Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Title: Sn-SUBSTITUTED LaNi_5 ALLOYS FOR METAL HYDRIDE ELECTRODES

56897

Author(s): Margot L. Wasz, Ricardo B. Schwarz, Supramaniam Srinivasan and M.P. Sridhar Kumar

Submitted to: Materials Research Society Proceedings
Spring 1995 Meeting Symposium W.
San Francisco, CA
April 17-21, 1995

By acceptance of this article, the publisher recognizes that the U.S. government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Los Alamos

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

FORM NO. 836 R4
ST. NO. 26295/81

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

GH

MASTER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Sn-SUBSTITUTED LaNi_5 ALLOYS FOR METAL HYDRIDE ELECTRODES

MARGOT L. WASZ,^{*} RICARDO B. SCHWARZ,^{*} SUPRAMANIAM SRINIVASAN,^{**} AND M. P. SRIDHAR KUMAR^{**}

^{*}Los Alamos National Laboratory, Center for Materials Science, Los Alamos, NM 87545

^{**}Texas A&M University, Center for Electrochemical Systems and Hydrogen Research, College Station, TX 77843-3402

ABSTRACT

Our research examines the efficacy of tin additions to LaNi_5 in improving the hydrogen storage capacity of the material during charging/discharging. Alloys were prepared using high energy ball milling (mechanical alloying), a technique superior to arc casting for alloying elements with a wide disparity in melting points. Characterization by x-ray diffraction and Rietveld analysis shows that tin preferentially occupies the Ni(3g) sites in the LaNi_5 structure, and the unit cell volume increases linearly with tin content to the maximum tin solubility of 7.33 atomic percent ($\text{LaNi}_{4.56}\text{Sn}_{0.44}$). We found that powders prepared by mechanical alloying and not exposed to air require no activation to induce hydrogen absorption. The hydrogen storage capacity in the gas and electrochemical phase was measured as a function of tin content. We found that with increasing tin, the plateau pressure decreases logarithmically, whereas the hydrogen storage capacity decreases linearly.

INTRODUCTION

Over the last twenty years, LaNi_5 -based intermetallic compounds have been widely researched as hydrogen storage materials because these compounds can store approximately one hydrogen atom per metal atom ($\text{H/M} = 6$) and the LaNi_5H_x ($x \approx 6$) hydride forms at near-ambient conditions of pressure and temperature.¹ Furthermore, the hydriding characteristics can be easily altered through the substitution of other elements on lanthanum and nickel sites.^{2,3} Metal hydrides based on the LaNi_5 structure for use in nickel/metal hydride batteries operating in KOH have met with growing success.⁴ However, factors contributing to capacity degradation upon hydrogen cycling, such as powder comminution due to the volume change between the hydrogen-free and hydrided material, as well as attack by the KOH electrolyte, continue to be obstacles in fully developing LaNi_5 -based electrodes.⁵ Generally, alloys showing little hysteresis between the pressures for hydride formation and decomposition suffer less degradation during cyclic charging and discharging.⁶

Previous studies have shown that $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ and $\text{LaNi}_{4.27}\text{Sn}_{0.24}$ can be hydrided at low hydrogen pressures and exhibit remarkably little cyclic degradation in the gas phase.⁶⁻⁸ These properties are similar to those of aluminum-substituted LaNi_5 .⁹ Unfortunately, in electrochemical applications, $\text{LaNi}_{5-y}\text{Al}_y$ is attacked by KOH and aluminum is lost from the structure. $\text{LaNi}_{5-y}\text{Sn}_y$ may prove to be more resistant to chemical attack in KOH.

This research investigates the effect of tin on the structure of LaNi_5 as well as the effect of tin on the hydrogen storage properties measured in the gas phase and electrochemically.

EXPERIMENTAL METHODS

The alloys, $\text{LaNi}_{5-y}\text{Sn}_y$ ($y = 0.0, 0.10, 0.29, \text{ and } 0.39$), were produced by mechanical alloying #100 mesh, 99.5 % purity LaNi_5 powder (CERAC, Milwaukee, Wisconsin) with #100 mesh, 99.999% purity tin powder (AESAR, Ward Hill, Massachusetts). Ball milling was chosen over conventional arc casting techniques because of the ease with which low melting point elements such as tin can be alloyed to high-melting point intermetallics like LaNi_5 . In addition, ball milling prevents the development of compositional inhomogeneities which are found in alloys prepared by conventional casting. The powder was processed and handled in an argon glovebox containing less than 1 ppm oxygen. Alloys were mechanically alloyed for four hours using a SPEX 8000 mixer/mill, a tungsten carbide vial, and a single 12.1-gram tungsten carbide ball. The powders were then annealed in a quartz tube in the same glovebox at 800°C for 30 minutes. X-ray diffraction of the powders, described elsewhere,¹⁰ indicate that following the annealing, all of the tin was incorporated either into the LaNi_5 structure or into a $\text{Ni}(\text{Sn})$ solid solution which precipitated to preserve the LaNi_5 stoichiometry.

The powders used for hydrogen storage studies from the gas phase were sieved to particle sizes between $45\mu\text{m}$ to $150\mu\text{m}$. One gram of alloy powder was mixed with an equal weight of copper powder to improve the thermal conductivity of the sample. This was necessary to minimize changes in temperature during hydride formation and dissolution. Alloys which were weighed, mechanically alloyed, and annealed in the glovebox, were also stored, sieved, and placed in the sample holder in the same glovebox without exposure to air.

The hydrogen storage characteristics were measured at 0°C using a computer-controlled Sieverts apparatus, described elsewhere.¹¹ For all compositions studied, the ball-milled alloys required no high hydrogen gas pressure or high temperature exposure to activate the surfaces for hydride formation. However for the first three cycles, the absorption plateau pressures consistently dropped with the number of cycles and reached a constant value thereafter. Therefore, prior to measuring each pressure-composition isotherm, the alloys were charged and discharged five times between 5000 torr and vacuum. At the conclusion of the pressure-composition measurements, absorption plateau pressures were measured at four different temperatures, ranging from 0°C and 40°C , for van't Hoff analysis. These pressures were measured at the midpoint of the absorption plateau at a constant hydrogen content since previous research has shown that reaction enthalpies can vary across the plateau region.¹²

Working electrodes for electrochemical characterization were prepared by mechanically pressing a 1:1 mixture of $\text{LaNi}_{5-y}\text{Sn}_y$ powder and binder onto nickel-mesh at a pressure of 200 kg/cm^2 . The binding material was carbon (Vulcan-XC-72) teflonized with 33% PTFE (polytetra-fluoroethylene). The geometrical area of the working electrode was 2 cm^2 . The counter electrode, obtained from Hughes Aircraft Company, consisted of sintered NiOOH and had a larger geometric area than the working electrode. Electrochemical measurements were performed in the flooded electrolyte condition using open cells containing a 31 wt. % KOH solution, which is the same concentration used in alkaline batteries. The electrolyte was prepared from reagent grade KOH and deionized water. The electrodes were tested for their charge/discharge characteristics, initial capacity, and cycle life. The potentials were measured with respect to a Hg/HgO reference electrode. Cycle life measurements were performed using

an Arbin Battery Testing System (College Station, TX, USA) by charging at a 0.5C rate for 2.5-3 hours and discharging at the same rate to a cut-off potential of -0.7 V.

RESULTS AND DISCUSSION

The lattice parameters of mechanically alloyed $\text{LaNi}_{5-x}\text{Sn}_x$ powders, ($0 < x < 0.6$), measured by x-ray diffraction, Figure 1, show that the unit cell volume increases linearly with increasing tin content to a maximum of 0.0908 nm^3 at the solubility limit of $\text{LaNi}_{4.56}\text{Sn}_{0.44}$. A Rietveld analysis of these diffraction patterns¹⁰ showed that tin replaces nickel in the 3g sites of the intermediate planes in the hexagonal LaNi_5 structure. Also derived in this work¹⁰ is the nickel-rich corner of the La-Ni-Sn ternary phase diagram with lattice parameter data and solubility data for fcc Ni(Sn).

Cohen et al.¹³ suggested that the degradation in the hydrogen storage capacity of LaNi_5H_6 is caused by the disproportionation of the hydride into LaH_2 and Ni. LaH_2 is undesirable because it is a stable hydride which does not decompose at room temperature. This disproportionation is thought to occur by the exchange of lanthanum and nickel at the nickel 3g sites.⁹ Although the room temperature mobility of lanthanum in LaNi_5 is small, the mobility is largely increased when the LaNi_5 unit cell is expanded in the hydrided condition. Recently, this theory has been supported by the observation of LaH_2 Bragg peaks in hydrogen-cycled LaNi_5 .⁸ Elements such as aluminum and silicon, which also substitute for nickel in 3g sites, have been linked with increased stability against cyclic degradation.^{9,14} By occupying this site, the aluminum atoms are thought to block the lanthanum/nickel exchange and thereby help retain the initial hydrogen capacity of the alloy.⁹ Since tin also occupies the nickel 3g sites in LaNi_5 , the same mechanism may operate in the present alloys.

Figure 2 shows the hydrogen absorption and desorption pressure plateaux as a function of tin content. The abscissa at the top of the figure shows the $\text{LaNi}_{5-y}\text{Sn}_y$ unit cell volume which is proportional to the tin concentration as shown in Figure 1. The logarithm of the plateau pressure decreases linearly with increasing unit cell volume. A similar dependence of plateau pressure on unit cell volume was found by Mendelsohn and Gruen,³ who substituted different

Figure 1 - $\text{LaNi}_{5-y}\text{Sn}_y$ unit cell parameters as a function of tin content, y.

Figure 2 - Pressure plateaux as a function of tin content and unit cell volume.

rare earth elements for lanthanum in LaNi_5 . However, the slope derived for the $\text{LaNi}_{5-y}\text{Sn}_y$ alloys in Figure 2 does not match that found by Mendelsohn and Gruen.

Although the LaNi_5 unit cell volume increases with tin content, the hydrogen storage capacity decreases, Figure 3. These capacities were measured at pressures equal to six times the absorption pressure plateau of alloy, listed in Table I. The decrease in hydrogen storage capacity is due to electronic effects. Gscheidner, et al.,¹⁵ attributed the loss in hydrogen capacity in $\text{LaNi}_{5-y}\text{Al}_y$ alloys to the partial filling of the alloys' 3-d band by electrons donated by the Al. This filling decreases the number of holes that can be occupied by electrons from the hydrogen. We believe a similar mechanism applies to the present tin-substituted alloys. The dashed line in Figure 3 is the predicted hydrogen storage capacity calculated assuming that each tin donates three electrons to the 3-d band of LaNi_5 .

Table I summarizes the gas phase results for the $\text{LaNi}_{5-y}\text{Sn}_y$ alloys including the van't Hoff analyses. Note that the enthalpy for hydride formation decreases with increasing tin content but the entropy stays approximately constant. The measured entropy is largely that lost by the hydrogen gas as it enters the LaNi_5 lattice.²

Figure 4 shows the electrochemical discharge capacity as a function of tin content. When tested electrochemically at room temperature, LaNi_5 and $\text{LaNi}_{5-y}\text{Sn}_y$ alloys containing low amounts of tin were observed to form bubbles on the surface of the working electrode. Hydrogen escaped to the air instead of entering the LaNi_5 lattice because the plateau pressures of these alloys were near one atmosphere and the partial pressure of hydrogen in air is low. Because the escaped hydrogen is not accounted for, the electrochemical discharge capacity measurements are low. Decreasing the cell temperature decreased the gas evolution and increased the apparent discharge capacity, as shown by the solid triangles in Figure 4.

Figure 3 - Gas phase hydrogen capacity in $\text{LaNi}_{5-y}\text{Sn}_y$ as a function of tin content, y.

Table I - Gas phase characterization of $\text{LaNi}_{5-y}\text{Sn}_y$

Composition	P_{abs} (torr)	P_{des} (torr)	Capacity at $6P_{\text{abs}}$ (H/ $\text{LaNi}_{5-y}\text{Sn}_y$)	ΔH (kJ/mol H_2)	ΔS (J/mol H_2 K)
LaNi_5	785 ± 14	396 ± 3	5.789	28 ± 6	104 ± 20
$\text{LaNi}_{4.90}\text{Sn}_{0.10}$	350 ± 8	226 ± 4	5.570	31.3 ± 3.8	107 ± 13
$\text{LaNi}_{4.80}\text{Sn}_{0.20}$	180 ± 2	130 ± 2	5.333	32.4 ± 2.0	106 ± 7
$\text{LaNi}_{4.71}\text{Sn}_{0.29}$	86 ± 5	65 ± 2	4.931	32.8 ± 0.6	102 ± 2
$\text{LaNi}_{4.61}\text{Sn}_{0.39}$	58 ± 8	43 ± 3	4.598	34.6 ± 0.2	104.0 ± 0.6

However, the electrochemical discharge capacities did not approach those measured in the gas phase until the tin content was increased to $\text{LaNi}_{4.71}\text{Sn}_{0.29}$. Further increases in the tin content of the alloys caused a decrease in the discharge capacity which is consistent with the gas phase results shown in Figure 4. The dashed line joining the open triangles in Figure 4 is the hydrogen capacity in mAh/g deduced from measurements in the gas phase at 0°C , (Figure 3). The solid circles for $y = 0.29$ and $y = 0.39$ are slightly below this line because the electrochemical charging was performed at room temperature. Thus, in the absence of gas evolution, the hydrogen storage capacities measured in the gas phase and electrochemically agree quantitatively. In a previous work,¹⁶ it was reported that LaNi_5 has a much lower electrochemical hydrogen storage capacity than $\text{LaNi}_{4.8}\text{Sn}_{0.2}$. The present experiments suggest that the capacity measured in LaNi_5 may have been low because of hydrogen evolution at the electrode. It may be possible to measure electrochemically the hydrogen storage capacity of LaNi_5 using a pressurized cell.

Figure 5 shows the effect of cycling on the discharge capacity of $\text{LaNi}_{4.71}\text{Sn}_{0.29}$ and $\text{LaNi}_{4.61}\text{Sn}_{0.39}$. The loss in hydrogen capacity q , per cycle n , was calculated as $1/q_0 (dq/dn)$, where q_0 is the highest measured discharge capacity for the alloy. Losses per cycle, in the range $10 < n < 60$, are approximately 0.22% in both alloys. This is half the loss rate previously reported for $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ which was measured at 0.46% per cycle.¹⁶ However in Ref. 16, the working electrode was discharged to a potential of -0.5V vs. the Hg/HgO reference electrode, and the $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ alloy was cast instead of ball-milled.

Figure 4 - Electrochemical discharge capacity in $\text{LaNi}_{5-y}\text{Sn}_y$ as a function of tin content, y .

Figure 5 - Discharge capacity as a function of cycle number in $\text{LaNi}_{4.71}\text{Sn}_{0.29}$ and $\text{LaNi}_{4.61}\text{Sn}_{0.39}$.

SUMMARY

Tin substitutes for nickel in the 3g sites of LaNi_5 . It is apparent that the substitution stabilizes the $\text{LaNi}_{5-y}\text{Sn}_y\text{H}_x$ intermetallic hydride against disproportionation to LaH_2 and Ni after repeated charging and discharging. By expanding the LaNi_5 unit cell volume, the pressure

for hydride formation and decomposition decreases logarithmically. The hydrogen storage capacity of $\text{LaNi}_{5-y}\text{Sn}_y$ from the gas phase decreases with increasing tin concentration. This decrease is also evident in the discharge capacity measured electrochemically provided hydrogen gas evolution is suppressed.

ACKNOWLEDGMENTS

This work was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences.

REFERENCES

1. J. H. N. van Vucht, F. A. Kuijpers, and H. C. A. M. Bruning, Philips Res. Repts. **25**, 133 (1970).
2. H. H. Van Mal, K. H. J. Buschow, and A. R. Miedema, J. Less Comm. Met. **35**, 65 (1974).
3. M. H. Mendelsohn and D. M. Gruen, Nature **269**, 45 (1977).
4. T. Sakai, K. Muta, H. Miyamura, N. Kuriyama, and H. Ishikawa, in Hydrogen Storage Material, Batteries, and Electrochemistry, edited by D. A. Corrigan and S. Srinivasan (The Electrochemical Society, Pennington, New Jersey, 1992), p. 59.
5. J. J. G. Willems and K. H. J. Buschow, J. Less-Comm. Met. **129**, 13 (1987).
6. S. W. Lambert, D. Chandra, and W. N. Cathey, J. of Alloys and Compounds **187**, 113 (1992).
7. M. H. Mendelsohn, D. M. Gruen, and A. Dwight, Inorganic Chem. **18**, 3345 (1979), Mater. Res. Bull. **13**, 1221 (1978).
8. R. C. Bowman, Jr., C. H. Luo, C. C. Ahn, C. K. Witham, and B. Fultz, J. Alloys and Comp. **217**, 185 (1995).
9. P. D. Goodell, J. Less-Comm. Met. **99**, 1 (1984).
10. M. L. Wasz, P. B. Desch, and R. B. Schwarz, submitted to Phil. Mag., 1995.
11. M. L. Wasz, S. Srinivasan, and R. B. Schwarz, unpublished results, Los Alamos National Laboratory, 1995.
12. T. B. Flanagan, W. Luo, and J. D. Clewley, in Hydrogen Storage Material, Batteries, and Electrochemistry, edited by D. A. Corrigan and S. Srinivasan (The Electrochemical Society, Pennington, New Jersey, 1992), p. 46.
13. R. L. Cohen, K. W. West, and J. H. Wernick, J. Less Comm. Met. **73**, 273, (1980).
14. A. Percheron-Guégan, C. Lartigue, and J. C. Achard, J. Less-Comm. Met. **74**, 1 (1980).
15. K. A. Gschneidner, Jr., T. Takeshita, Y. Chung, and O. D. McMasters, J. Phys. F: Met. Phys. **12**, L1 (1982).
16. B. V. Ratnakumar, C. Witham, B. Fultz, and G. Halpert, J. Electrochem. Soc. **141**, L89 (1994).