Journal of Power Sources 397 (2018) 280–287

Contents lists available at ScienceDirect

Journal of Power Sources

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

Relationship between H_2 sorption, electrochemical cycling and aqueous corrosion properties in A_5Ni_{19} hydride-forming alloys (A = Gd, Sm)

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HIGHLIGHTS

- Model A_5Ni_{19} (A = Sm, Gd) alloys have been elaborated and characterized.
- Sm_5Ni_{19} exhibits higher solid gas capacity up to 1.2 H/metal.
- Capacity decay for Sm is due to corrosion and crystallinity loss by hydrogenation.
- A_5Ni_{19} have similar corrosion behavior but Gd_5Ni_{19} shows better resistance.
- Gd_5Ni_{19} corrosion resistance is due to smaller Gd atomic radius.

ARTICLE INFO

Keywords:
Metallic hydrides
Ni-MH batteries
Corrosion
Rare earths
Magnetic measurements

ABSTRACT

A_5B_{19} compounds (A = rare earth, B = transition metal) are promising materials as negative electrodes in Ni-*M*H batteries. They are built from stacking along the c axis of one [A_2B_4] and three [AB_5] subunits. The former one exhibits a good ability to absorb hydrogen, and the later one a good cycling stability, thus A_5B_{19} compounds are expected to benefit the large capacity and the cycling stability of both units. In this paper, Gd_5Ni_{19} and Sm_5Ni_{19} were synthesized and their hydrogen sorption properties were investigated using the Sieverts' method. Calendar corrosion was also studied and X-ray diffraction, magnetic measurements and thermal gravimetric analysis were made to determine the amount of corroded alloy. Electrochemical cycling was performed for both compounds. After 100 cycles, the electrochemical capacity of Gd_5Ni_{19} remains constant whereas the Sm_5Ni_{19} one decreases sharply after five cycles. This good capacity retention is linked to the low corrosion rate of Gd_5Ni_{19} which corrodes 3 times less than Sm_5Ni_{19} after 18 weeks in KOH. For Sm_5Ni_{19}, we conclude that the capacity decrease was due for 19% to crystallinity loss and 53% to corrosion. Finally, a comparison is made between A_5Ni_{19} and A_2Ni_7-type compounds and the structure influence on the hydrogenation and corrosion properties is discussed.

1. Introduction

Materials for Ni-*M*H battery negative electrodes absorb and desorb hydrogen at room temperature. These electrodes are constituted of a hydride-forming element A and a non-hydride forming element B [1]. Most common active materials in Ni-*M*H battery negative electrodes are AB_5 compounds (A = rare earth (RE), B = transition metal) [2,3]. Nowadays, AB_y compounds with $2 \leq y \leq 5$ are also studied [4]. Those phases are described as stacking structures made of [A_2B_4] and [AB_5] units [5] and they are polymorphic adopting either rhombohedral (3*R*) or hexagonal (2*H*) structure. Indeed, there are three stacking periods for the rhombohedral structure, and two for the hexagonal one. The stacking period can be written as $n \times [AB_5] + [A_2B_4]$, for which n is an integer strictly greater than zero. The parameter y was first introduced by Khan [6] and is expressed as follows:

$$y = \frac{5n + 4}{n + 2}$$

AB_5 compounds are known for their good stability on hydrogen absorption-desorption cycling, whereas A_2B_4 compounds are able to absorb larger amount of hydrogen [7]. However, several authors have shown that hydrogen can induce amorphization in A_2B_4 systems [8,9].

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https://doi.org/10.1016/j.jpowsour.2018.07.033
Received 2 May 2018; Received in revised form 16 June 2018; Accepted 5 July 2018

This amorphization is related to the poor stability of the A_2B_4 phases due to the large value of the R_A/R_B ratio with RE ($R_{i,\ i=A,B}$: atomic radius), much larger than the ideal calculated one (1.225). However, benefit can be expected for these AB_y compounds exhibiting promising properties by combining the high capacity of the $[A_2B_4]$ subunits and the high cycling stability of the $[AB_5]$ ones.

Within these compounds, AB_3 alloys have been studied as they provide high capacity, but are also subject to high corrosion issues and hydrogen induced amorphization. We here study A_5B_{19} compounds, which brings a good compromise between high capacities and good corrosion resistance according to their lower $[A_2B_4]/[AB_5]$ subunit ratio. Prior to studying complex substitutions to reach high performance practical materials, we started as a first step to investigate basic properties of model alloys from this family. The A_5B_{19} stacking structures can be described as the stacking along *c*-axis of one $[A_2B_4]$ unit and three $[AB_5]$ units ($n = 3$). We chose A = Gd or Sm and B = Ni. Gadolinium and samarium have the benefit to have a smaller atomic radius than the most commonly used RE (La, Nd, and Pr). The ratio R_A/R_B is then smaller and consequently closer to 1.225, which stabilizes the A_2B_4 structure [8–12].

In this paper, we investigated Gd_5Ni_{19} and Sm_5Ni_{19} compounds in terms of structural and hydrogen sorption as well as electrochemical and corrosion properties.

2. Experimental

Gd_5Ni_{19} was synthesized using gadolinium (Alfa Aesar, 99.9%) and nickel (Praxair, 99.95%). The elements were introduced in stoichiometric proportions in an arc furnace under controlled atmosphere. They were melted several times, to obtain a homogeneous ingot. Subsequent annealing was performed for 7 days at 1000 °C in a silica tube under argon atmosphere before quenching in water to room temperature, to obtain the wanted Gd_5Ni_{19} structure at equilibrium.

Because of the high volatility of samarium, another method was used for Sm_5Ni_{19}. A small excess of samarium was added to the stoichiometric mixture of Sm (Alfa Aesar, 99.9%) and Ni (Praxair, 99.95%). They were melted together in an induction furnace under controlled atmosphere. Between each fusion, the ingot was weighted. Considering the loss in weight is only due to sublimation of samarium, this stepwise process ends when the ratio Sm/Ni reaches 5/19. The resulting ingot was crushed into powder ($\leq 100\,\mu m$) and pressed into a pellet under argon atmosphere, wrapped in tantalum foil, sealed in a stainless-steel crucible, annealed for 3 days at 950 °C, to reduce the samarium loss by evaporation, and water quenched.

Electron Probe Micro-Analysis (EPMA), CAMECA SX-100, was used to check chemical compositions. Samples were polished to 0.25 µm using diamond abrasive tape. X-ray diffraction (XRD) patterns were recorded using a Bruker D8 DA VINCI diffractometer with a Cu-K_α radiation, in a 2θ-range from 10 to 110° with a step size of 0.01°. Crystallographic properties and phase amounts were determined by Rietveld refinement using the program FULLPROF [13].

P-C isotherms were measured using the Sieverts' method. Samples were crushed into powder ($\leq 100\,\mu m$) under argon atmosphere and about 500 mg of sample were introduced in the sample holder. It was primary vacuumed and connected to a hydrogenation rig with gauged volumes. A known hydrogen pressure is introduced in the rig. During absorption, while opening the sample holder, measured hydrogen pressure decreases. Once a steady state is reached, NIST [14] equation is used to calculate the amount of absorbed hydrogen. Solid-gas cycling of Sm_5Ni_{19} was performed between 0 and 1 MPa (1st cycle) then up to 0.1 MPa for 20 cycles.

For determining the cycling properties, the right amount of hydrogen was introduced in the rig so that the final pressure equals to 0.1 MPa at equilibrium. We choose 0.1 MPa for sake of comparison as it corresponds to the maximal pressure reached in the open cell used during electrochemical measurements. The sample was desorbed at 150 °C under primary dynamic vacuum. Those two steps are equivalent to one hydrogenation-dehydrogenation cycle and were repeated to determine the stability of the hydride during solid-gas cycling.

For the electrochemical study, the sample was crushed into powder ($\leq 100\,\mu m$). A mixture of 90 wt% of the active material (Gd_5Ni_{19} or Sm_5Ni_{19}), 5 wt% of PTFE (binder) and 5 wt% of carbon black (electronic conductor) was spread out in a sheet of 250 µm in thickness. It was dried overnight under primary vacuum. Two $5 \times 5\ mm^2$ squares were cut from the resulting tape. They were pressed on both sides of a nickel grid current collector to make the negative electrode. The positive electrode was made of two $NiOOH/Ni(OH)_2$ plates. A two-electrode system was used, positive ($Ni(OH)_2/NiOOH$) and negative (M/MH_x) ones being separated by a nonwoven material in polypropylene and immersed in an open cell with KOH solution at 8.7 M. We selected KOH 8.7 M to emphasize the corrosion effect, without being detrimental to the specific conductivity of the solution [15]. Open cells were charged and discharged at a C/10 rate at room temperature, C being the capacity calculated from P-C isotherm up to 0.1 MPa. The charge duration was 11 h to assume 10% overcharge, and the end of discharge was set to a potential cutoff at 0.9 V. This value was selected to avoid entering the corrosion domain of the fully discharged cell.

For the corrosion study, samples were crushed into powder ($\leq 100\,\mu m$) and divided into several 200 mg-samples. They were introduced in different sample holders, immersed in KOH solution at 8.7 M and put in an oven at 25 °C with continuously renewed argon atmosphere. After different corrosion times (24 h, 48 h, 1w, 2 w, 3 w, 4 w, 8 w and 18 w; h = hour, w = week) KOH solution was removed with a Pasteur pipette. The powder was rinsed several times with a low concentrated KOH solution (10^{-2} M) with a pH high enough to avoid any dissolution of corrosion products. The powder was dried for 24 h under primary vacuum at 40 °C and was finally characterized using XRD and magnetic measurements.

Magnetic measurements were recorded with a Physical Properties Measurement System (PPMS) from Quantum Design. A small sample quantity (typically 20–50 mg) was used either as a massive sample (pristine alloy) or as a corroded powder fixed by a resin in a Teflon sample holder. The samples were placed in a gelatin capsule and fixed with glass wool. Diamagnetic contribution from the sample holder was measured and subtracted from the sample magnetization. Isotherm magnetization curves were measured at 300 K in an applied field range from 0 to 9 T. Amount of metallic nickel in the corroded samples was calculated by extrapolation of the magnetization curves to zero field and assuming it corresponds to the ferromagnetic Ni contribution. The mass percentage of Ni is then obtained by normalization with the saturation magnetization of nanoporous nickel isolated from a fully corroded sample ($42.74\ Am^2\,kg^{-1}$ at 300 K compared to $53\ Am^2\,kg^{-1}$ for bulk Ni).

Thermal gravimetric analysis (TGA) (Setaram instrumentation, Setsys Evolution model) experiments have been carried out on corroded samples. After 12–24 h under vacuum (10^{-4} mbar) in the apparatus, the samples were heated from room temperature to 1000 °C at $5\ K\,min^{-1}$ under argon (Linde 99.999%) in a platinum/rhodium crucible. This thermal profile was repeated two time and used as blank. In the corroded samples, the weight loss can be attributed to the loss of water from the RE hydroxide dehydration following the general formula of Eqs. (1) and (2) [16]

$$RE(OH)_3 \rightarrow REOOH + H_2O \quad (1)$$

$$2\ REOOH \rightarrow RE_2O_3 + H_2O \quad (2)$$

Thus, from TGA measurements it is possible to estimate the relative quantity of RE hydroxide.