ELSEVIER

Journal of Alloys and Compounds 330–332 (2002) 627–631

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

# Studies on the fluorination method for improving surface properties and characteristics of $AB_5$-types of hydrides

Y.-M. Sun*, S. Suda

*Department of Environmental and Chemical Engineering, Chemical Energy Laboratory, Kogakuin University, Nakano-machi 2665-1, Hachioji-shi, Tokyo 192-0015, Japan*

## Abstract

A fluorination technique aiming at increasing the specific surface area has been studied in this work. The fluorination process as a surface improvement procedure has been studied with regards to its fluoride formation mechanisms. In this paper, the proposed fluorination process is based on the control of pH values in a certain range by adding a buffer solution. Buffer solutions suitable for controlling pH change were considered and were selected. Surface structures and composition changes have been studied by ICPS, SEM, and EPMA.

*Keywords:* Fluorination; Surface properties; $AB_5$-type hydrides

## 1. Introduction

Among major rate-limiting factors that restrict hydrogen uptakes both in gas–solid and electrochemical reactions, surface properties and characteristics of hydriding alloy particles have been studied with regard to the improvements of the inherent shortcomings of hydriding alloy as pointed out previously [1]. A chemical treatment method in which a weak acid F-solution was applied to remove $La_2O_3$ and then to form a $LaF_3$ layer on the extreme surface of $LaNi_{4.7}Al_{0.3}$ particles has been developed [2]. It was found that judging from the three stepwise changes in pH values observed during fluorination processes of $LaNi_{4.7}Al_{0.3}$ particles, the first stage was found to be related to the removal of oxide layer, the second stage to the dissolution of Ni as $[NiF_4]^{2-}$ in the pH ranges of 5.5 and 6.5, and the third stage to the formation of fluorides (for example, $LaF_3$ or $AlF_3$) in the pH ranges of 6.5–8.0 [3]. It was experimentally confirmed that the formed fluorides contributes to increase of specific surface area and accelerates hydriding kinetics considerably.

This study is related to an F-treatment method developed that is based on the pH control during fluorination by using buffer solutions to maintain pH value within a certain level (6.0–8.0) for improving surface properties and characteristics of $AB_5$ hydriding alloys in order to increase the specific surface area and to enhance the initial activation characteristics.

## 2. Experimental details

$LaNi_5$-based alloys were ground mechanically to prepare average particle size of about 35 μm. The powder then was fluorinated by the free $F^-$ ions supplied from an aqueous solution composed of HF and KF where the pH value had been maintained within a certain range by adding $CH_3COOH$–$CH_3COONa$ buffer solutions. Fluorination conditions were consecutively varied under various constant pH value conditions in order to obtain the optimum fluorinated surfaces. Dissolution of specific metallic elements after the fluorination was analyzed by ICPS, and the surface composition of those samples was analyzed by SEM and EPMA. A BET method was used to determine the specific surface area of particles. Initial

---

*Corresponding author.

*E-mail address:* bq96002@ns.kogakuin.ac.jp (Y.-M. Sun).

0925-8388/02/$ – see front matter
PII: S0925-8388(01)01668-1

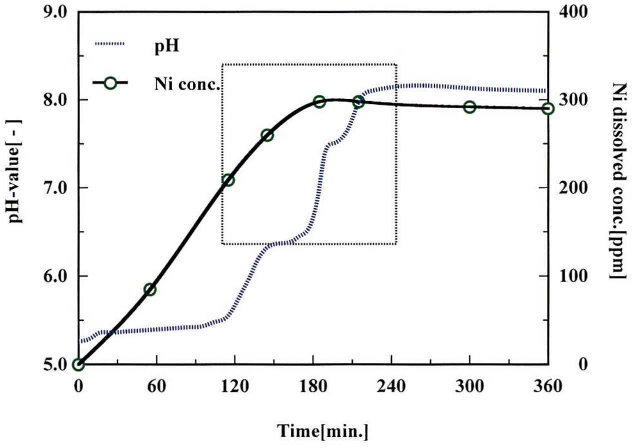

Fig. 1. pH change versus Ni concentration dissolved.

activation kinetics were measured at 40°C for both the fluorinated and unfluorinated samples by using a Sieverts apparatus as reported earlier [4].

## 3. Experimental results and discussions

### *3.1. The pH control by buffer solutions*

Figs. 1 and 2 illustrate the relations of pH changes with the concentration of Ni dissolved and the specific surface area change during fluorination of $LaNi_5$-based alloy. The pH value changes during 120 min resulted in Ni dissolution of ca. 200 ppm. After 120–240 min, the pH value was changed quickly but with less Ni dissolution, and the specific surface area was increased considerably during the later part of fluorination. The pH value regions of 6.0–8.0 were judged to contribute to increasing the specific surface area. However, it was concluded that the fluorination technique was not practical because of the time required (a few hours) to increase the specific surface area. Therefore, it would be more practical from engineering viewpoints to develop an alternative fluorination technique.

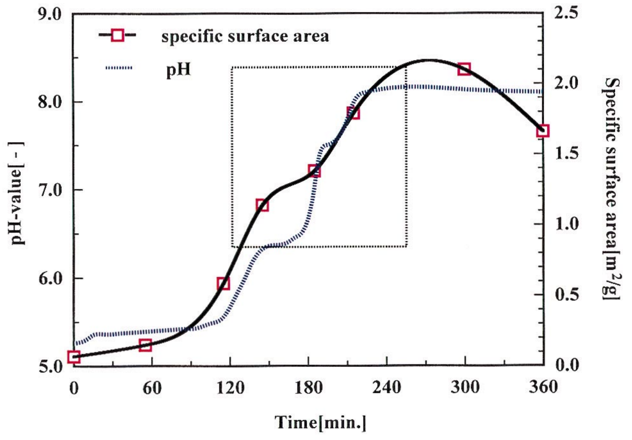

Fig. 2. pH change versus specific surface area change.

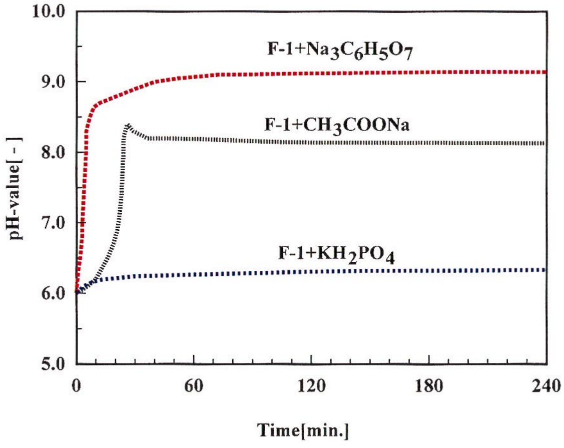

Fig. 3. Buffers effects on the fluorination process.

Buffer solutions that contain $KH_2PO_4$, $Na_3C_6H_5O_7$, and $CH_3COONa$ were tested in order to control the pH value between 6.0 and 8.0 during fluorination processes. As can be seen in Fig. 3, $KH_2PO_4$ solution with the pH value at 6.0 was found not effective to increase the specific surface area as has been expected. In the case of $Na_3C_6H_5O_7$ solution, the pH value was varied too fast up to 8.0 (in some cases, higher than 8.0) within a few minutes, but failed to form a fluoride layer without increasing the specific surface area. On the contrary, $CH_3COONa$ solution was found effective for both the formation of fluoride layer and the increase of specific surface area.

From these experimental results, it was concluded that the $CH_3COONa$ solution is a suitable buffer solution to maintain pH ranges of 6.0–8.0 during fluorination processes.

### *3.2. State of elements dissolved*

Fluorination treatments were performed under three different conditions in pH ranges of 6.0–6.5 (F-4a), 6.0–7.0 (F-4b), and 6.0–8.0 (F-4c), respectively, as shown in Fig. 4. It was found that the cycle numbers operated by controlling pH value decreased with widening of pH range by the use of a buffer solution, but the amount Ni dissolved into F-solution from the particle surface did not increase with the increasing of cycle numbers because of the formation of fluorides. The anionic complexes of La and Al were not detected in the F-solution by ICPS analysis because $LaF_3$ and $AlF_3$ were formed and stayed on the alloy surface.

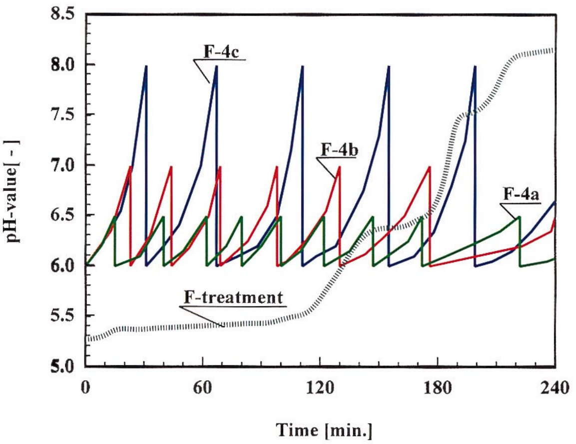

Fig. 4. The controls of pH changes during F-4 treatment process.

### 3.3. *Specific surface area and particle diameter*

The specific surface areas of fluorinated particles prepared under various conditions are shown in Fig. 5. The specific surface area treated by F-4b (pH 6.0–7.0) was three times larger than those treated by other conventional fluorination methods and 84 times larger than the untreated particles.

The diameters of particles treated under different conditions are shown in Table 1. The median particle diameter and the model particle diameter did not change. However, the calculated specific surface area diameter [5] decreased obviously.

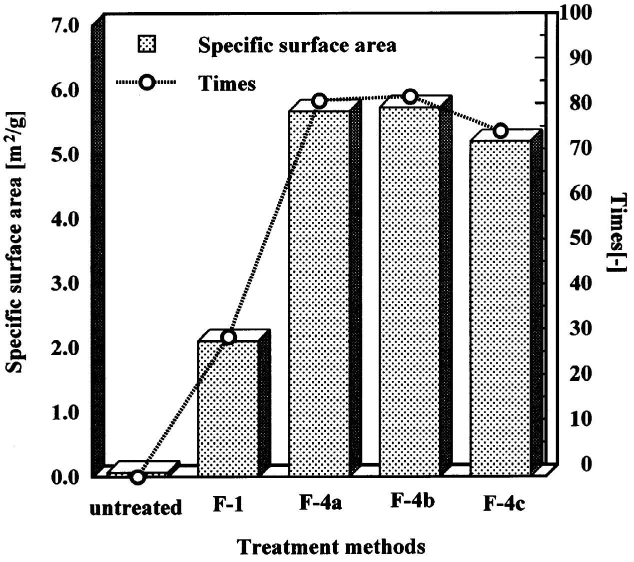

Fig. 5. The increases of specific surface area after F-4 treatment.

Table 1
The results of determined specific surface area and particle diameter

| Treatment | Median particle diameter (μm) | Model particle diameter (μm) | Specific surface area ($m^2/g$) | Specific surface area diameters (μm) |
|---|---|---|---|---|
| Untreated | 73.9 | 71.1 | 0.07 | 11.2 |
| F-1 | 74.8 | 71.1 | 1.79 | 0.424 |
| F-4a | 75.1 | 71.1 | 5.66 | 0.134 |
| F-4b | 75.3 | 71.1 | 5.72 | 0.133 |
| F-4c | 76.2 | 71.1 | 5.20 | 0.146 |

Specific surface area diameter $D_s = 6/\rho_p \cdot S_w$ ($\rho_p$, density; $S_w$, specific surface area),

### 3.4. *Surface state*

An SEM image of a $LaNi_5$-based alloy particle surface is shown in Fig. 6. The unfluorinated particle had a smooth surface morphology; however, the fluoride layer covered it uniformly after fluorination treatment. Furthermore, after F-4 fluorination treatment, the particle surface had a more complex structure, in which fine crystals of La-fluoride or Al-fluoride were formed, as seen in Fig. 7. The fine crystals have a size less than 1.0 μm; therefore, the formation of very large specific surface area is reasonable.

### 3.5. *F-4 fluorination effect on hydriding reaction*

The effects are attributed to the formation of La-fluoride layer, which is known to exhibit a high affinity to hydrogen, as proved in the $AB_5$ alloy [6]. Fluorination treatment further improves the activation kinetics in the gas–solid hydriding reaction compared with the untreated samples, as shown in Fig. 8. The oxides were removed from the particle surface by formation of fluorides, exhibiting more effective improvement for accelerating initial activation rate. After F-4 fluorination, the incubation time took 3 min, while the untreated alloy took 3 h.

## 4. Conclusion

For the F-4 treatment method, a $CH_3OOH$–$CH_3OONa$-containing buffer solution was found suitable for controlling pH change during fluorination. By controlling pH changes, fluorination was promoted due to the formation of fluoride layers in extremely fine structures over the surface. These fine structures were observed by an EPMA analysis and determined by a specific surface area measurement.

By applying the F-4 fluorination technique, the specific surface areas of particles were found to be three times larger than those treated by other conventional fluorination methods and 84 times larger than the untreated particles. In

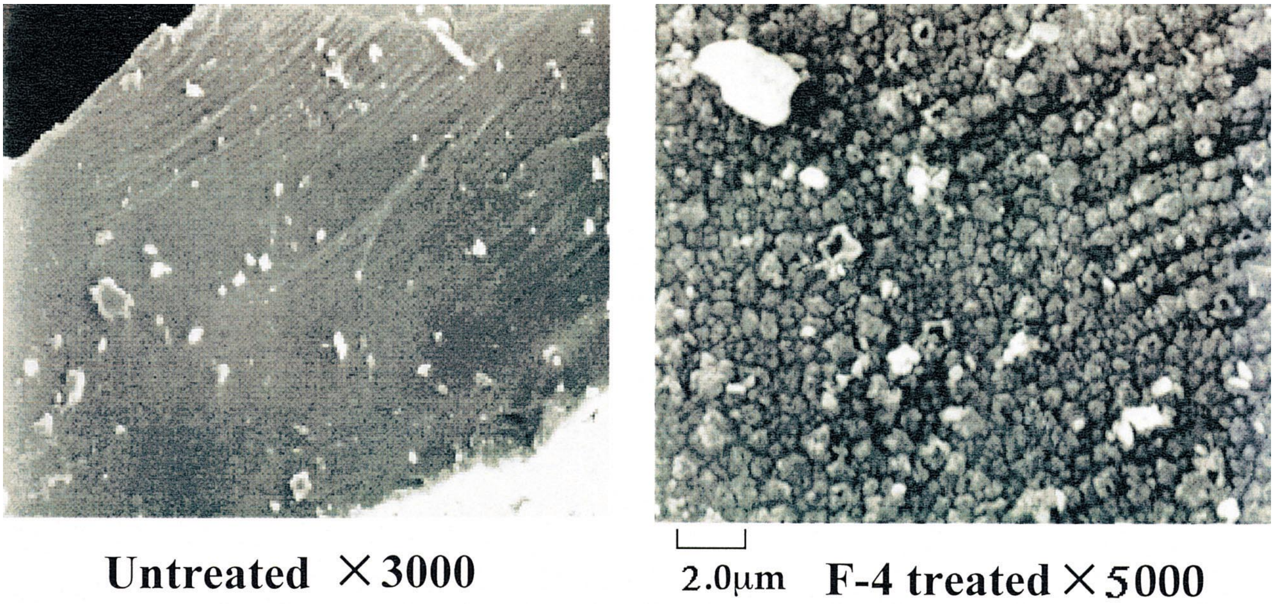

Fig. 6. SEM photographs of the alloy particle surface.

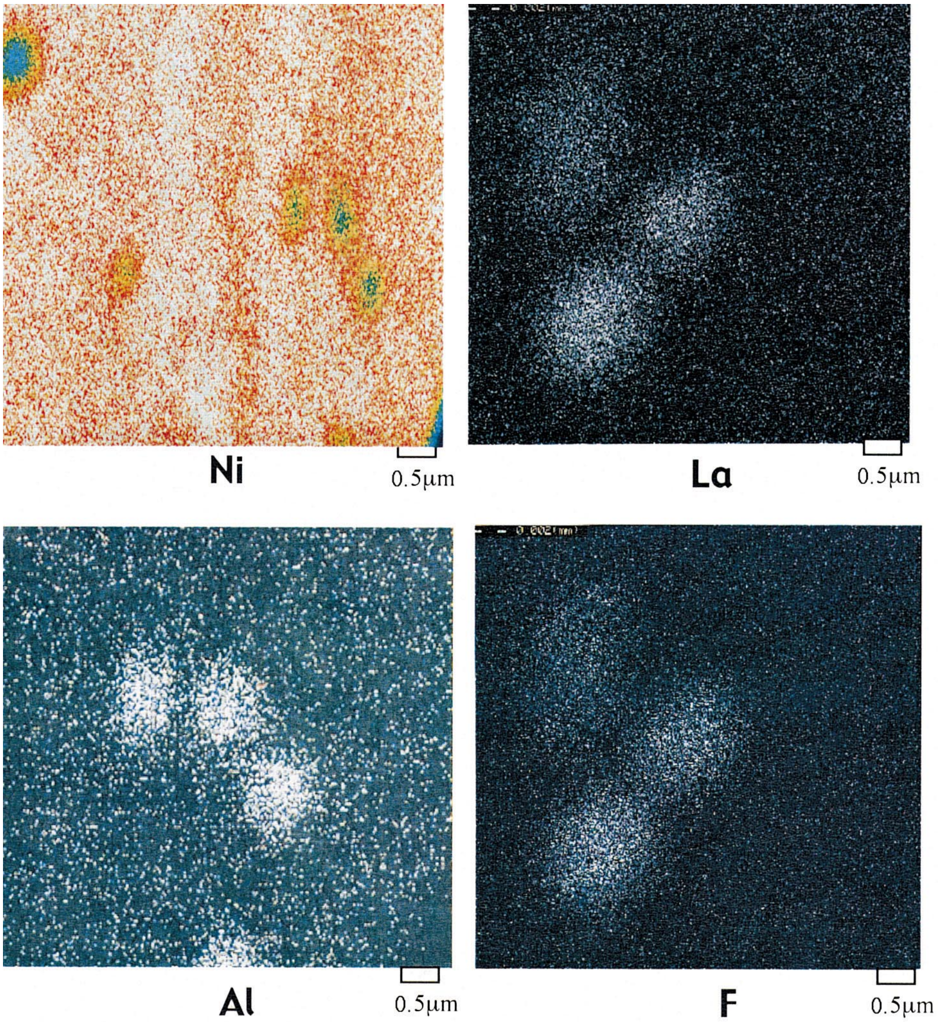

Fig. 7. Mapping photographs of elements on the particle surface.

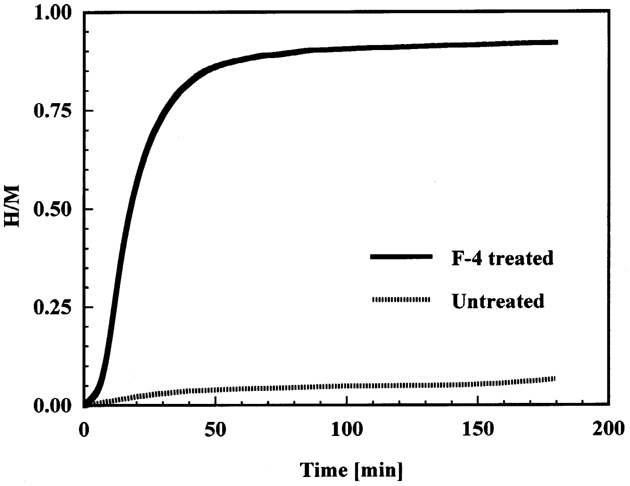

Fig. 8. F-4 treatment effect on the initial activation for gas–solid reaction.

view of the reaction rates, F-4 treated particles exhibited extremely high kinetics when compared with the untreated samples.

## References

[1] G.D. Sandrock, S. Suda, L. Schlapbach, Hydrogen in intermetallic compounds II, Top. Appl. Phys. 67 (1992) 200.

[2] S. Suda, H. Fuse, K. Nakajima, T. Okazaki, A. Hiromoto, Res. Rep. Kogakuin Univ. 75 (1993) 41–47.

[3] Y.-M. Sun, K. Iwata, S. Chiba, Y. Matsuyama, S. Suda, J. Alloys Comp. 253–254 (1997) 520–524.

[4] F.-J. Liu, M. Ito, S. Suda, Res. Rep. Kogakuin Univ. 72 (1992) 85–89.

[5] K. Kawakita, Powder processing (Japanese textbook), Maki Sho Ten, 1974, pp. 44–45.

[6] F.-J. Liu, G. Sandrock, S. Suda, J. Alloys Comp. 190 (1) (1992) 57–60.