INVESTIGATION OF INTERACTION OF HYDROGEN WITH IVB GROUP METAL ALLOYS IN THE COMBUSTION REGIME

Mayilyan D.G., Dolukhanyan S.K.*
A.B. Nalbandyan Institute of Chemical Physicis of Armenian NAS,
5/2 P.Sevak Str., Yerevan 0014, Republic of Armenia;
Fax: 37(410) 28 16 34; E-mail: seda@ichph.sci.am

Introduction

The hydrides of transition metals of IVB group have practical application in many fields of science and technique. Traditional methods of synthesis of these hydrides, based on thermal processing of metals in hydrogen atmosphere, are laborious and low-productive. Besides, it is difficult to obtain hydrogen-rich hydrides by these methods. Self-propagating High-temperature Synthesis (SHS) [1, 2] has appeared a perspective direction for receiving of metal hydrides.

In the present work, the results of study of processes of combustion of Ti-Hf, Zr-Hf, Ti-Zr-Hf alloys in hydrogen in SHS mode are presented. In "hydride cycle" method, developed last years at the laboratory of technology of SHS processes of IChPh of Armenian NAS [3, 4], the alloys of different compositions have been synthesized in these systems.

Results and discussion

The study of Ti-Hf, Zr-Hf, Ti-Zr-Hf alloys interaction with hydrogen and deuterium has shown that the compact alloys without crushing are capable to interact with hydrogen (deuterium), forming the hydrogen- (deuterium)-rich hydrides (deuterides), respectively, (H/Me = 2-2.28) and (D/Me = 1.8-2).

Process of hydrogen interaction with alloys can be presented by the following reactions:

$Ti_xHf_{1-x} + H_2 \leftrightarrow Ti_xHf_{1-x}H_y$

$Zr_xHf_{1-x} + H_2 \leftrightarrow Zr_xHf_{1-x}H_y$

$Ti_xZr_yHf_z + H_2 \leftrightarrow Ti_xZr_YHf_zH_к.$ (1)

These reactions are reversible – very important characteristic for cycling and usage the hydrides in the quality hydrogen accumulators.

In Table 1 the characteristics of hydrides and deuterides, synthesized in the systems under study, are presented. It is seen from this Table that the structure of a hydride depends on the composition of an initial alloy. At some compositions, the interaction of an alloy with hydrogen results in hydrides with cubic structure of fluorite, CaF_2; at other compositions – the hydrides with tetragonal structure of thorium dihydride, ThH_2, are formed. Data of X-ray analysis show, that the values of lattice parameters, **a** and **c,** depend on the structure of an initial alloy and increase with the growth of the zirconium and hafnium concentrations.

Table 1. Characteristics of hydrides.

Hydrides (deuterides) formula	Cryst. lat., struct. type	Cryst. lat. paramet., (Å)	H(D) cont., wt. %
TiH_2	FCC, CaF_2	a=4.44	4.01
ZrH_2	BCT, ThH_2	a=3.504 c=4.45	2.14
$HfH_{2.2}$	BCT, ThH_2	a=4.892 c=4.203	1.11
$Ti_{0.8}Hf_{0.2}H_2$	FCC, CaF_2	a=4.497	2.63
$Ti_{0.8}Hf_{0.2}D_{1.86}$	FCC, CaF_2	a=4.488	4.79
$Ti_{0.3}Hf_{0.7}H_{2.25}$	BCT, ThH_2	a=3.436 c=4.38	1.59
$Zr_{0.5}Hf_{0.5}H_2$	BCT, ThH_2	a=3.478 c=4.364	1.49
$Ti_{0.2}Zr_{0.4}Hf_{0.4}H_{2.03}$	BCT, ThH_2	a=3.452 c=4.395	1.7
$Ti_{0.22}Zr_{0.12}Hf_{0.66}$ - $-H_{2.28}$	BCT, ThH_2	a=3.435 c=4.378	1.61

The performed experiments had shown that the interaction of alloys with hydrogen proceeded as exothermal reactions.

In Fig.1, the thermogram of combustion of $Ti_{0.66}Hf_{0.34}$ alloy in hydrogen is shown. Combustion temperature of an alloy of any composition was in the interval 500-650°C. It is seen, that at interaction of alloy with hydrogen, the developed combustion temperature is rather low in comparison with the temperatures of combustion of metals (Ti, Zr, Hf) [1, 2].

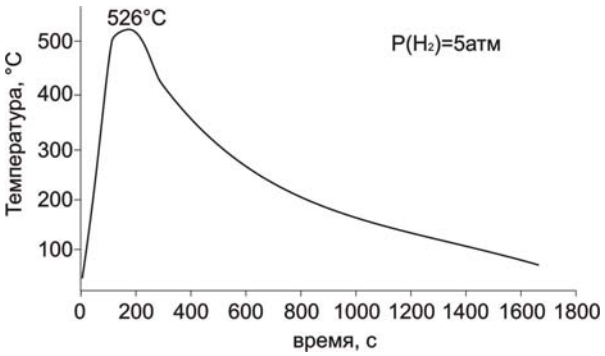

Fig. 1. Thermogram of combustion of $Ti_{0.66}Hf_{0.34}$ alloy in SHS mode at hydrogen pressure 5 atm.

The influence of hydrogen pressure on the process of alloy combustion was investigated on a sample of $Ti_{0.66}Hf_{0.34}$ alloy. The study had shown that the density of compact sample had not influence on the hydrogen content in the received hydride. With the increase of hydrogen pressure in the interval 1-30 atm, the combustion temperature grew from 450°C to 650°C.

The microstructures of the received hydrides of alloys have been studied on the scanning electron microscope (SEM). A hydride powder has been compacted to a tablet (d = 22 mm, t = 5-10 mm) on a hydraulic press at force loading 450 kN.

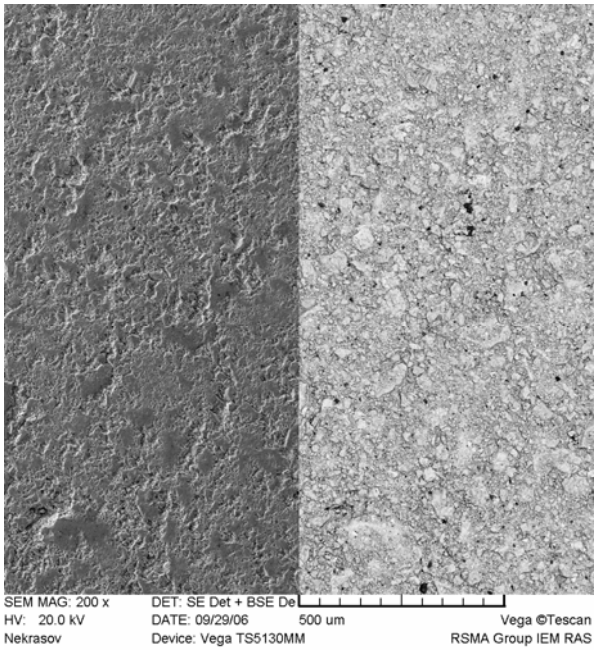

Fig.2. Microstructure of surface of tablet compacted from powder of $Ti_{0.8}Hf_{0.2}H_2$ hydride: at the left - shooting in the mode of reflected electrons (phase contrast), on the right – in the mode of secondary electrons (relief).

In Fig. 2 the microstructure of the same part of surface of the tablet pressed from powder of $Ti_{0.8}Hf_{0.2}H_2$ hydride is shown. According to SEM data, the surface structure is single-phase, rather dense, grains densely adjoin to each other, and the relief is flat. One can note the presence of a few small pores, with sizes from ~10 *microns* to a micron and less, dispersion is less than 5-10 microns.

Conclusions

For the first time it was shown, that compacted alloys (Ti-Hf, Zr-Hf, Ti-Zr-Hf) can interact with hydrogen and deuterium in combustion mode without preliminary crushing, and form the hydrogen- (deuterium-) rich hydrides (deuterides): H(D)/Me = 1.8-2.28. It was shown that the crystal structure of the received hydrides depended on the composition of initial alloys. It was established that the repeating the hydrogenation ↔ dehydrogenation cycle did not influence on the hydrogen content in the hydrides and on the structure of the alloys. The research of hydrides microstructure has shown that the surface structure of obtained compact hydride - was single-phase, rather dense, and its relief is flat.

References

1. Dolukhanyan S.K., Nersesyan M.D, Nalbandyan A.B., Borovinskaja I.P., Merzhjanov A.G. Combustion of transition metals in hydrogen. Dokl. AS of USSR. 1976; 231 (3): 675-678.

2. Dolukhanyan S.K., Hakobyan H.G., Aleksanyan A.G. Combustion of Metals in Hydrogen and Hydride Production by Self-Propagating High-Temperature Synthesis. Int. J. of SHS. 1992; 1 (4): 530-535.

3. Aleksanjan A.G., Mayilyan D.G., Dolukhanyan S.K., Shekhtman V.SH, Ter-Galstyan O.P. Sinthesis of hydrides and receiving of alloys in Ti-Hf-H system. Int. J. "Alternative energy and ecology". 2008, 9 (65): 22-26.

4. Aleksanyan A.G., Dolukhanyan S.K., Mantashyan A.A., Mayilyan D.G., Ter-Galstyan O.P., Shekhtman V.Sh. New technique for producing the alloys based on transition metals. Carbon Nanomaterials in Clean Energy Hydrogen Systems. NATO Science Series. 2008: 783-794.

This work was implemented in the frame of theme 0567 funded by the Ministry of Education and Science of Republic of Armenia, and at financial support of ISTC (grant A-1249).