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Preparation of hydrogen storage alloys for applications of hydrogen storage and transportation

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Abstract

This paper investigates the composition design and processing of hydrogen storage alloys (HSA) for H_2 storage and transportation (S&T) applications. A series of $Lm(NiX)_5$ intermetallic alloys were designed and prepared, where Lm indicates La-rich mischmetal, and X represents the metallic additives for improving hydrogen capacity and plateau pressure at various temperatures. PCT properties showed that $Lm(Ni_{1-x}Mo_x)_5$ intermetallics were among the best, x being in the range 0.01–0.1; the H_2 absorption capacity could extend to 1.7 wt.% without increasing plateau-slope. The processing improvement, a synthesizing technique based on the SMQ process, was established which allowed the segregation control and inhibited second-phase transformation, thus avoiding formation of a plateau-slope.

Keywords: Hydrogen storage alloy (HSA); Storage and transportation (S&T); Proton exchange membrane fuel cell (PEMFC); $Lm(Ni_{1-x}Mo_x)_5$ intermetallic alloy

1. Introduction

Hydrogen energy may solve the global problems of energy shortage and environmental pollution in the 21st century. The hydrogen fuel cell could become a major new energy resource to generate electricity. The supply, storage and transportation of hydrogen fuel are crucial problems for developing fuel cells, especially for the proton exchange membrane fuel cell (PEMFC) powered vehicle of the future.

Intermetallic compounds have important applications in reversible storage of hydrogen in three fields, namely electrochemical use in Ni/MH secondary batteries, hydrogen tanks for H_2 storage and transportation, and metal hydride heat engines for thermal applications. For electrochemical application, metal hydrides have been commercialized for Ni/MH rechargeable batteries for more than 10 years. In the case of hydrogen storage and transportation (S&T), several governing factors such as, hydrogen capacity, gravimetric energy density and manufacture cost, etc. have restricted progress. Sandrock [1] conducted a comprehensive survey from a gas-reaction point of view on hydrogen storage alloys, including the intermetallic families of AB_5, AB_2, AB, A_2B, and other novel approaches. He concluded that from the gas reaction point of view the conventional intermetallics that release H_2 at room temperature seem to be reaching their thermodynamic limits relative to PCT and reversible gravimetric densities, at no more than ~2 wt.%. Efforts toward increasing H_2 storage capacity with lightweight metal hydrides have been made [2]. However, no essential success was recorded in the development of light intermetallics operated at ambient temperature. In this paper, no attempt is made to break through the limitation of H storage capacity. In the contrast, this work is intended to improve the H capacity of the conventional $Lm(NiX)_5$ intermetallics within the limitation of the P–T realm, where X indicates substituting elements.

2. Experimental detail

The material studied is $Lm(Ni_{1-x}X_x)_5$ where Lm denotes La-rich mischmetal, X denotes Mn, Mo, Mg, Sn and Al and x denotes content of the additives; x=0.01–0.1 in this case. The alloys were separately prepared either by conventional vacuum arc re-melting (VAR) for lab-scale or by a new technique for a large quantity. With this new process, which we called synthesis–melting–quenching (SMQ) process [3], the powder billet containing the

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designated composition was first synthesized in an induction coil, and then locally melted in order to pour onto a fast rotating water-cooled conical drum surface. Via the inclined drum surface, the molten drops were spun-off and quenched by hitting a vertical cooling wall in the reactor. The solidified drops became round-shaped flakes before falling into a pre-cooled container. The alloys, prepared either by VAR or by the SMQ process, were crushed by a cyclone system into an average particle size of 2 mm. The particle size and powder distribution were measured using a HORIBA 'LA-910' laser scattering particle size analyzer if the size was less than 20 μm.

Microstructure of the alloys was analyzed using XRD and SEM equipped with electron probe micro-analyzer (EPMA).

Pressure–concentration–temperature (PCT) measurement and hydrogen absorption/desorption characteristics based on a conventional Sievert's apparatus were performed by use of a fully automatic P-C-I monitor (GfE product).

Intermetallic powder was filled into a vacuum stainless steel tank in glove box. High purity hydrogen charged easily. A cooling device surround the tank was necessary during charging.

3. Results and discussion

3.1. Alloy optimizing design

As described above, the intermetallic compounds have three important applications in the reversible storage of hydrogen, namely electrochemical use, H_2 storage and transportation, and engines for thermal application. For electrochemical application, the prime requirements of metal-hydrides are electrical capacity and attainable cycle life at specific capacity. Optimization design of hydrogen storage alloys (HSA) is important because hydriding/dehydriding reaction during hydrogen absorption/desorption kinetics is an ion-exchange action which takes place at the interface between solid phase of HSA and liquid phase of the electrolyte. Each element in the multi-element intermetallic alloy has its specific function on the hydrogen A/D kinetics. For instance, cobalt addition can inhibit decrepitation of the alloy during electric charging/discharging cycle, but the manufacture cost will be increased due to the expensive raw material.

Design criteria of HSA for the application of hydrogen storage and transportation (S&T) would be different. The main requirement for S&T application is aimed at hydrogen storage capacity in a narrow band of $P–T$ in the PCT diagram. The secondary requirements are energy density (both the gravimetric and the volumetric) and manufacture cost. Since the hydriding/dehydriding kinetics is a consequent result of gas reaction of hydrogen and solid phase intermetallics, tailoring the PCT diagram could be a crucial step in alloy design.

3.2. PCT properties of HSA for S&T applications

For an application as a PEMFC-powered scooter, the temperature would be in the range of 253–353 K and the operating pressure would be hopefully in the range of 1–10 atm. Based on the Van't Hoff relationship (log P_d vs. $1/T$), very few intermetallics fall in this narrow $P–T$ range. For a rare earth metal based AB_5 system, only X=Al, Sn, Mn, Fe, and Ni-containing $La(NiX)_5$ alloys could meet this requirement. Unfortunately, when the PCT properties were evaluated, as reviewed by Sandrock [1], it was found that most existing hydrides fall far short of what is desired. $LaNi_5$ has a relatively long width along with flat plateau pressure, however, its absorption pressure is considered too high to be use in a hot climate. In order to decrease the plateau pressure, a second element of Al or Mn was added to replace part of Ni in the B-side. Decreasing of plateau pressure was obvious, however, shortening of the length of the plateau or increasing of the plateau slope were encountered. Most HSA do not show a perfectly flat plateau but exhibit concave upward curvature with a plateau slope or multiple plateaus. The feature of the plateau slope indicates that some second phases, inclusions, impurities and/or segregation etc. may be presented in the HSA. As a result, both $\Delta(H/M)$ and $(H/M)_{max}$ in weight percent were reduced.

3.3. Modification of $Lm(NiX)_5$ intermetallic compound

Fig. 1 illustrates PCT properties of $Lm(Ni_{1-x}X_x)_5$ intermetallics tested at 40°C, where X represents substitution elements Mo, Mg, Mn, Al, and Sn, respectively, and $x=0.01–0.1$ in our case. It is worth noting that Mo-modification not only depresses the plateau pressure to the application range but also increases the H_2 capacity $(H/M)_{max}$ to 1.7 wt.% without changing the plateau slope of $LmNi_5$. The study of the effect of Mo additive on HSA was initiated from this work. Mo modification was able to improve electrochemical capacity as well [4], but degraded

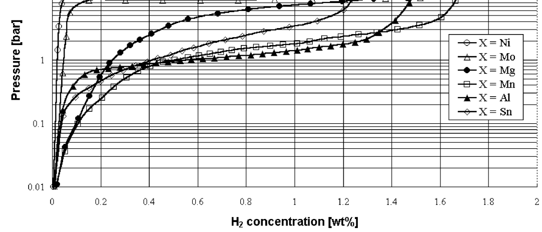

Fig. 1. PCT properties of $Lm(Ni_{1-x}X_x)_5$ intermetallics tested at 40°C, where X=Mo, Mg, Mn, Al and Sn, respectively.

cycle life due to forming Co_3Mo with cobalt. In this case of gas reaction with HSA for S&T application, Mo plays an important role in changing the microstructure solely on the B-side of the alloy (in AB_5 system), for ease of hydriding/dehydriding kinetics, but is inert on the A-side without forming any rare earth based second phase. As for Al or Mn modification, the effect of decreasing plateau pressure is apparent, however, shortening of the plateau pressure or increase plateau slope was a side-effect. Regarding Mg modification of HSA, there have been extensive studies on Mg_2Ni (A_2B system) because of its cost effective, high H-absorption capacity and high-energy density. Unfortunately, attempts to decrease plateau pressure at ambient temperature have not been successful. As shown in Fig. 1, Mg modification of $Lm(Ni_{1-x}Mg_x)_5$ does not reveal any improvement in PCT property at 40°C. It was concluded that the Mo modified HSA, $Lm(Ni_{1-x}Mo_x)_5$, seems to be one of the best candidates for PEMFC application. The thermodynamic data of the $Lm(Ni_{1-x}Mo_x)_5$ intermetallics are listed in Table 1. The PCT properties of $Lm(Ni_{1-x}Mo_x)_5$ as a function of temperature are shown in Fig. 2.

3.4. Preparation of $Lm(Ni_{1-x}Mo_x)_5$ intermetallics for S&T applications

Most of the rare earth based intermetallics such as $SmCo_5$ are subject to a peritectic reaction during solidification. From a metallurgical point of view it is inevitable that one or multiple second-phases are generated from conventional melting. The existence of a second phase causes an increase of plateau-slope, which is undesirable in S&T applications. For commercial mass production of a large quantity of HSA, environment control and segregation control are the two items which must be considered. An innovative design of the reactor with the SMQ process, as described in Experimental detail, was established in the factory. The key point of the SMQ process is mainly based on the phenomena of spontaneous reaction synthesis (SRS) [5]. Nearly single phase of $Lm(Ni_{1-x}Mo_x)_5$ was synthesized spontaneously by its own exothermic reaction-heat at a temperature below melting point. For the purpose of quenching, the ingot was locally melted by an induction coil and then flowed onto the drum surface for spin-off.

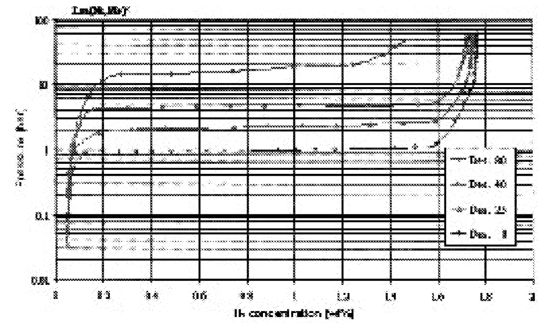

Fig. 2. PCT properties of $Lm(Ni_{1-x}Mo_x)_5$ as a function of temperature, T=0, 25, 40 and 80°C, respectively.

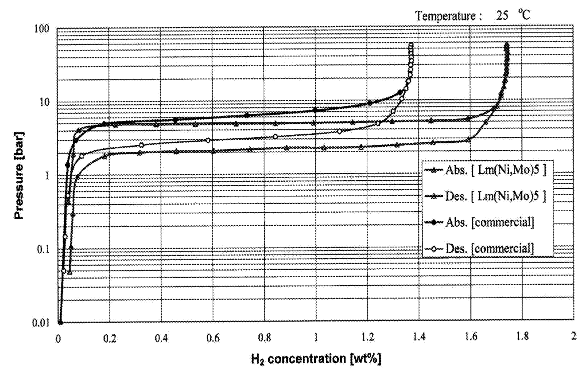

Fig. 3. A/D hysteresis loop of $Lm(Ni_{1-x}Mo_x)_5$ compared with commercial product tested at 25°C.

Fig. 3 shows the PCT hysteresis loop of $Lm(Ni_{1-x}Mo_x)_5$ at 25°C, and another loop of commercial product is also shown for comparison. It is verified from the comparison that the properties of the $Lm(Ni_{1-x}Mo_x)_5$ intermetallics prepared by the SMQ process not only lengthen the H_2 absorption capacity $(H/M)_{max}$ to 1.7 wt,%, but also maintain the plateau pressure flat and horizontal even without further homogenization.

4. Conclusions

In order to improve H_2 desorption capacity of the $Lm(NiX)_5$ intermetallics in the P_{des}–T realm (P_{des} of 1–10 atm and temperature of 253–353 K) for hydrogen storage

Table 1
PCT and thermodynamic properties of selected $La(NiX)_5$ alloys

Alloy	H (KJ mol^{-1})	S (KJ mol^{-1})	P_d at 25°C	T for P_d =1 atm (°C)	Plateau	
					Hysteresis	Slope
$MmNi_5$[a]	21.1	0.097	23	−56	1.65	0.54
$LaNi_5$[a]	30.8	0.108	1.8	12	0.13	0.13
$LmNi_5$	33	0.120	2.9	3	0.75	0.11
$Lm(NiMo)_5$	32.9	0.118	2.28	6	0.8	0.25

The slope in the table is given for the desorption plateau.
[a] Data quoted from Ref. [1].

application, a series of X substitutions was investigated. It was found that $Lm(Ni_{1-x}Mo_x)_5$ was among the best, not only to lengthen the H_2 capacity, $(H/M)_{max}$, from 1.4 (commercial grade) to 1.7 wt.% in this work, but also to maintain the horizontal plateau-slope.

Composition design and a manufacturing process obtained this optimal result. For the manufacturing process, a synthesizing technique based on the SMQ process was established, which allowed segregation control and inhibited second-phase transformation thus avoiding formation of plateau-slope.

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