

## Deterioration of Laves phase alloy electrode during cycling

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### Abstract

A study is made of the deterioration mechanism of a Laves phase alloy electrode without addition of Ni powder by means of electrochemical impedance spectra (EIS), X-ray diffraction (XRD), inductively coupled plasma (ICP) and X-ray photoelectron spectroscopy (XPS). The XRD analysis shows that after cycling, the alloy bulk still has the capability to store hydrogen. The deterioration mechanism is considered to be mainly a surface process. In particular, particle pulverization (increased specific surface area and reduced the particle size) is the main reason for electrode deterioration. Dissolution of V and Mn increases gradually during cycling. On the other hand, particle pulverization increases further the dissolution rates of V and Mn, which are proportional to the specific surface area due to the generation of a new, fresh surface. In addition, it is demonstrated by XPS that the depth of oxide layers of Zr and Mn increases with cycling and results in an increase in the reaction impedance and a decrease in the surface electronic conductivity. Therefore, a change in the structure of the particle surface layer, due to particle pulverization and dissolution of V and Mn, contributes to the deterioration of the Laves phase electrode. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Laves phase alloy; Electrode materials; Element dissolution; Particle pulverization; Oxidation

### 1. Introduction

Laves phase alloy hydrides are attractive materials because of their high theoretical hydrogen-storage capacity. It is well known, however, that they display the disadvantages of poor initial activation, limited charge–discharge cycle life and poor high-rate capability. Many efforts have been made [1–3] to improve the initial activation and the high-rate capability by changing the alloy composition, by modifying the particle surface with Ni and Co, and by treating the surface to remove the oxide layer. In particular, the fluorination technique developed in this laboratory has proved effective for improving the initial activation and high-rate discharge capability of the Zr-based Laves phase alloy during electrochemical reaction [4–6]. Nevertheless, the cycle-life of the Laves phase electrode remains a serious problem in practice applications [7]. Therefore, elucidation of the deterioration mechanism of the Laves

phase electrode is very important in order to improve the cycle life for future applications in Ni/MH batteries.

In this study, particle surface state, crystallographic structure, dissolution of constituent elements and electro-

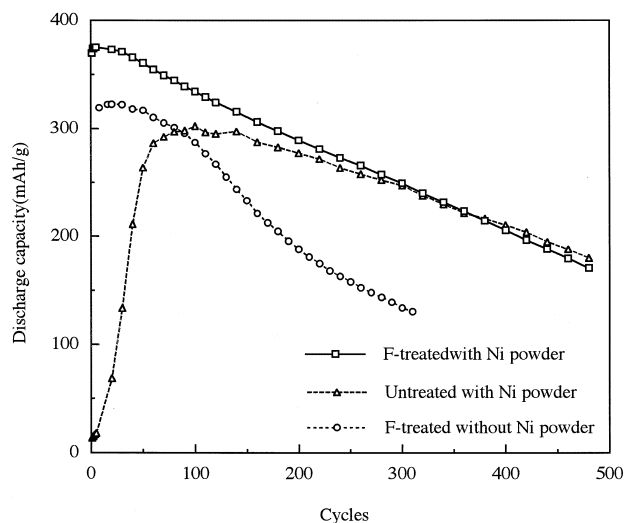


Fig. 1. Cycle life of untreated F-treated and alloy electrodes with and without Ni powder.

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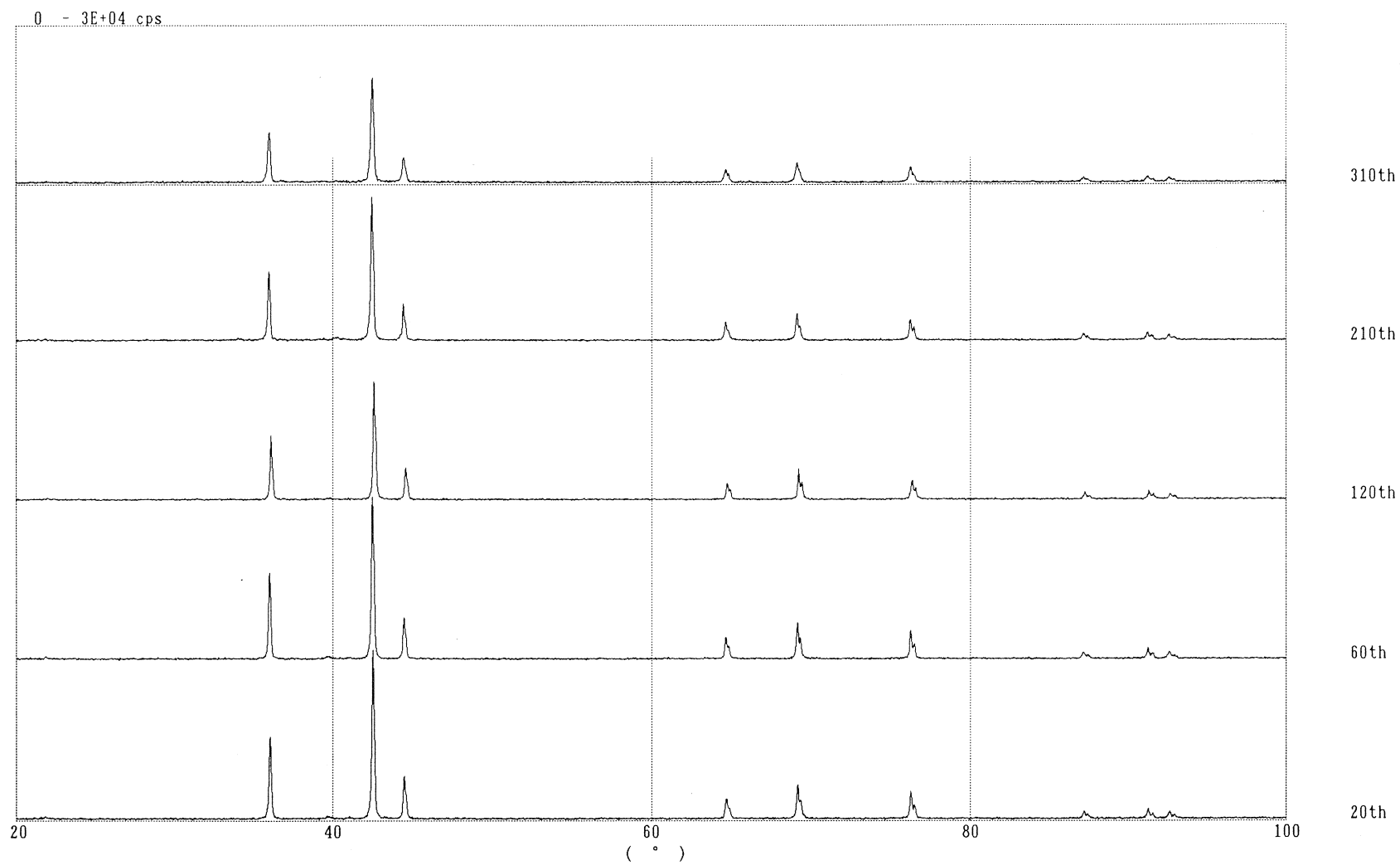


Fig. 2. XRD patterns of F-treated alloy after different numbers of cycles.

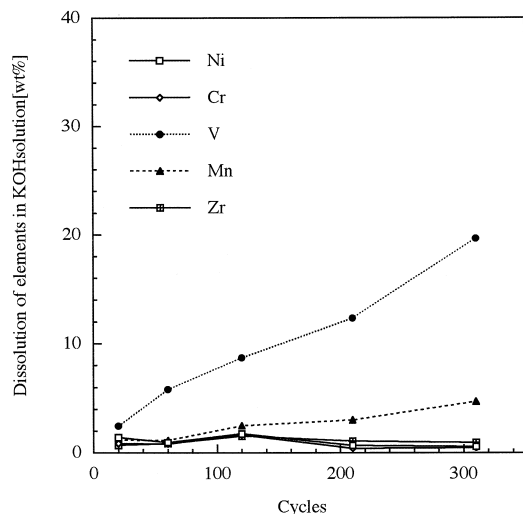


Fig. 3. Dissolution of surface elements from a F-treated alloy electrode without addition of Ni powder during cycling.

chemical properties of  $\text{ZrV}_{0.2}\text{Mn}_{0.6}\text{Cr}_{0.1}\text{Ni}_{1.2}$  alloy after the fluorination treatment are investigated. The effects of surface element dissolution, surface oxidation and particle pulverization on cycle life are examined by means of experimental surveys with inductively coupled plasma (ICP) analysis, electrochemical impedance spectra (EIS), specific surface area, scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS).

## 2. Experimental

The  $\text{ZrV}_{0.2}\text{Mn}_{0.6}\text{Cr}_{0.1}\text{Ni}_{1.2}$  alloy was prepared by arc-melting under an argon atmosphere. The alloy was pulverized to an average size less than  $25\ \mu\text{m}$  after annealing at  $1100^\circ\text{C}$  for 18 h under an argon atmosphere. The powder was treated by the F5 method as described previously [5]. The surface microstructure and chemical state were investigated by SEM (EPMA 8705, Shimadzu) and XPS. The specific surface area was determined by the BET method.

For electrochemical evaluation, a button-type hydride electrode was made by mixing the alloy powder with PTFE powder in a weight ratio of 1.0:0.05 (with Ni powder pellet: alloy/Ni/PTFE = 0.25/0.75/0.05). The mixture was then compressed into a pellet with a diameter of 13 mm and a thickness of 1.5 mm under a mechanical load of  $4\ \text{ton cm}^{-2}$ . The electrodes were placed in a half-cell with a sintered nickel counter-electrode and a Hg/HgO (6 M KOH) reference electrode. The electrochemical properties of the electrode were measured by charging at a current density of  $68\ \text{mA g}^{-1}$  for 6 h and then discharging at the same current density after resting for 1 h at  $20^\circ\text{C}$ . The cut-off potential was set at  $-0.6\ \text{V}$ . EIS were measured from 10 kHz to 10 MHz at 5 mV of the amplitude of perturbation by using an IM6 (ZAHNER).

## 3. Results and discussion

### 3.1. Cycle life

The cycle lives of the untreated and F-treated alloy electrodes with and without addition of Ni powder are presented in Fig. 1. The F-treated electrode added with Ni powder has a faster initial activation, and reaches a maximum discharge capacity of  $375\ \text{mA h g}^{-1}$  after only 5 cycles. The initial discharge capacity is about 95% of its maximum discharge capacity. By contrast, the untreated electrode with addition of Ni powder requires at least 100 cycles to reach its maximum capacity of  $305\ \text{mA h g}^{-1}$ . The cycle life for both the untreated and F-treated electrodes is almost identical in their capacity decay tendency. In summary, the fluorination technique employed in this study is effective in improving the initial activation.

As is known, it is impossible to use many Ni powders in MH electrodes in practice applications. Therefore, electrochemical properties of the electrode without Ni powder are more important. The discharge capacity of the F-treated electrode without the addition of Ni powder is lower than that of the F-treated electrode with addition of Ni powder owing to the poor electronic conductivity. In particular, the deterioration rate of the F-treated electrode without addition of Ni powder is faster than that of the electrode containing Ni powder.

### 3.2. X-ray diffraction (XRD) patterns

XRD patterns of the F-treated alloy for the electrode without addition of Ni powder after different cycles are presented in Fig. 2. It is seen that the alloy bulk consists merely of a single phase, which is identified as a cubic

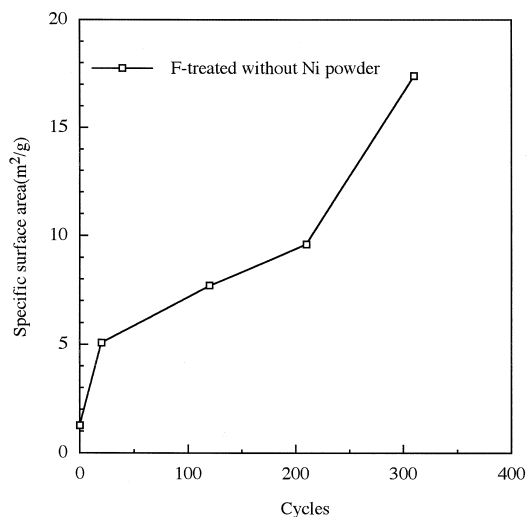
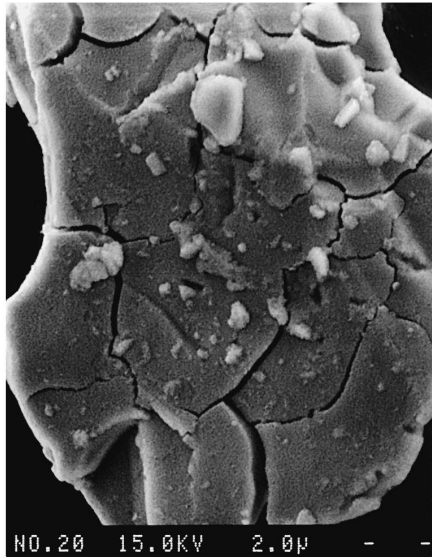
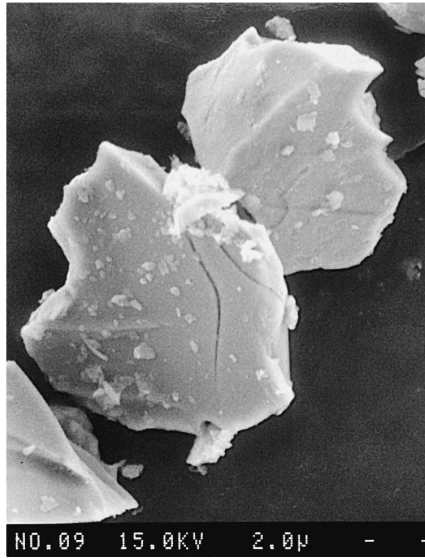


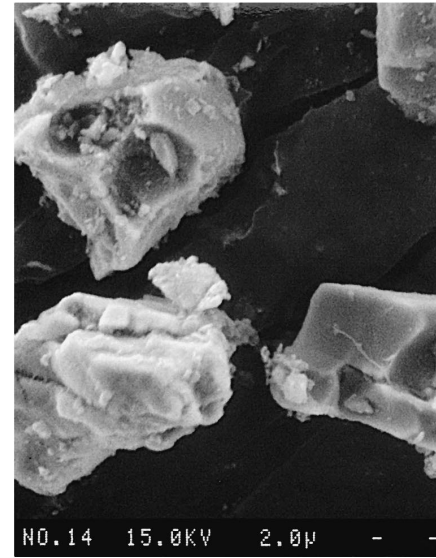
Fig. 4. Specific surface area of F-treated alloy after different numbers of cycles.



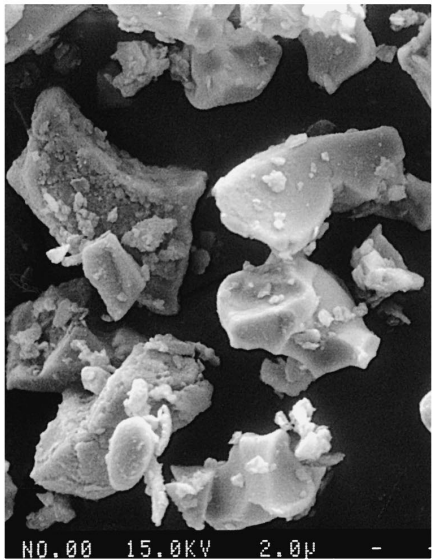
(a)



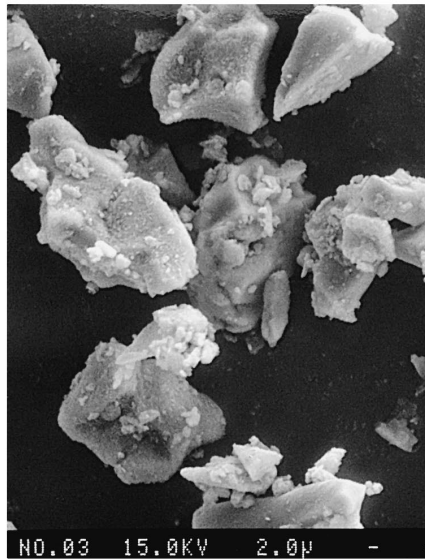
(b)



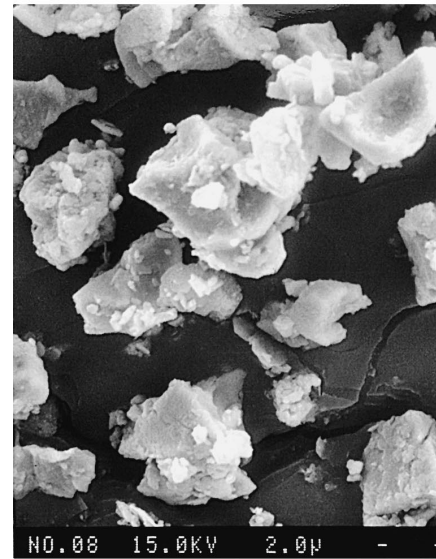
(c)



(d)



(e)



(f)

Fig. 5. Surface morphology of F-treated alloy before and after cycling (magnification  $\times 5000$ ): (a) before cycling; (b) 20 cycles; (c) 60 cycles; (d) 120 cycles; (e) 210 cycles; (f) 310 cycles.

C15 type structure after different cycles. There are no residual phases such as oxides of Zr and Mn. Moreover, there is no reflection peak of a free Ni with a face-centered cubic structure, which appears in  $\text{LaNi}_5$  and  $\text{LaNi}_4\text{Cu}$  electrodes due to a disproportionation reaction after prolonged cycling [10]. Therefore, the Laves phase alloy bulk retains capability for storing hydrogen. The deterioration mechanism is different between  $\text{AB}_2$  and  $\text{AB}_5$  electrodes during charge–discharge cycling. The deterioration mechanism of the Laves phase electrode is considered to be mainly a surface process.

### 3.3. Dissolution of particle surface elements

The relative dissolution of V and Mn from the electrode without the addition of Ni powder in KOH solution increases gradually during cycling (Fig. 3). Impedance spectra (see Section 3.5) show that there is an obvious oxidation of the particle surface. Metallic vanadium and manganese in the particle surface easily form oxides of  $\text{VO}_x$  and  $\text{Mn}(\text{OH})_2$  during cycling, respectively. The vanadium metallic oxides are the most soluble in alkaline solution. Manganese metallic hydroxides, in turn, form a precipitate of  $\text{MnO}_2$  due to oxidation by atmospheric  $\text{O}_2$ . ICPS analysis shows that V and Mn dissolution in KOH solution form a deposit which is approximately 25 wt.% after 310 cycles. The hydrogen-storage capacity of the electrode during cycling is proportional to the total amount of uncorroded and unoxidized active materials. It is concluded that V and Mn dissolution on the particle surface is one of the contributors to the deterioration of the electrode during cycling.

### 3.4. Particle pulverization

The specific surface area of the F-treated alloy after cycling was measured by the BET method and is shown in Fig. 4. It is evident that the specific surface area increases significantly with increasing cycle number. After 310 cycles, the specific surface area has increased 10 times due to particle pulverization. The oxidation and dissolution of V and Mn easily occur at the new generated surface without a covering Ni network formed by fluorination.

The surface morphology of the particle after cycling is shown in Fig. 5. The particle size becomes smaller with increasing cycle number due to the volume expansion. On the other hand, the particle surface morphology changes from smooth to rough due to the dissolution of V and Mn from the particle surface. These results are in agreement with measurements of the specific surface area of particles after different numbers of cycles. The surface oxide layer becomes thicker due to the dissolution of V and Mn, and also the oxidation of Zr.

It has been shown qualitatively by Boonstra et al. [10] that the cycling stability of the  $\text{AB}_5$  electrode is influenced strongly by the particle size or the specific surface area of

the MH powder. The deterioration rate is attributed to differences in the specific surface area of the starting materials of the  $\text{AB}_5$  alloy [11]. It is important to note that the specific surface area of the Laves phase alloy changes dramatically due to particle pulverization during cycling. In addition, the oxidation and dissolution rates of the elements are proportional to the specific surface area of the particles during cycling. Therefore, the deterioration rate of a Laves phase electrode is faster than the conventional  $\text{AB}_5$  alloy used currently in Ni/MH batteries; the latter has good pulverization resistance upon hydrogen uptake or cycling [8]. Particle pulverization is identified as the main cause for deterioration of the MH electrode during cycling.

### 3.5. Surface oxidation and passivation

EIS of a F-treated electrode without Ni powder were measured at open circuit after different numbers of cycles and are presented in Fig. 6. The electrochemical impedance increases gradually with increasing cycle number, as found in  $\text{AB}_5$  hydride electrodes [9]. This implies that the particle surfaces oxidation and passivation intensity during cycling.

XPS analysis (Fig. 7) shows that a Ni-rich layer is formed and peaks of  $\text{Zr}_{3d}$ ,  $\text{V}_{2p}$ ,  $\text{Mn}_{2p}$  and  $\text{Cr}_{2p}$  core level almost disappear on the top surface after fluorination. The formation of Ni-rich layer is beneficial to the improvement of the initial activation and to the achievement of maximum discharge capacity. The amount of V at the subsurface decreases considerably during cycling on account of dissolution in KOH solutions, as mentioned above (ICP analysis). The amount of Mn at the subsurface increases slightly because of the precipitation of  $\text{MnO}_2$  by oxidation. Metallic Zr is gradually transformed into  $\text{ZrO}_2$ , and Zr tends to segregate in the top surface by oxidation induction during cycling. This result is in agreement with impedance measurements. It is found that Cr exists in the metallic

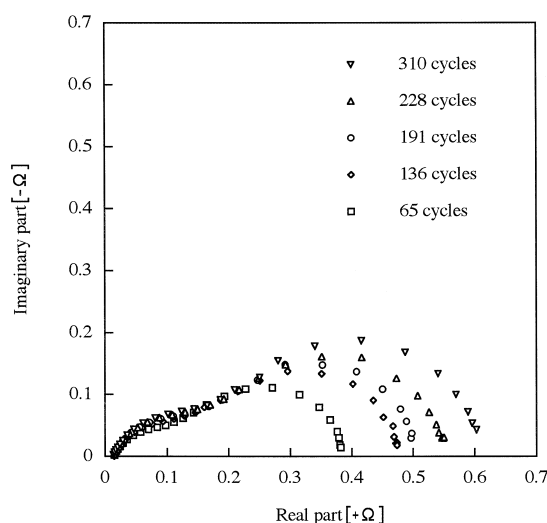


Fig. 6. Impedance spectra of F-treated alloy electrode without addition of Ni powder after different numbers of cycles.

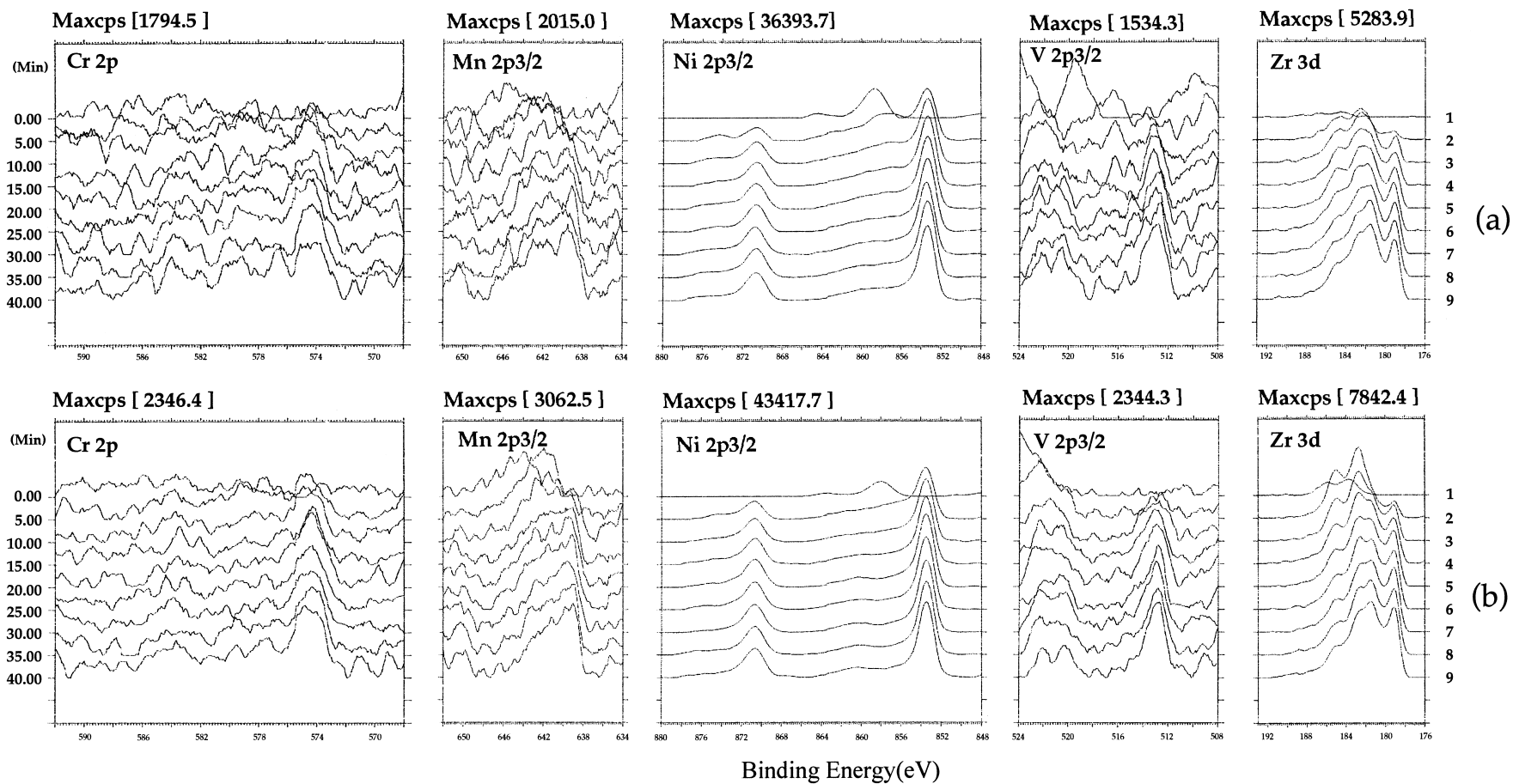
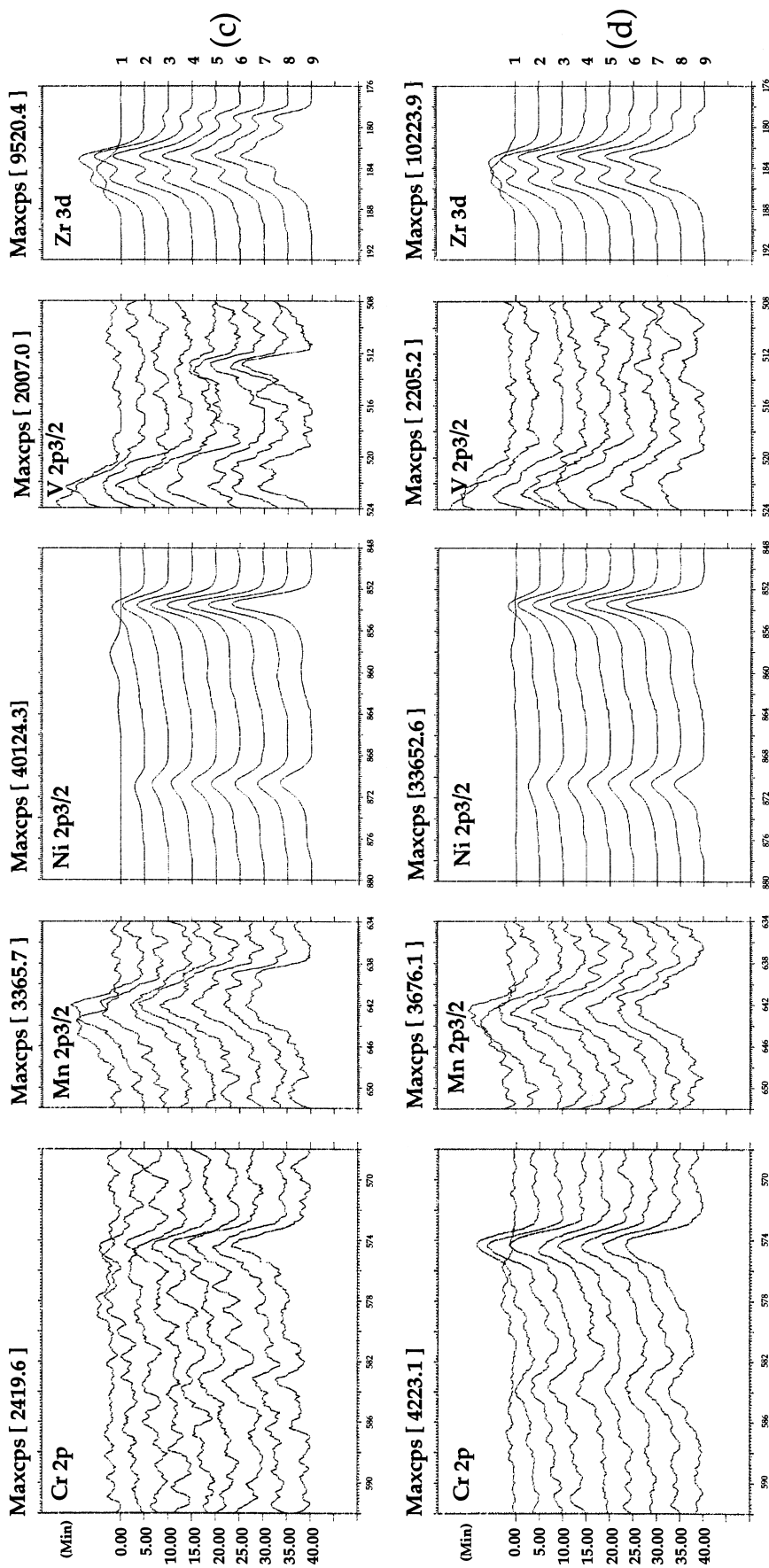


Fig. 7. XPS spectra of Zr<sub>3d</sub>, Ni<sub>2p</sub>, V<sub>2p</sub>, Mn<sub>2p</sub> and Cr<sub>2p</sub> core level of F-treated alloy before and after cycling at different sputtering times: (a) before cycling; (b) 60 cycles; (c) 210 cycles; (d) 310 cycles.



Binding Energy(eV)

Fig. 7 (continued).

state and has a good corrosion resistance in KOH solution during cycling. The Cr cannot, however, protect V from dissolution and Zr from segregation. The amount of Ni on the top surface decreases dramatically and this results in decrease of the surface electronic conductivity and the surface reaction activity. The depth of the corrosion layers, concentrated with oxides of Zr and Mn, and also with metallic Ni and Cr, increases gradually with cycling.

#### 4. Conclusions

Fluorination treatment is very effective for improving the initial activation of Laves phase alloy electrodes with or without Ni powder.

The deterioration mechanism of the Laves phase electrode without Ni powder has been investigated. After cycling, the alloy bulk retains the capability for storing hydrogen and the deterioration mechanism of the electrode is considered to be mainly a surface process. Particle pulverization is identified as the main reason for causing deterioration of the electrode. The dissolution of V and Mn increases gradually during cycling. Particle pulverization further increases the dissolution rate of V and Mn, which is proportional to the specific surface area due to generation of a new, fresh surface. In addition, it is demonstrated by XPS that the depth of the oxide layers of Zr and Mn

increases with cycling and this, in turn, leads to an increase in the particle surface impedance and to a decrease in the surface electronic conductivity. Therefore, a change in the structure of the alloy surface layer due to the particle pulverization and dissolution of V and Mn contributes to the deterioration of the Laves phase electrode.

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