



Effects of rare-earth element additions to Laves phase-related body-centered-cubic solid solution metal hydride alloys: Thermodynamic and electrochemical properties



Lingkun Kong^{a, b}, Xinhai Li^a, Kwo Young^{c, *}, Jean Nei^c, Xingqun Liao^{a, b}, Wenliang Li^b

^a School of Metallurgy and Environment, Central South University, Changsha, 410083, Hunan, China

^b Shenzhen Highpower Technology Co., LTD, Luoshan Industrial Zone, Pinghu, Longgang, Shenzhen, Guangdong, China

^c BASF/Battery Materials-Ovonic, 2983 Waterview Drive, Rochester Hills, MI 48309, USA

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ABSTRACT

The influences of rare-earth element additions on the structural, gaseous phase hydrogen storage, and electrochemical properties of Laves phase-related body centered cubic (BCC) metal hydride alloys were studied using a series of alloys with the design composition of $\text{Ti}_{14.6}\text{Zr}_{2.1}\text{V}_{44.1}\text{Cr}_{12.2}\text{Mn}_{6.9}\text{Fe}_{2.7}\text{Co}_{1.4}\text{Ni}_{14.7}\text{Al}_{0.3}\text{RE}_{1.0}$, where RE (rare earth) = Y, La, Ce, Nd. Samples were prepared by induction melting and then annealed, and only 0.2 to 0.3 at% of the rare-earth element was included in the final samples in the elemental form, which varies from the RENi phase formed in the C14-predominated metal hydride alloy. The Al-content in the final alloy is about 1 at% because of a small reaction to the crucible material. The beneficial effects of rare-earth element addition on the low-temperature performance of the C14-predominated alloy was not observed in this group of BCC/C14 alloys. The gaseous phase and electrochemical hydrogen characteristics were influenced by the rare-earth elements addition mainly through changes in both compositions and abundances of the constituent phase. Y increased reversibility of gaseous phase hydrogen storage. La raised plateau pressure, decreased discharge capacity, and hindered activation and surface electrochemical reaction. Ce increased BCC phase abundance and discharge capacity with reduced room temperature surface charge-transfer resistance. Nd increased C14 phase abundance, decreased the plateau pressure, increased gaseous phase hydrogen storage capacities, and increased discharge capacity and bulk hydrogen diffusion.

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1. Introduction

Nickel/metal hydride (Ni/MH) batteries have been used to power more than 10 million hybrid electric vehicles (HEV) [1] because of their wide operating temperature range, proven durability, and excellent abuse tolerance. In the competition for plug-in HEV and battery-powered electric vehicle (EV) applications with the rival Li-ion battery technology, Ni/MH batteries lost the leading position because of their relatively low gravimetric energy density [2]. In a recent U.S. DOE-funded ARPA-E program, a group of metal hydride (MH) alloys with a mixed body-centered-cubic (BCC)/C14 phase structure exhibited a high discharge capacity (400 mAh g^{-1}) at a moderate discharge rate (100 mA g^{-1}), which is adequate for EV

applications [3]. Inoue et al. also reported a series of high-capacity MH alloys with similar microstructures, suitable for Ni/MH battery applications [4]. Iba and Akiba named the alloy group “Laves phase-related BCC solid solution” and it exhibits a characteristic two-phase microstructure composed of a BCC phase and a Laves phase (mostly C14), with a general formula of AB_x , where A is an element or any combination of elements from Group 4A (typically Ti), B is from Group 5A, 6A, or 7A (mainly V), and x is between 1 and 6 [5,6]. This group of alloys combine the high hydrogen storage capability of the BCC phase [7,8] and electrochemical catalytic ability of the C14 phase [9–14] through synergetic effects [15]. Pan and his group had made lots of contributions in this field [16–25].

Rare-earth (RE) elements have been used extensively to improve the activation, low-temperature, and high-rate dischargeability (HRD) characteristics of C14-based MH alloys [26–30]. For the Laves phase-related BCC solid solution alloys, only a few reports regarding RE substitutions are available, and the results are

* Corresponding author.

E-mail address: kwo.young@basf.com (K. Young).

mixed; 0.8 at% Y was found to improve both HRD and cycle stability [31], 1 at% La improved HRD but not the cycle stability [32], 1 at% Ce was reported to increase both capacity and diffusion rate in the gaseous phase [33], electrochemical activation [34], and cycle stability [34], 0.5 at% Gd increased the initial discharge capacity [35], 1 at% Dy improved the discharge capacity [34], and 0.5 at% Ho improved HRD. Therefore, this study addresses a need to re-investigate the effects of adding REs to this group of alloys. The testing results from sealed Ni/MH cells using these RE-containing BCC/C14 alloys will be published in a separate article [36].

2. Experimental setup

In order to prepare electrode materials for sealed Ni/MH cell experiments, an induction melt technique operated in a vacuum with a MgAl₂O₄ crucible and a steel mold with an average batch size of 2 kg was used instead of the conventional arc melt method, which prepares smaller samples. The ingots obtained were annealed under vacuum at 900 °C for 12 h following a recipe developed from a previous process optimization study [37]. The chemical compositions of the annealed ingots were analyzed with a Varian Liberty 100 inductively-coupled plasma optical emission spectrometer (ICP-OES, Agilent Technologies, Santa Clara, CA, USA). A Philips X'Pert Pro X-ray diffractometer (XRD, Philips, Amsterdam, the Netherlands) and a JEOL-JSM6320F scanning electron microscope (SEM, JEOL, Tokyo, Japan) equipped with energy dispersive spectroscopy (EDS) capabilities were used to examine the microstructures of the as-prepared samples. Pressure-concentration-temperature (PCT) analysis was performed with a Suzuki-Shokan multi-channel PCT (Suzuki Shokan, Tokyo, Japan) system. In the PCT analysis, each sample (a single piece of ingot with newly cleaved surface and a weight of approximately 2 g) was first activated by a 2 h thermal cycle between 300 °C and room temperature at 5 MPa H₂ pressure, after which PCT isotherms were measured at 30, 60, and 90 °C. Alloy samples, after PCT measurements, were ground into –200 mesh powder and used as the raw materials for electrode fabrication. Electrochemical testing was performed at room temperature using a CTE MCL2 Mini (Chen Tech Electric MFG. Co., Ltd., New Taipei, Taiwan) cell test system with standard Ni(OH)₂ positive electrodes (AP50 from BASF-Ovonac [38]) and 30 wt% KOH as the electrolyte. Details of electrode preparation, as well as the measurement methods, were reported previously [39,40]. AC impedance measurements were conducted using a Solartron 1250 Frequency Response Analyzer (Solartron Analytical, Leicester, England) with a sine wave amplitude of 10 mV and a frequency range of 0.5 mHz–10 kHz. Prior to the experiments, the electrodes were subjected to one full charge/discharge cycle at a rate of 0.1C, using a Solartron 1470 Cell Test galvanostat, discharged to 80% state-of-charge, and then cooled to –40 °C. Magnetic susceptibility was measured using a Digital Measurement Systems Model 880 vibrating sample magnetometer (MicroSense, Lowell, MA, USA).

3. Results and discussion

3.1. Alloy composition

The base alloy (alloy P9) in this study with a composition of Ti_{14.6}Zr_{2.1}V_{44.1}Cr_{12.2}Mn_{6.9}Fe_{2.7}Co_{1.4}Ni_{15.7}Al_{0.3} was selected from a previous study on the Ti/Cr content in Laves phase-related BCC solid solution alloys, because of its excellent balance between discharge capacity and HRD [41]. In this experiment, 1 at% of REs—Y, La, Ce, and Nd were added to alloys P45, P46, P47, and P48, respectively, partially replacing Ni. The design compositions and ICP results from the annealed samples are listed in Table 1. Large

Table 1
Design compositions (in **bold**) and ICP results in at%.

Alloy#	Ti	Zr	V	Cr	Mn	Fe	Co	Ni	Al	RE
P9	14.6	2.1	44.1	12.2	6.9	2.7	1.4	15.7	0.3	0.0
ICP	14.7	1.2	43.4	12.2	6.8	3.3	1.4	15.6	1.4	0.0
P45 (RE = Y)	14.6	2.1	44.1	12.2	6.9	2.7	1.4	14.7	0.3	1.0
ICP	14.8	1.8	43.6	12.4	6.9	3.0	1.4	14.8	1.1	0.2
P46 (RE = La)	14.6	2.1	44.1	12.2	6.9	2.7	1.4	14.7	0.3	1.0
ICP	14.6	1.9	43.7	12.4	6.9	3.1	1.4	14.8	1.0	0.2
P47 (RE = Ce)	14.6	2.1	44.1	12.2	6.9	2.7	1.4	14.7	0.3	1.0
ICP	14.9	1.5	44.2	12.4	6.9	2.8	1.4	14.5	1.2	0.2
P48 (RE = Nd)	14.6	2.1	44.1	12.2	6.9	2.7	1.4	14.7	0.3	1.0
ICP	14.6	2.0	43.8	12.2	6.9	3.0	1.5	14.5	1.2	0.3

discrepancies are found in the Al- and RE-contents between the design compositions and the corresponding ICP results, as only 0.2 to 0.3 at% RE is found in the final alloys, in exchange for an additional ~1 at% Al. The composition of the alloys determined by ICP is closer to Ti_{14.7}Zr_{1.8}V_{43.8}Cr_{12.3}Mn_{6.9}Fe_{3.0}Co_{1.4}Ni_{14.7}Al_{1.2}RE_{0.2}. Because of the higher melting temperature of the high V-content BCC alloy, the temperature and duration at that temperature in the induction melting process were higher than those used for the Laves phase MH alloy. Thus, more RE was oxidized and reacted with the spinel crucible, resulting in less RE and more Al in the final ingot. This phenomenon was not observed in the RE-containing Laves phase MH alloys [28–30]. The reaction between REs and the spinel crucible was also absent in the sample prepared by arc melting with a water-cooled Cu crucible [15]. ICP results from the as-cast ingot confirmed that the loss of RE originated from melting/casting, not annealing. Furthermore, the Zr-content in the final alloy was reduced because of the same oxidation observed with REs during the high temperature stage of induction melting.

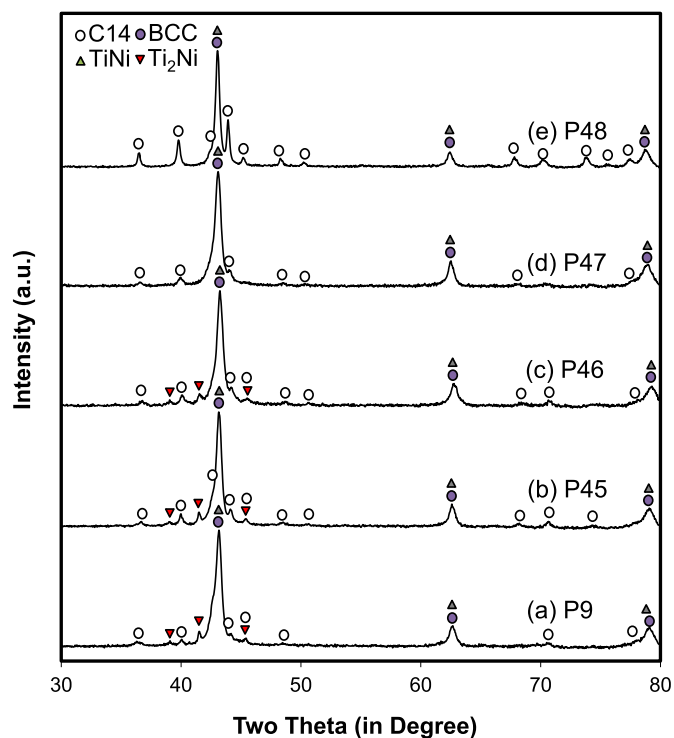


Fig. 1. XRD patterns for alloys P9 (a), P45 (b), P46 (c), P47 (d), and P48 (e) using Cu-K α as the radiation source.

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