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Fluorination mechanism and its effects on the electrochemical properties of metal hydrides

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Abstract

Fluorination of hydriding alloys has been found effective for improving durability and initial discharge characteristics of hydride electrodes in Ni–MH rechargeable batteries. However, it has also been found that it decreases the discharge capacity because of the fluoride formed on the surface which decreases the electrical conductivity of the electrode. A more advanced technique has been developed in this laboratory to implant metallic Ni in the fluoride layer to form a functionally graded surface layer. The proposed fluorination technique considerably improves the durability and initial activation characteristics of AB_5-types of hydride, electrodes and also the initial activation characteristics of AB_2 electrodes. The fluorination was found effective for removing the oxide layer which acts as an impedance to electrochemical hydrogen uptake.

Keywords: Fluorination; Fluorinated hydriding alloy; Functionally graded surface layer; Hydride electrode; Discharge capacity; Durability

1. Introduction

In general, AB_2-type alloys have comparatively higher discharge capacities than those of AB_5-type alloys, but it is well-known that they have poor activation characteristics and slower kinetics [1]. It has been observed that fluorination usually decreases the discharge capacity due to the formation of a Ni-lean fluoride layer with poor electrical conductivity, although it can improve the durability in the charge/discharge cycle life [2]. A chemical plating technique has been proposed by Sakai et al. [3,4] in view of the electrical conductivity improvement, but at the expense of capacity.

In this paper, a more advanced technique is studied for formation of a functionally graded surface layer in which metallic Ni is distributed in the fluoride layer.

An aqueous fluorine-containing solution (denoted as F-solution) which is made by mixing KF and HF solutions has been applied for fluorinating the surface of AB_5 hydriding alloy particles. The F-solution exhibits a pH value between 4.5 and 6.5 where the F^- ions (so called ‘free F^- ions’ are supplied from HF_2^- ions and HF in equilibrium with H^+, F^- and HF_2^- under the presence of K^+ and OH^- ions. During the fluorination process, a Ni-lean fluoride layer is formed by reaction with rare earth metals contained in AB_5 alloys and the process accompanies the dissolution of a considerable amount of Ni into the F-solution [5]. Reduction of the electrical conductivity of the fluorinated particle is attributed to Ni dissolution during the fluorination process.

The conventional fluorination technique has been observed to be effective in eliminating the oxide layer from the surface but not effective for forming insoluble and stable fluorides in the case of AB_2 alloys where the Ti- and Zr-fluorides dissolve easily in F-solutions by forming complex ions.

An F-solution which contains a Ni-salt (NiF_2), reductant (sodium phosphinate monohydrate) and ligand (trisodium citrate dihydrate) for stabilizing Ni^{2+} was developed in order to implant metallic Ni in the surface layer. Details of the F-solution are described in Japanese patents [6,7]

2. Electrochemical measurements

The hydride electrodes were made by mixing alloy powders with Ni and PTFE powders in a weight ratio of 5:15:1, packed with a Ni-grid of 100 mesh and then pressed into pellets with diameters of 13 mm and thicknesses of 1.5 mm under a load of 4 $\mathrm{ton\,cm^{-2}}$. The electrodes were cycled by charging with a current of 200 $\mathrm{mA\,g^{-1}}$ for 3 h and then discharging at a current of 150 $\mathrm{mA\,g^{-1}}$ to a cut-off voltage of −0.6 V with respect to the

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Hg/HgO electrode in 6 N KOH after resting for 10 min at 20 °C.

3. Results and discussion

3.1. Fluorination

During the fluorination treatments with a conventional F-solution, the pH value changes from pH=5.3 up to 7.9, as shown in Fig. 1. The changes were caused by the removal of an oxide layer on the surface and the dissolution of metallic elements (mostly Ni) into the solution.

A typical example of the fluorination reactions of $LmNi_{4.0}Co_{0.4}Al_{0.3}Mn_{0.3}$ alloy (Lm=La rich mischmetal) can be illustrated by the following equations:

$$CeO_2 + La_2O_3 + 10F^- + 5H_2O = CeF_4 + 2LaF_3 + 10OH^- \quad (1)$$

$$Ce + La + 5F^- + 7H_2O = CaF_4 + LaF_3 + 3.5H_2 + 7OH^- \quad (2)$$

$$Ni + 6F^- + 2H_2O = [NiF_6]^{4-} + H_2 + 2OH^- \quad (3)$$

The $[NiF_6]^{4-}$ ion in Eq. (3) is an octahedral complex.

In the case of fluorination of the AB_2 alloy, it is not possible to obtain insoluble fluoride layers of Ti and Zr by the conventional F-solution where surface oxides are removed and Ti and Zr form complex ions to dissolve into the solution. When $ZrNi_2$ is treated, for instance, the ZrO_2, metallic Zr and Ni react with the F-solution to form $[ZrF_6]^{2-}$ and $[NiF_6]^{4-}$ which leave from the surface into the solution.

An F-solution which contains a reductant such as sodium phosphinate monohydrate was prepared in order to implant metallic Ni on hydriding alloy surfaces. A ligand such as trisodium citrate dihydrate was added to stabilize Ni ions by preventing the precipitation of metallic Ni out of the surface.

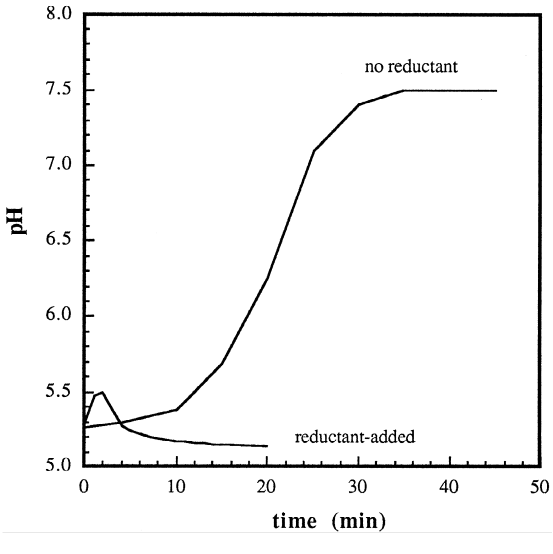


Fig. 1. pH value change of $LmNi_{4.0}Co_{0.4}Al_{0.3}Mn_{0.3}$ during fluorination.

The pH value first increased from pH=5.3 up to 5.5 and then decreased to 5.1 during treatment. After that, the value decreased slowly. Increases of the pH value are understood from the reactions for the removal of the oxide layer, dissolution of metallic elements and formation of fluorides. On the other hand, the decreases of the pH value can be attributed to the deposition of metallic Ni on the particle surfaces by the following reaction:

$$2H_2PO_2^- + 2H_2O + [Ni^{2+} \cdot C_6H_5O_7^{3-}] \rightarrow Ni^0 + 2HPO_3^{2-} + 4H^+ + H_2 + C_6H_5O_7^{3-} \quad (4)$$

where $C_6H_5O_7^{3-}$ is the ligand, and $H_2PO_2^-$ is the reductant.

The reactions of Eqs. (1)–(3) proceed rather quickly when oxide layers are removed to form fluorides at the beginning of the fluorination processes by increasing the pH value. After that, the reaction in Eq. (4), for implanting Ni on the surface, takes place slowly after the oxide layers are removed. The reaction in Eq. (4) becomes faster at the latter part of the fluorination reactions due to the increase of active sites for Ni implantation and the pH value starts to return to more acidic ranges. After that, the rate of Ni implantation slows down due to a decrease of the pH value of the F-solution. All details regarding the fluorination technique and procedures are given in the Japanese patents [6,7].

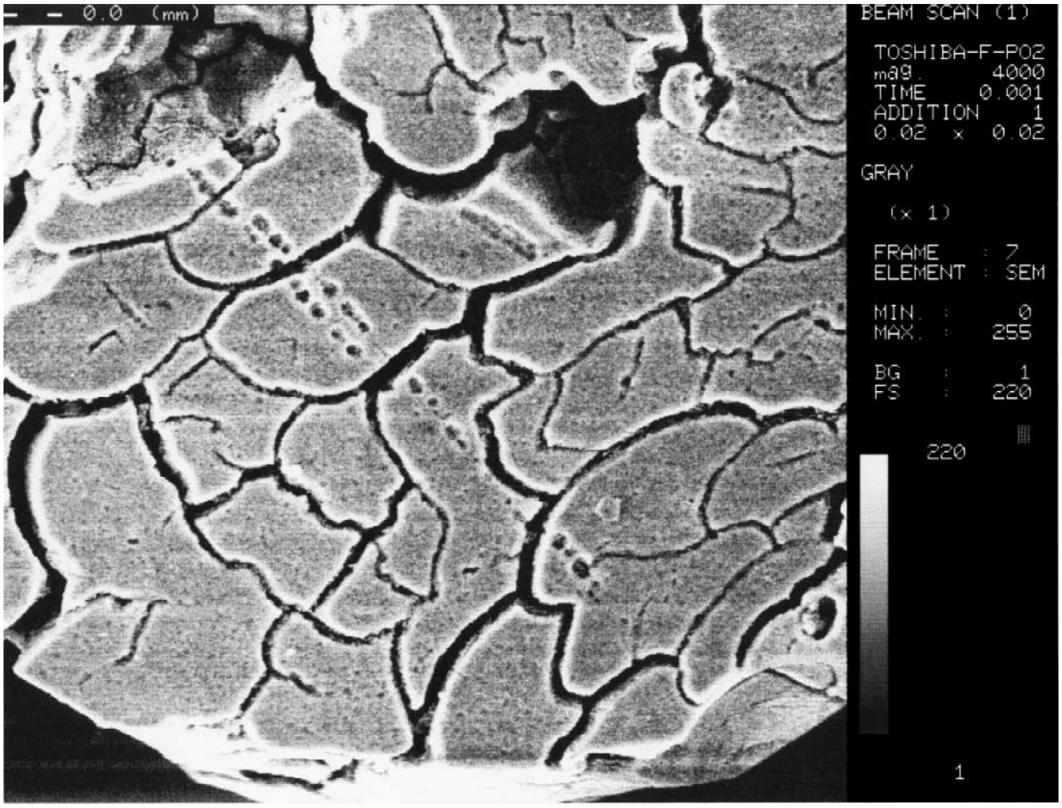
3.2. Surface

By changing the treatment condition, it is possible to control the speed of fluoride growth and Ni implantation as a functionally graded layer and to get different kinds of surface structure. The existence of fluoride and metallic Ni over the surface can be observed by XPS and EPMA analyses for the $LmNi_{4.0}Co_{0.4}Al_{0.3}Mn_{0.3}$ as a typical example of AB_5 hydriding alloys (shown in Fig. 2 Fig. 3).

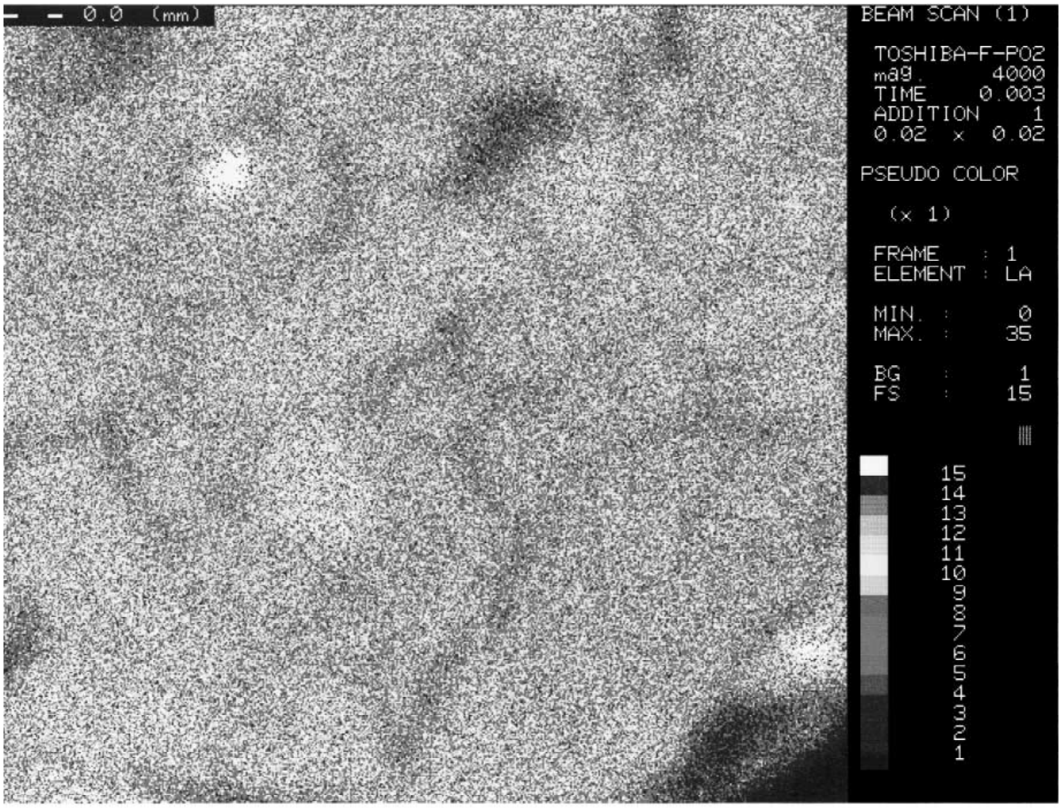
In the case of AB_2 alloys such as $Zr_{0.9}Ti_{0.1}V_{0.2}Ni_{1.1}Co_{0.1}Mn_{0.6}$, the treatment technique is applied for controlling the amount of the metallic Ni distributed on the surface layer by changing the treatment condition in those cases where the existence of the F^- ion was proven necessary for removing the oxide layer and providing active sites for Ni implantation.

3.3. Discharge capacity

The treatment technique reported here is very effective for the discharge characteristics of the $LmNi_{4.0}Co_{0.4}Al_{0.3}Mn_{0.3}$ alloy as shown in Fig. 4. A stable Ni by the fluoride layer protects not only the particle

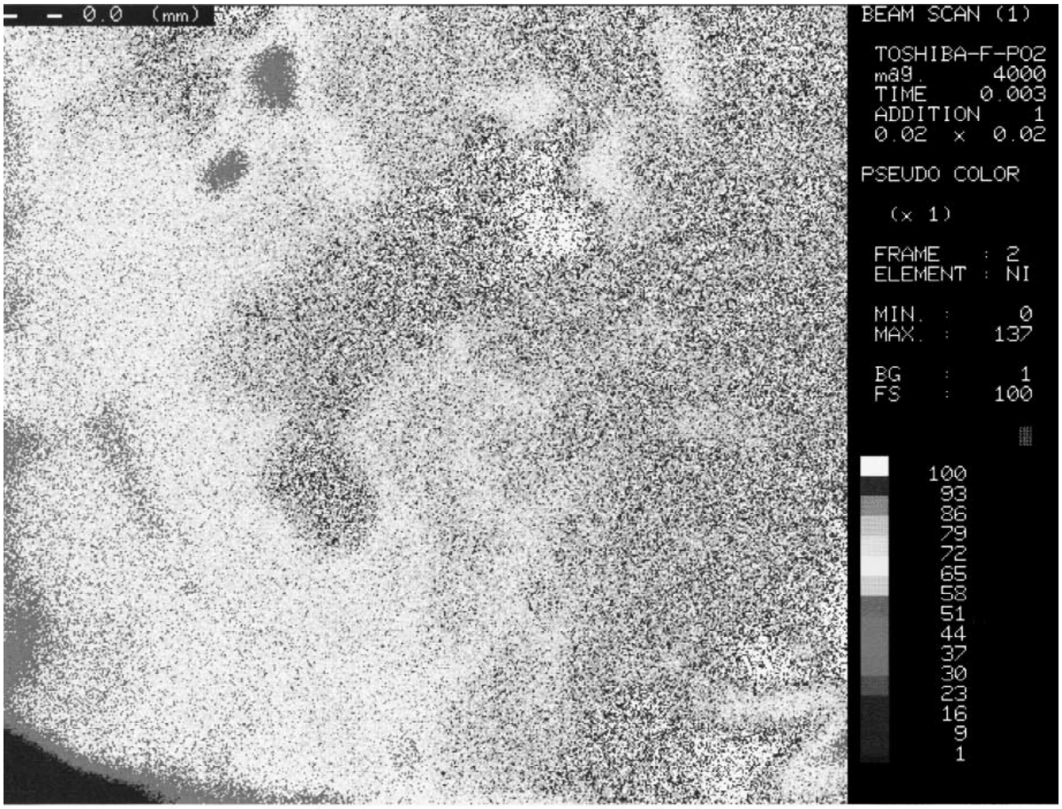


SEM

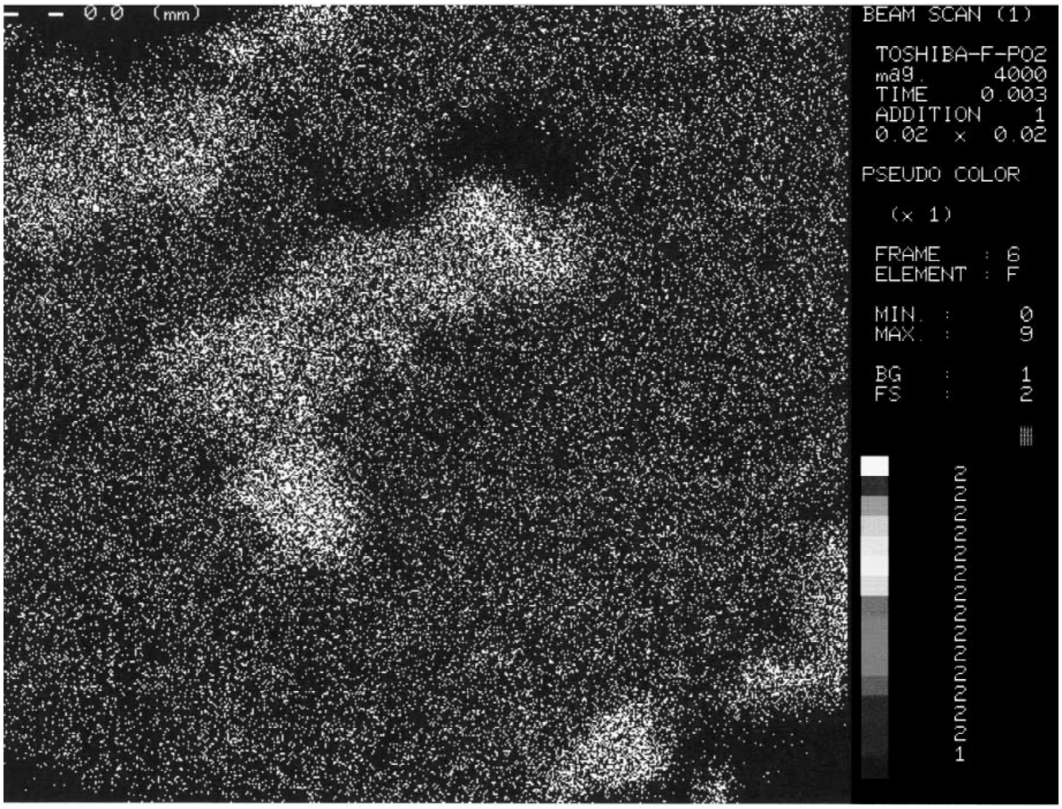


La distribution

Fig. 2. EPMA of F-Ni-fluorinated $LmNi_{4.0}Co_{0.4}Al_{0.3}Mn_{0.3}$ alloy.



Ni distribution



F distribution

Fig. 2. (*continued*)

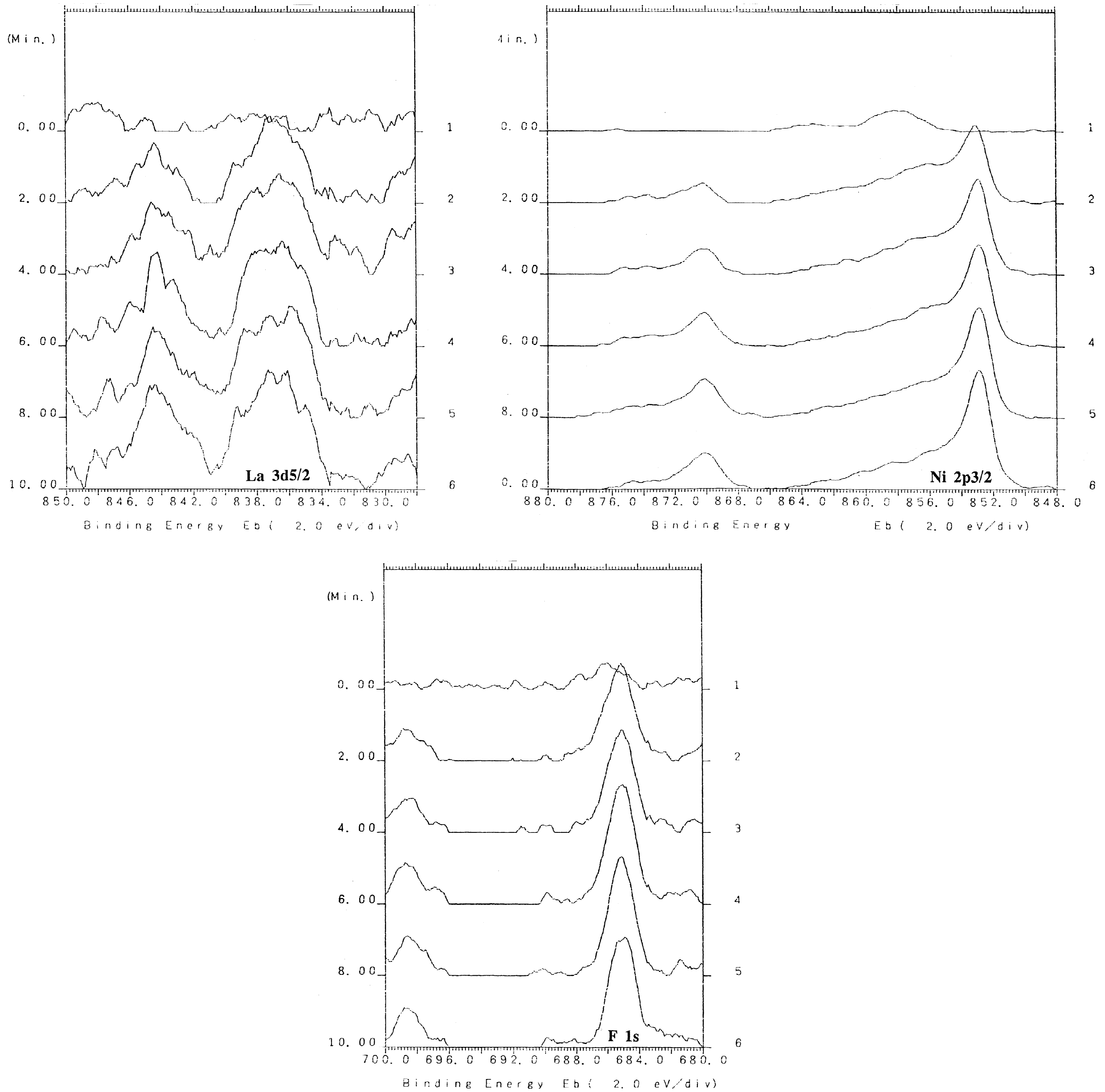


Fig. 3. XPS of F-Ni-fluorinated $LmNi_{4.0}Co_{0.4}Al_{0.3}Mn_{0.3}$ alloy.

surface from corrosion of the KOH electrolyte, but is also effective for increasing the initial discharge capacity.

In the treatment of an AB_2-type alloy such as $Zr_{0.9}Ti_{0.1}V_{0.2}Ni_{1.1}Co_{0.1}Mn_{0.6}$, the surface oxide layer was easily removed and the metallic Ni-containing structure was formed. The Ni-implanted layer activated the surface for hydrogen uptake during charging and improved significantly the initial discharge characteristics, as shown in Fig. 5.

4. Conclusions

By treatment of the hydriding alloy surfaces with Ni-containing F-solution, it has been found possible to synthesize a Ni-implanted surface layer as one of the typical functionally graded materials which is effective for removing oxides and protecting the surface from corrosion, and also improving the electrochemical properties and characteristics.

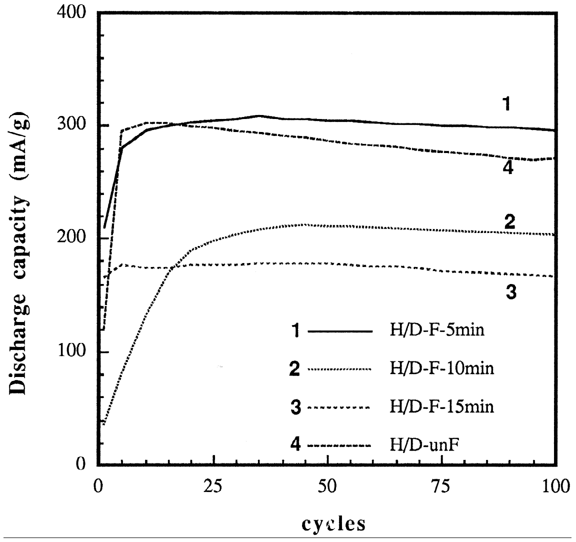


Fig. 4. Fluorination effect of fluorination time on electrochemical cycling behaviour of $LmNi_{4.0}Co_{0.4}Al_{0.3}Mn_{0.3}$ alloy under discharge current of 150 mA g^{-1} at 20 °C.

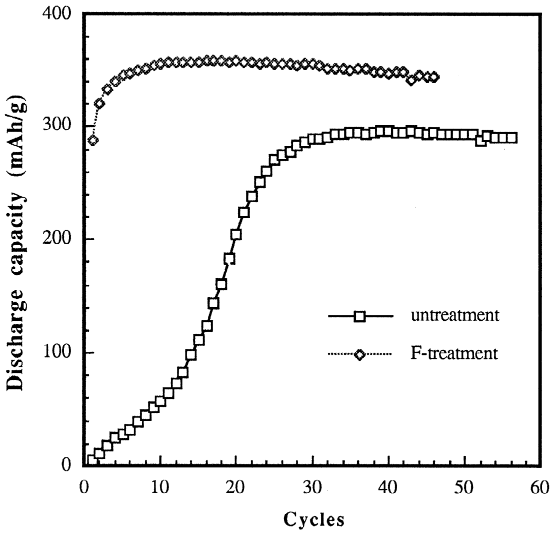


Fig. 5. Effect on electrochemical cycling behavior of $Zr_{0.9}Ti_{0.1}V_{0.2}Ni_{1.1}Co_{0.1}Mn_{0.6}$ alloy under discharge current of 150 mA g^{-1} at 20 °C.

References

[1] H. Sawa, M. Ohta, H. Nakano and S. Wakao, *Z. fur Phy. Chem. N.F., 164* (1989) 1527.

[2] Z.-P. Li, D.-Y. Yan and S. Suda, *Trans. Mat. Res. Soc. Jpn., 18B* (1994) 1209.

[3] T. Sakai, H. Ishikawa, K. Oguro and C. Iwakura, *Prog. Batteries Sol. Cells, 6* (1987) 221.

[4] T. Sakai, H. Ishikawa, K. Oguro, C. Iwakura and H. Yoneyama, *J. Electrochem. Soc., 134(3)* (1987) 558.

[5] S. Suda, H. Fuse, K. Nakajima, T. Okazaki and A. Hiromoto, *Research Reports of Kogakuin University, 75* (1993) 41.

[6] S. Suda, *Jpn. Tokyo Patent*, No. 4-199231, 1992.

[7] S. Suda, *Jpn. Tokyo Patent*, No. 8-118098, 1996.