

HYDRIDES OF TRANSITION METALS AND THEIR ALLOYS AS CONDENSED HYDROGEN CARRIERS

**S. K. DOLUKHANYAN^{*}, A. G. ALEKSANYAN, G. N. MURADYAN^{*},
V. Sh. SHEKHTMAN^{**}, O. P. TER-GALSTYAN^{*}, H. G. HAKOBYAN^{*},
N. N. AGHAJANYAN^{*} and N. L. MNATSAKANYAN^{*}**

^{*} A. B. Nalbandyan Institute of Chemical Physics, NAS RA
5/2, P. Sevak Str., Yerevan, 0014, Armenia

^{**} Institute of Solid State Physics of Russian Academy of Sciences
Chernogolovka, Moscow region, 142432, Russia
E-mail: seda@ichph.sci.am

The review of the work of the Laboratory of High-Temperature Synthesis and Technology of Inorganic Materials, ICP NAS of Armenia, is presented. For the first time, more than 200 binary and multicomponent hydrides and deuterides of metals and alloys were synthesized by the method of self-propagating high-temperature synthesis (SHS). These studies became the physico-chemical basis of SHS processes in Me-H systems and led to the formulation of technological works having huge industrial prospects. Hydrides of transition metals and alloys are of great value as condensed hydrogen carriers. Further studies of hydrides synthesized in the SHS regime made it possible to develop yet another fundamentally new method for the synthesis of alloys and intermetallics of transition metals, which we called the "Hydride cycle-HC" method. The method is based on reactions of interaction of two or more metal hydrides, for example, $x\text{Me}_1\text{H}_2 + (1-x)\text{Me}_2\text{H}_2 \rightarrow \text{alloy Me}_x\text{Me}_{(1-x)} + \text{H}_2\uparrow$. It is shown that when a compacted mixture of two or more hydrides, as well as hydride and metal powder (for example, TiH_2 and Al) is heated, the removal of hydrogen from the compacted charge at temperatures slightly above the dissociation temperatures of the hydrides leads to the formation of strong, nonporous, compact binary, ternary alloys of these metals. More than 100 alloys and intermetallics in Ti-Zr systems were synthesized in the HC mode; Ti-Hf; Ti-Nb; Ti-V; Zr-Hf; Ti-Zr-Hf; Ti-Ni; Zr-Co; Ti-Al; Nb-Al, etc. Some of the obtained compact alloys without preliminary grinding interact with hydrogen in the SHS mode, forming hydrides with a high hydrogen content.

Figs. 18, tables 4, references 25.

1. Hydrides of transition metals

When the reserves of fossil fuels such as oil, natural gas and coal are depleted and disappear, they will be replaced by water decomposed to hydrogen and oxygen. Hydrogen is a fuel of the future. Although it was shown that hydrogen has a great future, its accumulation, storage and usage is dangerous. Gaseous hydrogen is stored in gas cylinders at a pressure of 150 atm with explosion hazard. Hydrogen is liquefied at temperatures between -253– -259°C and stored in special containers – tanks.

It is worth noting that at present, the modern technology offers a more advantageous way of hydrogen storage by incorporation it into a metal, storage without loss for a long time at ambient temperature and pressure, and extraction at a right time applying heating. The extracted hydrogen is of as high purity as 99.99% because at the temperature of its extraction no other gases or impurities are released from the metal. There is a huge literature devoted to metal-hydrogen compounds named hydrides. Actually, the term "hydrides" combines a very broad class of substances with cardinally different properties, chemical composition and type of inter-atomic bonds.

Fig. 1 shows the elementary crystal lattice of titanium hydride, TiH_2 .

The hydrides of transition metals and alloys having "metallic bonds", the so-called metal hydrides, are the subject of the present article. Hydrogen, embedded in the metal can radically change the properties of the latter. The interaction of transition metals with hydrogen results in formation of structures, in which the hydrogen atoms are located in the interstices of the metal sublattice, for example, in tetrapores.

Hydrides of transition metals are of wide interest as a large class of compounds with unique physical and chemical characteristics. Table 1 presents some characteristics of several hydrides of transition metals and hydrogen containing materials.

Table 1

The most important characteristics of some transition metal hydrides and hydrogen containing materials

Compound	Atomic concentration of H_2 , $N_{\text{H}} \times 10^{22} \text{ at. H/cm}^3$	Content of H_2 , wt. %	Dissociation temperature, °C
ZrH_2	7.34	2.01	800-1000
TiH_2	9.5	4.02	600-800
MgH_2	6.7	7.6	
VH_2	11.4	3.78	
$\text{ZrV}_2\text{H}_{4.3}$	7.06	1.85	550-600
ZrNiH_3	7.73	1.96	250-350
ZrCoH_3	7.64	1.95	250-350
TiFeH_2	5.5	1.5	80
LaNi_5H_7	7.6	1.5	30-50
Mg_2NiH_4	5.9	3.8	200-250
Gaseous H_2 at 100 atm	0.65	—	—
Liquid H_2	4.2	—	—
H_2O	6.7	—	—
Lithium borohydride, LiBH_4	7.6	18.5	—
Polystyrene, $(\text{C}_8\text{H}_9)_n$	5.4	1.05	—

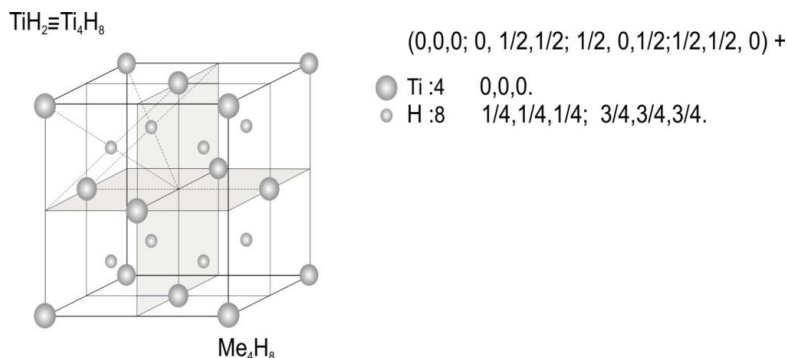


Fig. 1. Elementary crystal lattice of TiH_2 .

The data in Table 1 show that the hydrogen content in a unit volume of metal hydride is much higher than in a unit volume of many hydrogen-containing materials including liquid hydrogen and water. Consequently, hydrides of transition metals and alloys are of great value as condensed hydrogen carriers.

The interest in hydrogen and metal hydrides is associated with two global problems: protection of environment and depletion of fossil carbon and hydrocarbon fuels. Metal hydrides are multifunctional materials. The range of application of hydrides of metals and alloys is very wide.

1. In hydrogen energy, the metal hydrides serve as hydrogen accumulators and are promising as components of environmentally pure fuel. In this sense, the hydrides with dissociation temperatures below 300°C are of particular interest [1].
2. In nuclear power, the metal hydrides are used as biological protection against ionizing radiation and fast neutron flux. The mass of hydrogen atom is closer to the mass of neutron than the mass of any other element; therefore, upon interaction with neutron, it exhibits a unique property: is the most effective absorber of neutron energy. The content of hydrogen atoms in volume unit, $N_{\text{H}} \times 10^{22} \text{ at. H/cm}^3$, is the most important characteristic determining the effectiveness of any protective material in slowing down neutron flux. The data in Table 1 show that this characteristic for metal hydrides is the best [2].
3. In powder metallurgy, the metal hydrides are used as most convenient compounds for dispersing the refractory metals. It is known that the introduction of hydrogen into the crystal lattice of a metal brings to its embrittlement [3]. The hydrides of transition metals can be easily ground to micron and submicron grain sizes, besides they consist of crystallites of nanoscale sizes. In metallurgy, the term "hydrogen fragility" is known. In steel and cast iron, this very undesirable phenomenon can appear due to the hydrogen impurity even not exceeding 0.1 wt.%.
4. Metal hydrides can serve as sources of the purest hydrogen, $\approx 99.4444\%$.
5. Metal hydrides are successfully used as catalysts in the chemical industry.

Many other original and unexpected applications of metal hydrides have been described in the literature.

The current method of metal hydride producing consists in the heat treatment of metal at high temperature ($\sim 1000^{\circ}\text{C}$) in inert atmosphere and stepwise cooling it in the hydrogen atmosphere. The process lasts from 10 to 40 *hours*, depending on the metal. For preparation of hydride of stoichiometric composition, multiple cycling, deep purification of hydrogen, etc. are required. The obvious difficulty of producing hydrogen rich, single-phase metal hydrides hinders their wide application in industry, studying their physical and chemical properties for finding new areas and expanding application fields [4].

The SHS method has appeared a perspective direction for the synthesis of metal hydrides.

The essence of SHS method consists in the usage of heat of exothermic reaction after local instantaneous initiation of combustion in a thin layer of non-heated mixture of metal and solid metalloid (C, B, Si), or metal and gaseous metalloid (N_2). The heat of the initiated exothermic reaction creates a front of high temperature, which propagates with a constant linear velocity through the mixture at the expense of transferring the heat from layer to layer. The process proceeds exclusively at the expense of heat of chemical reaction without input of external energy [5].

At the Institute of Chemical Physics of the AS of Armenian SSR in the Laboratory of high-temperature synthesis, the SHS processes in Me-H systems were predicted and implemented for the first time [6-9]. The study of metal combustion in hydrogen in the SHS mode resulted in the synthesis of hydrides of transition metals. Therefore, a promising SHS method for the synthesis of hydrides of transition metals and alloys was elaborated. The interaction of a transition metal with hydrogen occurs with release of significant heat. For example, $\text{Ti} + \text{H}_2 \leftrightarrow \text{TiH}_2 + \text{Q}$ (ΔH of TiH_2 formation is equal to 39 kcal/mol). The released heat ensures the propagation of the combustion front along the unheated metal tablet with constant linear velocity.

Fig. 2 shows the scheme of the exothermic reaction flow in the Ti- H_2 system.

Fig. 3 shows the photo of titanium hydride formed in SHS mode.

Fig. 4 shows the thermograms of combustion of zirconium, titanium and ZrCo intermetallic in hydrogen atmosphere at $P = 3 \text{ atm}$.

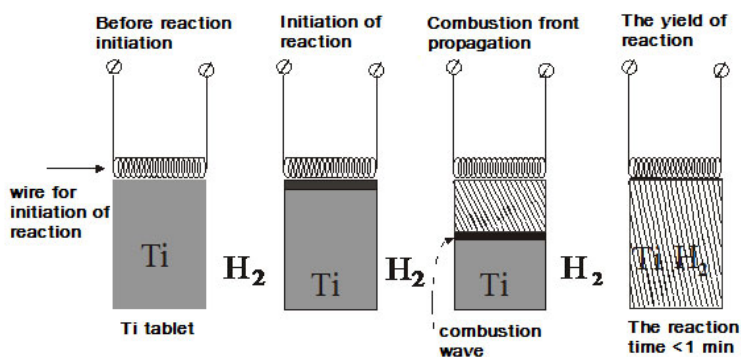


Fig. 2. Scheme of exothermic reaction in Ti- H_2 system.



Fig. 3. Photo of non-crushed SHS-synthesized TiH_2 sample.

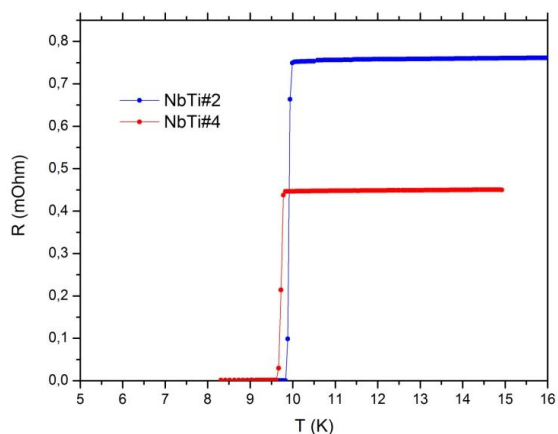


Fig.10. The dependences from the temperature of resistance of $\text{Ti}_{0.4}\text{Nb}_{0.6}$ and $\text{Ti}_{0.5}\text{Nb}_{0.5}$ alloys.

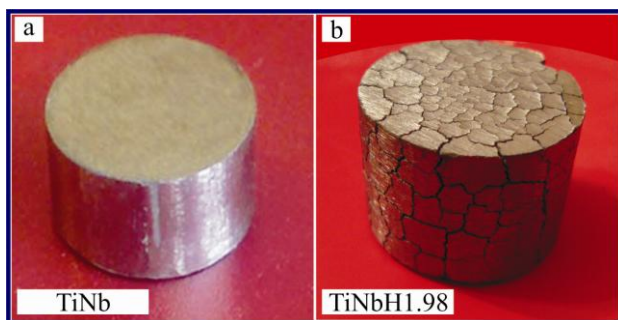


Fig. 12. The pictures of $\text{Ti}_{0.5}\text{Nb}_{0.5}$ alloy and its hydride.

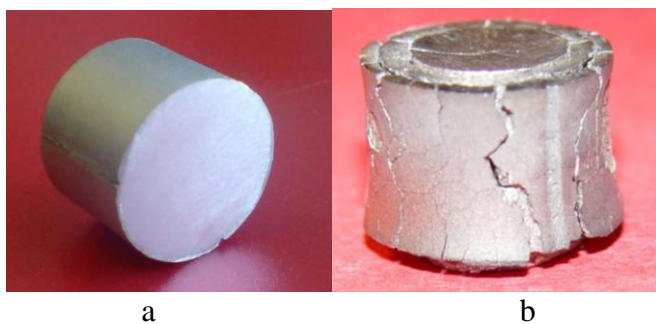


Fig. 18. The pictures of: a – $\text{Ti}_{0.5}\text{Al}_{0.25}\text{Nb}_{0.25}$ alloy; b – its hydride.

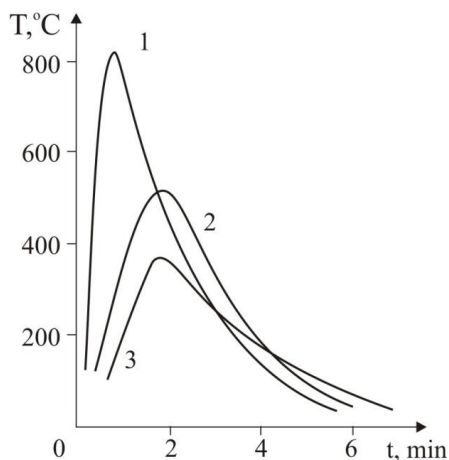


Fig. 4. The thermograms of combustion of zirconium (1), titanium (2) and ZrCo intermetallic (3) in hydrogen atmosphere at $P = 3 \text{ atm}$.

Numerous hydrogen-containing systems, such as Me-H, Me-Me¹-H, Me-nonmetal (C, N) - H have been investigated, including:

1. III, IV and V group and rare earth metals – hydrogen (or deuterium) [6];
2. IV and V group metals – carbon – hydrogen [7];
3. IV and V group metals – nitrogen – hydrogen [8];
4. Zr₂Ni, Zr₂Co, ZrNi, ZrCo, Ti₂Co and other intermetallics – hydrogen [9].

The implemented researches resulted in:

- synthesis of more than 200 compounds: binary hydrides and deuterides of III-V group transition metals and lanthanoids (TiH₂, ZrH₂, HfH₂, NbH_{1.23}, PrH₂, etc.), as well as of carbohydrides, hydridonitrides, hydrides of intermetallics, based on titanium, zirconium, nickel, cobalt, etc. [6, 9, 10];
- elucidation of the scientific basis for SHS processes proceeding in hydrogen atmosphere in various condensed systems [10];
- clarification of the factors, controlling the characteristics of combustion wave, velocity of its propagation, the temperature and completeness of combustion and other conditions demanded for production of compounds of given chemical and phase composition [11];
- proof of a two-stage mechanism of combustion and formation of hydrides in SHS: in the first stage, a solid solution of hydrogen in metal is formed in the combustion front; this stage is followed by the second stage, when a stoichiometric hydride is formed by saturation of sample with hydrogen (after-hydrogenation) [6-11];
- description of the physical and chemical characteristics of synthesized hydrides (heat resistance, dissociation kinetics, etc.) [6-11].

Fig. 5 shows the diffraction patterns of TiH₂, NbH_{1.3}, TiC_{0.4} H_{1.2} and TiN_{0.21}H_{1.34} hydrides.

Fig. 6 shows the microstructure of synthesized in SHS mode niobium hydride.

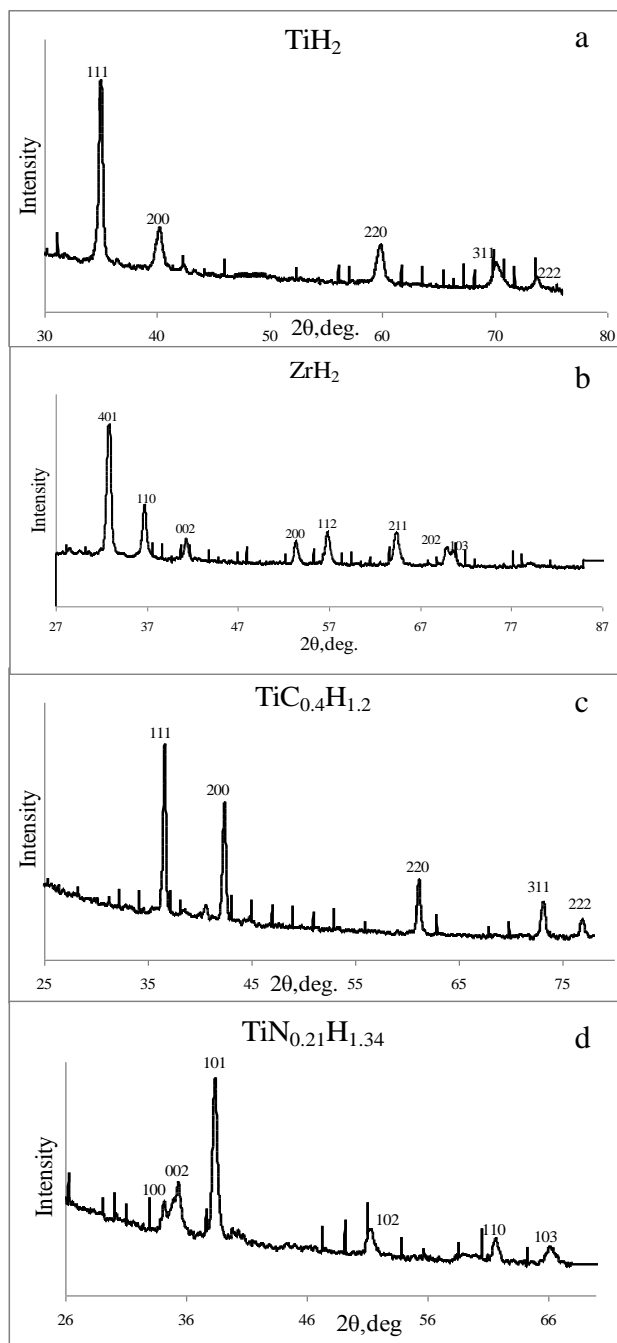


Fig. 5. X-ray patterns of SHS hydrides: a) TiH_2 , b) $\text{NbH}_{1.3}$, c) $\text{TiC}_{0.4}\text{H}_{1.2}$, d) $\text{TiN}_{0.21}\text{H}_{1.34}$.

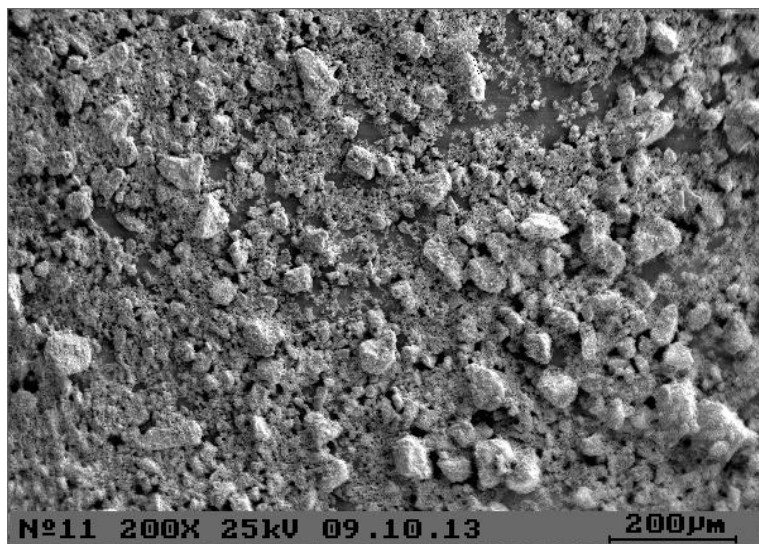


Fig. 6. Microstructure of SHS-synthesized niobium hydride, $\text{NbH}_{1.23}$.

Tables 2 and 3 show some characteristics of SHS-synthesized binary hydrides, deuterides, carbohydrides and hydridonitrides.

Table 2

Characteristics of SHS-synthesized binary hydrides and deuterides

Metal	H ₂ , D ₂ content, wt. %	Crystal structure	Lattice parameters, Å	Calculated formula
Sc	4.25	FCC	a=4.782	ScH ₂
	3.01	FCC	a=4.698	ScD _{0.73}
Y	3.255	HCP	a=3.661; c= 6.630	YH _{2.9}
	4.41	FCC	a= 5.197	YD _{2.1}
Ti	4.01	FCC	a= 4.460	TiH ₂
	7.03	FCC	a=4.51	TiD _{1.82}
Zr	2.16	tetragonal	a= 3.527; c= 4.476	ZrH ₂
	4.16	tetragonal	a= 3.520; c= 4.476	ZrD _{1.96}
Hf	1.09	tetragonal	a= 4.911; c= 4.405	HfH ₂
	2.11	tetragonal	a= 4.911; c= 4.405	HfD _{1.93}
V	1.71	tetragonal	a= 3.310; c= 3.339	VH _{0.8}
Nb	0.95	orthorhombic	a=4.451; b=4.878; c=3.453	NbH
Nd	1.78	FCC	a=5.446	NdH _{2.6}
	3.61	FCC	a=5.364	NdD _{2.5}
Sm	1.87	HCP	a=3.771; c=6.782	SmH ₃
Ho	1.78	HCP	a=3.653	HoH ₃
Gd	1.79	HCP	a=3.373; c=6.71	GdH _{2.88}

Table 3

Characteristics of SHS-synthesized carbohydrides and hydridonitrides

Formula	Content, wt. %			Crystal structure and lattice parameters, Å	Dissociation temperature, °C
	H ₂	C	N ₂		
TiC _{0.4} H _{1.2}	2.2	8.45	—	HCP, a=3.09; c= 5.08	400-840
TiC _{0.45} H _{0.5}	0.95	10.08	—	FCC, a=4.296	380-840
ZrN _{0.3} H _{1.52}	1.52	—	3.81	HCP, a=3.27; c= 5.519	370-795
TiN _{0.28} H _{1.33}	2.2	—	7.6	HCP, a=3.044; c= 5.09	455-610
Ti _{0.7} V _{0.3} C _{0.69}	—	14.42	—	FCC, a=4.272	—
Ti _{0.7} V _{0.3} C _{0.60} N _{0.30}	—	12.65	6.78	FCC, a=4.205	—
Ti _{0.7} V _{0.3} C _{0.7} H _{0.16}	0.28	14.57	—	FCC, a=4.249	—
Ti _{0.7} V _{0.3} N _{0.69} H _{0.2}	—	14.39	3.35	FCC, a=4.252	—
Ti _{0.7} V _{0.3} C _{0.7} N _{0.13} H _{0.1}	0.17	14.42	3.1	FCC, a=4.249	—
Zr _{0.5} Nb _{0.5} C _{0.42} N _{0.34}	—	5.17	4.34	FCC, a=4.57	—

The study of combustion in hydrogen of various condensed systems permitted the elucidation of the physical and chemical basis of SHS process in metal-hydrogen systems and led to the carrying out technological researches having enormous industrial prospects. High-performance technological processes for the synthesis of various hydrides have been developed, which have no analogues in the world. The developed methods can provide production of large assortment of cheap high-quality hydrides. At the experimental plant “ArmNIItsvetmet” (Yerevan) more than 20 tons of titanium and zirconium hydrides were produced.

The SHS method for the synthesis of hydrides has several significant advantages over traditional methods: high productivity, high quality of hydrides, practically no energy consumption, ecological purity and safety of the process, etc. The SHS synthesis of hydrides excludes a number of laborious operations demanded in the traditional methods, such as preliminary activation of the metal, deep purification of hydrogen, fine dispersion of metal powders, etc.

A special advantage of SHS is the possibility of metal sponge, chips and other industrial waste utilization using them as raw material. It means that the SHS hydrogenation can be applied in the high-efficiency recycling of the waste of refractory metals (Ti, Zr, Hf, Nb, V, etc.) and alloys, formed in huge quantities during their mechanical processing. This is a very cheap way of synthesis of valuable hydrides of expensive metals.

2. Synthesis of alloys and intermetallics of transition metals by hydride cycle method

Further study of SHS synthesized hydrides of transition metals brought to the development of a fundamentally new, early unknown method for formation of the

alloys and intermetallics of transition metals, which we called the "Hydride cycle" (HC) method.

The hydrogen-rich metal hydrides are very plastic. It means that they can be effectively pressed (compacted). Fig. 7 shows the microstructures of the initial powder of titanium hydride and of the surface of the tablet compacted from TiH_2 . The tablet has a very dense structure. The particles perfectly conform with one another.

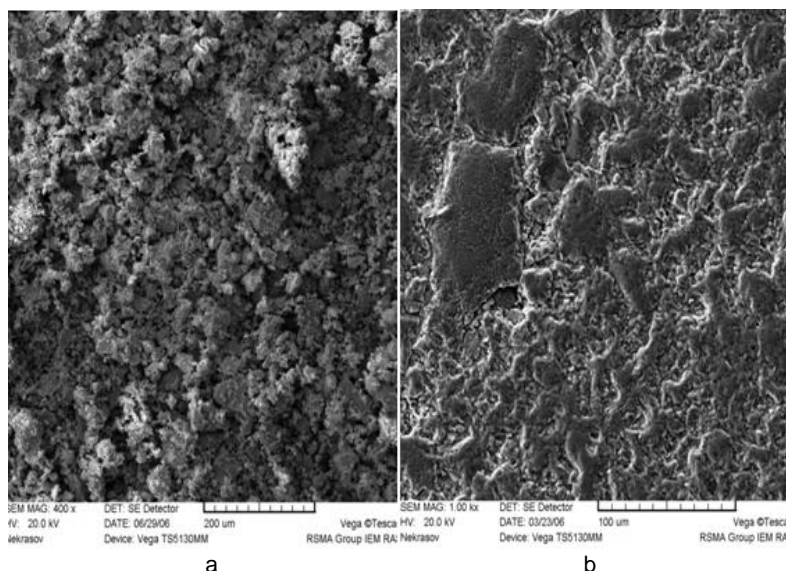
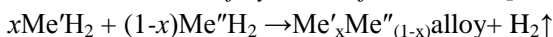


Fig.7. The initial surface of titanium hydride powder (A) and the microstructure of surface of the pressed from it tablet (B).

We used the compatibility of hydrides for elaboration of method for the synthesis of alloys. It was shown that upon heating a compacted mixture of powders of two (for example, TiH_2 and ZrH_2 , TiH_2 and NbH_x , TiH_2 and VH_x , etc.) or more hydrides, as well as powders of a hydride and metal (for example, TiH_2 and Al, TiH_2 and Fe, TiH_2 and Re, ZrH_2 and Y, etc.), hydrogen was removed a little above the hydride dissociation temperature (far below the melting points of the used metals). This process brought to the formation of strong, nonporous, compact binary (or ternary) alloy of taken metals. In HC mode, more than 100 alloys and intermetallics were synthesized in Ti-Zr, Ti-Hf, Ti-Nb, Ti-V, Zr-Hf, Ti-Zr-Hf, Ti-Ni, Zr-Co and other systems [12-16], among them – the alloys with structure of α -, β -, γ - and ω -phases.

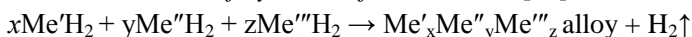
The HC process is based on the reactions:

1. *The interaction of hydrides of two metals* [12-15]:



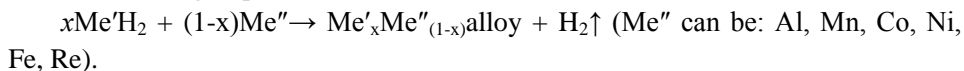
For example, $\text{TiH}_2 + \text{ZrH}_2 \leftrightarrow \text{TiZr} + \text{H}_2\uparrow$ or $\text{TiH}_2 + \text{NbH}_x \leftrightarrow \text{TiNb} + \text{H}_2\uparrow$ etc. These reactions resulted in synthesis of $\text{Ti}_x\text{Zr}_{(1-x)}$, $\text{Ti}_x\text{Hf}_{(1-x)}$, $\text{Zr}_x\text{Hf}_{(1-x)}$, $\text{Ti}_x\text{Nb}_{(1-x)}$, $\text{Ti}_x\text{V}_{(1-x)}$; etc. binary alloys.

2. *The interaction of hydrides of three metals* [16]:



For example, $\text{TiH}_2 + \text{ZrH}_2 + \text{HfH}_2 \rightarrow \text{Ti}_{0.66}\text{Zr}_{0.22}\text{Hf}_{0.12} + \text{H}_2\uparrow$ ternary alloys formed

3. *The interaction of hydride of any metal of III, IV, V groups with any metal of III, VI, VII, VIII groups* [17-19]:



For example, TiH_2 and Al, TiH_2 and Fe, TiH_2 and Re, ZrH_2 and Y, ZrH_2 and Co (Ni), ZrH_2 and Al, etc. These reactions resulted in formation of ZrCo, ZrNi, TiFe, TiAl, ZrAl, etc. intermetallics.

In [12-20], HC method is described and the experimental results of synthesis of alloys of IV-V group metals are presented. The influence on the characteristics (the crystal structure, density, adsorption properties, etc.) of the synthesized alloys and intermetallics of various parameters: ratio of metal hydride and metal in the reaction mixture; grain size in hydride powder (micro- and nanoscale); compaction pressure, conditions of dehydrogenation and sintering (temperature and rate of heating) was defined. Based on the experimental results, the following mechanism of HC-formation of alloys and intermetallics was suggested. During heating of the compacted mixture $x\text{Me}'\text{H}_2 + (1-x)\text{Me}-\text{H}_2$, due to breaking of the Me-H bonds at 800-1100°C, the metals become strongly activated. Simultaneously, hydrogen atmosphere reduced the oxide film, which usually exists on the surface of fine powders. The "open bonds" and the cleaned surface of the powders ensure the solid-phase diffusion of refractory metals at relatively low temperatures. For a more precise description and confirmation of the mechanism of formation of alloys and intermetallics in the HC, a differential thermal analysis (DTA) of the initial charge was carried out under conditions close to the HC. The comparison of these two processes clarified the nature of thermal effects at dissociation of hydrides and formation of alloys.

As starting powders, the metals of high purity were used: zirconium (98.9%), niobium (99.9%), titanium (98.9%), nickel (99.5%), cobalt (99.1%) and aluminum (99.7%). The hydrides of titanium (TiH_2 , H_2 content 4.01 wt.%), zirconium (ZrH_2 , H_2 content 2.0 wt.%) and niobium ($\text{NbH}_{1.23}$, H_2 content 1.31 wt.%) were synthesized and crushed down to $<50 \mu\text{m}$ particles. In SHS hydrides of transition metals of III, IV, V and RE groups, the hydrogen content is very high, between 2-4 wt.% (60 at.%). As it was mentioned above, due to introducing of hydrogen into the crystal lattice, the metal becomes brittle, it can be easily crushed to micron, submicron grain sizes, consisting of nanoscale crystallites [21]. The powders of one (or more) hydride(s) of transition metals and the same with aluminum, nickel or cobalt were carefully mixed and pressed in collet molds into cylindrical tablet with a diameter of 22-25 mm and a height of 8-10 mm by hydraulic press, using pressing force between of 20000-45000 kgf.

The alloys were produced in a specially designed hermetic unit consisting of a quartz reactor, a furnace, and devices for monitoring the vacuum and temperature in the reactor. A tablet sample was placed into the reactor, evacuated and heated. The HC process was carried out at temperatures of 600÷1100°C. The samples were identified using the chemical, differential-thermal (Derivatograph Q-1500) and X-ray diffraction (Diffractometer DRON-0.5) methods. DTA was carried out by heating the samples up to 1000°C at a rate of 20°C per minute.

2.1. Synthesis of alloys in Ti-Nb system.

Synthesis of alloys in Ti-Nb system proceeds in accordance with the reaction:

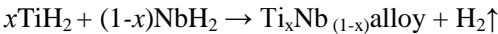


Fig. 8a shows the thermograms of HC-formation of $\text{Ti}_{0.6}\text{Nb}_{0.4}$ alloy [13]. At heating of 60% TiH_2 + 40% $\text{NbH}_{1.23}$ charge up to 1000°C, no thermal effect was registered on the HC thermogram. The sample was kept for about 30 min at this temperature, and the heater was turned off. According to XRD data, the sample, cooled down to the ambient temperature, represented a single-phase $\text{Ti}_{0.6}\text{Nb}_{0.4}$ alloy. Obviously, during heating to 1000°C, the TiH_2 and $\text{NbH}_{1.23}$ hydrides dissociated, but because of the high rate of heating, these processes were not reflected on the thermogram in Fig. 8a.

At the heating of the same charge at thermal analysis (Fig. 8b), DTA curve 2 shows three endo-effects at 130, 470 and 580°C, reflecting dissociation of titanium and niobium hydrides. No other thermal effects were registered at the temperature increasing up to 1000°C (8b, curve 1).

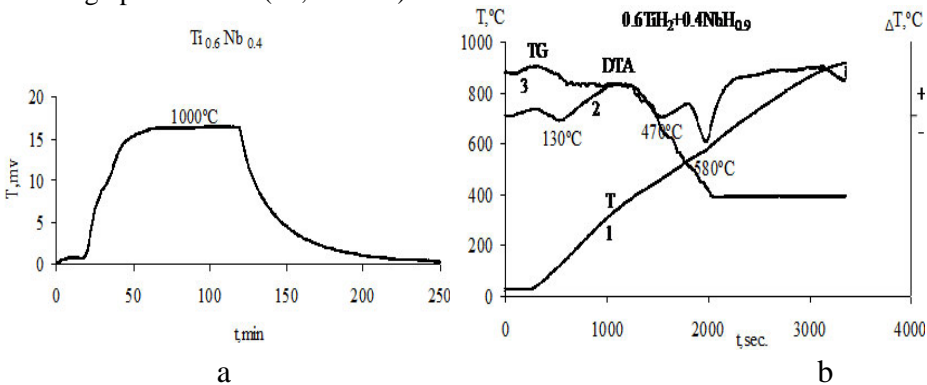


Fig. 8. (a) thermograms of HC-formation of TiNb alloy from $\text{TiH}_2 + \text{NbH}_{1.23}$; (b) DTA curves at heating of the same charge up to 1000°C.

Fig. 9 shows the diffraction patterns of $\text{TiH}_2 + \text{NbH}_{1.23}$ mixture, of two Ti-Nb based alloys and their hydrides.

The superconductivity of HC synthesized Ti-Nb-based alloys was investigated. Fig. 10 shows the dependences of resistance on the temperature of $\text{Ti}_{0.4}\text{Nb}_{0.6}$ and $\text{Ti}_{0.5}\text{Nb}_{0.5}$ alloys with BCC crystal lattice. In excellent accordance with the literature ($T_c = 9.5\text{-}10.5\text{K}$), the critical temperatures (transformation to overconductivity) of the studied alloys were registered at $T_c = 9.8$ and 9.9K .

Ti_{0.5}Nb_{0.5}-based alloys without preliminary crushing interacted with hydrogen in SHS mode and formed reversible hydrides. For example, Ti_{0.5}Nb_{0.5} + H₂ ↔ Ti_{0.5}Nb_{0.5}H_{0.99}. Fig. 11 shows the thermogram of combustion in hydrogen of Ti_{0.5}Nb_{0.5} alloy.

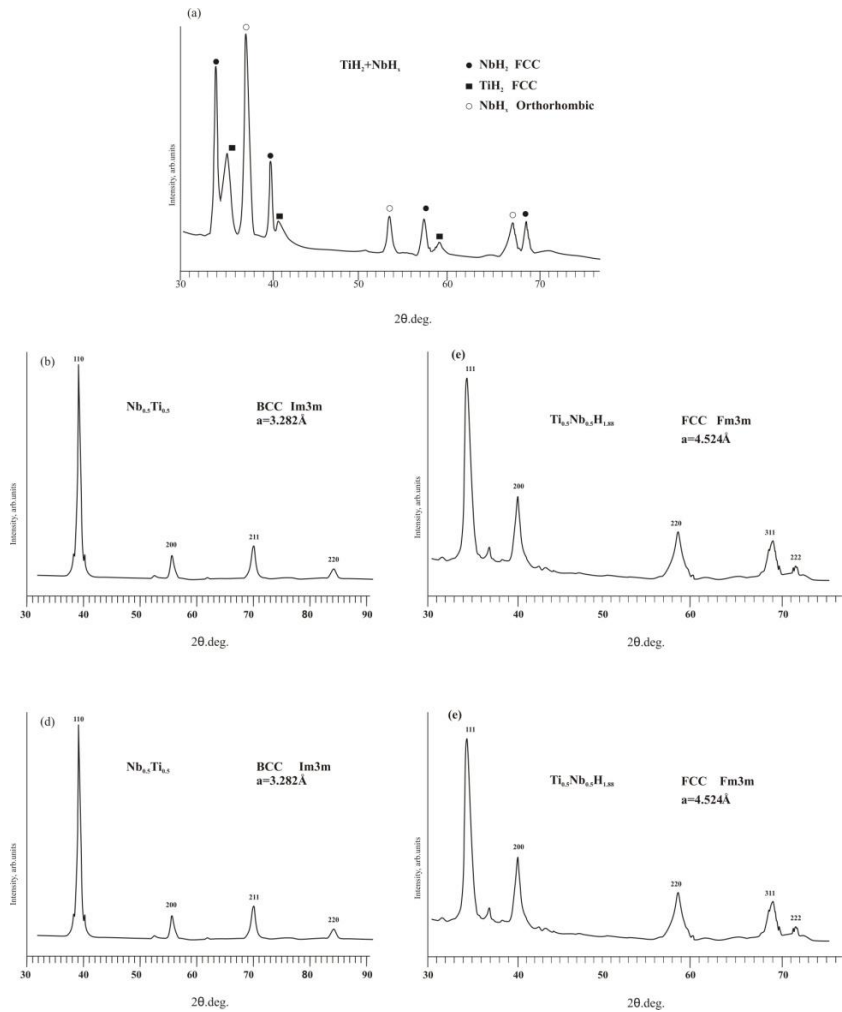
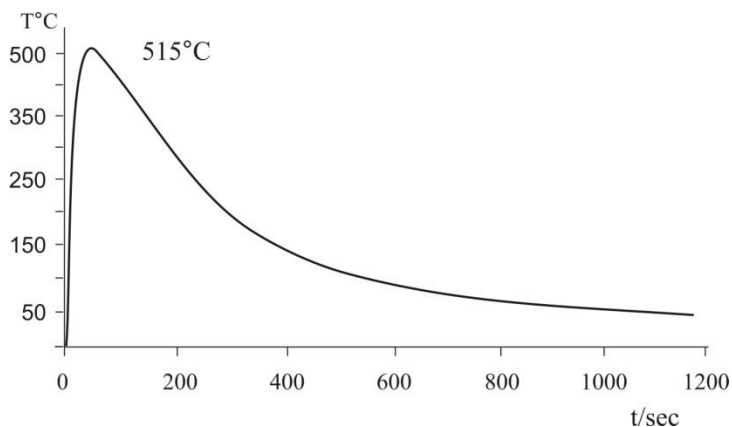


Fig. 9. Diffraction patterns of TiH₂ + NbH_{1,23} mixture (a), two Ti-Nb based alloys (b, c), and the hydrides of these alloys (d, e).



. Fig. 11. Thermogram of combustion in hydrogen of $\text{Ti}_{0.5}\text{Nb}_{0.5}$ alloy.

Fig. 12 shows the pictures of $\text{Ti}_{0.5}\text{Nb}_{0.5}$ alloy and its hydride.

Similarly, the alloys were formed in the systems: $x\text{TiH}_2 - (1-x)\text{ZrH}_2$; $x\text{TiH}_2 - (1-x)\text{HfH}_2$; $x\text{TiH}_2 - (1-x)\text{VH}_{0.8}$; $x\text{TiH}_2 - y\text{ZrH}_2 - z\text{HfH}_2$, etc., where the HC alloy formation takes place in solid phase mechanism, excluding melting [12-16]. Fig. 13 shows the diffraction pattern of HC synthesized $\text{Ti}_{0.2}\text{Zr}_{0.4}\text{Hf}_{0.4}$ alloy.

Fig. 14 shows the microstructure of Ti_2Zr alloy, taken on a thin section of flat surface of a sample by scanning electron microscope.

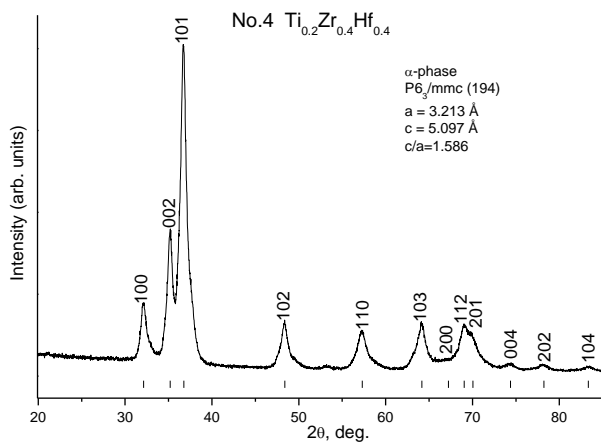


Fig. 13. Diffraction patterns of HC-synthesized alloys of $\text{Ti}_{0.2}\text{Zr}_{0.4}\text{Hf}_{0.4}$.

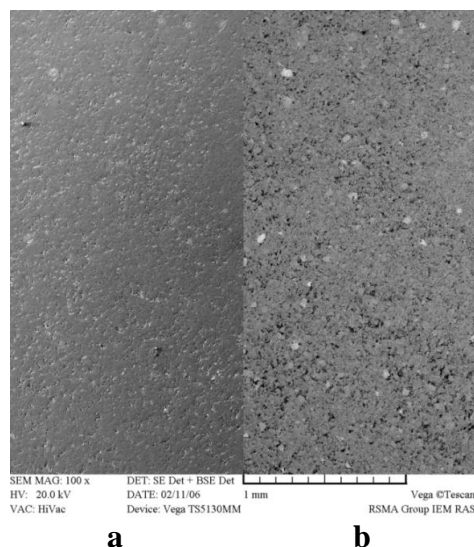


Fig. 14. Microstructure of Ti_2Zr alloy: *a* – surface relief (surveyed in secondary electrons); *b* – image of the surface in the phase contrast mode (surveyed in reflected electrons).

2.2. Investigation of HC processes in Ti-Al, Zr-Al and Nb-Al systems. Synthesis of Ti, Zr and Nb based aluminides

A distinctive feature of aluminum containing systems is that the formation of aluminides in HC proceeds via exothermic reactions. Fig. 15 shows the thermograms of HC formation of aluminides of titanium, zirconium, hafnium (a, b, c) and the DTA curves (d, e, f) registered upon heating up to 1000°C of three compositions: 75 at.% TiH_2 + 25 at.% Al (Ti_3Al); 75 at.% ZrH_2 + 25 at.% Al (Zr_3Al) and 75 at.% $\text{NbH}_{1.3}$ + 25 at.% Al (Nb_3Al).

On the HC thermograms of all three compositions in Fig. 15 a, b, c, the exo-effects are registered at the temperature interval of $670\text{--}940^\circ\text{C}$. The registration of these exo-effects indicates that the reactions of aluminide formation are exothermic. On the DTA curves (Fig. 15 d, e, f), in the temperature interval of $140\text{--}600^\circ\text{C}$, the endo-effects are registered at temperatures corresponding to the dissociation of titanium, zirconium and niobium hydrides. Only in the case of $3\text{NbH}_{1.3} + 25\%\text{Al}$ system (Fig. 15f) on curve 2, the additional endo-effect is observed at 660°C due to aluminum melting. Simultaneously, on the HC thermogram of the same composition (Fig. 15c), no endo-effects, corresponding to the dissociation of the initial hydrides and/or the aluminum melting were registered.

DTA curves 3 in Fig. 15 d, e, f manifest sharp loss of weight by all the samples due to the dissociation of hydrides and liberation of hydrogen. On the HC thermograms (Fig. 15 a, b, c) and DTA curves 2 (Fig. 15 d, e, f), the temperatures of the exo-effects due to interaction of aluminum with titanium, zirconium and niobium coincide for the same compositions (Fig. 15 a and d, b and e, c and f).

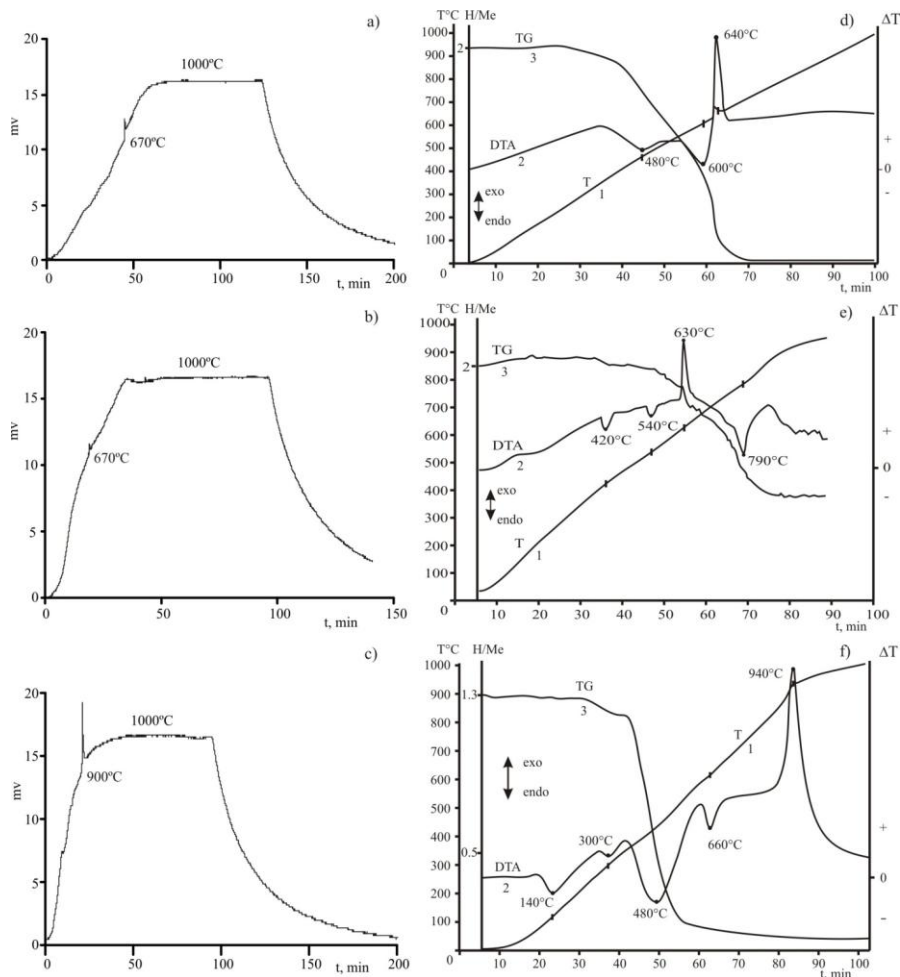
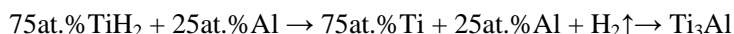


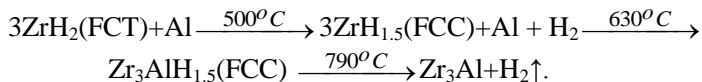
Fig. 15. The thermograms of HC-formation of aluminides (a, b, c) and DTA curves (d, e, f) upon heating up to 1000°C of three compositions: (a, d) – 75at.%TiH₂ + 25at.%Al(Ti₃Al), (b, e) – 75%ZrH₂ + 25%Al(Zr₃Al) and (c, f) – 3NbH_{1.3} + 25%Al(Nb₃Al).

Each of the titanium, zirconium and niobium hydrides shows its own specific feature of interaction with aluminum. The process of titanium aluminide formation in HC (Fig. 15 a) upon heating the initial mixture can be described by:



The dissociation of titanium hydride is reflected in the endo-effect at 600°C, which smoothly turns to the exoeffect at 640°C (DTA curve 2 in Fig. 15d) [17].

The behavior of ZrH₂ is different (Fig. 15e) [18]. When the temperature of the charge reaches 540°C (endoeffect on curve 2), the hydride partially decomposes to ZrH_{1.5}. A phase transition occurs: the tetragonal crystal lattice transforms to FCC lattice. The future temperature increase brings to the exo-effect at 630°C, indicating the formation of zirconium aluminide-hydride. The latter decomposes at 790°C (reflected in the endo-effect), resulting in Zr₃Al formation.



As it was noted above, only in the $3\text{NbH}_{1.3}$ -25%Al system, beside the endo-effect due to dissociation of $\text{NbH}_{1.23}$, an endoeffect due to aluminum melting is observed at 660°C (Fig. 15f). Then, on DTA curve 2, the exoeffect at 940°C indicates the formation of Nb_3Al (proved by X-ray analyses) [19]. These results from the differences in the conditions of the HC and DTA processes.

Judging by the HC thermograms (Fig. 15 a, b, c) and the DTA curves (Fig. 15 d, e, f), the formation of binary and ternary aluminides of titanium, zirconium and niobium proceeds identical to the alloy formation in HC. At heating of corresponding charge in the reactor, the initial hydrides dissociate. As a result, the metals became activated and quickly interacted exothermically with aluminum in solid-phase mechanism, without aluminum melting. At first, regardless of the aluminum content, solid solution of aluminum in metal is formed. It is worth noting that, according to the phase diagrams, the melting points of aluminum solid solutions in titanium, zirconium and niobium are much higher, in the interval of 1680 - 2100°C . Hence, the temperatures registered as exo- endo-effects in the DTA curves do not reflect the aluminum melting. This is evidenced by the external view of the samples – no trace of melting is seen. An exception is $3\text{NbH}_{1.23}$ -Al system (Fig.15 c), in which an endo-peak is observed on the DTA curve at 660°C due to aluminum melting.

In the HC mode, more than 30 binary aluminides are synthesized: single-phase titanium aluminides: α_2 - Ti_3Al , γ - TiAl and TiAl_3 [17]; solid solutions of aluminum in zirconium of Zr_3Al composition, accompanied by various zirconium aluminide phases (Zr_4Al_3 , ZrAl and Zr_2Al_3); single-phase zirconium aluminides ZrAl_2 ; ZrAl_3 [18]; single-phase niobium aluminides NbAl_3 , Nb_2Al and Nb_3Al , containing about 10% Nb_2Al [19]. Some of aluminides reacted with hydrogen in the SHS mode forming reversible hydrides.

2.3. The HC-formation of ternary aluminides

The processes of HC-formation of ternary aluminides were studied in the following systems: $x\text{TiH}_2+y\text{Al}+z\text{NbH}_{1.23} \rightarrow \text{Ti}_x\text{Al}_y\text{Nb}_z+\text{H}_2\uparrow$ (where $x+y+z=1$) and $x\text{TiH}_2+(1-x)\text{ZrH}_2+\text{Al}$ (Al content between 25-75 at.%)

Depending on the $\text{TiH}_2/\text{NbH}_{1.23}$ and $\text{TiH}_2/\text{ZrH}_2$ ratios, single or double phase bimetallic aluminides formed with FCC (D0_{23}) and (D0_{22}), orthorhombic O-phase, BCC, β or B_2 structures. The experiments resulted in the synthesis of the following aluminides: $\text{Ti}_{0.35}\text{Zr}_{0.4}\text{Al}_{0.25}$; $\text{Ti}_{0.55}\text{Zr}_{0.2}\text{Al}_{0.25}$; $\text{Ti}_{0.15}\text{Zr}_{0.1}\text{Al}_{0.75}$; $\text{Ti}_{0.1}\text{Zr}_{0.15}\text{Al}_{0.75}$; $\text{Ti}_{0.5}\text{Al}_{0.23}\text{Nb}_{0.27}$; $\text{Ti}_{0.33}\text{Al}_{0.34}\text{Nb}_{0.33}$; $\text{Ti}_{0.125}\text{Al}_{0.75}\text{Nb}_{0.125}$; $\text{Ti}_{0.52}\text{Al}_{0.15}\text{Nb}_{0.33}$; TiAl_6Nb ; $\text{Ti}_{0.25}\text{Al}_{0.5}\text{Nb}_{0.25}$; $\text{Ti}_{0.45}\text{Al}_{0.28}\text{Nb}_{0.27}$; etc. [20, 22]. Fig. 16 shows the diffraction patterns of $\text{Ti}_{0.1}\text{Zr}_{0.15}\text{Al}_{0.75}$ (a) and $\text{Ti}_{0.2}\text{Zr}_{0.05}\text{Al}_{0.75}$ (b) three-aluminides.

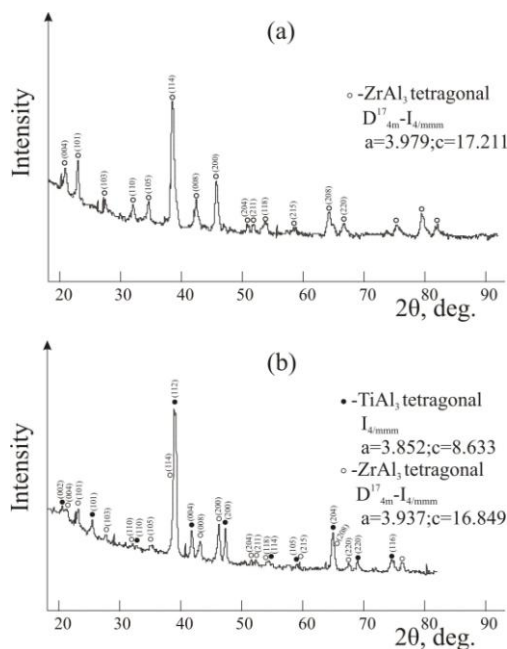


Fig.16. Diffraction patterns of: a – Ti_{0.1}Zr_{0.15}Al_{0.75}; b – Ti_{0.2}Zr_{0.05}Al_{0.75}.

Fig. 17 shows the diffraction patterns of Ti_{0.5}Al_{0.23}Nb_{0.27}, Ti_{0.333}Al_{0.333}Nb_{0.334} and Ti_{0.125}Al_{0.75}Nb_{0.125} aluminides.

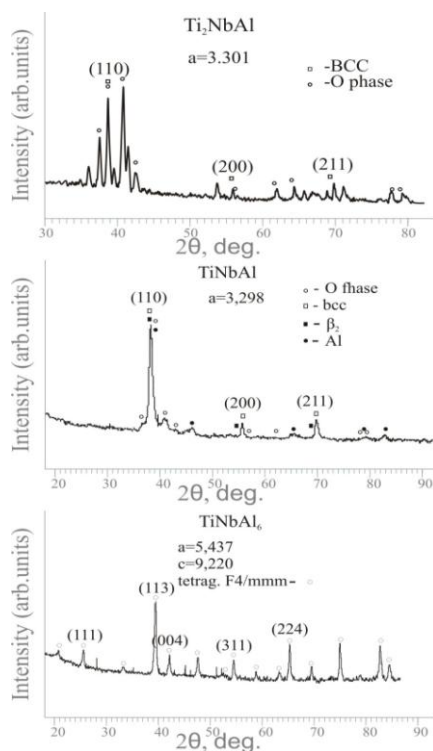


Fig. 17. Diffraction patterns of: a – Ti_{0.5}Al_{0.23}Nb_{0.27}; b – Ti_{0.333}Al_{0.333}Nb_{0.334}; c – Ti_{0.125}Al_{0.75}Nb_{0.125} aluminides.

It was shown that some aluminides reacted with hydrogen in the SHS mode at $P_H = 5\text{-}10 \text{ atm}$ ($T_{\text{comb.}} = 300\text{-}500^\circ\text{C}$), forming reversible hydrides, which dissociated with one endo-effect at $\sim 300\text{-}380^\circ\text{C}$.

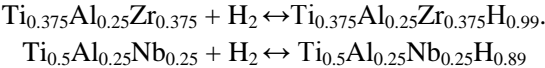


Fig. 18 shows the pictures of $\text{Ti}_{0.5}\text{Al}_{0.25}\text{Nb}_{0.25}$ alloy and its hydride.

2.4. Synthesis of Ti, Zr and Ni, Co based aluminides

The other example of HC-process is the reaction of a metal (titanium or zirconium) hydride interaction with any metal of VII or VIII groups (Ni, Co, Mn) [23-25]: $\text{TiH}_2 + \text{Ni} \rightarrow \text{TiNi} + \text{H}_2\uparrow$; $\text{ZrH}_2 + \text{Ni} \rightarrow \text{ZrNi} + \text{H}_2\uparrow$; $\text{TiH}_2 + \text{Co} \rightarrow \text{TiCo} + \text{H}_2\uparrow$; $\text{TiH}_2 + \text{ZrH}_2 + \text{Ni} \rightarrow \text{Ti}_{44-52}\text{Zr}_{40-32}\text{Ni}_{16} + \text{H}_2\uparrow$; $\text{TiH}_2 + 1.2\text{VH} + 0.8\text{Mn} \rightarrow \text{TiV}_{1.2}\text{Mn}_{0.8} + \text{H}_2\uparrow$; etc. The synthesized compact intermetallics in the combustion (SHS) mode ($T_{\text{comb.}} = 480\text{-}600^\circ\text{C}$) interacted without crushing with hydrogen at a pressure of $10\text{-}30 \text{ atm}$. These interactions brought to the formation of reversible hydrides of intermetallics with rather high hydrogen content (Table 2). For example:

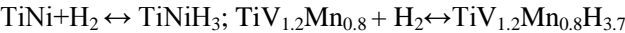


Table 4

Characteristics of intermetallics and their hydrides

Compound	H ₂ content, wt. %	Crystal structure and lattice parameters, Å	Dissociation temperature, °C
Ti ₂ Co	–	Cubic, a = 11.31	–
Ti ₂ CoH ₃	1.7	Cubic, a = 11.89	240 – 360
Zr ₂ Co	–	Tetragonal, a=6.387, c=5.542	–
Zr ₂ CoH ₅	2.02	Tetragonal; a=6.906, c=5.55	190 - 360
ZrCo	–	Cubic, a= 3.197	–
ZrCoH ₃	1.68	Orthorhombic, a= 3.37, b=10.57, c= 4.318	300
Zr ₂ Ni	–	Tetragonal, a=6.54, c=5.34	–
Zr ₂ NiH ₅	2.08	Tetragonal, a=6.86, c=5.657	170-250
ZrNi	–	Orthorhombic, a= 3.29, b=9.998, c= 4.080	–
ZrNiH ₃	1.96	Orthorhombic, a= 3.53, b=10.62, c= 4.328	220-260
Ti ₂ Co	–	Cubic, a= 11.31	–
Ti ₂ CoH ₃	1.7	Cubic, a= 11.89	220-260
Ti ₄₄₋₅₂ Zr ₄₀₋₃₂ Ni ₁₆	2.10-2.15	C14 hexagonal Laves phase	–
Ti ₄₄₋₅₂ Zr ₄₀₋₃₂ Ni ₁₆ H ₃	–	–	170-260
TiV _{1.2} Mn _{0.8}	–	BCC, (HCP traces); a =3.039 (6)	–
TiV _{1.2} Mn _{0.8} H _{3.67}	2.36	BCT- monohydride, a = 3.069(6), c = 3. 510(5)	280; 330

2.5. The applications of alloys and intermetallics

Interest in alloys is associated with their numerous and important practical applications. They are used in the high-tech areas of nuclear and hydrogen power

engineering, aerospace, shipbuilding, chemical, automotive, metalworking, machine and machine tool industry, tool manufacturing, radio and electrical engineering, electronics, as composite materials in nuclear power plants, as biocompatible materials in medicine, etc. Particularly, the titanium- and zirconium-based alloys are interesting for the production of construction materials that can work in various chemically active environments (sea water, steam, gas turbines), at low temperatures (for example, in liquid oxygen). The main advantages of titanium alloys are lightness and corrosion resistance. Alloys of zirconium and hafnium are used in nuclear reactors.

In modern materials science, the problem of development of new light, heat-resistant alloys with operating temperatures higher than 550-600°C is acute. From this point of view, transition metal alloys and intermetallics are very promising construction materials. Their advantages are low density, high melting points, high mechanical strength, high heat and electrical conductivity, superconductivity, heat and corrosion resistance, etc. These characteristics condition their use in aerospace and ground engine construction, in the defense industry, in many branches of machine building, chemical and food industry, electronics, medicine, etc. Titanium aluminides are used in the first wall of thermonuclear reactor (TNR) as constructive materials. Aluminides of IV-V group metals are 3 times cheaper than such competing materials as, for example, nickel alloys. The aluminides are known as construction materials and can absorb high amounts of hydrogen and serve as hydrogen storage materials.

The current methods for producing binary and multicomponent alloys and intermetallics are based on melting (induction, electric arc, electron beam), powder metallurgy and mechano-chemistry. Each of these methods bears considerable laboriousness and instrumental complexity. The powder metallurgy methods are characterized by long-duration processes: the interaction of metals in the initial mixtures is mainly determined by the diffusion rates in the solid state. Specific difficulties in obtaining high-quality alloys and intermetallics are associated with the presence of a dense oxide film on the surface of refractory metal particles, which hinders the process of mutual diffusion. In the mechano-chemical methods of producing alloys and intermetallics, the initial components are mixed in drums for 10-40 *hours* or more, when the sticking of the reaction components to the drum wall can occur changing their ratio; besides, the contamination of the reaction mixture by the ball and drum materials can occur.

The differences in melting and evaporation temperatures, in densities of titanium, niobium, zirconium and aluminum also complicate the current technologies. Therefore, new effective methods for producing binary and multicomponent alloys with given physical and technical properties are urgently demanded in modern materials science. The described in the present work Hydride Cycle method can be such a promising technique.

The significant advantages of "Hydride Cycle" method over the above presented traditional methods are listed below.

1. The alloys and intermetallics are formed in lower temperatures (600-1200°C instead of 1800-2600°C) and with a shorter duration (1.5-2 hours instead of tens of hours) processes. Because of alloy formation via solid-phase mechanism excluding melting, the energy consumption is low.

2. The binary and multicomponent alloys and intermetallics of the defined composition are produced in one technological stage.

3. The processes of formation of alloys and intermetallics are safe, wasteless and highly effective.

4. Instead of the expensive fine-dispersed powders of refractory metals demanded as starting materials, cheap SHS hydrides are used, formed in a highly efficient, low-energy technological process, utilizing the wastes appeared during machining of refractory metals.

5. More than 100 HC-synthesized alloys, intermetallics and their hydrides have been produced. Among them – the alloys with structure of α -, β -, γ - and ω -phases.

6. The elaborated method for synthesis of alloys and intermetallics of transition metals can be very attractive for industry and be of commercial interest. Hydrides of synthesized alloys and intermetallics potentially can serve as hydrogen storage materials.

ԱՆՅՈՒՄԱՅԻՆ ՄԵՏԱՂՆԵՐԻ ԵՎ ՆՐԱՆՅ ՆԱՄԱՁՈՒՎԱԾՔՆԵՐԻ ՆԻՂԲԻՆԵՐԸ ՈՐՊԵՍ ԽՏԱՅՎԱԾ ՋՐԱԾՆԻ ԿՐՈՂՆԵՐ

**Ս. Կ. ԴՈՒՈՒԽԱՆՅԱՆ, Ա. Գ. ԱԼԵՔՍԱՆՅԱՆ, Գ. Ն. ՄՈՒՐԱԴՅԱՆ, Վ. Շ. ՇԵԽՏՄԱՆ,
Օ. Պ. ՏԵՐ-ԳԱԼՍՏՅԱՆ, Ն. Գ. ՆԱԿՈՔՅԱՆ,
Ն. Ն. ԱՂԱՋԱՆՅԱՆ և Ն. Լ. ՄՆԱՅԱԿՅԱՆ**

ՀՀ ԳԱԱ ՔՖԻ բարձրջերմաստիճանային սինթեզի և անօդաչուական միացությունների տեխնոլոգիայի լաբորատորիայում ԲԻՍ(Բարձրջերմաստիճանային Ինքնատարածվող Սինթեզ) մեթոդով սինթեզվել են 200-ից ավելի մետաղների և համաձուլվածքների երկ- և բազմակոմպոնենտ հիդրիդներ և դեյտերիդներ: Հետազոտությունները $Me-H$ համակարգերում ֆիզքիմիական հիմք դարձան ԲԻՍ պրոցեսների համար և հանգեցրին տեխնոլոգիական աշխատանքների կատարմանը: Մշակված են պրոցեսների բարձրարտադրողական տեխնոլոգիաներ ամենատարբեր հիդրիդների սինթեզի համար, որոնք կարող են ապահովել բարձր որակով էժան հիդրիդների մեծ տեսականու սինթեզ և արտադրություն: «ԱրմՆԻԿվետոն» փորձնական փոքրիկ գործարանում (ք. Երևան) արտադրվել է տիտանի և ցիրկոնիումի ավելի քան 20 տոննա հիդրիդներ: Անցումային մետաղների և նրանց համաձուլվածքների հիդրիդները՝ որպես կոնդենսված ջրածնի կրիչներ, մեծ արժեք են ներկայացնում: Մշակված է անցումային մետաղների համաձուլվածքների և միջմետաղական միացությունների սինթեզի ևս մեկ սկզբունքորեն նոր մեթոդ, որն անվանվեց մեր կողմից «Հիդրիդային Յիկլի-ՀՅ» մեթոդ: Մեթոդի հիմքում ընկած են երկու և ավելի մետաղների հիդրիդների փոխազդեցության ռեակցիաները, ինչպես օրինակ՝ $xMe'H_2 + (1-x)Me''H_2 \rightarrow \text{համաձուլվածք } Me'xMe''(1-x) + H_2\uparrow$: Ցույց է տրված, որ երկու և ավելի հիդրիդների սեղմված խառնուրդի, օրինակ՝ TiH_2 և ZrH_2 , ինչպես նաև հիդրիդի և մետաղական փոշու՝ TiH_2 և Al , տաքացման ղեպքում սեղմված սկզբնական խառնուրդից ջրածնի անջատումը հիդրիդների քայքայման ջնմաստիճաններից քիչ բարձր ջերմաստիճաններում բերում է նշված մետաղների ամուր, հոծ, կոմպակտ երկ- և եռկոմպոնենտ համաձուլվածքների առաջացման: ՀՅ ռեժիմում սինթեզվել են 100 և ավելի

Համաձուլվածքներ և միջմետաղական միացություններ $Ti-Zr$; $Ti-Hf$; $Ti-Nb$; $Ti-V$; $Zr-Hf$; $Ti-Zr-Hf$; $Ti-Ni$; $Zr-Co$; $Ti-Al$; $Nb-Al$ և այլ Համակարգերում: Ստացված որոշ կոմպակտ Համաձուլվածքները առանց նախնական մանրացման փոխազդում են ջրածնի հետ RbU ռեֆինում առաջացնելով ջրածնի բարձր պարունակությամբ Հիդրիդներ:

ГИДРИДЫ ПЕРЕХОДНЫХ МЕТАЛЛОВ И ИХ СПЛАВОВ КАК НОСИТЕЛИ КОНДЕНСИРОВАННОГО ВОДОРОДА

С. К. ДОЛУХАНИЯН, А. Г. АЛЕКСАНИЯН, Г. Н. МУРАДЯН, А. Г. АКОПЯН,
Н. Н. АГАДЖАНИЯН, Н. Л. МНАЦАКАНИЯН и О. П. ТЕР-ГАЛСТЯН

Институт химической физики им. А.Б. Налбандяна НАН Республики Армения
Армения, 0014, Ереван, ул. П. Севака, 5/2
E-mail: seda@ichph.sci.am

Представлен обзор работ Лаборатории высокотемпературного синтеза и технологии неорганических материалов ИХФ НАН Армении. В первой части статьи описаны исследования процессов горения переходных металлов в водороде. Впервые методом СВС (самораспространяющегося высокотемпературного синтеза) было синтезировано более 200 бинарных и многокомпонентных гидридов и дейтеридов металлов и сплавов. Эти исследования стали физико-химической основой СВС процессов в системах $Me-H$ и привели к постановке технологических работ, имеющих огромные промышленные перспективы. Разработаны не имеющие аналогов в мире высокопроизводительные технологические процессы синтеза различных гидридов, которые могут обеспечить синтез и производство большого ассортимента дешевых гидридов высокого качества. На опытном заводе АрмНИИцветмет (г. Ереван) было изготовлено более 20 т гидридов титана и циркония. Гидриды переходных металлов и сплавов представляют большую ценность как конденсированные носители водорода. Интерес к водороду и металлгидридам связан с двумя глобальными проблемами: охрана окружающей среды и истощение запасов ископаемого углеродного и углеводородного топлива. Спектр применения гидридов металлов и сплавов очень широк.

Дальнейшие исследования синтезированных в режиме СВС гидридов позволили разработать еще один, принципиально новый метод синтеза сплавов и интерметаллидов переходных металлов, названный нами методом «Гидридного цикла – ГЦ». Вторая часть работы посвящена исследованиям процесса формирования сплавов и интерметаллидов в ГЦ. В основе метода лежат *реакции взаимодействия двух и более гидридов металлов*, как например, $xMe'H_2 + (1-x)Me''H_2 \rightarrow \text{сплав } Me'_xMe''_{(1-x)} + H_2\uparrow$. Показано, что при нагреве компактированной смеси двух и более гидридов, например TiH_2 и ZrH_2 , а также гидроксида и металлического порошка (например TiH_2 и Al) удаление водорода из компактированной шихты при температурах чуть выше температур диссоциации гидридов приводит к образованию прочных, беспористых, компактных бинарных, тройных сплавов указанных металлов. В режиме ГЦ синтезировано более 100 сплавов и интерметаллидов в системах $Ti-Zr$; $Ti-Hf$; $Ti-Nb$; $Ti-V$; $Zr-Hf$; $Ti-Zr-Hf$; $Ti-Ni$; $Zr-Co$; $Ti-Al$; $Nb-Al$ и др. Некоторые полученные компактные сплавы без предварительного измельчения взаимодействуют с водородом в режиме СВС, образуя гидриды с высоким содержанием водорода. Установлено влияние параметров – соотношения гидридов металлов и порошков металлов в реакционной смеси, размеров зерен порошков гидридов (микро- и наноразмеры), давления прессования при компактировании гидридов, а также режимов дегидрирования и спекания (температуры и скорости

нагрева) на характеристики полученных сплавов и интерметаллидов – кристаллическую структуру, плотность, адсорбционные свойства и др. Предложен механизм их формирования. Перспективы метода ГЦ для синтеза сплавов и интерметаллидов могут быть очень привлекательны для индустрии. Разработанные технологии по методу ГЦ могут представлять коммерческий интерес, поскольку имеют большие преимущества перед традиционными.

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