti_{0.2}V_{0.8}$ alloy with hydrogen.

4. Conclusions

1. A number of Ti and V based alloys were formed from their hydrides, TiH_2 and $VH_{0.9}$, using technique named "hydride

cycle". Parameters of process of alloys formation were defined. In general, the alloys were formed containing mainly BCC crystal structure with small amount of α-phase.
2. It was shown that the alloys in Ti–V system formed hydrogen-rich hydrides in SHS regime.
3. The temperatures of formation and decomposition of hydrides defined in the investigations by SHS, DSC and DTA techniques are well concordant.

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References

[1] S.K. Dolukhanyan, A.G. Aleksanyan, O.P. Ter-Galstyan, V.Sh. Shekhtman, et al., Russ. J. Phys. Chem. B 2 (6) (2007) 563–569.
[2] A.G. Aleksanyan, S.K. Dolukhanyan, A.A. Mantashyan, D.G. Mayilyan, O.P. Ter-Galstyan, V.Sh. Shekhtman, in: B. Baranovski, et al. (Eds.), Carbon Nanomaterials in Clean Energy Hydrogen Systems. NATO Science Series, Springer, 2008, pp. 783–794.
[3] A.G. Merzhanov, I.P. Borovinskaya, Dokl. AN SSSR. 204 (2) (1972) 366–369.
[4] S.K. Dolukhanyan, A.G. Aleksanyan, V.Sh. Shekhtman, H.G. Hakobyan, D.G. Mayilyan, N.N. Aghadjanyan, K.A. Abrahamyan, N.L. Mnatsakanyan, O.P. Ter-Galstyan, Int. J. Self-Propagating High-Temp. Synth. 19 (2) (2010) 87–95.
[5] S.K. Dolukhanyan, in: A.A. Borisov, L. De Luca, A.G. Merzhanov (Eds.), Self-Propagating High-Temperature Synthesis of Materials, Taylor and Francis, New York, 2002, pp. 219–237.
[6] S.K. Dolukhanyan, J. Alloys Compd. 253–254 (1997) 10–12.
[7] J. Huot, H. Enoki, E. Akiba, J. Alloys Compd. 453 (2008) 203–209, 1-2 3.
[8] H.G. Schimmel, J. Huot, et al., J. Am. Chem. Soc. 127 (41) (2005) 14348–14354.
[9] J. Huot, L. Cranswick, I. Swainson, Phys. Can. 62 (5) (2006) 289–294.
[10] S. Ono, K. Nomura, Y. Ikeda, J. Less-Common Met. 72 (1980) 159–165.