



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/hydro](http://www.elsevier.com/locate/hydro)

# Hydride cycle formation of ternary alloys in Ti–V–Mn system and their interaction with hydrogen

A.G. Aleksanyan<sup>\*</sup>, S.K. Dolukhanyan, O.P. Ter-Galstyan,  
N.L. Mnatsakanyan

A.B. Nalbandyan Institute of Chemical Physics of Armenian NAS, 5/2 P. Sevak Str., Yerevan 0014, Armenia

## ARTICLE INFO

### Article history:

Received 18 January 2016

Received in revised form

16 June 2016

Accepted 16 June 2016

Available online 11 July 2016

### Keywords:

Hydride cycle

Ternary alloys

Dehydrogenation-sintering

Combustion mode

## ABSTRACT

Metal hydrides are promising as compact and safe hydrogen storage materials. Among them, the hydrides of ternary and more complex alloys are provided with properties required in modern hydride material science. In this work, the mechanism of formation of ternary alloys in Ti–V–Mn system in the “hydride cycle” mode was investigated.  $\text{TiV}_{1.2}\text{Mn}_{0.8}$ ,  $\text{TiV}_{0.8}\text{Mn}_{1.2}$ , and  $\text{Ti}_{0.37}\text{V}_{0.25}\text{Mn}_{0.25}$  alloys were synthesized, their interaction with hydrogen was observed in: a) combustion mode; b) at rather low temperature (25–50 °C) after short-term activation. X-ray, DTA and chemical analysis evidenced that the hydrogen interaction with the alloys, formed in both modes, resulted in the formation of  $\text{TiV}_{1.2}\text{Mn}_{0.8}\text{H}_{3.7}$ ,  $\text{TiV}_{0.8}\text{Mn}_{1.2}\text{H}_{2.35}$  and  $\text{Ti}_{0.37}\text{V}_{0.25}\text{Mn}_{0.25}\text{H}_{1.56}$  hydrides of identical structure, hydrogen content and thermal properties. These hydrides were stable at sorption-desorption cycling and during long-term (1 year) storage. Conclusion: the “hydride cycle” is an easy and affordable method of creation the ternary alloys with high hydrogen sorption properties, needed in hydrogen accumulators.

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

In the technically developed countries (USA, Japan, Norway, EU, etc.), hydrogen and fuel cells are considered as fundamental technologies in the 21st century, important for economic progress. Obviously, hydrogen-based sources of energy can greatly contribute to a more sustainable and less carbon dependent energetic. Vast financial and human resources are involved in the research programs in these fields [1]. The prospect of use of hydrogen as an energy source of the future is based on such properties of molecular hydrogen as:

1. high energy content per unit mass – 120.7 MJ/kg, higher than in any organic fuel;
2. ecologically pure combustion (end product is water) [2].

In order to create hydrogen economics, many important scientific, technological and technical problems must be solved, among them the quest for: a) a reliable way of producing large quantities of cheap hydrogen, b) capacities for storage, delivery and effective use of hydrogen.

Currently, the most spread in the world technologies of hydrogen producing are based on the water electrolysis, and on the steam reforming of methane (natural gas) in the

<sup>\*</sup> Corresponding author. Tel./fax: +374 286316.

E-mail address: [a.g.aleks\\_yan@mail.ru](mailto:a.g.aleks_yan@mail.ru) (A.G. Aleksanyan).

<http://dx.doi.org/10.1016/j.ijhydene.2016.06.145>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

chemical reformers in the presence of steam and a nickel catalyst. The resulting exothermic reaction breaks up the methane molecules and forms carbon monoxide (CO) and hydrogen (H<sub>2</sub>). Since the aim of a hydrogen economy is to reduce carbon emissions, it would be necessary to deploy carbon capture and storage systems on these plants, and this would only be economic for large-scale production [1–4].

The other methods for hydrogen production (Alkaline electrolysis, Polymer electrolyte membrane electrolysis, High-temperature electrolysis, Photo-electrolysis, biophotolysis, hydrogen from biomass, etc.) are further away from commercialization and need additional R&D. The researches for creation of new photocatalyst materials and study of their potential abilities are in the field of interests in the development of these technologies [1–6].

First of all, the problem of hydrogen storage and transportation is associated with its very low density in gaseous state ( $\approx 0.09 \text{ kg/m}^3$  under ambient atmospheric pressure and temperature). The existing relatively advanced storage methods (high-pressure gaseous or liquid hydrogen container) cannot meet the future goals for hydrogen storage. It seems that the storage of hydrogen in solid materials has the best potential to become a safe and efficient way both for stationary and mobile applications. A valuable alternative of hydrogen storage is the storage in the form of metal hydrides. The volume content of hydrogen in metal hydrides is higher than in liquid hydrogen ( $>4.2 \times 10^{22} \text{ cm}^{-3}$ ), therefore they are considered prospective as compact and safe hydrogen storage materials. However, some features of binary hydrides and intermetallic hydrides (for example, equilibrium pressure and temperature of hydrogen absorption/desorption, etc.) often do not meet the requirements of specific technical problems, such as: transportation, stationary and mobile storage of hydrogen, hydride compressors, hydrogen getters, batteries, etc. At the same time, the hydrides of ternary and more complex alloys are most likely to be the metal hydrides meeting the requirements of above mentioned technical problems. The replacement or addition of one or more components to a binary alloy can decrease the temperature and pressure of hydrogen absorption, and increase the hydrogen absorption/desorption rate, the storage capacity and the number of stable charging–discharging cycles.

Simultaneously, there is also a problem of developing new approaches for designing and synthesis of multicomponent single-phase alloys, alloys with combined phases (bcc, C14, etc.), high-hydrogen-absorbing nanostructure alloys, etc., which can serve as hydrogen storage materials [7–11,13–15].

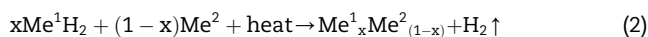
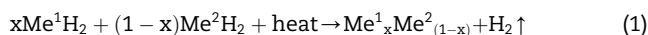
In the Laboratory of High Temperature Synthesis of A.B. Nalbandyan Institute of Chemical Physics of NAS RA (SHS Laboratory), a new method of synthesis of binary and multi-component alloys has been developed, named “hydride cycle” (HC). HC is a highly effective, hitherto unknown highly efficient method of producing refractory metal alloys. Current technologies of alloy production (mechanical alloying, arc melting, powder metallurgy techniques, etc.) are associated with certain technological difficulties, while the HC method avoids most of them (particularly, it excludes melting). HC is based on the combination of self-propagating high-temperature synthesis (SHS) of transition metal hydrides and heat

treatment of a mixture of hydrides, resulting in alloy formation [11,13–15].

The gist of SHS method is the use of the heat of exothermal reaction, initiated by ignition in the thin layer of metal-solid nonmetal (C, B, Si) mixture, or of metal in gas (H<sub>2</sub>, N<sub>2</sub>) environment. The high temperature, developed in the front of combustion, proceeds through a solid substance via a heat transfer from layer to layer with constant linear velocity. This high-efficient SHS process proceeds without external power input. Hydride is synthesized on account of the exothermal  $\text{Me} + \text{H}_2$  reaction in combustion mode with the velocity 1–10 cm/s. The yield of end-product is almost 100%. The process is mono-stage, low-energy-consuming, ecologically pure, cheap, wasteless and safe. It is worth to note that, besides powders, in the synthesis of hydrides of transition metals of III–IV–V groups, also shavings, sponge and the waste, appearing at metal machining, can be used. Earlier we have developed the technological processes for synthesis of TiH<sub>2</sub> and ZrH<sub>2</sub> suitable for industrial application [16].

The gist of the HC method is that, as starting materials, powders of cheap SHS-synthesized metal hydrides are used. They are mixed, compacted and dehydrogenated-sintered at 900–1150 °C. The use of a mixture of powders of hydrides of two or more III–V group transition metals, or of powders of metal(s) and metal hydride(s) results in the formation of alloy of corresponding metals [11,13–15]. HC is a low power input, high productivity, wasteless process, yielding high quality alloys and intermetallics of a given composition from not expensive SHS-hydrides. The main advantage of HC is the alloy formation at relatively low temperature (900–1150 °C) during a short time (1–2 h). Another very significant advantage of HC is that the metals with very different melting points and different densities can be alloyed without melting.

In general, the reactions of binary alloy formation can be expressed as:



The HC concept is a perfect solution for creating multi-component hydrogen storage alloys. In HC, a small addition of any transition element (i.e. Cr to Ni) to the main components can result in a doped alloy. It is suggested, that the alloys, doped by different metals, would be of a higher hydrogen storage capacity, higher stability in charging–discharging cycles and higher rate of hydrogen absorption/desorption. The use of transition metal hydrides as starting materials enables formation of alloys through a process, which radically differs from the melting processes. HC is an easier way to synthesize transition metal alloys of various structures (hcp, bcc,  $\omega$ -phase, approximants, etc.) [11,13–15,17,18].

We assume that in HC, the described below physical and chemical processes occur: a) the compaction of a hydride mixture leads to plastic deformation and shredding of the starting powders; b) the further sintering leads to dissociation of hydrides and hydrogen removal from the system, which brings to: reconstructive phase transitions, cleavage of atomic bonds, creation of new bonds, and restructuring of the system as a whole; c) the cleavage of Me–H bonds results in formation

Download English Version:

<https://daneshyari.com/en/article/1276466>

Download Persian Version:

<https://daneshyari.com/article/1276466>

[Daneshyari.com](https://daneshyari.com)