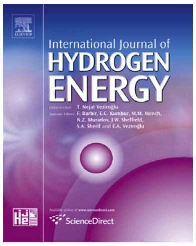
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 41 (2016) 425–430

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Hydrogen occlusion behaviors of ZrVFe alloys under mild hydrogen pressures and lowering of their hydrogen desorption temperatures

Yasuhiro Watanuki, Takeshi Toyama, Yoshiyuki Kojima, Nobuyuki Nishimiya[*]

Department of Materials & Applied Chemistry, College of Science & Technology, Nihon University, 1-8-14, Kanda-Surugadai, Chiyoda-Ku, Tokyo 101-8308, Japan

ARTICLE INFO

Article history:
Received 26 June 2015
Received in revised form
30 October 2015
Accepted 10 November 2015
Available online 9 December 2015

Keywords:
Hydrogen storage materials
Intermetallics
Zirconium-based alloy

ABSTRACT

Four kinds of ZrVFe alloys with the C14 Laves phase structure had high hydrogen storage capacity under mild pressures, and those alloys would be promising for widespread application such as recovery of hydrogen derived from water splitting. Addition of titanium to ZrVFe lowered hydrogen desorption temperatures through increase of equilibrium pressures. Substitution of ferrovanadium for vanadium did not deteriorate hydrogen occlusion performance of ZrVFe, and provided with lower cost alloys. Another way to reduce the cost would be elimination of purifying step of vanadium prepared by the thermite process, but remaining aluminum proved to bring about lower hydrogen capacity, as evidenced by comparative experiments including a ZrVFe alloy with aluminum intendedly added. Every alloy had fairly good cycling durability except the one contaminated with aluminum.

Introduction

Typical zirconium-based AB2 alloys with the C14 Laves phase structure such as $ZrMn_2$ and ZrV_2 have high hydrogen storage capacity [1–3]. ZrVFe is also an excellent hydrogen storage material [4], and particularly known as a tritium getter that can be used at room temperature under mild pressures [5,6]. ZrVFe is thus promising for storage of hydrogen derived from water splitting at room temperature under atmospheric pressures. Bio-hydrogen from microorganisms [7–10] is generally sparse, and ZrVFe would play an important role to recover hydrogen from as-produced mixtures.

In our preliminary experiments, hydrogen production by anabaena or spirulina was enhanced in the presence of hydrogen storage alloys, presumably owing to the shift of the equilibrium [11]. While ZrVFe readily sorbed hydrogen, desorption proceeded with difficulty due to its low equilibrium pressures. ZrVFe would become practically prominent, if higher equilibrium pressures are attained.

Many intermetallic compounds such as TiFe and $TiCr_2$ desorb hydrogen at low temperatures [12,13] despite of high hydrogen affinity of titanium. In the cited example [4], substitution of larger vanadium atoms for smaller iron atoms increased the stability of $ZeFe_2$ hydride. It is thus likely that

---

[*] *Corresponding author*. Tel.: +81 3 3259 0797; fax: +81 3 3293 7572.
E-mail address: nishimiya.nobuyuki@nihon-u.ac.jp (N. Nishimiya).

http://dx.doi.org/10.1016/j.ijhydene.2015.11.051
0360-3199/

Table 1 – Compositions (mass%) of ZrVFe and modified alloys.

	Zr	V	Fe	Ti	Al	C	N	O
ZrVFe	46.0	25.68	28.9	–	0.327	0.013	0.005	0.066
ZrVFe (Ti)	42.2	26.24	29.3	2.35	0.283	0.014	0.006	0.066
ZrVFe (Ti–Al)	42.0	25.38	28.5	2.34	2.21	0.012	0.005	0.052
ZrVFe (FeV)	46.5	25.97	29.2	–	0.45	0.081	0.018	0.078

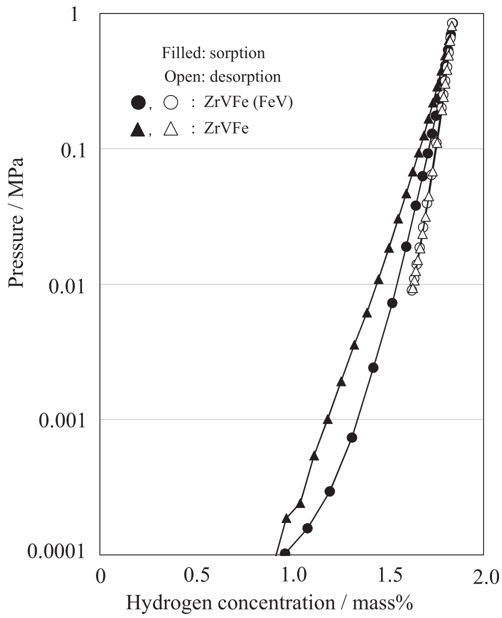


Fig. 1 – Hydrogen sorption and desorption isotherms at 298 K for ZrVFe and ZrVFe (FeV).

the equilibrium pressure of ZrVFe is heightened by substitution of smaller titanium for larger zirconium. Addition of titanium would also bring about kinetic improvement. For example, kinetics of magnesium were actually improved by milling with titanium [14].

Another barrier against practical applications of ZrVFe is high price of pure vanadium. Using ferrovanadium as a cheap vanadium source would be preferable for low cost alloys. However, ferrovanadium often carries impurities such as aluminum and carbon. Influences of the impurities on hydrogen sorption and desorption properties of ZrVFe are thus to be investigated. When the thermite process is employed for production of vanadium, removal of aluminum is necessary and that makes vanadium costly. If ZrVFe alloys containing small amounts of aluminum have similar hydrogen sorption and desorption behaviors as pure ZrVFe, the purification process is able to be avoided to reduce the cost.

In the present study, hydrogen storage capacity, hydrogen desorption temperatures and cycling durability of ZrVFe were studied with titanium or aluminum added or with ferrovanadium substituted for vanadium.

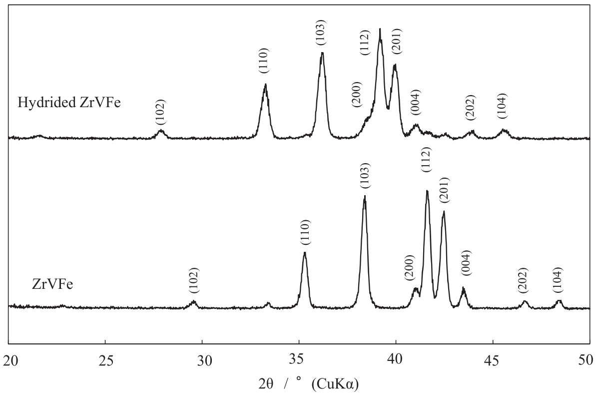


Fig. 2 – XRD patterns of ZrVFe and hydrided ZrVFe.

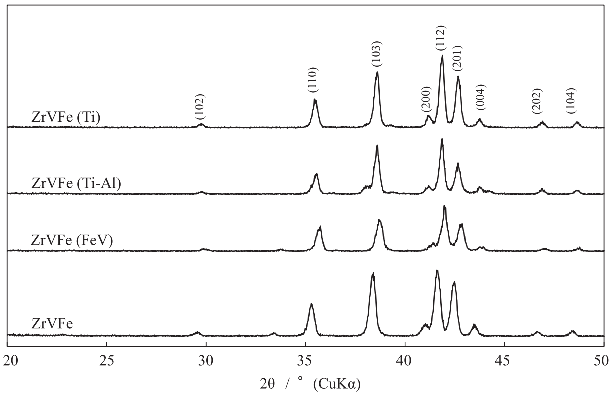


Fig. 3 – XRD patterns of ZrVFe alloys.

Experimental

Four kinds of alloys, ZrVFe, ZrVFe (Ti), ZrVFe (FeV) and ZrVFe (Ti–Al), where the elements in parentheses were added or substituted, were prepared by Taiyo Koko Co., Ltd. by means of arc melting method using high purity vanadium grains (99.9%), iron grains (99.9%), zirconium grains (98%) and

Table 2 – Hydrogen sorption and desorption behaviors of ZrVFe alloys.

Alloy	Hydrogen concetration at 1.0 MPa on sorption/mass %	Hydrogen concetration at 0.1 MPa on sorption/mass %	Hydrogen concetration at 0.01 MPa on desorption/ mass%
ZrVFe	1.84	1.66	1.64
ZrVFe (Ti)	1.88	1.66	1.69
ZrVFe (Ti –Al)	1.73	1.60	1.52
ZrVFe (FeV)	1.84	1.73	1.64