



The structural peculiarities of the transition metals carbohydrides produced by combustion synthesis

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Abstract

We present experimental data regarding the combined influence of hydrogen and carbon on obtaining titanium carbohydrides. For processing, the self-propagating high-temperature synthesis (SHS) technique was used. The parameters of the SHS process were established by producing two modifications for ternary phases: fcc, TiC_xH_y ($0.43 < x < 1$); and hcp, $\text{TiC}_{0.38-0.41}\text{H}_{1.12-1.20}$. It is shown that the addition of a V^a group metal led to significant changes in structure and composition of combustion products. On the concentration triangle Ti–V–C–H the fcc carbohydride regions are separated. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Carbohydride; SHS; Combustion synthesis; Solid solution

1. Introduction

The carbohydrides are interesting advanced materials; for example, they provide good opportunities for nuclear energy systems as materials for biological protection.

It is known that the presence of carbon in hydride lattices leads to change of properties, including thermal stability, etc. [1]. Earlier it was also established that the refractory carbides of 1V–V group transition metals with a wide range of homogeneity on interaction with hydrogen formed ternary compounds. In the Ti–C–H system, carbohydrides with an fcc structure, obtained on the basis of non-stoichiometric carbides ($\text{TiC}_{0.47}$ – $\text{TiC}_{0.99}$), are known. Upon insertion of hydrogen, the fcc structure remains, but the lattice parameter (a) increases. In this system, besides the fcc, a new ternary compound with a hexagonal close packed structure was discovered [2].

Normally such compounds have been obtained by hydrogenation on preliminary prepared non-stoichiometric carbide powders. The hydrogenation was carried out by a graded method at temperatures of 1000°C down to room temperature. Such multi-stage processes are too hard, require complicated furnace equipment and are not adequate to prepare single-phase ternary compounds with high hydrogen content. In this case, the combustion technique, self-propagating high-temperature synthesis (SHS), seems to be more suitable [3]. In SHS processes

the heat of the exothermic chemical reaction is used. The essence of the method consists of instantaneous local initiation of combustion reaction in the metal–hydrogen system (in a thin metal–non-metal layer). High temperature arising in the reaction zone propagates due to the heat transfer throughout the material from layer to layer with a constant linear rate.

Up to now more than 500 different oxides, borides, carbides, nitrides and other inorganic compounds have been synthesized by the SHS technique [3].

In our laboratory, the principal opportunity of using SHS for hydrides was predicted and realized. Since 1975, systematic investigations of the combustion processes in the Me–H, Me–Me'–H, Me–nonmetal–H and other systems have been elaborated. More than 150 binary and complex hydrides and deuterides have been synthesized [4–6].

Here we present the data on SHS of carbohydrides, on the basis of Ti and Ti–V, and investigation of their structures depending on the parameters of the process (composition, hydrogen pressure, etc).

2. Experimental

Titanium (99.9%), vanadium (99.9%), hydrogen (99.9%), argon, the lamp soot were used. The hydrogen pressure was changed within 1–10 atm. The chemical

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composition (H , C_{free} , C_{total} content) and phase composition were determined by X-ray diffraction (DRON-2).

2.1. Ti–C–H system

The mixture of metal and soot powders of non-stoichiometric compositions ($\text{Me}+x\text{C}$, where $x=0.1-0.9$) were prepared in a preliminary stage. From this mixture, the cylindrical tablets ($d=20$ mm) were pressed. Then the combustion was started in a hydrogen environment.

The analysis of the SHS process in the Ti–C–H system showed that the type of reaction can vary either towards carbide or hydride formation, depending on the pressure as well as on the composition of the initial reagents.

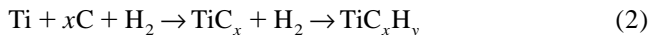
Thus, the combustion of the Ti–C–H system exhibits challenging characteristics of titanium interaction either with carbon and hydrogen.

(1) At $x \leq 0.35$ the combustion front propagation is related with the reaction:



In this case the base mixture carbon plays the role of a ballast and does not take part in the reaction.

(2) At $x \geq 0.38$ the combustion front propagation is related with the reaction:



Here the process is initiated by carbon, but for each composition with respect to carbon there exists a critical hydrogen pressure. Upon reaching this pressure the reaction goes toward hydride formation. There are also critical values for the sample density and for the initial titanium dispersion, which effect the combustion behavior and give rise to one or another phase [7].

The diagram of hydrogen pressure versus composition (Fig. 1) demonstrates two regions of the above reaction: in region I only reaction of hydride formation take place; in region II only carbohydrides are formed. The region boundary depends on the critical combustion parameters.

It has been shown that, in the carbide formation region the combustion temperatures and rates are high and do not depend on the hydrogen pressure. On reaching the critical parameters of the process, the combustion temperatures and rates fall abruptly, and their changes with H_2 pressures become typical for the reaction of hydride formation (Figs. 2 and 3, respectively).

Thus, the competition of reaction is a very interesting peculiarity of the Ti–C–H systems.

In the case, when combustion reaction is 'led' by carbon, two modifications of carbohydrides are formed: face centered cubic (fcc) and hexagonal close packed (hcp). It is necessary to emphasize that single carbohydrides with an hcp structure were synthesized for the first time by SHS. Attention should be paid to the fact that

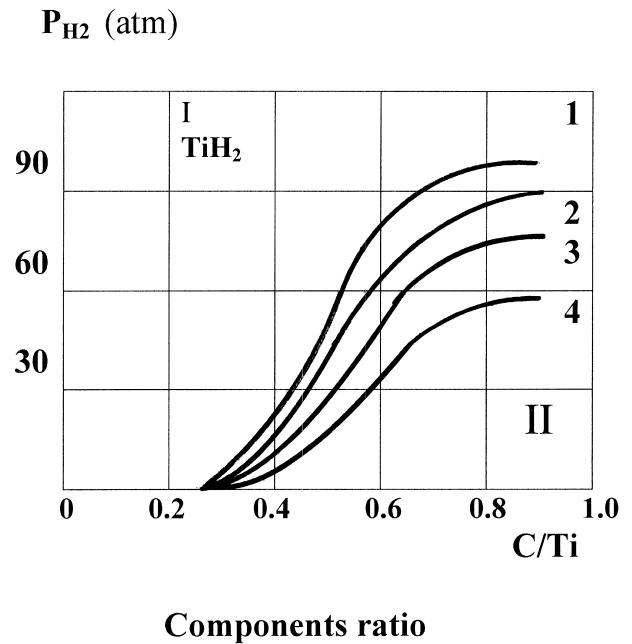
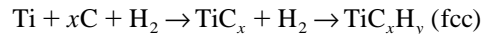


Fig. 1. The diagram of hydrogen pressure versus composition.

the hydrogen content in hcp carbohydrides is twice that for fcc modification.

Table 1 presents the main characteristics of titanium carbohydrides.

The fcc carbohydrides are formed by a two-stage mechanism. In the first stage, the non-stoichiometric carbide in the combustion front is formed. After combustion, at the cooling zone, the hydrogen enters into the carbide structure.



The formation of carbohydrides with an hcp structure proceeds similarly by a two-stage mechanism, but in the first high temperature stage a hexagonal phase carbide is formed ($\text{TiC}_{0.38-0.43}$). In second stage this phase is rapidly stabilized by introduction of hydrogen.

The direct formation of the ternary compound with hcp in the combustion front is also possible.

The NMR data evidenced that the hydrogen in fcc carbohydrides occupies the octahedral positions. Actually, in non-stoichiometric carbides, hydrogen fills up the deficit carbon positions.

In the hcp carbohydrides the hydrogen mainly occupies the tetrahedral positions and partially the octahedral positions. According to the DTA data, titanium carbohydrides are more stable than titanium hydride. The dissociation temperature of hexagonal titanium carbohydride is 200°C higher.

The parameter ratio c/a for hcp carbohydrides increases in comparison with that of $\alpha\text{-Ti}$ and approaches the ideal value. It takes place by virtue of the growth of both parameters a and c . The incremental volume $\Delta V/V$ of the unit cell in this case is equal to 18.6%.

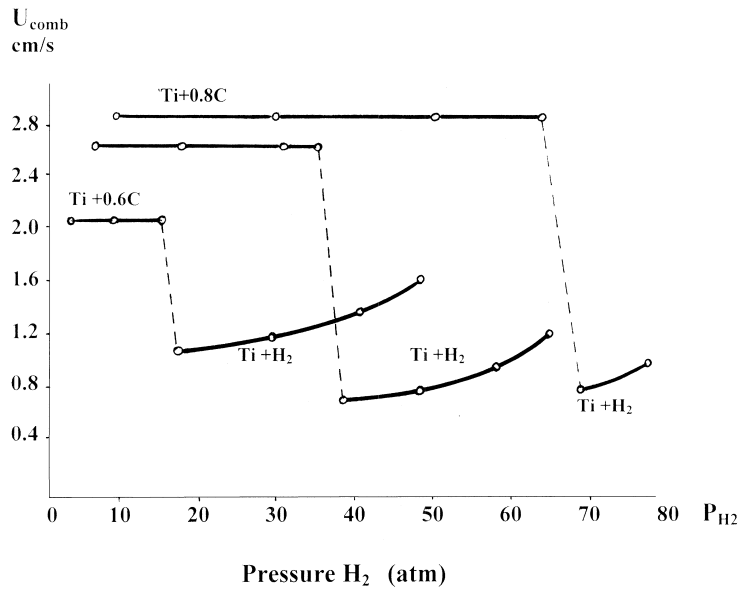


Fig. 2. Combustion rates of titanium-carbon mixtures of various composition as a function of hydrogen pressure.

2.2. Ti-V-C-H system

The multi-component interstitial phases are interesting because their physico-chemical properties differ from those of the binary systems. Let us consider the vanadium influence on the combustion process in the Ti-C-H system and formation of final products.

The synthesis of the carbohydrides with the participation both Ti and V were carried out in one technological stage. The mixture $x\text{Ti} + (1-x)\text{V} + y\text{C}$, where $0.1 < x < 0.9$ and $0.3 < y < 0.9$, was ignited in a hydrogen atmosphere. The addition of V to the Ti-C-H system leads to the decrease of both the temperature and the rate of the combustion

process. On the basis of chemical and XRD data one say that the influence of V on the formation of the structure of the final products is significant. For example, upon combustion of the Ti-V-C-H system at all Ti/V ratios used, only the complex carbides and carbohydrides with cubic structure were observed.

In Table 2 the structural data of complex carbides and carbohydrides and, for comparison, of binary titanium and vanadium carbide, are presented. At higher vanadium concentrations the lattice parameters of the complex carbides all decrease. On insertion of hydrogen, the fcc structure was maintained, with the lattice parameters increasing slightly, but remaining lower than those of

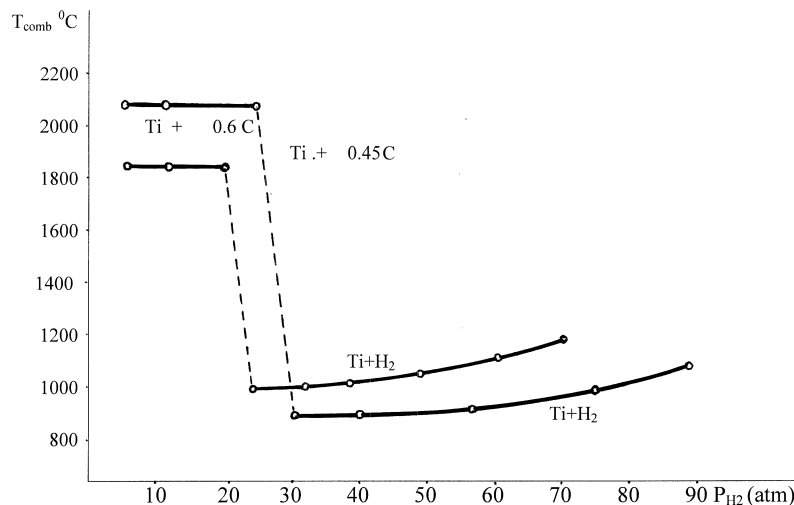


Fig. 3. Combustion temperatures of titanium-carbon mixtures of various compositions as a function of hydrogen pressure.

Table 1
Characteristics of combustion products in the Me–C–H system

N	Composition of base mixture	Phase composition of products and actual formula	Lattice parameters (Å)			Non-metal content (wt.%)		Ratio (C+H)/Me
			a	c	c/a	C	H	
1	Ti+0.10C	TiH ₂ fcc	4.450	–	–	– ^a	3.84	2.00
	Ti+0.35C	TiH ₂ fcc	4.450	–	–	– ^a	3.45	2.00
	Ti+0.38C	TiC _{0.38} H _{1.2} hcp	3.091	5.062	1.63	8.48	2.23	1.58
	Ti+0.40C	TiC _{0.40} H _{1.16} hcp	3.076	5.033	1.63	8.92	2.15	1.56
	Ti+0.43C	TiC _{0.41} H _{1.12} hcp	3.095	5.089	1.60	9.15	2.08	1.53
	Ti+0.45C	TiC _{0.42} H _{0.68} hcp + fcc	3.076 4.287	5.042	1.60	9.31	1.27	1.10
	Ti+0.47C	TiC _{0.44} H _{0.65} hcp + fcc	3.084 4.315	5.069	1.60	9.15	1.21	1.09
4	Ti+0.50C	TiC _{0.50} H _{0.58} fcc	4.295	–	–	10.99	1.06	1.08
5	Ti+0.55C	TiC _{0.53} H _{0.55} fcc	4.296	–	–	11.58	1.00	1.08
6	Ti+0.65C	TiC _{0.65} H _{0.41} fcc	4.300	–	–	13.88	0.73	1.06
7	Ti+0.80C	TiC _{0.79} H _{0.21} fcc	4.300	–	–	16.43	0.36	1.00
	Ti (ASTM)	hcp	2.950	4.686	1.58	–	–	–
	TiC _{0.47–0.98}	fcc	4.260–4.328	–	–	–	–	0.47–0.98

^a Free carbon (<4.00 wt.%).

cubic TiC. In contrast to ternary Ti–C–H, in the presence of vanadium the hcp carbohydrides were not observed, even at low carbon concentrations. The hydrogen concentration in fcc carbohydrides increased with the decline of carbon content.

The Ti/V ratio also influenced the hydrogen content in the final combustion products (Table 2).

Special attention must be paid to the carbohydrides having a common non-metals index of >1 (for example, Ti_{0.7}V_{0.3}C_{0.40}H_{0.81}).

The XRD data indicated that the fcc packing of the C and H atoms arrangement is possible:

- We can assume the first variant to be of NaCl structure, characteristic for the cubic titanium carbide. In this case the main reaction is the filling up of octahedral positions by the carbon atoms. The hydrogen atoms occupy the remaining octahedral vacancies and accommodate also the tetrahedral positions of the crystalline lattice after filling up the octahedral vacancies.

Table 2
Characteristics of Ti–V carbides and carbohydrides with fcc structure

N	Actual formula	Non-metal content (wt.%)		Ratio (C+H)/Me	Parameters of lattice a (Å)
		C	H		
1	TiC _{0.47–0.99} [8]	10.0–19.4	–	0.47–0.98	4.296–4.236
	Ti _{0.9} V _{0.1} C _{0.70}	14.81	–	0.70	4.292
	Ti _{0.9} V _{0.1} C _{0.70} H _{0.24}	14.75	0.42	0.94	4.230
2	Ti _{0.9} V _{0.1} C _{0.40}	9.04	–	0.4	4.290
	Ti _{0.9} V _{0.1} C _{0.40} H _{0.79}	8.91	1.47	1.19	4.231
3	Ti _{0.8} V _{0.2} C _{0.90}	18.18	–	0.90	4.289
	Ti _{0.8} V _{0.2} C _{0.90} H _{0.15}	18.14	0.25	1.05	4.290
4	Ti _{0.8} V _{0.2} C _{0.59}	12.72	–	0.59	4.301
	Ti _{0.8} V _{0.2} C _{0.59} H _{0.38}	12.63	0.68	0.97	4.305
5	Ti _{0.7} V _{0.3} C _{0.90}	18.09	–	0.90	4.306
	Ti _{0.7} V _{0.3} C _{0.90} H _{0.13}	18.05	0.22	1.03	4.320
6	Ti _{0.7} V _{0.3} C _{0.70}	14.66	–	0.70	4.264
	Ti _{0.7} V _{0.3} C _{0.70} H _{0.20}	14.61	0.35	0.90	4.295
7	Ti _{0.7} V _{0.3} C _{0.40}	8.94	–	0.4	4.269
	Ti _{0.7} V _{0.3} C _{0.40} H _{0.81}	8.81	1.49	1.21	4.288
8	Ti _{0.7} V _{0.3} C _{0.30}	6.86	–	0.30	4.257
	Ti _{0.7} V _{0.3} C _{0.30} H _{0.90}	6.74	1.69	1.20	4.270
9	Ti _{0.5} V _{0.5} C _{0.70}	14.51	–	0.70	4.250
	Ti _{0.5} V _{0.5} C _{0.70} H _{0.28}	14.44	0.48	0.98	4.263
	VC _{0.73–0.87}	14.68–17.50	–	0.73–0.87	4.131–4.165

- We can assume the second variant to be of the CaF_2 structure, specific for binary hydrides. In this case non-metal atoms fill up mainly the tetrahedral voids of the fcc metal lattice. Here we have doubts regarding the inserting the carbon atoms into smaller voids.

The data received so far did not allow us to make a definite judgement about the exact structure of the synthesized carbohydrides. The undergoing neutron diffraction investigations will enable us to make a choice from the models proposed.

3. Discussion

On the basis of the present investigations and on the known published data [8,9] it is possible to arrange the fcc and hcp carbohydride regions on the concentration triangle (Figs. 4 and 5).

Usually, the ternary phase diagrams are built on the basis of a series of isothermal sections by rapid quenching of the samples followed by phase analysis.

The diagrams represented in this work are not the state diagrams in an exact sense. Each point of our triangle corresponds to a concrete combustion temperature, determined by the composition. Taking into account the high velocity of the SHS reactions (1–15 cm/s), as well as the rate of the cooling of sample (several minutes), we can say that the SHS products are quenched to some extent from their own combustion temperature. Accordingly, Figs. 4 and 5 do not present the isothermal cuts of the ternary diagram, but a useful phase region in the systems investi-

gated. For example, on the triangle for the Ti–C–H diagram (Fig. 4), phase regions of hcp carbohydrides are found. This is significantly distant from the binary solid solutions of carbon or hydrogen in α -Ti and are rather close to the MeH_2 composition.

Regarding the nature of hcp $\text{Ti-C}_x\text{-H}_y$, it is not reasonable to consider them as simple solid solution of H and C in α -Ti. The main objection is the solution of great amounts of C and H in Ti in contrast to the narrow α -regions on binary diagrams Ti–C and Ti–H.

It would be preferable to consider the hcp carbohydrides of titanium as new individual ternary compounds, for the following reasons:

1. the position of their region on the concentration triangle; and
2. the essential change of the unit cell volume $\Delta V/V=18.6\%$ and the parameter ratio $c/a=1.63$.

In Figs. 4 and 5 concentration triangles for complex carbohydrides of the Ti–C–H and Ti–V–C–H systems are presented. In each case, the triangles show that the phase regions of carbohydrides can be found.

3.1. Conclusion

This work demonstrates the new possibilities of the SHS method for the synthesis of multi-component compounds, as well as methods to analyze the structural peculiarities of the obtained materials. The possibility of diverse conditions for SHS synthesis enabled us to collect enough data about the single-phase regions on three and more com-

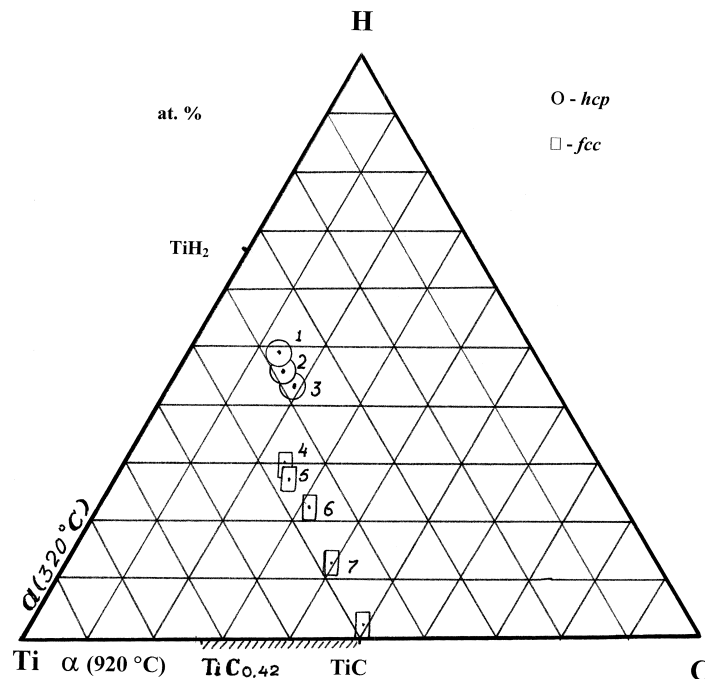


Fig. 4. The concentration triangle for carbohydrides of the Ti–C–H system with structures: (○) hcp and (□) fcc.

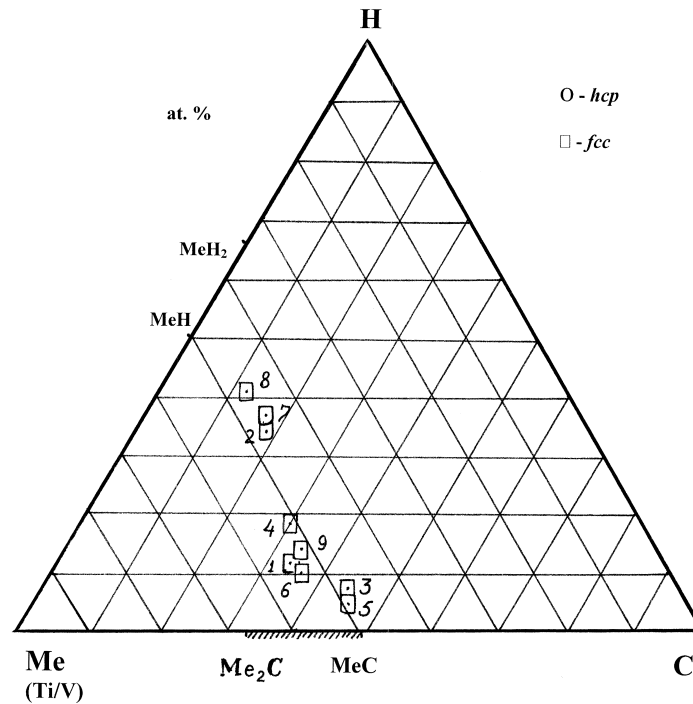


Fig. 5. The concentration triangle for complex carbohydrides of the Ti–V–C–H system with fcc structures.

ponent state diagrams in experiments for the study of different systems.

References

- [1] G.V. Samsonov, M.M. Antonova, V.V. Morozov, *Poroshk. Metall.* 4 (1970) 66–69.
- [2] K. Yvon, H. Novotny, R. Kiffer, *Monatschr. Chem.* 98 (6) (1967) 2164–2172.
- [3] A.G. Merzhanov, I.P. Borovinskaya, *Dokl. Akad. Nauk SSSR* 219 (2) (1979) 366–368.
- [4] S.K. Dolukhanyan, M.D. Nersesyan, I.P. Borovinskaya, A.B. Nalbandyan, A.G. Merzhanov, *Dokl. Akad. Nauk SSSR* 231 (3) (1976) 675–678.
- [5] S.K. Dolukhanyan, H.G. Hakobian, A.G. Aleksanian, *Int. J. Self-Propagating High Temp. Synthesis* 1 (4) (1992) 530–535.
- [6] S.K. Dolukhanyan, A.G. Aleksanian, H.G. Hakobian, *J. Hydrogen Energy* 20 (5) (1995) 391–395.
- [7] N.A. Martirosian, S.K. Dolukhanyan, A.G. Merzhanov, *Fiz. Goreniya Vzriva* 4 (1981) 24–29.
- [8] E. Storms, *Refractory Carbides*, Atomizdat, Moscow, 1970.
- [9] K.M. Mackay, *Hydrogen Compounds of the Metallic Elements*, Mir, Moscow, 1968, 244 pp.