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# Improvement of the electrochemical properties of Zr-based $AB_2$ alloys by an advanced fluorination technique

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## Abstract

An advanced fluorination technique has been developed for improving the electrochemical performances of Zr-based $AB_2$ alloys. During the procedure, alloys were ball milled in a complex fluoride solution. It was found that the electrode of the treated alloy exhibited excellent electrochemical performance. Its activation property and high-rate discharge capability were found to be satisfactory compared with the conventional $AB_5$-based electrodes. The electrode demonstrated a significant decrease of the reaction resistance measured by an impedance spectrometric method. The F-treated alloy was found to give a larger specific surface area and to form a highly Ni-covered surface. © 1999 Published by Elsevier Science S.A. All rights reserved.

*Keywords:* Surface treatment; Ball milling; Electrochemical performance; Activation; Rate capability

## 1. Introduction

With a relatively larger storage capacity than the conventional $AB_5$ alloys, Zr-based $AB_2$ Laves phase alloys have long been considered as potential candidates for the negative electrode material in the Ni–MH battery. However Zr-based alloy electrodes have some inherent drawbacks such as poor initial activity and low discharge capability at high discharge rates compared with their $AB_5$ counterpart. These shortcomings have to be cleared away before they can be put into practical use.

Extensive efforts have been made to improve the electrochemical performance of Zr-based alloys. Modification of alloy composition is one of the conventional ways. Incorporating some rare earth elements [1], increasing the amount of Ti, Mn etc, are found to be effective to enhance the surface activity of alloys. However, change of alloy composition has its limitations and sometimes induces undesirable damage on other properties. On the other side, surface treatments were proven to be an effective way to improve the surface properties while keeping the bulk untouched. Hot alkaline etching [2], hot-charging treatment [3] were such kinds of examples.

A series of so-called F-treatments have been developed in this laboratory [4], during which alloys were treated by a weakly acidic fluoride solution. These treatments were proven to be very effective for improving the initial surface activity of alloys both in the medium of $H_2$ gas and the electrolyte. Recently, a new F-treatment called F5-treatment was developed for the Zr-based $AB_2$ electrode materials [4]. Alloys were first pulverized by several hydriding–dyhydriding cycles and then treated by a Ni ion-containing complex fluoride solution at 50–80°C. After the treatment, it was found that the surface activity of these alloys was significantly improved because of the formation of a functional Ni layer. However, the high-rate discharge capacity of the treated alloy electrode was still inferior to that of $AB_5$ alloys. In this paper, an advanced F-treatment named F9-treatment will be reported, in which the alloy was treated by the complex fluoride solution during a ball milling process. A highly active surface with a large specific area was achieved through the treatment. The treated alloy electrode was easily activated and its high-rate discharge capability was comparable to the conventional AB5 alloy.

XRD, SEM, ICPS analysis and surface area measurements were performed in order to elucidate the reasons of the improvement.

## 2. Experimental details

A multi-component alloy $Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$ was used as a standard material in this study. The alloy sample was prepared by vacuum induction melting and then annealed at 1100°C for 18 h. After being mechanical-

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ly crushed to less than 200 mesh, alloy powder was ready for the F9 treatment.

During the so-called F9 treatment, alloy samples were put in a stainless steel bowl together with several small stainless steel balls. Then a certain volume of a Ni ion-containing complex fluoride solution was added. There was no reduction agent included in the solution. The bowl was sealed in the air and then set on a Fristch pulverisette 7 planetary micro mill. A typical ball milling parameter is 2750 rpm for 90 min. After the ball milling, the alloy sample was rinsed by deionized water for five times and then dried in a vacuum dryer.

An typical $AB_5$ alloy $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ prepared by gas atomization with a size of less than 100 μm was used in order to compare its electrochemical property with the F-treated $AB_2$ alloy.

Pellet-type alloy electrodes were prepared by mixing 1 g of alloy powder with 0.05 g of PTFE, wrapping the mixture in a nickel net and then pressing at 4 ton/cm$^2$. The pellets have a size of 13 mm in diameter and 1.5 mm in thickness.

Electrochemical tests were performed on a multi-channel automatic charger–discharger. Electrochemical characteristics of the alloy electrodes were tested in a three-electrode system consisting of a negative electrode, two counter electrodes and a Hg/HgO reference electrode. Alloy electrodes were first activated by five charging–discharging cycles during which the electrodes were charged at 68 mA/g (0.2 C) for 6 h, rested for 1 h and then were discharged at 68 mA/g to −0.6 V versus Hg/HgO. Then discharge capacities at different discharge rates were measured, where the charging condition was kept at 68 mA/g for 6 h. After that, the charge rate capability was measured by changing the charge current while keeping the charge capacity at 100% and discharge current at 68 mA/g.

## 3. Results and discussion

### 3.1. Electrochemical charateristics

The employed multi-component alloy has a C15 single phase structure after being annealed at 1100°C for 18 h. When compacted with a large amount of Ni powder, the alloy can finally reach a capacity as high as 380 mAh/g at 0.2 C rate.

### *3.1.1. Activation behavior*

The initial activation behaviors of the untreated and F-treated alloy electrodes are illustrated in Fig. 1. The untreated alloy electrode was prepared with an alloy powder pulverized to less than 25 μm by five hydriding–dehydriding cycles in $H_2$ gas. The F5-treated alloy electrode was made of the same H/D pulverized alloy powder but treated by the fluoride solution at 70°C for 30 min. As can be seen in Fig. 1, the untreated alloy shows a very poor activation behavior. Its capacity gradually climbs up during the first few cycles. However, far from reaching the potential value, the capacity begins to decline only after several cycles. The maximum capacity can only reach half of the potential value. In contrast, as can be seen from Fig. 1, the electrodes of F-treated alloys exhibit a superior activity even at the first cycle. The maximum capacity could be reached within 2–3 charging–discharging cycles for the F9-treated alloy electrode.

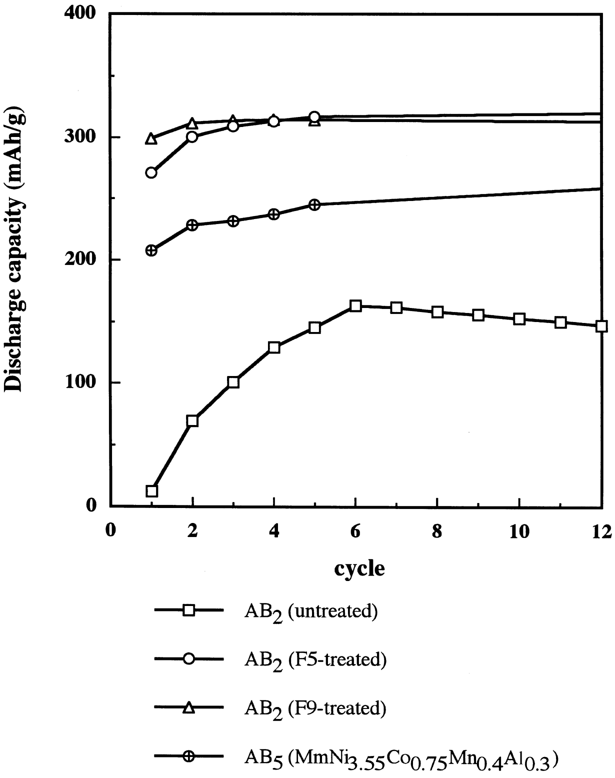


Fig. 1. Activation characteristics of the untreated and F-treated alloy electrodes.

### *3.1.2. High-rate discharge capability*

After five charging–discharging cycles at a 0.2 C rate for activation, the rate discharge capacities of the electrodes were measured by varying the discharge currents from 0.1 C to 2 C. As shown in Fig. 2, the F-treated alloys demonstrated rather good high-rate discharge capability. An even higher capacity at 2 C rate was obtained for the F9-treated alloy. Its high-rate discharge capability is comparable to the conventional $AB_5$ alloy $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$, as can be seen in the figure.

### *3.1.3. High-rate charge capability*

Charge rate capabilities of the electrodes were measured by changing the charge current from 0.1 C to 2 C while keeping the charge capacity at 100% and discharge current at 0.2 C. As can be seen from Fig. 3, the F-treated alloy electrodes also show rather good charge rate capability.

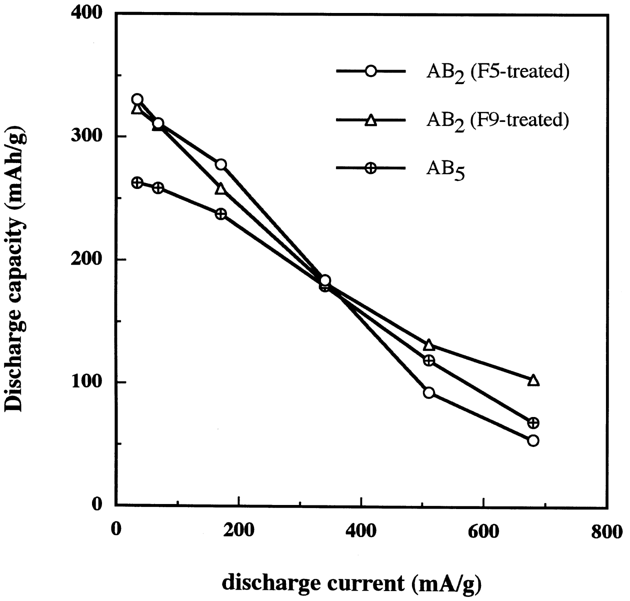


Fig. 2. Discharge capacity versus discharge current for the F-treated alloy electrodes.

### 3.1.4. Electrochemical impedances

The kinetics of electrode process can be well characterized by its electrochemical impedance spectrum. In this study, electrochemical impedance spectra of the electrodes were examined right after above properties were obtained. As can be seen from Fig. 4, the F9-treated electrode shows a remarkably reduced reaction resistance. The small reaction resistance can explain the excellent rate capability of the treated alloy.

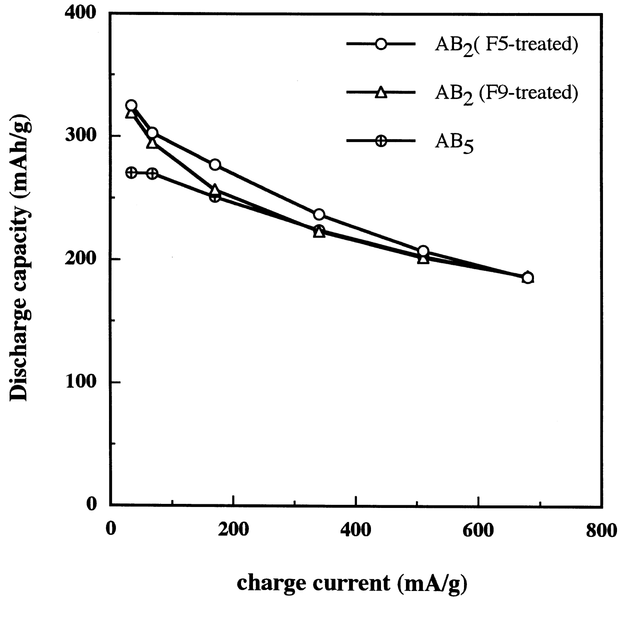


Fig. 3. Discharge capacity versus charge current for the F-treated alloy electrodes.

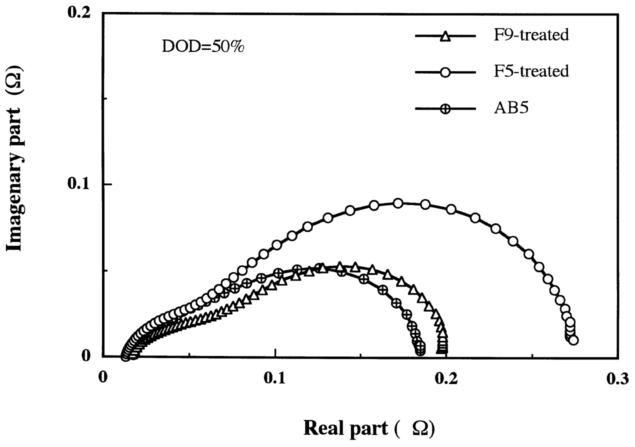


Fig. 4. Impedance spectra of the electrodes at DOD=50%.

### 3.2. Structure and micro-analysis

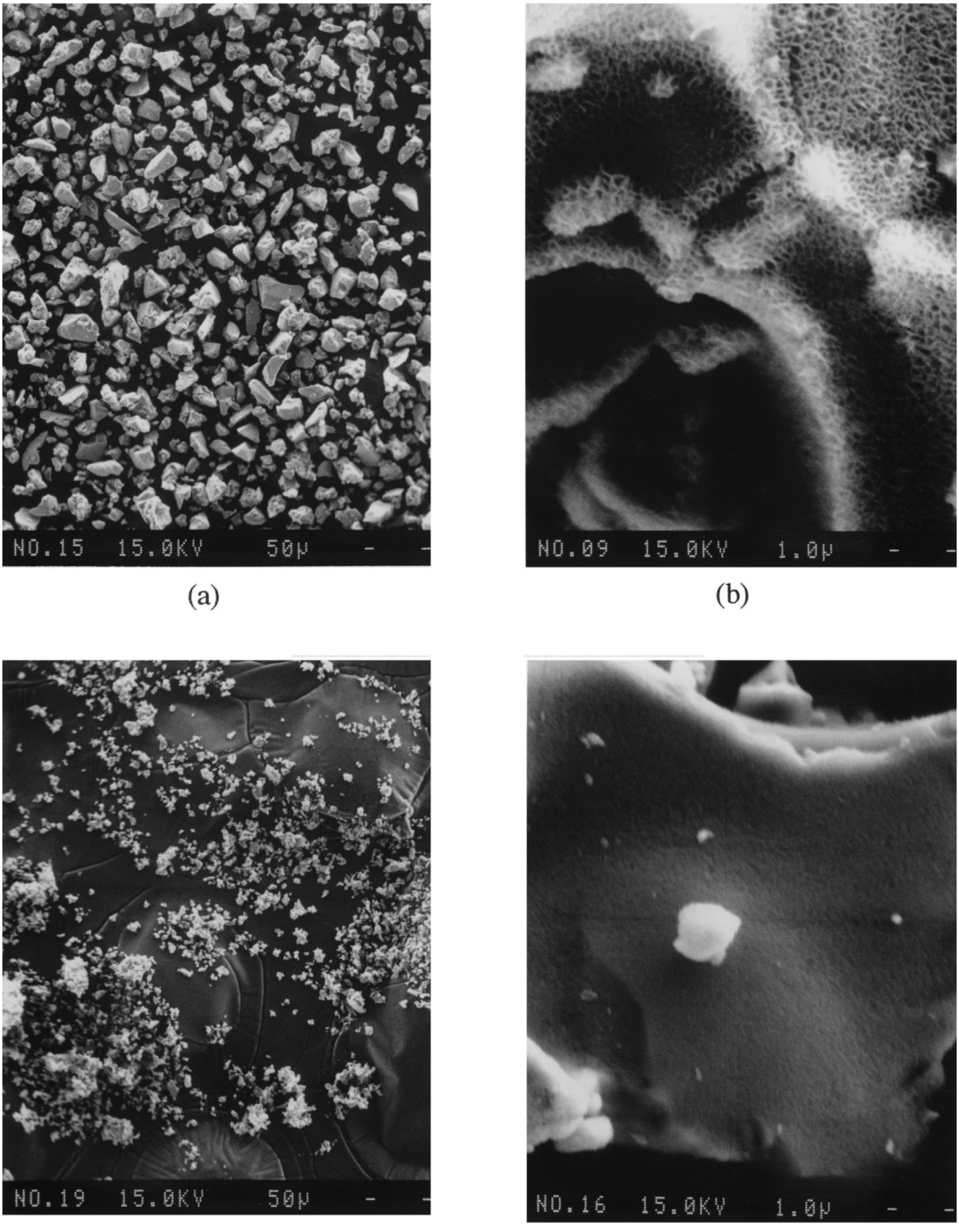
According to XRD analysis, no obvious structural change occurred after the ball milling process. Through SEM examination, it was found that a very fine powder with a size of a few micron was formed after the ball milling, as shown in Fig. 5. The reduction of alloy particle size will increase the surface area and shorten diffusion distance in the alloy, which favor electrode kinetics. However, the decrease of particle size will show positive effects on the electrochemical performance only when the surface is active, otherwise, the drastic decrease of particle size will decrease the use efficiency of alloy particle and inversely harm the properties [5]. Hence, the surface state of the treated alloy is believed to play a more crucial role in determining its performance. Based on the ICPS analysis, as shown in Fig. 6, it can be deduced that following process took place during the F9 treatment, similarly to the F5-treatment:

$$Zr+[NiF_6]^{4-}\rightarrow[ZrF_6]^{2-}+Ni^0$$

$$Mn+[NiF_6]^{4-}\rightarrow[MnF_6]^{4-}+Ni^0$$

which means that a oxidation–reduction reaction occurred on the alloy surface during the ball milling process. It is imaginable that during the ball milling, a lot of new surfaces were continually created, $Ni^{2+}$ ions in the solution were then reduced by the metallic elements like Zr and Mn on the new created surface and implanted back on the surface. Through the treatment, not only a fine powder was created, but also an active surface with a functional layer of metallic Ni was formed. As shown in Fig. 7, a larger specific surface area was achieved after the F9-treatment.

Although Zr-based $AB_2$ alloys have high hydrogen storage capacity, their poor surface activity in the electrolyte makes it difficult to show their advantages as a hydrogen holder. The compact and inert nature of Zr oxide and relatively low Ni content in alloys lead to a poor electric conductivity and inferior catalytic activity on the



(a) (b)

(c) (d)

Fig. 5. SEM photographs of the F-treated $AB_2$ alloy particles. (a), (b): F5-treated; (c), (d): F9-treated.

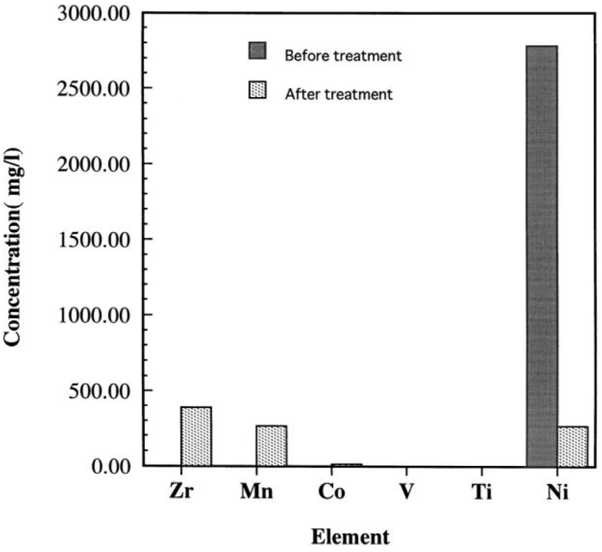


Fig. 6. ICPS analysis result of the treating solution before and after the F9 treatment.

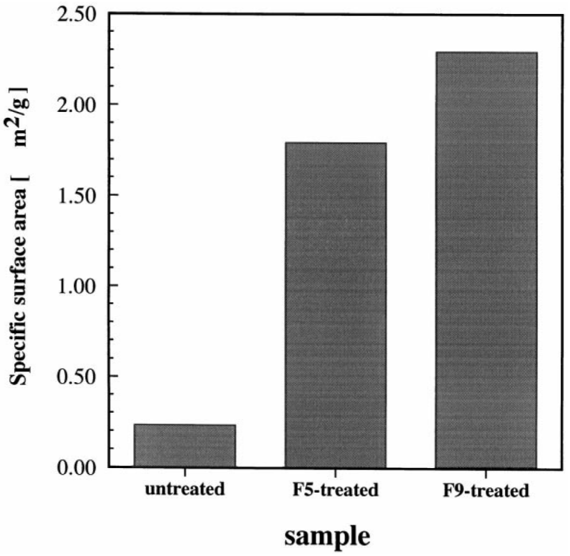


Fig. 7. Comparison of specific surface area for the untreated and F-treated $AB_2$ alloy powders.

charge transfer reaction of alloy electrodes. In the case of the untreated alloy, the low surface conductivity resulted in a low use efficiency of active material, a part of the alloy particles eventually lost electric contact and could not participate in the electrochemical reaction. That is why the untreated alloy electrode could only reach a low maximum capacity. As discussed above, after F-treatment, a functional Ni-rich layer was formed on the alloy surface by the Ni reduction and implantation. The treated surface is highly conductive and electrochemically active. A large exchange current density can be expected on this kind of surfaces. Moreover, a fine particle size was formed after F9-treatment, which provides a large reaction area and a short diffusion distance. All these effects are favorable for the kinetics of electrode processes and can account for the excellent activation behavior and high-rate discharge capability of the F9-treated alloy electrode.

## 4. Conclusions

1. The activation process and the high-rate discharge capability of the Zr-based $AB_2$ alloy were successfully improved by a wet ball milling process.
2. The improvements are believed to be brought on by a Ni-rich surface and a fine powder created during the ball milling process.

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