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Synthesis of novel compounds by hydrogen combustion

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Abstract

The combustion of metals and intermetallic compounds in hydrogen and deuterium were studied. The products of synthesis in this technique are the hydrides and deuterides of transition metals and their alloys. We determined the formation mechanism in self-propagating high-temperature synthesis mode; the effect of second non-metal (C, N) and metal (VA, VIIIA groups) components on the combustion of IVA group metals in hydrogen was established.

Keywords: Combustion; SHS; Hydride; Carbohydride; Hydrides of intermetallics

1. Introduction

The report is devoted to the application of the self-propagating high-temperature synthesis (SHS) process to metal–hydrogen systems. That technique is based on the use of the exothermic interactions between two or more chemical components [1]. Initially one would think that it is impossible to use the SHS process in Me–H systems, although the thermodynamic data are favourable, as in a number of cases the metal–hydrogen interaction occurs with a heat release. The doubts were based on the known instability of the hydrides at the temperatures produced by the combustion process. Nevertheless, it was found in 1975/1976 that the combustion reaction in transition metal–hydrogen systems proved to be feasible in principle, and the final products were hydrides [2].

2. Experimental

The combustion processes in Me–H systems were realized in the regime of self-propagating high-temperature synthesis. A large series of experiments on the combustion of transition and rare earth metals in hydrogen and deuterium enables us to synthesize over 30 hydrides and deuterides. Some of them are listed in Table 1. After measurements of the combustion rates (U_{comb}) and temperatures (T_{comb}), the main attention was focused on the determination of the conditions ensuring the completeness of the combustion and the yield of single-phase hydrides having stoichiometric compositions. In order to determine the mechanism of the hydride formation the intermediate products of combustion were quenched and annealed. This data combined with gravimetric analysis gives evidence for a two-stage combustion process. The first stage is a rapid one and corresponds to the propagation of the combustion front throughout the sample, which was prepared from powder as a pellet. The reaction in this case occurs in a narrow zone, forming a solid solution of hydrogen in the metal. The second stage is slow and the reaction takes place in the bulk heated by the combustion wave. It results in the formation of a dihydride or trihydride phase. These are the main processes occurring in Me–H combustion. It was intriguing to see that the formation of intermetallic hydrides by the same technique can also be accomplished. The combustion of intermetallics in hydrogen was found to occur at anomalously low temperatures (T_{comb}=250–350 °C), corresponding to the ‘invisible’ range of the radiation spectrum. In this case the products obtained were the hydrides of the intermetallic compounds (Table 2). By increasing the hydrogen pressure up to 20 atm the T_{comb} of this system increases so that the combustion reaction shifts to the visible range of the spectrum. The variety of phases observed in this case and the decrease of hydrogen concentration in the hydride can be attributed to the effect of hydrogenolysis. This reaction has been revealed after combustion, for example:

$$Zr_2Co + H_2 \rightarrow Zr_2CoH_5 \rightarrow ZrH_2 + ZrCo_2$$

Interesting results were also obtained from a study of ternary systems including carbon or nitrogen. The addition of a second nonmetal element changed the behaviour of hydrogen during combustion. The main characteristics of the SHS process in the Me–N–H and Me–C–H system are

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Table 1
Characteristics of binary SHS hydrides and deuterides

Metal	U_{comb} (cm s^{-1})	T_{comb} (°C)	H_2 and D_2 content (wt.%)	Crystal structure; Lattice parameters (Å)	Actual formula
Sc	8.79	1450	4.25	fcc; $a=4.782$	ScH_2
	7.15	1100	3.01	fcc; $a=4.688$	$ScD_{0.35}$
Y	9.65	1500	2.21	fcc; $a=5.224$	$YH_{2.2}$
	–	—	3.255	hcp; $a=3.661$ $c=6.630$	$YH_{2.9}$
Ti	1.00	820	4.01	fcc; $a=4.460$	TiH_2
	–	–	7.03	fcc; $a=4.451$	$TiD_{1.82}$
Zr	1.20	980	2.10	sct; $a=3.527$; $c=4.476$	ZrH_2
	–	–	4.16	sct; $a=3.527$; $c=4.476$	$ZrD_{1.96}$
Hf	0.80	900	1.09	sct; $a=4.911$; $c=4.405$	HfH_2
	–	–	2.11	sct; $a=4.911$; $c=4.405$	$HfD_{1.93}$
V	–	–	1.71	sct; $a=4.460$; $c=3.666$	$VH_{0.9}$
Nb	0.83	850	0.95	orthorhombic $a=4.859$; $b=4.878$; $c=3.453$	$NbH_{0.9}$
Pr	8.31	1265	1.49	fcc; $a=5.509$	PrH_2
	–	–	2.08	fcc; $a=5.491$	$PrH_{2.4}$
	4.01	800	3.29	fcc; $a=5.508$	$PrD_{2.4}$
Nd	8.25	1240	1.52	fcc; $a=5.451$	$NdH_{2.2}$
	–	–	1.78	fcc; $a=5.446$	$NdH_{2.6}$
	5.95	1050	3.61	fcc; $a=5.364$	$NdD_{2.3}$
Sm	10.27	1210	1.24	fcc; $a=5.380$	$SmH_{2.24}$
	–	–	1.87	hcp; $a=3.771$; $c=6.672$	SmH_3

as follows. The type and course of the reactions depend on hydrogen pressure and partial ratio P_{H_2}/P_{N_2}. For example:

$$Ti+(1-x)C+H_2 \begin{array}{ll} \nearrow TiH_2+(1-x)C & x>0.4;\ P_{H_2}>10\ \text{atm} \\ \rightarrow TiC_{1-x}+H_2 \rightarrow TiC_{1-x}H_y & x>0.4;\ P_{H_2}<10\ \text{atm} \\ \searrow TiC_{0.4}H_{1.02} & x=0.4;\ P_{H_2}<10\ \text{atm} \end{array}$$

$$Zr+N_2+H_2 \begin{array}{ll} \nearrow ZrN+Zr(N)\ \text{solid solution} & P_{N_2}/P_{H_2}>2 \\ \rightarrow ZrH_2 & P_{N_2}/P_{H_2}<0.5 \\ \searrow ZrN_{0.3}H_{1.6}\ \text{hcp} & 1>P_{N_2}/P_{H_2}>1.5 \end{array}$$

The main characteristics of carbohydrides and hydridonitrides of titanium and zirconium are listed in Table 3.

It was also useful to analyze the role of a second metal component by combustion in more complicated systems with hydrogen, nitrogen, carbon, such as Me(IV)–Me(V)–C–H, Me(IV)–ME(V)–N–H, Me(IV)–Me(V)–C–N–H. It is clear that in such systems it is possible to develop many variants of competitive reactions. As a result it was possible to direct these processes so as to obtain a series of multicomponent interstitial alloys containing hydrogen (Table 4). It was found that group VA metals are the most convenient for the production of hydrogen-containing phases with an fcc lattice at low nitrogen contents.

3. Discussion

On the basis of systematic investigations of the SHS process optimal parameters have been found for combustion in hydrogen. The time of operation is of the order of

Table 2
Characteristics of intermetalic compounds and their hydrides

Compound	H_2 content (wt.%)	Crystal structure; Lattice parameters (Å)	Temperature range of dissociation (°C)
Zr_2Co	–	Tetragonal; $a=6.387$; $c=5.542$	–
Zr_2CoH_5	2.02	Tetragonal; $a=6.906$; $c=5.550$	190–360
ZrCo	–	Cubic; $a=3.197$	–
$ZrCoH_3$	1.68	Orthorhombic; $a=3.370$; $b=10.570$; $c=4.318$	200–370
Zr_2Ni	–	Tetragonal; $a=6.540$; $c=5.340$	–
Zr_2NiH_5	2.08	Tetragonal; $a=6.860$; $c=5.657$	170–250
ZrNi	–	Orthorhombic; $a=3.290$; $b=9.998$; $c=4.080$	–
$ZrNiH_3$	1.96	Orthorhombic; $a=3.530$; $b=10.620$; $c=4.328$	220–260
Ti_2Co	–	Cubic; $a=11.310$	
Ti_2CoH_3	1.70	Cubic; $a=11.890$	240–360

Table 3
Characteristics of carbohydrides and hydridonitrides of Ti and Zr

Formula	Content (wt %)			Crystal structure; Lattice parameters (Å)	Temperature range of dissociation (°C)
	H_2	C	N_2		
$TiC_{0.4}H_{1.2}$	2.20	8.45	–	hcp; $a=3.090$; $c=5.089$	400–840
$TiC_{0.5}H_{0.5}$	0.90	10.39	–	fcc; $a=4.296$	425–800
$ZrN_{0.3}H_{1.52}$	1.52	–	3.81	hcp; $a=3.270$; $c=5.519$	370–795
$ZrN_{0.28}H_{1.33}$	2.20	–	7.60	hcp; $a=3.044$; $c=5.090$	455–610

seconds because of the high velocity of the combustion wave (1–10 cm s^{-1}) in the sample. Note that the SHS technique does not need large external heat sources. An important advantage is also the possibility of instantaneous sample homogenization, i.e. the quick formation of single-phase hydrides from a powder mixture of metals, metal nitrides or carbides. In conclusion we note that the SHS process can produce complicate and novel compounds with high concentrations of hydrogen. The results of our investigations suggest a competition between several reactions during combustion in hydrogen or gaseous mixtures. This competition can be exploited to obtain products of various types.

Table 4
Characteristics of complicated materials based on Ti-V and Zr-Nb

Compound	Content (wt.%)			Crystal structure; Lattice parameters(Å)
	C_{tot}	N	H	
$Ti_{0.7}V_{0.3}C_{0.7}$	14.84	–	0.08	fcc; $a=4.268$
$Ti_{0.7}V_{0.3}C_{0.65}N_{0.27}$	12.82	6.35	0.10	fcc; $a=4.253$
$Ti_{0.7}V_{0.3}C_{0.69}H_{0.2}$	14.39	–	0.35	fcc; $a=4.273$
$Ti_{0.7}V_{0.3}N_{0.13}H_{0.78}$	14.42	3.08	0.17	fcc; $a=4.264$
$Ti_{0.8}V_{0.2}N_{0.21}H_{1.36}$	–	5.62	2.55	hcp; $a=3.021$; $c=4.223$
$Zr_{0.7}Nb_{0.3}C_{0.54}$	6.6	–	–	fcc;$a=4.697$
$Zr_{0.7}Nb_{0.3}N_{0.33}H_{1.06}$	–	4.40	1.08	$a=4.602$
$Zr_{0.7}Nb_{0.3}C_{0.61}H_{0.24}$	7.04	–	0.24	fcc; $a=4.692$
$Zr_{0.7}Nb_{0.3}C_{0.44}N_{0.3}H_{0.1}$	5.44	4.07	0.10	fcc; $a=4.680$

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