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Characteristics of surface-modified metal hydride electrode with flake Ni by the ball-milling process

Sang-Min Lee*, Ji-Sang Yu, Paul S. Lee, Jai-Young Lee

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-Dong, Yusong-Gu, Taejon, South Korea

Abstract

In order to improve the electrochemical cyclic durability of the Ti-based hydrogen storage alloy electrode, the ball-milling process was applied to the Ti-based alloy using flake Ni as a surface modifier. Flake Ni powder is a very useful material to modify the surface of metal hydrides. While the as-cast Ti-based alloy electrode is completely degraded within ten cycles, the ball-milled Ti-base alloy electrode using flake Ni as a surface modifier shows only 8% of capacity decay even after 180 cycles. It is also noticeable that the ball-milled alloy electrode shows just a little decreased discharge capacity (429 mAh/g) by ball-milling with flake Ni powder. These results are closely related to the higher strain and higher coverage area of flake Ni powder. The residual strain of flake Ni powder can promote the diffusion reaction in the impact event of ball-milling. Consequently, the flake Ni as a new surface modifier can modify the alloy surface without changing the bulk properties of the alloy, resulting in an effective surface coating within a shorter ball-milling time.

Keywords: Cycle life; Ti-based alloy; Flake Ni; Ball-milling process

1. Introduction

The developed rechargeable batteries have been presented as follows: Ni–Cd, Ni–MH, and Li-ion batteries. Among these batteries, Nickel–metal hydride (Ni–MH) batteries using hydrogen storage alloys as the negative electrode have been developed and commercialized to meet a strong market demand as a power source with a high performance/cost ratio. The energy density per weight of Ni–MH batteries has also improved from 60 to 100 Wh/Kg, which is still lower than that of Li-ion batteries [1,2]. On the other hand, the cost per cell has greatly decreased to about one-third of the initial value, reaching almost the same level as that of Ni–Cd batteries and less than half of that of the Li-ion batteries [3]. For maximizing the performance/cost ratio of Ni–MH batteries compared with other batteries, further studies on the alloy design should be performed for the development of hydrogen storage alloys with higher discharge capacity. Among various alloys as anode materials of the Ni–MH battery, Ti-based hydrogen-storage alloys have become known as promising negative electrode materials because their gravimetric hydrogen storage capacities are higher than those of Zr-based or La and Mm-based metal hydrides. However, there still remains an unsettled question of how to improve its cycle life, because Ti-based hydride electrodes abruptly degrade within ten electrochemical charging–discharging cycles even though their initial discharge capacities are very high as previously reported [4]. It has been reported that the fast degradation of the Ti–Zr–V–Mn–Ni-based alloy is caused by the deterioration of surface properties caused by the growth of Ti-oxide on the surface [5]. Therefore, the deterioration of the alloy surface should be prevented through surface modification methods.

In this work, ball-milling was applied to a $Ti_{0.8}Zr_{0.2}Mn_{0.5}V_{0.5}Ni_{0.8}$ alloy using various surface modifiers (Ni, Cu, Zr, and Cr). The changes in thermodynamic and electrochemical properties of the modified alloy were investigated. Finally, the effects of the ball-milling process on the cyclic characteristics of Ti-based hydrogen storage alloy were characterized on the basis of electrochemical and phenomenological analyses.

2. Experimental details

The base alloy ($Ti_{0.8}Zr_{0.2}Mn_{0.5}V_{0.5}Ni_{0.8}$) was prepared

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*Corresponding author.

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in an arc-melting furnace under an argon atmosphere. The purity of individual components was not less than 99.5 weight percent (wt.%). To assure the homogeneity of the alloy, the alloy ingots were turned over and remelted at least five times. The alloys were crushed and ground into powder with a characteristic particle diameter of less than 45 μm. This powder was employed in the ball-milling process. The surface modified alloy samples were prepared by ball milling with various surface modifiers (Ni, Cu, Zr, and Cr). Mechanical alloying was performed with an attrition mill (Simoloyer: CM01 model, Zoz GmbH) at different ball-milling times in an Ar atmosphere. For electrochemical measurements, electrodes were made by mixing the ball-milled powder with copper powder in a weight ratio of 2:1 and pressing it at a pressure of 10^4 N/m^2 into porous pellets with a diameter of 10 mm. The experimental cell for the electrochemical measurements consisted of a working electrode (metal hydride), counter electrode (Pt wire) and reference electrode (Hg–HgO electrode). The reference electrode was equipped with a Luggin probe to reduce the IR drop in the polarization measurements. The electrolyte was 30 wt.% KOH solution whose temperature was held at 30±1°C. The alloy electrode was galvanostatically charged at 100 mA/g for 6 h, and then after resting for 5 min it was discharged at 100 mA/g until the potential reached −0.75 V vs. Hg–HgO. The cyclic voltammetry measurements were recorded with an EG&G 273A potentiostat.

The morphological changes of ball-milled powders with increasing ball-milling time were imaged by scanning electron microscopy (SEM) and the chemical compositions of the alloy constituting elements in the interface were estimated by energy dispersive spectroscopy (EDS) analysis. In order to analyze the changes in surface composition of the alloy by ball-milling, Auger electron spectroscopy (AES) analysis was performed. In AES analysis, a Perkin–Elmer PHI4300-SAM instrument with a base pressure of 1×10^{-9} Torr was used and depth profiling was performed using Ar^+ ions at 3 kV for sputtering.

3. Results and discussion

3.1. Optimization of surface modification condition

Various spherical type shaped metal powders (Ni, Cu, Cr, and Zr) were applied as surface modifiers in the ball-milling process. In view of electrode performances (discharge capacity and cycle life), it is assured that Ni is the best element for effective surface modification of the Ti-based hydrogen storage alloy. First of all, the ball-milling condition (i.e. the amount of Ni powder addition, ball-to-powder weight ratio, and ball-milling time) should be optimized for effective surface modification. As the degree of ball-milling increases (Ni amount, ball-to-powder weight ratio, and ball-milling time increases), the cyclic durability improves, but the discharge capacity decreases. Based on the above results, the optimal ball-milling condition for effective surface modification is set to be Ni of 10 wt.%, a ball-milling time of 40 min, and a ball-to-powder weight ratio of 5:1.

The electrochemical properties are generally related to changes in thermodynamic properties. Especially, it is considered that the decreased discharge capacity is due to the change of hydrogen storage capacity with ball-milling time, as shown in Fig. 1. As the degree of surface alloying increases, the hydrogen storage capacity decreases, which is related to the structural damage of the alloy (Fig. 2). It is necessary to effectively modify the alloy surface minimizing the change of the bulk properties of the alloy. A new modifier should be qualified for promoting the surface alloying within shorter ball-milling time. A new surface modifier should have a large surface coverage area, leading to fast diffusion reactions at the cold welding event. It has been reported that the metal flake pigments can increase the surface coverage compared to spherical metal powder [6]. Moreover, metal powder with high strain can promote the diffusion reaction at the cold-welding events [7]. Therefore, in this work, we intended to prepare flake Ni with higher strain and higher surface coverage area by the ball-milling process. If flake Ni is to be used as a new surface modifier in ball-milling process, it is possible to

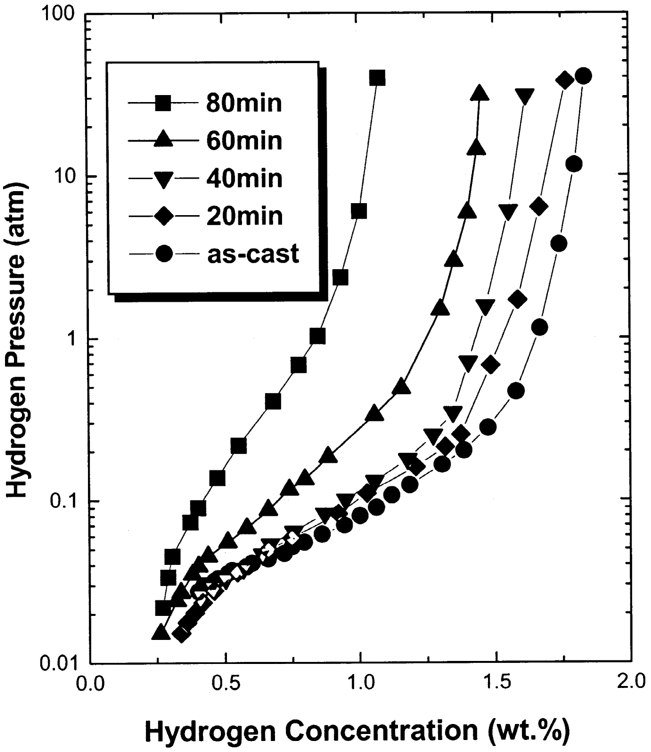

Fig. 1. Changes in P–C–T curves of ball-milled alloy with ball-milling time.

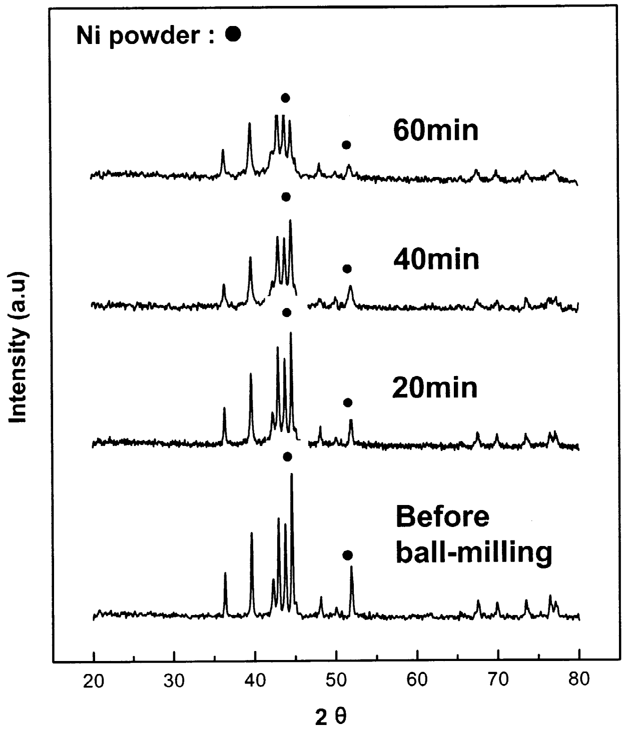

Fig. 2. Changes in X-ray diffraction patterns of ball-milled alloys with ball-milling time.

effectively modify the alloy surface minimizing the change of the bulk properties of the alloy.

3.2. Preparation of flake Ni by the ball-milling process

Fig. 3 shows the morphologies of flake Ni prepared by the ball-milling process. As the ball-milling time increases, the particle size increases and particle thickness decreases. It is also observed that the surface coverage area of flake Ni is higher than that of conventional spherical Ni powder. The XRD pattern of flake Ni is measured in Fig. 4. The peak intensity decreases while the broadness increases in XRD patterns of flake Ni with increasing ball-milling time. It means that the high strain energy is incorporated into the flake Ni, which is closely related to the reactivity of Ni powder versus Ti-based alloy. Therefore, it is expected that a large surface-alloying effect be obtained by ball-milling with flake Ni. Fig. 5 shows the change of discharge capacity with cycling for the alloy electrode prepared with various types of flake Ni. The alloy shows a better cycle life and higher discharge capacity when it is ball-milled with flake Ni with higher strain.

In the case of ball-milling with flake Ni, it is possible to shorten the ball-milling time and decrease the structural damage of the alloy, which is related to the loss of interstitial sites and the decay of hydrogen storage capacity. Fig. 6 shows the comparison of PCT characteristics of a ball-milled alloy with flake Ni and an as-cast one. It is observed that the hydrogen storage capacity of ball-milled alloy has decreased within only 6% compared to that of the as-cast one. Fig. 7 shows the change of discharge capacity of the ball-milled alloy electrode with electrochemical cycling. It can be shown that the cycle life is strikingly improved by ball-milling with flake Ni. It is also observed that the discharge capacity of the ball-milled alloy electrode is as high as that of the as-cast one. Consequently, it is suggested that the flake Ni can modify the alloy surface without damaging the inner part of the alloy.

3.3. Analysis on the improvement in cycle life of Ti-based alloy electrode

In order to investigate the effect of the surface modification on the cycle life of the alloy electrode, the surface composition of the ball-milled alloy should be examined. Fig. 8 shows the cross-sectional view of the ball-milled alloy with flake Ni imaged by SEM. Based on this observation, it is clear that the Ni content of the alloy surface increases after ball-milling with flake Ni. In order to identify the variations in the surface properties of the ball-milled and as-cast alloys with cycling, EIS analyses were performed. It is generally known that the degradation of an alloy electrode is caused by changes of surface properties. In the case of the as-cast Ti-base alloy electrode, the smaller semicircle in the high-frequency region (contact resistance between alloy particles) hardly changes, but the semicircle in the low-frequency region (charge transfer resistance for hydrogenation reaction) markedly changes during cycling [8,9]. The phenomena means that the rapid degradation of the Ti-based alloy electrode is ascribed to the increase of charge transfer resistance during cycling. On the other hand, as the flake Ni content increases, the contact and charge transfer resistance decreases for the electrochemical reaction. It is also known that the increment of reaction resistance with cycling decreases with the increasing flake Ni content.

The results of the AES analyses are shown in Fig. 9a and b. It was observed that the surface composition of the as-cast alloy electrode was characterized by higher oxygen concentration after 15 cycles. It was demonstrated that the degradation of the Ti-substituted alloy electrode is caused by the penetration of oxygen into the alloy surface during cycling. On the other hand, the surface of the ball-milled alloy electrode is mainly composed of Ni-enriched regions even after 180 cycles. It can be assured that the Ni-enriched surface serves as a protective layer to prevent the formation of a Ti-oxide layer.

The proposed mechanism of the mechanical alloying with flake Ni can be suggested as follows: The high-strained flake Ni can promote the diffusion reaction at lower temperature, which leads to the effective surface alloying within shorter ball-milling time. It is possible to effectively modify the alloy surface minimizing changes in the bulk properties of the alloy.

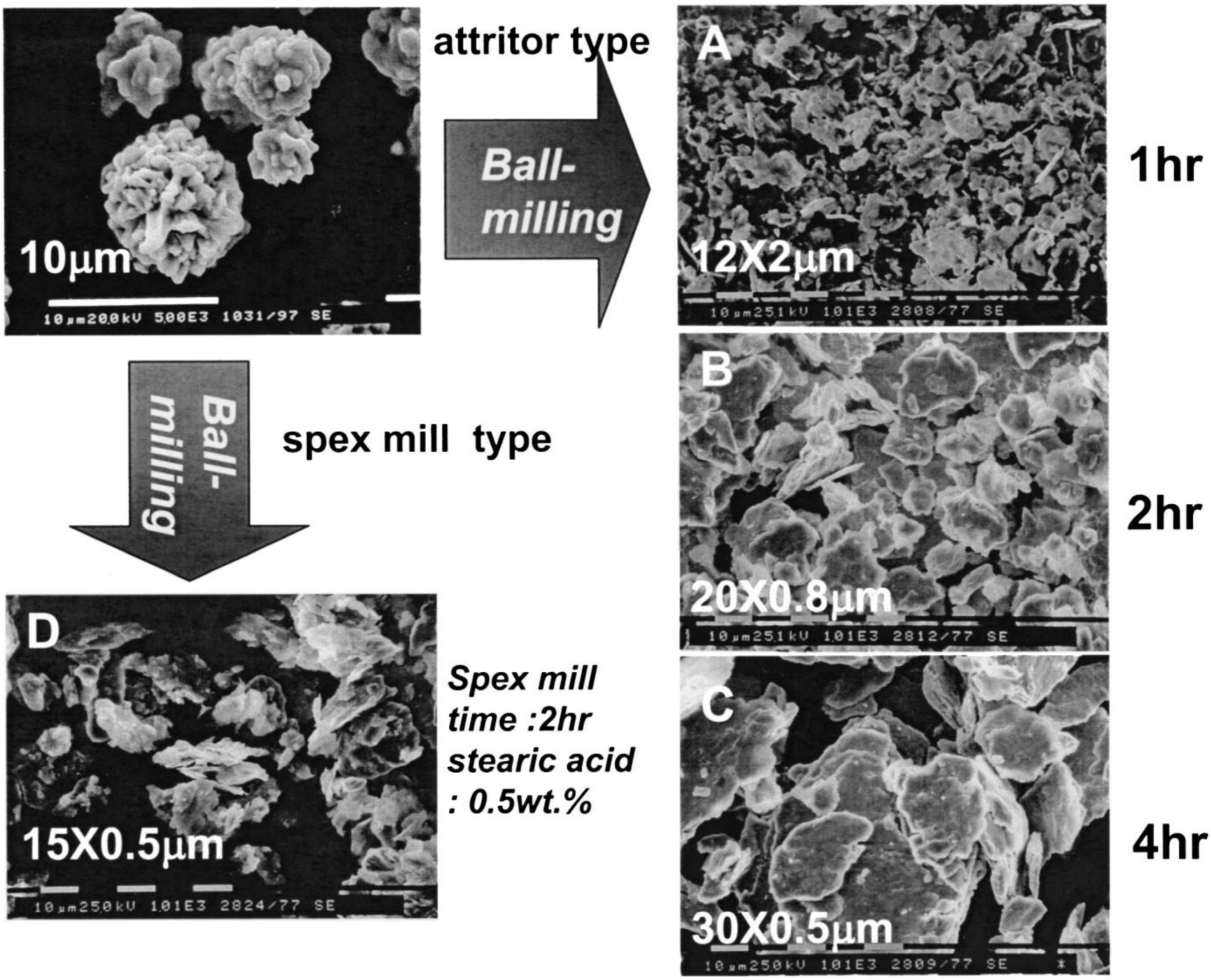

Fig. 3. SEM images of ball-milled Ni powder. Type A (1 h), type B (2 h), type C (4 h) by attritor type and type D (2 h) by spex type.

4. Conclusions

In order to improve the cyclic durability of Ti-based alloy electrodes, the ball-milling process was directed to prevent a Ti-oxide layer growing on the alloy surface. The cycle life of the alloy electrodes greatly improved, but the discharge capacity decreased by surface-alloying with Ni powder. As the degree of surface alloying increases, the hydrogen storage capacity decreases, which is related to the structural damage of the alloy. To effectively modify the alloy surface minimizing changes in the bulk properties of the alloy, we intended to prepare flake Ni with higher strain, higher surface coverage area, which has a better cold-weld ability than spherical Ni powder. The optimal surface condition is 10 wt.% of flake Ni content, 25 min of ball-milling, and a 5:1 ball-to powder weight ratio. After the surface was modified with flake Ni, the $Ti_{0.8}Zr_{0.2}Mn_{0.5}V_{0.5}Ni_{0.8}$ alloy showed a high discharge capacity (429 mAh/g) and a good cycle life (92% after 180 cycles). The improvement of the cycle life by surface modification is due to the formation of a surface alloying layer providing a protective and high-catalytic site. Consequently, the surface modification using flake Ni effectively leads to improvement of in cycle life while minimizing the discharge capacity of the alloy electrode.

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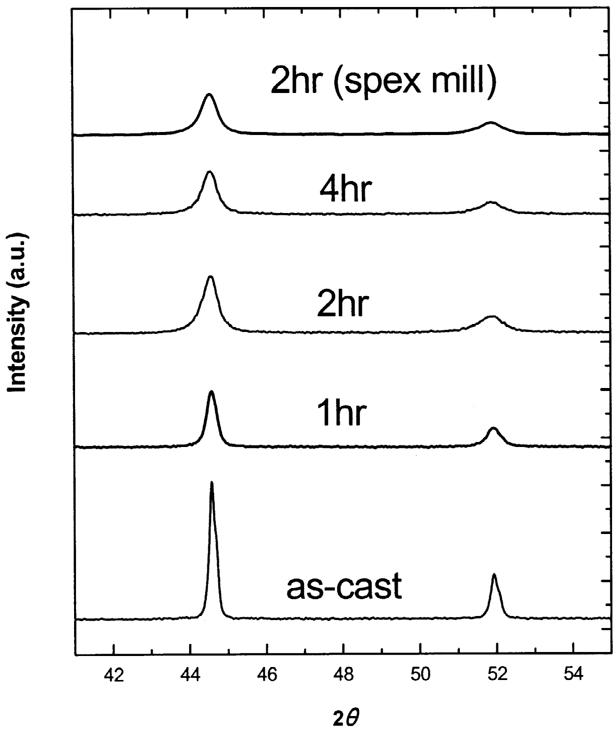

Fig. 4. X-ray diffraction patterns of ball-milled Ni powder (Ni flake) with various ball-milling times.

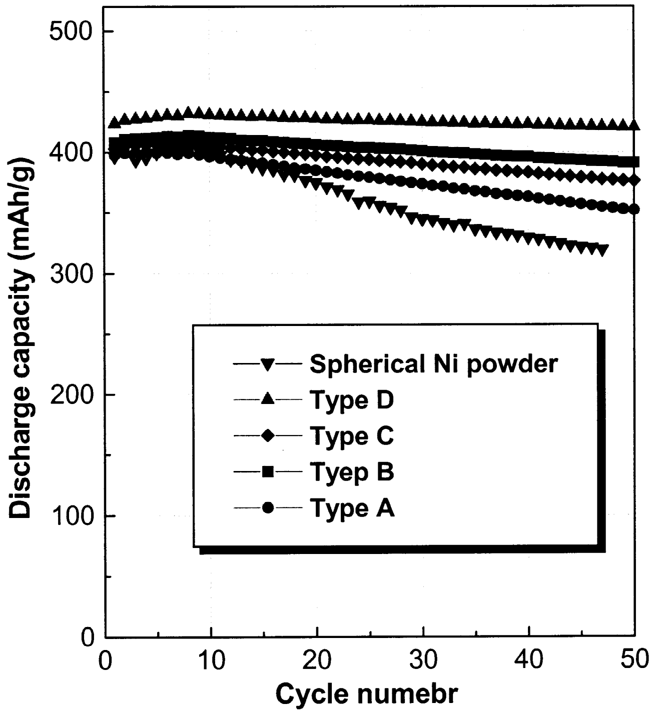

Fig. 5. Comparison of cycle life of ball-milled alloy electrode with various Ni flake powders.

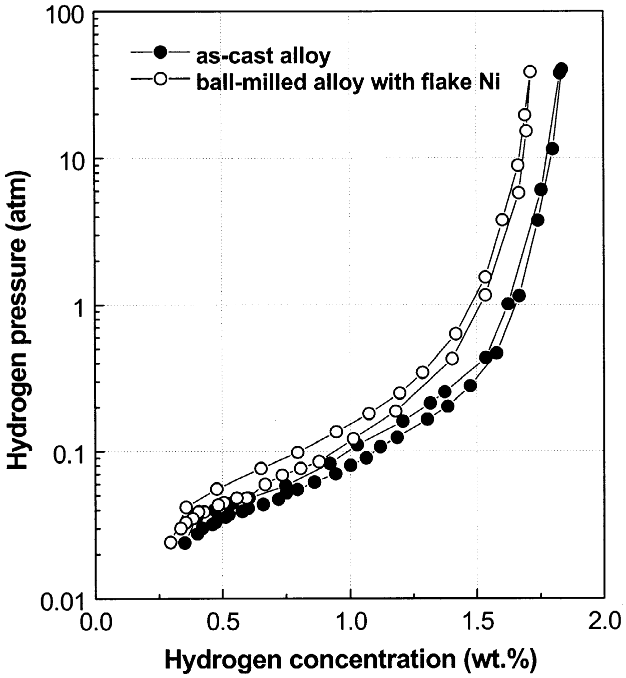

Fig. 6. P–C–T curves of as-cast and ball-milled alloys with Ni flake for 25 min.

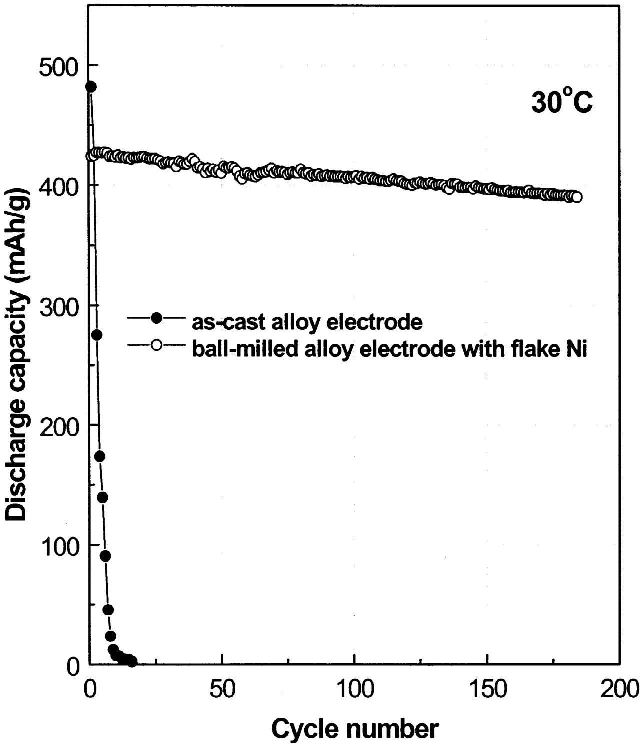

Fig. 7. Comparison of cycle life of as-cast and ball-milled alloy electrode with Ni flake.

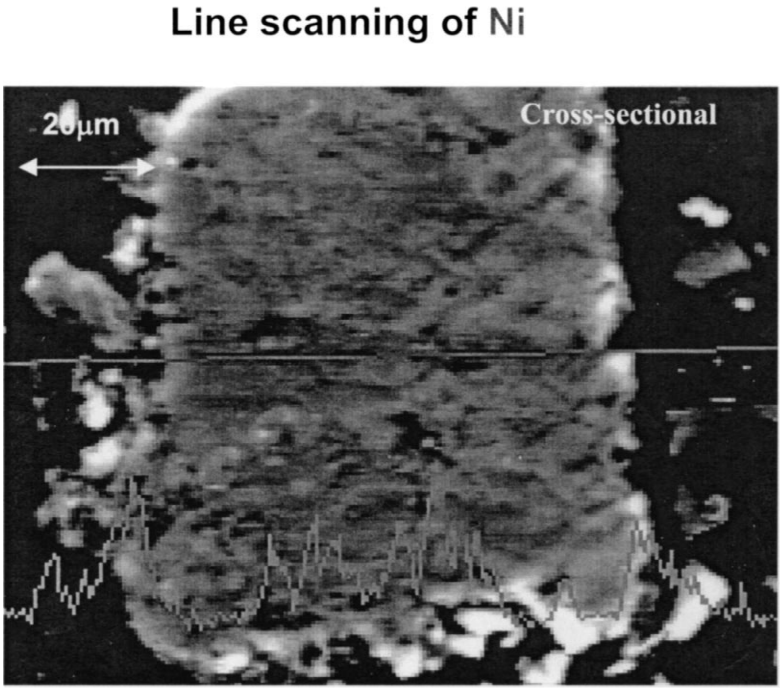

Fig. 8. Cross-sectional view of ball-milled alloy with flake Ni imaged by SEM.

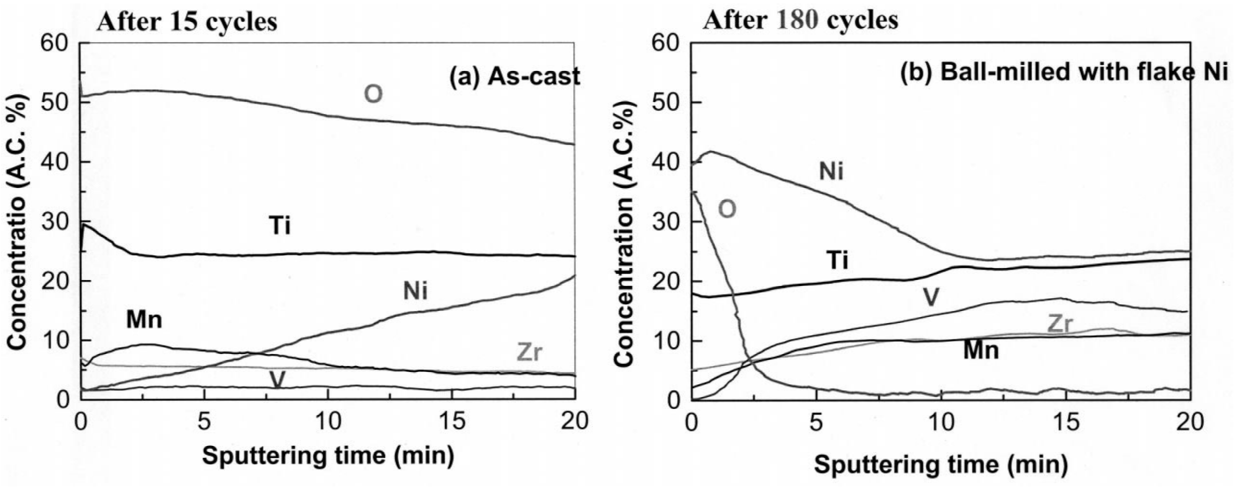

Fig. 9. AES depth profiles for (a) as-cast alloy electrode and (b) ball-milled alloy electrode with flake Ni after electrochemical cycling.

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