Journal of Alloys and Compounds 253–254 (1997) 520–524

Studies on the properties and characteristics of the fluorinated AB_5 hydrogen-absorbing electrode alloys

Y.-M. Sun*, K. Iwata, S. Chiba, Y. Matsuyama, S. Suda

Faculty of Engineering, Department of Chemical Engineering, Chemical Energy Laboratory, Kogakuin University 2665-1, Nakano-machi, hachioji-shi, Tokyo 192, Japan

Abstract

Fluoride layers have been known to contribute to the selective permeability of hydrogen molecules in the gas–solid reaction and provide a protective barrier against impurities such as water vapor, carbon monoxide, air, and others. One of the important roles of the fluorination processes is the removal of the oxide layer from the surface which considerably improves the initial charge/discharge characteristics. However, it has also been found that during fluorination, metallic Ni on the surface dissolves rapidly into the aqueous F^- and HF_2^- ion containing solution (here after, denotes F-solution) and as the result, the electric conductivity is significantly reduced in the fluoride layer. This paper is aimed at investigating the effects of fluorination conditions on the electrochemical properties and characteristics of the AB_5 electrodes for Ni–metal hydride batteries. Special care has been taken to control fluoride formation and its thickness on the particle surface. Ni^{2+} ions were added to the F-solution in order to protect Ni from being dissolved and lost in the vicinity of the particle surface. The thickness of the fluoride layer depends largely upon the specific surface area to be treated as a function of time. The thickness of the fluoride layer and the state of metallic Ni near the surface region was investigated by EPMA and ICPS and they were correlated with the initial discharge capacity, charge/discharge cycle life, and durability, against a 6 M KOH electrolyte solution.

Keywords: Fluorination mechanism; Fluorinated metal hydride; Fluorination reaction; Electrochemical properties

1. Introduction

Most of the hydriding alloys have been suffering from a lack of durability of surfaces exposed to air and water [1,2], impurities [3], and electrolyte solutions [4]. Past efforts in modifying the surface sensitivity have not necessarily succeeded when they are applied in KOH solution as for the electrode in Ni/MH rechargable batteries [5,6]. The poor surface durability for impurities has been pointed out as one of the major shortcomings of hydriding alloys by Suda and Sandrock [7].

The purpose of this paper is, (1) to develop a fluorination procedure which can prevent Ni-dissolution from particle surface to solution during the fluorination process, (2) to develop a fluorination solution which is suitable for treating AB_5 compounds as electrodes in Ni/MH rechargable batteries, (3) to optimize Ni-contents in the fluorination solution in view of the improvements of initial activation characteristics, discharge capacity, and charge/discharge cyclic life, (4) to find a novel pulverization technique to produce hydriding alloy particles with an increase in the specific surface area.

To increase the specific surface area is especially important for preventing pulverization during charge/discharge cycles. The authors stand by the idea that the smaller the particle size, the better the electrochemical property and characteristics. Enlarging the specific surface area of hydriding alloys which have the improved surface is believed to be a way to discover new materials suitable for use as electrodes.

2. Experiments

2.1. Fluorination solution

The original solution which was invented by one of the authors in 1991 [8] was designated as F-1 solution and the F-1 solution which contains Ni^{2+} was designated as F-2 in which Ni^{2+} contents are ranging from 10:0 to 0:10 as the ratio of F-1 to F-2. Preparation of the F-1 solution is described in elsewhere [8].

---

*Corresponding author.

PII S0925-8388(96)03055-1

2.2. Fluorination procedures

The AB_5 powders of $LaNi_{4.7}Al_{0.3}$ which have been used as the standard material in this laboratory, and $LmNi_{4.0}Co_{0.4}Mn_{0.3}Al_{0.3}$ (Lm:La-rich mischmetall) as an electrode material, were treated to make the fluorinated layers on the particle surface. The fluorination was performed under a specific ratio s/V of 0.35 $m^2/200$ ml at 30°C where s denotes the total surface area of alloy powder and V denotes the volume of fluorination solution. The pH value changes from 5.3 to 7.5 in three step-wise changes, as a function of time during the fluorination processes.

2.3. Analytical measurements

The metallic elements which dissolve in the fluorination solution were analyzed by ICPS analyzer and the results were correlated as a function of the pH value changes. The surface distribution of constituent metals was measured by an EPMA. A BET method was introduced to measure the specific surface area and it was correlated with the fluorination conditions.

2.4. Evaluation of electrochemical properties

The 0.25 g of alloy samples before and after the fluorination were mixed with 0.75 g of Ni powder (INCO #255) and 0.05 g of PTFE, and then cold-pressed under 4 tons/cm^2 loads to make coin-shaped pellets which were sandwiched between the Ni wire nets of 100 mesh.

The discharge capacity, especially at the initial stages of the charge/discharge cycles, were measured in a 6 M KOH electrolyte solution where the experimental conditions were set as the followings: charging at 200 mA/g for 3 h, resting for 10 min, and discharging at 150 mA/g to −0.6 V vs. Hg/HgO reference.

3. Results and discussion

3.1. Chemical status of the fluorination solution

The following equilibrium conditions have been supposed to express the characteristic nature of the free F^- ions which are believed to contribute to the fluorination reactions to make fluoride layers on particle surfaces.

$$2HF \leftrightarrow HF_2^- + H^+$$

$$HF_2^- \leftrightarrow 2F^- + H^+$$

$$HF \leftrightarrow F^- + H^+$$

The pH value changes stepwise up to 7.5 in the course of the fluorination reaction. The HF^{2-} ions in the solution act as the free F^- ion supplier which react directly with the surface to form the fluoride layer, reduce rapidly as the fluorination reaction proceeds.

3.2. Fluorination reactions

The fluorination reaction by an F-1 solution is considered to proceed along with the following equations:

$$Ma_xOy + xnF^- + 2yH^+ \leftrightarrow xMaF_n + yH_2O \tag{1}$$

$$M + nH^+ + nF^- \leftrightarrow MaF_n + n/2H_2\uparrow \tag{2}$$

$$nH^+ + ne + M \rightarrow MH_n \tag{3}$$

The fluorination processes which is initiated from the removal of the oxide layer (oxides are replaced by fluorides) is counted as one of the significant features of the fluorination processes (Eq. (1)). The fluorination reaction itself begins instantly after the removal of the oxide layer. The metallic transition elements react individually with the free F-ions to form soluble ionic fluorides, and the rare earth metals react to form solid fluorides at the surface of the alloys (Eq. (2)).

The excess hydrogen ions existing in the fluorination solution have two optional reactions, i.e., to generate hydrogen gas as bubbles at the interface between fluorination solution and particle surface, and to penetrate into the surface to form hydride (Eq. (3)). The latter is a hydriding reaction at the vicinity of the surface region and it causes pulverization with the generation of countless number of cracks in the order of micrometers. The hydriding reaction during fluorination processing plays important roles not only to improve the initial activation characteristics, but also to increase the specific surface area of the fluorinated alloy particles. This can be considered as the second significant feature of the fluorination processes.

The specific surface area can be controlled by controlling the pH value changes during the fluorination processes as seen in Fig. 1 where the thickness of the fluoride layer may be correlated with the time elapsed as a function of the pH value changes. The physical structures of the fluorinated layer have been reported elsewhere in [9,10].

3.3. Prevention of Ni dissolution in the fluorination solution

The washing (oxides removal) effects of the fluorination has been confirmed experimentally in the F-1 solution. However, it has been found that the metallic Ni distributing near the surface dissolves easily to the fluorination solution at a high level, up to 350 ppm as shown in Fig. 2. Due to the formation of the Ni-lean fluoride layer with less electric conductivity, the apparent discharge capacity was found to decrease significantly in spite of the improvement of the initial C/D characteristics and the cyclic durability.

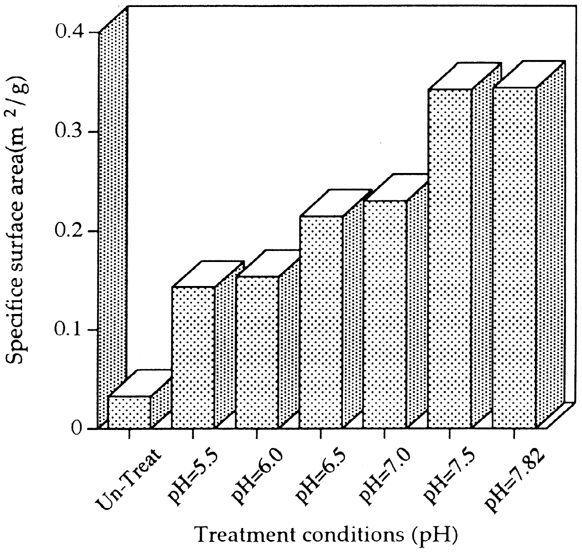

Fig. 1. The changes of the specific surface area after fluorination.

The Ni^{2+} containing solution as F-2 was developed in order to prevent the Ni dissolution and also to modify the electric conductivity at the surface. The amount of Ni dissolved in the solution correlates inversely proportional with the amounts of Ni^{2+} in F-2 solution can be seen from Fig. 3. The pH value changes during fluorination process is illustrated in Fig. 4. Those reactions are summarized in the following equations for a $LaNi_{4.7}Al_{0.3}$ specimen

$$Ni^{2+}\text{ (added into solution)} + nF^{-} \leftrightarrow [NiF_n]^{2-n} \tag{4}$$

$$NiO\text{ (on alloy surface)} + nF^{-} + 2H^{+} \leftrightarrow [NiF_n]^{2-n} + H_2O \tag{5}$$

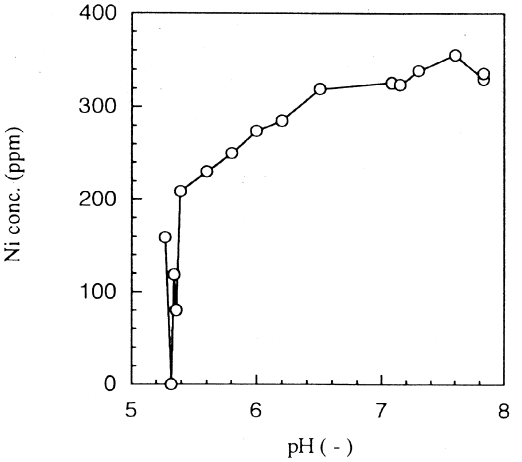

Fig. 2. Concentration curve of Ni dissolved in the fluorination solution.

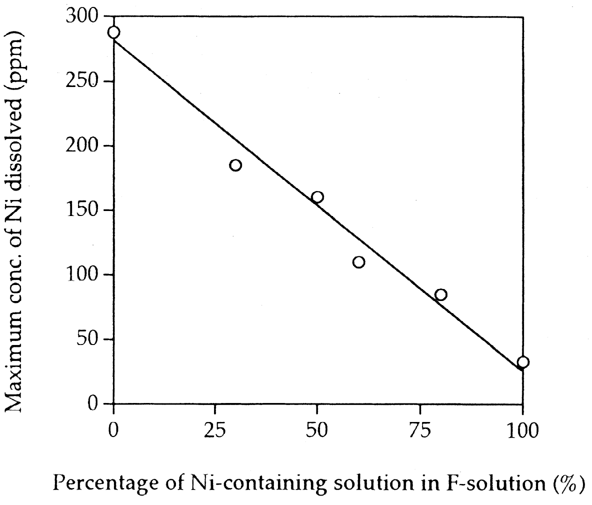

Fig. 3. Relationship between the amount of dissolved Ni and the amount of Ni contained in the fluorination solution.

$$Ni\text{ (in alloy)} + nF^{-} + 2H^{+} \leftrightarrow [NiF_n]^{2-n} + H_2\uparrow \tag{6}$$

$$2La\text{ (in alloy)} + 6F^{-} + 6H^{+} \leftrightarrow 2LaF_3 + 3H_2\uparrow \tag{7}$$

Those reactions initiated from the formation of $[NiFn]^{2-n}$ in the Ni-containing F-2 solution (Eq. (4)), and then oxide layer is removed by free F^{-} ions in the solution (Eq. (5)). The last reaction followed after those two preceding reactions for forming LaF_3 (Eq. (7)). The reactions (Eq. (4)) and (Eq. (5)) are quicker than the reaction (Eq. (6)) because they have not needed the oxidation process included in the reaction (Eq. (6)) so that metallic Ni dissolution from alloys is prevented.

The control of the Ni^{2+} contents in the F-2 solution results in a considerable variation in the pH value changes during fluorination. During the course of changing the pH, formation of LaF_3 was strongly dependent on the acidity of the solution. At the pH value lower than 6.5, $[NiFn]^{2-n}$

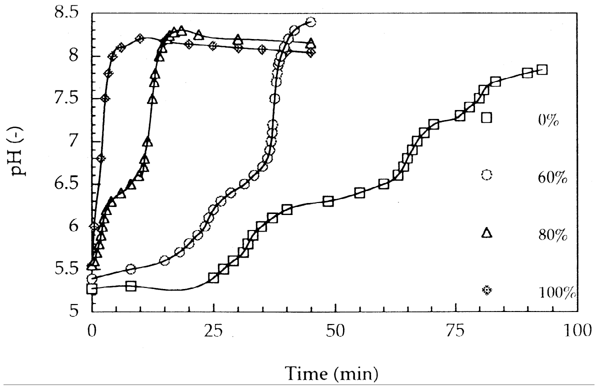

Fig. 4. Curves of pH-change vs time during fluorination.

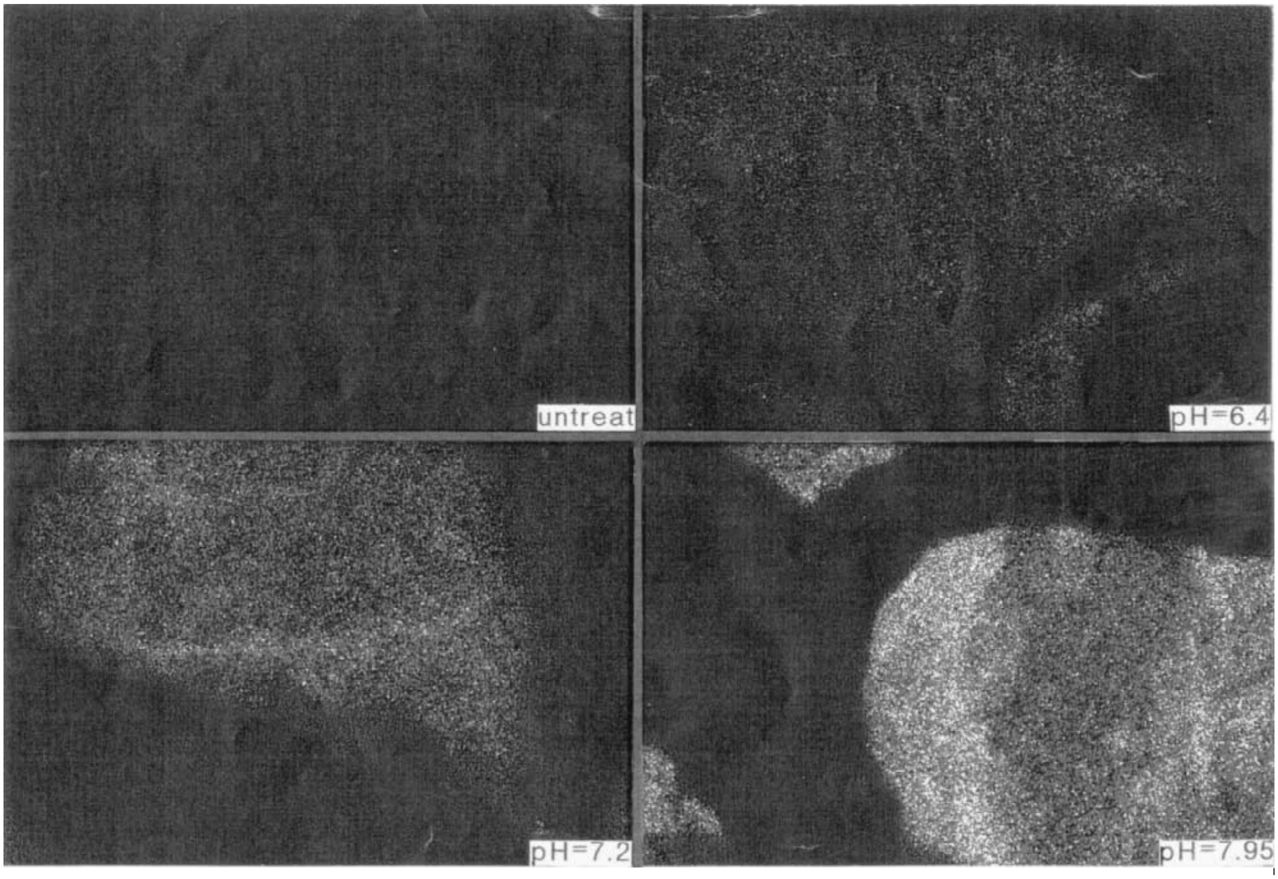

Fig. 5. An EPMA photo-mapping of F-element on $LaNi_{4.7}Al_{0.3}$ alloy surface after F-1 fluorination.

formation in the solution was regarded as the dominating reaction and the formation of fluoride layer at the surface started after pH value exceeding 6.5 as seen in Fig. 5.

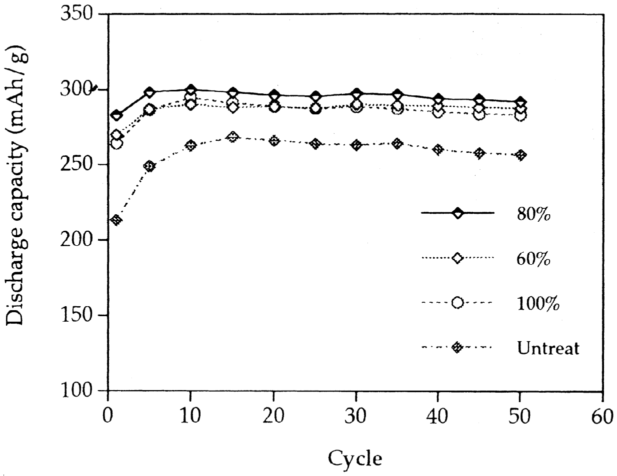

Fig. 6. Effects of F-2 fluorination on the electrochemical characteristics of AB_5 alloy.

3.4. Electrochemical characteristics of the fluorinated alloy electrodes

Fluorination effects by applying F-2 solution were examined by evaluating the initial discharge characteristics, discharge capacity, and *C*/*D* cycle life under the experimental conditions listed in Section 2.4. The data were taken by varying the Ni^{2+} ratio in the F-2 solution and the results were given in Fig. 6. It can be seen from the figure that the combination of the specific surface area and the Ni^{2+} put in F-2 solution decides the optimum electrochemical characteristics of the fluorinated electrode materials.

4. Conclusions

1. Fluorination by F-2 solution is effective for removing the surface oxides, increasing the specific surface area and improving the initial activation characteristics at the starting *C*/*D* cycles.
2. Ni dissolution in F-1 solution is prevented by using F-2

solution, and it contributes to the improvement of the surface electric conductivity.

3. The pH value control results in the optimum formation of the fluoride layer at the surface.

Acknowledgments

The authors wish to express their gratitude to NEDO (New Energy Technology Development Organization) and ATST (Agency of Industrial Science & Technology) of MITT (Ministry of International Trade and Industry) for their funding. The authors thank Dr. Z-P. Li, an invited researcher at Kogakuin University, for his assistance in the evaluation of electrochemical performance of the fluorinated electrodes.

References

[1] F.-J. Liu, G. Sandrock and S. Suda, *Trans. Mat. Res. Soc. Jpn.*, 18B (1994) 1237–1244.
[2] F.-J. Liu and S. Suda, *J. Alloys Comp.*, 231 (1995) 411–416.
[3] X.-L. Wang and S. Suda, *J. Alloys Comp.*, 22 (1995) 58–62.
[4] M. Nogami and O. Furukawa, *J. Japanese Chemical Association*, 1 (1995) 1.
[5] F.-J. Liu and S. Suda, *J. Alloys and Compounds*, 230 (1) (1995) 58–62.
[6] H.-Y. Zhu, C-P. Chen, Y.-Q. Lei, J. Wu and Q.-D. Wang, *J. Less-Common Met.*, 873 (1991) 172–174.
[7] S. Suda and G. Sandrock, *Phys. Chemie*, 183 (1994) S. 149–156.
[8] Japanese Patent, TOKUKAI HEI 5-213601, *Methods for Stabilizing or Activating Metallic Materials*, Japan Research & Development Corporation, 1993.
[9] S. Suda, *Research Repots of Kogaguin University*, 74 (1993) 28–34.
[10] X.-L. Wang and S. Suda, *J. Alloys Comp.*, 231 (1995) 380–386.