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A study on the electrode characteristics of Zr-based alloy surface-modified with Ti-based alloy by ball-milling process as an anode material for Ni–MH rechargeable batteries

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Abstract

In order to improve the kinetic properties of the Zr-based hydrogen storage alloy electrode, the ball-milling process is applied to the Zr-based alloy using the Ti-based alloy powder as a surface modifier. While the Zr-based alloy electrode is not fully activated before 50 cycles, the ball-milled Zr-based alloy electrode using Ti-based alloy as a surface modifier is fully activated within only four cycles. In order to analyze the strikingly improved kinetic characteristics after ball-milling, the microstructure of ball-milled alloy is examined by transmission (TEM), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). It is observed that there is a surface-alloying region at the contact points between the two alloy powders from the TEM bright-field image. Furthermore, the local quantitative analysis by EDS clearly reveals that the atomic concentration of the constituting elements in the surface-alloying region is gradually changed between the two alloy powders. From the above results, it is suggested that the high kinetic energy applied in the ball-milling process causes cold-welding or surface alloying at the points of impact where Zr-based alloy particles collide with Ti-based alloy particles by the action of steel balls at high speed. The SEM analysis demonstrates that the particle size is decreased as the ball-milling time increases, which implies an increase in the surface area of Zr-based alloy particles touching Ti-based alloy particles. Eventually, it can be suggested that Ti-alloy powder serves as a window for hydrogen to penetrate into the Zr-based alloy, which leads to easy absorption/desorption of hydrogen and also to improvement in the kinetic properties of the Zr-based alloy electrode at initial cycles.

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Keywords: Ball-milling process; Activation characteristics; Rate-capability; Ti-based hydrogen storage alloy; Electrocatalytic activity; Dense oxide film

1. Introduction

Nickel–metal hydride (Ni–MH) batteries using hydrogen storage alloys as negative electrodes have been developed and commercialized to meet the strong market demand for a power source with high energy density, high rate capability, long cycle life, and good environmental compatibility. A number of metals, alloys, and intermetallic compounds capable of forming hydrides have been studied extensively as a potential electrode, among which the rare earth metal-based and Ti or Zr-based alloys are considered to be most promising [1,2]. However, rare earth metal and Ti-based alloys are limited in developing high-capacity and high-performance Ni–MH batteries, because these alloys have a small discharge capacity and poor cycle life, respectively [3,4].

The Zr-based hydrogen storage alloy is attractive as an anode material in Ni–MH secondary batteries because of its large hydrogen storage capacity in gas–solid reactions and long cycling life in KOH electrolyte. However, kinetic characteristics of the alloy electrode is very poor because of the dense oxide film on its surface, which forms a surface structure impermeable to hydrogen [5]. Many investigations have been directed on the surface treatments such as hydrogen-fluorine acid treatment, hot immersion treatment, anodic oxidation treatment for stripping the dense oxide film from the alloy surface [6–9]. However, the previous surface treatments are not effective surface modification methods even if a toxic and high temperature (>80°C) process is applied. Recently, ball-milling has been suggested as a surface modification method for improving the activation properties of the alloy electrode instead of previous ones. Sun et al. have studied the effect of surface modification on the Zr–Cr–Ni hydrogen storage alloy with Ni powder by ball-milling and found that the activation characteristics of the alloy were improved,

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whereas discharge capacity was decreased as compared with their intrinsic discharge capacity [10]. Therefore in order to have a more effective surface modification, it is necessary to improve the activation properties while retaining the real discharge capacity of the matrix. Yu et al. have also found that sintering an $TiMn_{0.5}$ alloy electrode with $LaNi_{4.7}Al_{0.3}$, which has a higher discharge capacity and can serve as an alternative for Ni in sintering, has a lower loss of discharge capacity of matrix phase than that of a Ni-sintered one [11].

If the conventional surface modifiers such as Cu, Ni powders are replaced by new candidate materials having high discharge capacity and high electrocatalytic activity, the ball-milling process is possible to improve the activation properties while maintaining the discharge capacity.

In this work, ball-milling was applied to a $Zr_{0.65}Ti_{0.35}(Mn_{0.30}V_{0.14}Cr_{0.11}Ni_{0.45})_{1.76}$ alloy using $Ti_{0.8}Zr_{0.2}V_{0.5}Mn_{0.5}Ni_{0.7}$ as a surface modifier. The changes in the thermodynamic and electrochemical properties of the modified alloy were investigated. Finally, the effects of the ball-milling process on the kinetic characteristics of the Zr-based hydrogen storage alloy were revealed on the basis of electrochemical and phenomenological analyses.

2. Experimental

The base alloy [$Zr_{0.65}Ti_{0.35}(Mn_{0.30}V_{0.14}Cr_{0.11}Ni_{0.45})_{1.76}$] and surface modifier alloy ($Ti_{0.8}Zr_{0.2}V_{0.5}Mn_{0.5}Ni_{0.7}$) were prepared in an arc-melting furnace under an argon atmosphere, respectively. The purity of the metals 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 a powder with a characteristic particle diameter less than 45 μm. This powder was employed in the ball-milling process. The surface modified alloy samples were prepared by ball milling with Zr-, and Ti-based alloy powders. Mechanical alloying was performed with an SPEX mill at different ball milling times in Ar atmosphere. For the electrochemical measurement, electrodes were made by mixing the ball-milled powder with copper powder in a weight ratio of 2:1 and pressing this mixtures at a pressure of 10^4 Pa to porous pellets having 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 which temperature was held at 30±1°C. The alloy electrode was galvanostatically charged at 100 mA/g for 6 h, and 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. Before cyclic voltammograms were measured, the working electrode was repeatedly swept at 0.025 mA/s between −1.0 and −0.7 V vs. Hg/HgO.

The interface in the cross-section of ball-milled alloy powders was examined by transmission electron microscopy (TEM) and the chemical compositions of the alloy constituting elements in the interface were estimated by energy dispersive spectroscopy (EDS) analysis. The morphological changes of ball-milled powders with increasing ball-milling time were imaged by scanning electron microscopy (SEM) to determine the factor affecting the activation characteristics of ball-milled alloys. 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 (1 Torr=133.322).

3. Results and discussion

3.1. Analysis of X-ray diffraction patterns

The change of the crystallographic structure after ball-milling is shown in Fig. 1. It is seen that the crystallinity of the alloy is maintained even though the ball-milling was applied. This opens the possibility of modifying the alloy surface without changing the bulk characteristics.

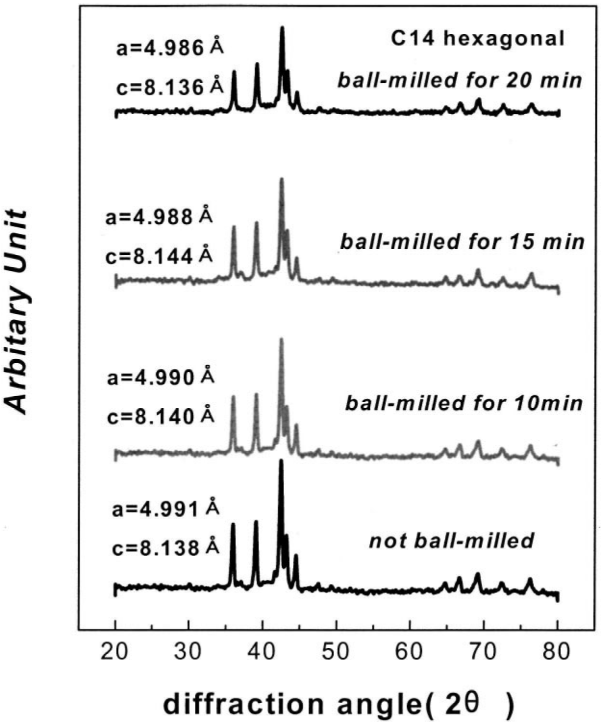

Fig. 1. X-Ray diffraction patterns of ball-milled powders for various ball-milling times.

3.2. Establishment of ball-milling conditions

To improve the kinetic characteristics of the base alloy (Zr-based alloy) electrode effectively, optimization of ball-milling condition is required. Generally, the main optimized parameters are ball-milling time (5, 10, 15, and 20 min), ball-to-powder weight ratio (6:1), and weight ratio of Ti alloy powder (3, 5, and 10 wt.%). First of all, to optimize the ball-milling time, the surface of Zr-based alloy was modified with 10 wt.% of Ti-based alloy. The ball-milling time, at the constant ball-milling speed of 500 rpm was varied and the ball-to-powder weight ratio was kept constant (6:1). We can assure that the Zr-based alloy electrode surface modified by ball-milling for 15 min is fully activated in the first electrochemical cycle. However, the surface modified electrode with 10 wt.% of Ti alloy powder seems to become degraded gradually with cycling. Therefore, the weight ratio of the Ti alloy powder should be reduced for securing the durability of the surface modified Zr-based alloy electrode.

In Fig. 2, the change of the initial activation characteristics for Zr-based alloy electrodes surface modified with Ti alloy powder in weight ratio of 0.95:0.05. We define C_{real} as the discharge capacity calculated from the corresponding weight ratio of the base alloy (Zr-based alloy) and the surface modifier (Ti-based alloy), considering the discharge capacity of each alloy. The C_{real} values of the ball-milled systems with various weight ratios of Ti alloy powder are presented in Table 1.

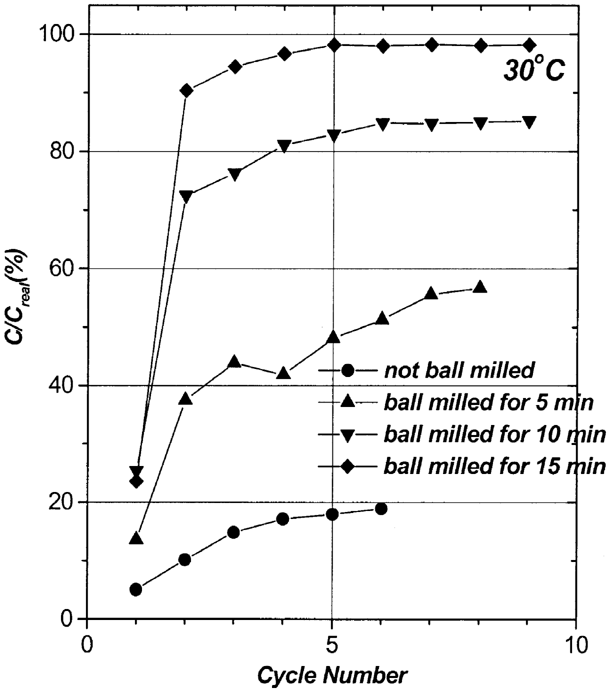

Fig. 2. Changes in the initial activation characteristics of a Zr-based alloy electrode surface modified with Ti alloy powder in the weight ratio 9.5:0.5.

Table 1
The expected discharge capacity (C_{real}) of ball-milled Zr-based alloy with the various weight ratios of the Ti-based alloy as a surface modifier

	W_{Ti} (%)		
	10	5	3
C_{real} (mAh/g)	418	419	420

C_{real} (mAh/g)=($W_{\mathrm{Ti}} \times C_{\mathrm{Ti}}$)+($W_{\mathrm{Zr}} \times C_{\mathrm{Zr}}$), where $W_{\mathrm{Ti}}+W_{\mathrm{Zr}}=1$. W_{Ti}: Weight fraction of Ti-based alloy to total weight of mixed alloy before ball-milling. W_{Zr}: Weight fraction of Zr-based alloy to total weight of mixed alloy before ball-milling. C_{Ti}: Discharge capacity of Ti-based alloy at 100 mA/g of discharge current density at 30°C. C_{Zr}: Discharge capacity of Zr-based alloy at 100 mA/g of discharge current density at 30°C.

It is clear that the surface modified Zr-based alloy electrode with 5 wt.% of Ti alloy powder is easily activated within four cycles without any degradation at the initial cycling stage. The surface of the Zr-based alloy mixed with 5 wt.% Ti alloy powder is modified effectively by ball-milling for 15 min in respect to the electrochemical properties such as activation characteristics, discharge capacity, and cyclic stability.

3.3. Rate-capability of surface modified alloy at initial cycles

For ball-milled alloy electrode with 5 wt.% of Ti-based alloy powder for 15 min, As shown in Fig. 3a and b, the rate-capability of Zr-based alloy electrode at initial cycles is abruptly improved by surface modification through ball-milling process.

3.4. P–C–T characteristics of surface modified alloy

From the above results, we can derive that the discharge capacity of the surface modified alloy is nearly equal to C_{real}. Fig. 4 shows the change of P–C–T characteristics of the surface modified alloy with increasing ball-milling time. The hydrogen equilibrium pressure is slightly increased, but the reversible hydrogen storage capacity is little changed, which can explain that real discharge capacity is maintained even after ball-milling.

3.5. Cyclic voltammetry experiment

In order to demonstrate the activation process with electrochemical cycling, cyclic a voltammetry experiment is performed. Cyclic voltammograms of the untreated and ball-milled alloy electrodes, obtained at a scan rate of 0.025 mV/s in the potential range of −0.7 to −1.0 V, are shown in Fig. 5a and b. For the both samples, hydrogen is absorbed in the cathodic direction and then oxidized in the anodic direction. However, the hydrogen absorption/desorption peak of the ball-milled samples in this potential range becomes more strikingly apparent than that of the non-treated alloy sample with electrochemical cycling. It is

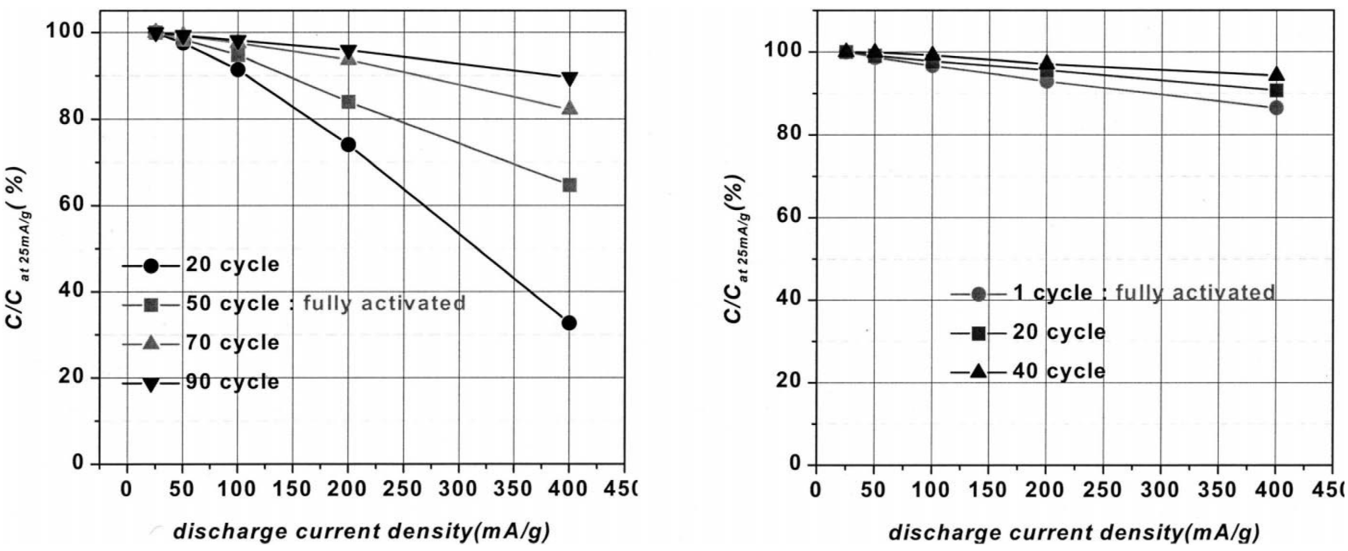

Fig. 3. Comparison of rate-capability of alloy electrode (a) before ball-milling, and (b) after ball-milling at initial cycles.

obvious that the initial hydrogen charging/discharging proceeds more easily for the ball-milled alloy electrode than for the non-treated alloy electrode does.

3.6. Microstructural analysis for ball-milled alloy sample

In order to identify the origin of the formation of a hydrogen permeable surface structure after ball-milling, TEM and EDS analyses were performed. Fig. 6 shows the TEM bright-field images of the cross section of ball-milled alloy powder magnified by 1.15×10^5. It is observed that there is a surface-alloying region at the contact points between the two alloy powders. Moreover, EDS analysis clearly shows that the atomic concentration of constituting elements in surface alloying region is gradually changed between the two alloy powders (Fig. 7). From the above results, it can be inferred that the high kinetic energy causes cold-welding or surface alloying at the points of impact where the Zr-based alloy particles collide with the Ti-based alloy particles by the action of steel balls at high speed.

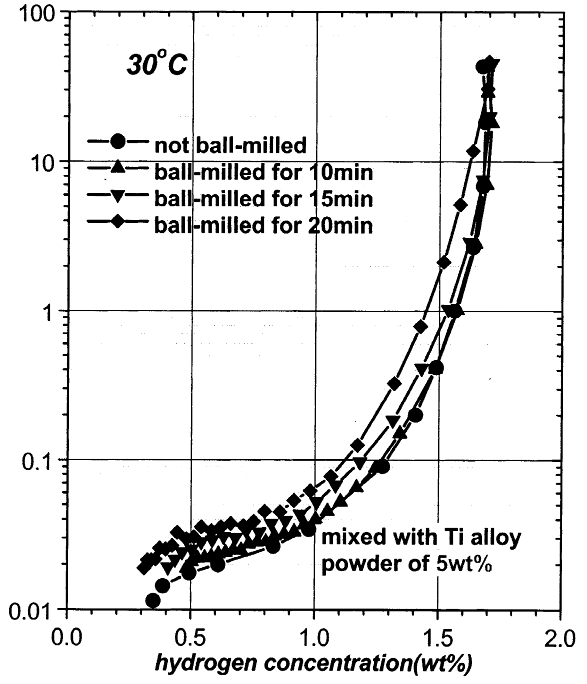

Fig. 4. Changes in the P–C–T characteristics of a surface modified Zr-based alloy with variation of ball-milling time.

Züttel et al. have suggested that the strategy of substitution of Ti for Zr in Zr-based alloys is effective for improving the kinetic characteristics due to a hydrogen permeable Ti oxide film leading to easier absorption/desorption of hydrogen [12]. Eventually, it can be suggested that Ti-alloy powder serves as a window for hydrogen to penetrate into the Zr-based alloy, which leads to the easy absorption/desorption of hydrogen, and also to the improvement in kinetic properties of the Zr-based alloy electrode.

4. Conclusions

Ball-milling has been applied to a Zr-based alloy using Ti-alloy powder as a surface modifier. It is shown that the ball-milled alloy has crystalline characteristics similar to those of the as-cast one, which indicates that it is possible to modify the alloy surface without changing the bulk characteristics. Furthermore, the measurements of P–C–T characteristics also show that the reversible hydrogen storage capacity is little changed even though a ball-milling process was applied. The above results are responsible for maintaining the inherent discharge capacity(about 360 mAh/g) of the matrix alloy (Zr-based alloy) after

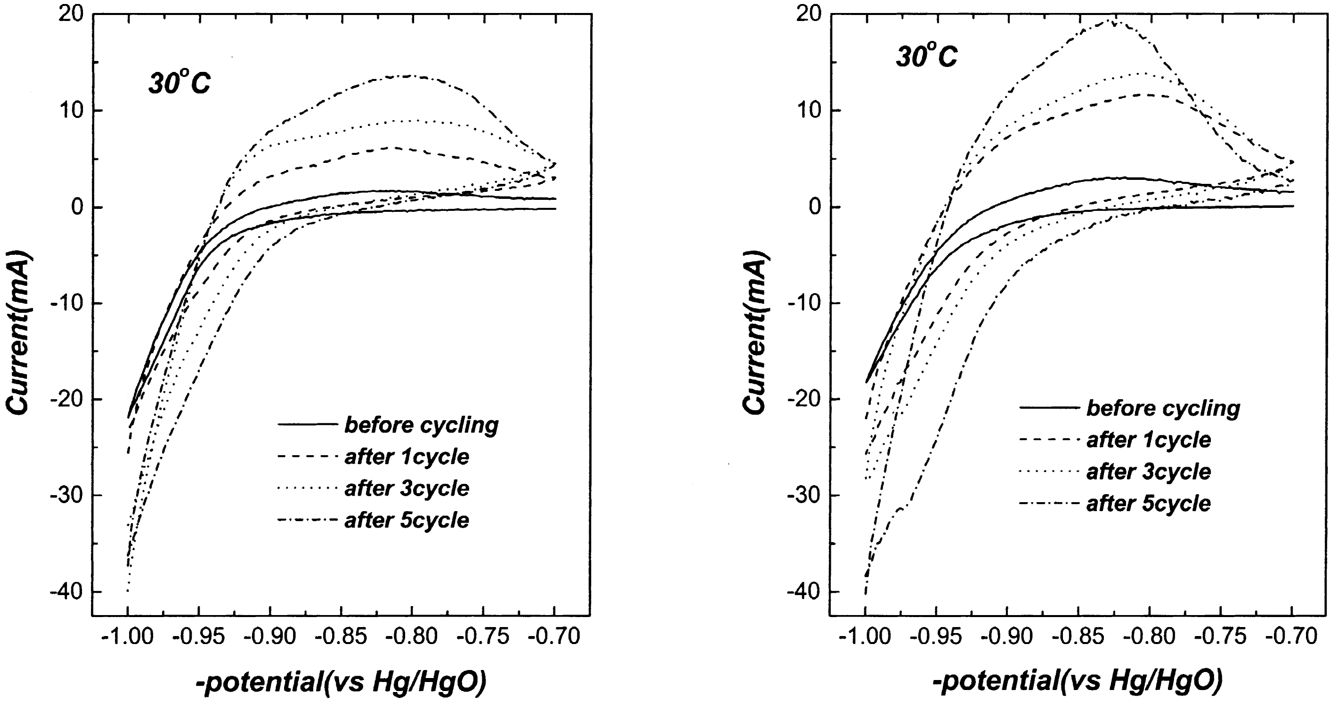

Fig. 5. Cyclic voltammograms of (a) an as-cast alloy electrode and (b) ball-milled alloy electrode with 5 wt.% of Ti alloy powder with cycling.

ball-milling. Consequently, while the Zr-based alloy electrode is not fully activated before 50 cycles, the ball-milled one is fully activated within only four cycles. It is evident that the surface of the Zr-based alloy mixed with 5 wt.% Ti-based alloy powder is effectively modified by ball-milling for 3 h with regard to the electrochemical properties such as activation characteristics, discharge capacity and cycle stability. It is derived from the TEM and EDS analyses that there is a surface alloying region at the contact points between the two alloy powders. The particle size is decreased with increasing ball-milling time. It means an increase in the surface area of Zr-based alloy particles in contact with Ti-based alloy particles resulting in an improvement of the kinetic characteristics for the ball-milled alloy electrode with increasing ball-milling time. Eventually, it can be suggested that the Ti-based alloy powder serves as a window for hydrogen to penetrate into the Zr-based alloy which leads to easy absorption/

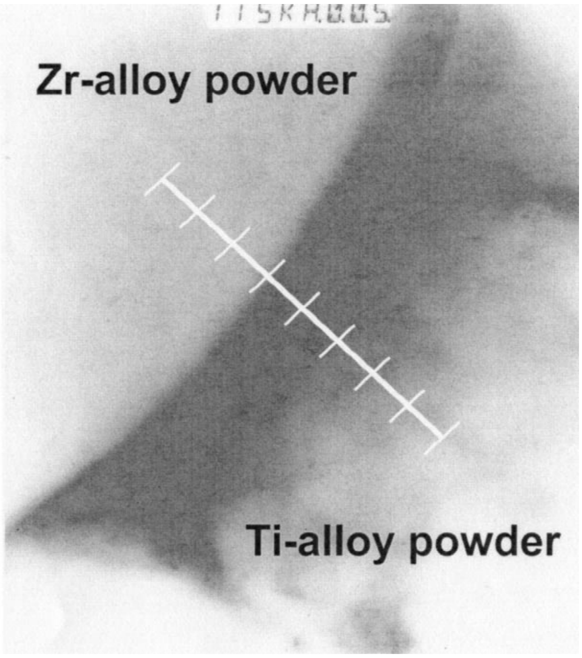

Fig. 6. TEM bright-field image of the cross section of ball-milled alloy powder magnified by 1.15×10^5.

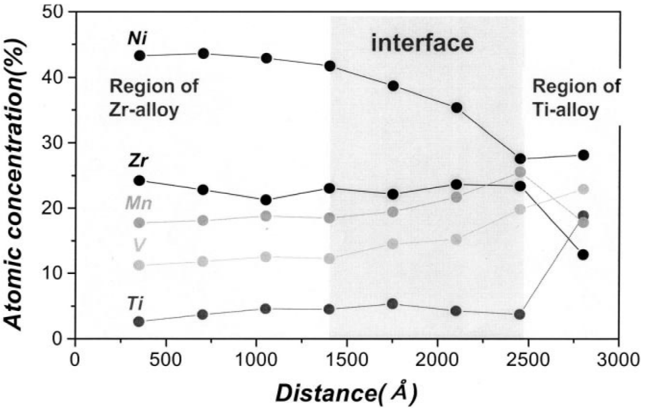

Fig. 7. Changes in the atomic concentration of the constituting elements in the surface-alloying region after ball-milling for 15 min.

desorption of hydrogen and also to an improvement in the kinetic properties of the Zr-based alloy electrode at initial cycles.

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