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Improvement in −40 °C electrochemical properties of AB_2 metal hydride alloy by silicon incorporation

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ABSTRACT

The ultra-low temperature (−40 °C) charge transferred resistance of a Laves phase based-AB_2 metal hydride alloy was reduced by a factor of 5 by a partial substitution of Ni with Si in $Ti_{12}Zr_{21.5}V_{10}Cr_{7.5}Mn_{8.1}Co_{8.0}Ni_{32.2-x}Si_xSn_{0.3}Al_{0.4}$, where $x = 0$–4. This improvement was due to the increases in surface area from the higher leaching-rate of the oxidation product of Si and to the surface catalytic effect with the incorporation of Si. The microstructure, gaseous phase hydrogen storage, and electrochemical properties of these alloys were investigated and reported. With the addition of Si in the formula, the abundances of both C15 and TiNi minor phases increased, which resulted in decreases in both maximum gaseous phase hydrogen storage and electrochemical capacities. Some changes on the chemical compositions of the minor phases from the Si-incorporation were observed but cannot be correlated to the improvement in low-temperature performance. These changes are the transition from Zr to ZrO_2, the decrease in Ti/Zr ratio in the TiNi phase, and the higher Sn-content in the TiNi phase. An amount of 1 at.% of Si is recommended from the balance among capacity, bulk diffusion, surface area, and catalytic properties of the alloys. In addition, a special sample preparation method for using inductively coupled plasma analysis to determine the Si-content in the sample was developed and presented.

1. Introduction

Nickel/metal hydride (Ni/MH) battery is a very versatile rechargeable battery technology. In the consumer market, it is widely used to replace the nickel–cadmium (Ni/Cd) battery, which is considered toxic and environmentally unfriendly. The only drawback of Ni/MH battery compared to Ni/Cd battery is its inferior performance at ultra-low temperatures (<−30 °C). In the propulsion application, most of the commercially available hybrid electric vehicles employ Ni/MH batteries. However, the recent price hike of rare-earth metals has put the Ni/MH battery at a disadvantageous position to compete with the lithium-ion battery. AB_2 alloy, which has long been used as the negative electrode material for Ni/MH battery [1–6], is free of rare-earth elements and has a price advantage in today's raw material market. The multi-phase nature of AB_2 metal hydride (MH) alloy allows the incorporation of many transition and non-transition metals [3]. For example, substitutions with Mo [7], Fe [8], Cu [9], and Y [10] were reported previously, but the improvements over the base alloy were limited. Si, a light element with electronegativity (1.90) similar to that of Ni (1.91), is a candidate to substitute in the B-site with the intention to improve the low-temperature dischargeability of AB_2 alloys. The metallic radius of Si (1.669 Å) [11] in Laves phase inter-metallic compound is between that of Ti (1.614 Å) and Zr (1.771 Å) and much larger than those of the commonly used B-site elements, such as Ni (1.377 Å), Co (1.385 Å), Cr (1.423 Å), Mn (1.428 Å), and V (1.491 Å), which makes Si also a candidate to substitute in the A-site.

In AB_5 alloys, Si was first added in $LaNi_5$ alloys by J.J.G. Willems to extend the cycle life of the MH electrode with a trade-off in capacity [12]. The same author also reported the improvement in high-rate dischargeability (HRD) with Si-addition [13]. The extension in cycle life from Si-incorporation was mainly due to the reduction in unit cell expansion during hydriding [12,14,15]. Suppression of Al-dissolution into the electrolyte by Si also contributed positively to the cycle stability of AB_5 electrode [15]. Sakai et al. attributed the increase in cycle stability to the formation of a thick layer of silicon oxide on the surface [16], but the proposition was rejected by later works with X-ray photoemission spectroscopy [14]. Besides the improvement in cycle life and HRD, Si also facilitated the formation process, according to reports from Meli et al. [14,17]. Opposite contributions were also reported previously: Si in a low-Co misch metal-based AB_5 MH alloy decreased both HRD and activation [18]. In the gaseous phase, the partial replacement of Ni by Si in $MmNi_5$ decreased both the maximum storage capacity and the hydrogen equilibrium plateau pressure [19]. In a similar misch metal-based A_2B_7 alloy system, the

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incorporation of Si resulted in improvement in cycle stability but also lead to deterioration in activation and reductions in capacity, HRD, bulk diffusion, and surface reaction [20].

Si was also added in a few Laves phase-based AB_2 MH alloys previously, and its effects are summarized here. In the binary alloy $ZrCr_2$, the partial replacement of Cr by Si reduced the unit cell volume (C14), decreased the volume expansion during hydriding, lowered the gaseous phase maximum storage capacity, and increased the equilibrium plateau pressure [21]. In another binary alloy, $TiCr_2$, the effects of the same replacement are similar: reductions in both unit cell volume and maximum storage capacity [22]. In the ternary alloy $ZrV_{0.8}Ni_{1.2}$, the addition of Si decreased the reaction impedance and facilitated the electrochemical reaction [23]. In the multi-phase Zr-rich systems (A-site composition of either $Zr_{0.9}Ti_{0.1}$ or $Zr_{0.8}Ti_{0.2}$), Si promoted the formation of the C14 phase [24] due to its fewer number of outer-shell electrons, which lowered the average electron density (e/a) – a parameter that determines the C14/C15 phase abundances [25–27], lowered the discharge capacity [28,29], increased the cycle stability and charge retention from the formation of stable silicon oxide on the surface [29], impeded [28] or facilitated [24] the formation process, and improved the high-temperature discharge characteristic [29]. In the Ti-rich multi-phase AB_2 alloys, as the Si-content in the alloy increased, the secondary TiNi phase abundance increased at the expense of the main C14 phase, the cycle stability increased, and the lattice parameters, c/a ratio, electrochemical capacity, and ease of formation all decreased [30]. Among several similar body-center-cubic solid solution MH alloys (also transition metal-based), the addition of Si increased Laves phase abundance, decreased the maximum storage capacity, increased the equilibrium plateau pressure, and facilitated the formation process [31–34]. Finally, Si was also found to play a crucial role as a catalyst in improving the electrochemical discharge property of the crystalline Co metal [35]. Although many works on Si-substitution have been reported previously, none of them focused on its effect on the low-temperature performance and relationship to the alloy microstructure. Therefore, a complete study on the microstructure, gaseous phase hydrogen storage, and electrochemical properties, especially at −40 °C, of the Si-substitution in AB_2 MH alloy was conducted and presented in this paper.

2. Experimental setup

Arc melting was performed under a continuous argon flow with a non-consumable tungsten electrode and a water-cooled copper tray. Before each run, a piece of sacrificial titanium underwent a few melting-cooling cycles to reduce the residual oxygen concentration in the system. Each 12-g ingot was re-melted and turned over a few times to ensure uniformity in chemical composition. The chemical composition for the ingot was analyzed using a Varian *Liberty* 100 inductively coupled plasma optical emission spectrometer (ICP-OES). A typical ICP analysis involves a sample preparation that starts with an acid dissolution of the MH alloy followed by a dilution into 0.5 l solution. A second 10:1 dilution is typical for measuring bulk elements. While relatively straightforward, there are some limitations for Si detection by conventional ICP-OES. Most lanthanide and transition metals are readily soluble in conventional mineral acids, e.g. HNO_3 and/or HCl; however, dissolution of Si requires an addition of hydrofluoric acid (HF). The presence of HF causes compatibility problems between the sample matrix and the ICP introduction system components, e.g. torch, nebulizer, etc., which are typically made of borosilicate glass and quartz. When glass or quartz is exposed to HF, it is attacked to a degree relative to the HF concentration, which ultimately results in "false positives" for any or all of Si, B, Na, etc. There are options for the analyst to mitigate this effect, but they each have tradeoffs. Corrosion resistant introduction components, e.g. alumina based components, are not easily attacked by HF; however, detection limits and relative standard deviation suffer greatly when they are used compared to when standard glass concentric nebulizers and quartz torch assemblies are used. Furthermore, the similar situation now exists with false positive of Al and poses the same challenge when analyzing for trace Al, which is a constituent element in the alloys of the current study. The MH alloys in the current study have relatively low levels of Si ranging from 0 to 4 at.%. A reasonable approach for ICP analysis would be to determine the lowest HF concentration necessary to dissolve the alloy and prepare an equivalent blank in order to evaluate the Si contribution from the ICP components. About 100 mg of each sample was placed in a Teflon beaker with 4 ml HCl and heated at 90 °C for 2 h. Next, it was found that the addition of 1 ml HCl with 3 drops of HF together with the heat treatment of 90 °C for 1 h was sufficient for the complete digestion of the alloy. A blank was prepared in exactly the same manner. All solutions were diluted into 0.5 l and analyzed for Si using 3 Si emission lines: 251.611 nm, 212.412 nm, and 288.158 nm. The blank exhibited a negligible Si background, i.e. approximately equivalent to that of a blank without HF. The background counts were collected versus time as the HF blank was aspirated to determine the possible cumulative effects of HF in the system. No cumulative effects were observed for a period greater than required for running a sample. In conclusion, despite concerns regarding the Si measurement, the digestion method adopted proved to be sufficient for complete dissolution while the HF concentration was low enough to avoid false positives.

A Philips *X'Pert Pro* X-ray diffractometer (XRD) was used to study the microstructure, and a JEOL-*JSM6320F* scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) capability was used to study the phase distribution and composition. The gaseous phase hydrogen storage characteristics for each sample were measured using a Suzuki–Shokan multi-channel pressure-concentration-temperature (PCT) system. In the PCT analysis, each sample was first activated by a 2-h thermal cycle between 300 °C and room temperature at 25 atm H_2 pressure. The PCT isotherms at 30 °C and 60 °C were then measured. Details of both electrode and cell preparations as well as the measurement methods have been reported previously [36,37]. AC impedance measurements were conducted using a Solartron 1250 Frequency Response Analyzer with sine wave of amplitude 10 mV and frequency range of 10 mHz to 10 kHz. Prior to the measurements, the electrodes were subjected to one full charge/discharge cycle at 0.1 C rate using a Solartron 1470 Cell Test galvanostat, discharged to 80% state-of-charge, and then cooled to −40 °C.

3. Results and discussion

Five alloys with Si substituting for Ni at various levels from 0 to 4 at.% ($Ti_{12}Zr_{21.5}V_{10}Cr_{7.5}Mn_{8.1}Co_{8.0}Ni_{32.2-x}Si_xSn_{0.3}Al_{0.4}$, $x = 0$–4) were prepared, and the design compositions are listed in Table 1. The base alloy (Si0) was selected due to its good HRD and was also used in the studies of effects of Mo [7] and Fe [8] modifiers on structural, hydrogen storage, and electrochemical properties. The average electron density (e/a) for each alloy, calculated from averaging the numbers of outer-shell electrons of the constituent elements, is listed in Table 1. These e/a values are lower than the

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

		Ti	Zr	V	Cr	Mn	Co	Ni	Sn	Al	Si	e/a	B/A
Si0	**Design**	**12.0**	**21.5**	**10.0**	**7.5**	**8.1**	**8.0**	**32.2**	**0.3**	**0.4**	**0.0**	**6.82**	**1.99**
	ICP	11.9	21.3	10.2	7.7	8.5	7.6	31.7	0.3	0.7	0.0	6.79	2.01
Si1	**Design**	**12.0**	**21.5**	**10.0**	**7.5**	**8.1**	**8.0**	**31.2**	**0.3**	**0.4**	**1.0**	**6.76**	**1.99**
	ICP	12.0	21.3	10.1	7.5	8.2	8.0	31.4	0.3	0.4	0.7	6.77	2.00
Si2	**Design**	**12.0**	**21.5**	**10.0**	**7.5**	**8.1**	**8.0**	**30.2**	**0.3**	**0.4**	**2.0**	**6.70**	**1.99**
	ICP	12.2	21.4	10	7.3	8.1	8.0	30.6	0.3	0.5	1.5	6.72	1.97
Si3	**Design**	**12.0**	**21.5**	**10.0**	**7.5**	**8.1**	**8.0**	**29.2**	**0.3**	**0.4**	**3.0**	**6.64**	**1.99**
	ICP	12.3	21.4	10.1	7.2	8.1	8.0	29.8	0.3	0.5	2.0	6.66	1.96
Si4	**Design**	**12.0**	**21.5**	**10.0**	**7.5**	**8.1**	**8.0**	**28.2**	**0.3**	**0.4**	**4.0**	**6.58**	**1.99**
	ICP	12.2	21.5	10.2	7.5	8.1	8.0	28.4	0.3	0.5	3.2	6.59	1.96