# An electroless copper plating method for Ti, Zr-based hydrogen storage alloys

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## Abstract

An acidic electroless copper plating method using HF has been developed and applied to the hydrogen storage alloy: $Zr_{0.5}Ti_{0.45}V_{0.54}Ni_{0.87}Cr_{0.15}Co_{0.21}Mn_{0.24}$. It is shown that the copper plating mechanism is an ion-exchange process between alloy elements and copper ions. The resulting copper coating is metallic. The coated copper layer significantly improved activation properties of the alloy electrode for a Ni–MH secondary battery. Anodic polarization curves and SEM micrographs showed that the reason for this improvement is due to the dissolution of a surface oxide film by HF during the copper plating. This coating method was also successfully applied to eight other Zr(Ti) alloy powders with different compositions. It can be concluded that this electroless copper plating method can be widely applied to Ti(Zr)-based hydrogen storage alloys of various compositions which had been regarded to be difficult to coat by conventional electroless copper plating methods.
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## 1. Introduction

Ti, Zr-based hydrogen storage alloys have been extensively studied for use as the negative electrode of Ni–MH batteries, for fuel storage for hydrogen vehicles and as heat pumps; it has a high hydrogen storage capacity, over 2 wt%, and the alloy cost is low compared to rare earth-based hydrogen storage alloys [1–4]. For practical use this alloy has problems such as delayed activation and a shorter cycle life than rare earth-based hydrogen storage alloys [5,6]. It is known that a dense Zr oxide film formed on alloy surfaces hinders the reaction between the proton ($H^+$) and electron as well as adsorption of hydrogen molecules [7]. For these reasons $AB_2$-type alloys have not been used as the negative electrode for Ni–MH secondary batteries whereas $AB_5$-type alloys have commercial use.

In order to prevent $AB_2$-type alloys from forming a Zr oxide film or else to remove it, great efforts have been made, such as modification of alloy composition [6],

fluorination of the alloy surface [8], alkaline etching [9] and ball-milling [10,11].

On the other hand, for the case of $AB_5$-type hydrogen storage alloys, the micro-encapsulation by copper on the alloy surface was introduced as a very effective way to improve electrical and thermal conductivity and remove the oxide layer [12–16]. Park and co-workers [14–16] reported that $AB_5$-type hydrogen storage alloys could be easily coated by copper using an acidic electroless copper plating solution containing copper ions and $H_2SO_4$ as a catalyst. They reported that the copper coated alloy electrode showed a higher discharge capacity, better activation properties, longer cycle life and a better formability compared to the uncoated alloy electrode. For the Ti, Zr-based hydrogen storage alloys, however, this method could not be applied because $H_2SO_4$ was not able to dissolve the Zr and Ti oxide films, consequently the necessary ion-exchange between metal ions in the alloy and copper ions in solution could not occur. The use of HCl or $HNO_3$ instead of $H_2SO_4$ was unsuccessful. HF is more corrosive than these and therefore, we have tried to use it for electroless copper plating of the Zr(Ti) based

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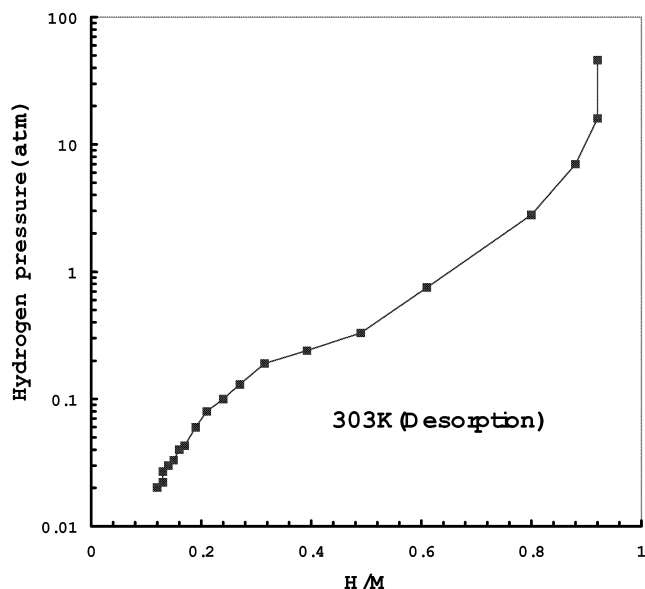*E-mail address:* cnpark@chonnam.ac.kr (C.N. Park).

Fig. 1. Pressure–composition isotherm of the $Zr_{0.54}Ti_{0.45}V_{0.54}Ni_{0.87}Cr_{0.15}Co_{0.21}Mn_{0.24}$ alloy.

alloys. In this paper we report on the results of this experiment.

## 2. Experimental

The $AB_2$-type hydrogen storage alloy used in this experiment was $Zr_{0.5}Ti_{0.45}V_{0.54}Ni_{0.87}Cr_{0.15}Co_{0.21}Mn_{0.24}$ alloy powder with particle size below 75 μm. This alloy was developed for an electrode of a Ni–MH secondary battery. The alloy has the hydrogen storage capacity of 0.92 H/M and a desorption plateau pressure approximately 1 atm at 303 K. The $P$–$C$ isotherm of this alloy is shown in Fig. 1. The alloy powder (0.3 g) was immersed in the copper plating solution of 50 ml containing $CuSO_4$ 0.298 g (about 25 wt% Cu with respect to alloy weight) with 0.2 ml of HF at room temperature for times between 1 and 5 min. Chemical analyses of the plating solutions and alloy powder and SEM observation of the powder before and after coating for given time periods were performed. After

plating, the alloy powder was washed in distilled water and methanol and dried in vacuum to avoid oxidation. About 0.2 g of the powder was cold compacted (6 tonnes cm$^{-2}$) into disk shape electrodes of 10 mm diameter. The disks were connected to a holder made of nickel grid and used for electrochemical measurements. The measurements were conducted in a half cell which contained the metal hydride electrode, a platinum counter electrode, a Hg/HgO reference electrode and 6 M KOH solution as electrolyte. Charging–discharging cycles were automatically carried out up to 100 cycles. The charging and discharging currents were of equal magnitude (15 mA). Discharging was interrupted at −650 mV (vs. Hg/HgO) to avoid any oxidation of copper. A rest time of 20 s were allowed for every change of the current direction.

Potentiodynamic polarization tests were also performed on the electrodes.

## 3. Results

### 3.1. Mechanism of copper plating

In order to confirm the coating mechanism, the compositions of the alloy and coating solution was analysed by ICP–AES before and after coating. As shown in Table 1, all elements in the alloy were dissolved into the coating solution with the almost same composition before dissolution and all of the copper ions in the solution were precipitated on the alloy surface as metallic copper [14].

The alloy surfaces observed by SEM during coating process is shown in Fig. 2. The SEM results of the copper plating process can be summarized as follows:

1. HF erodes the oxide film on the alloy surfaces
2. The alloy dissolves into the solution and simultaneously copper precipitates on the alloy surfaces
3. The precipitated copper grows and covers all alloy surfaces

In order to analyse the coating process the pH of the coating solution was examined during coating and the results are represented in Fig. 3. With dissolution of $CuSO_4$, the pH value of the coating solution fell from 7.0

Table 1
Result of ICP–AES analysis (numbers are wt% with respect to alloy weight)

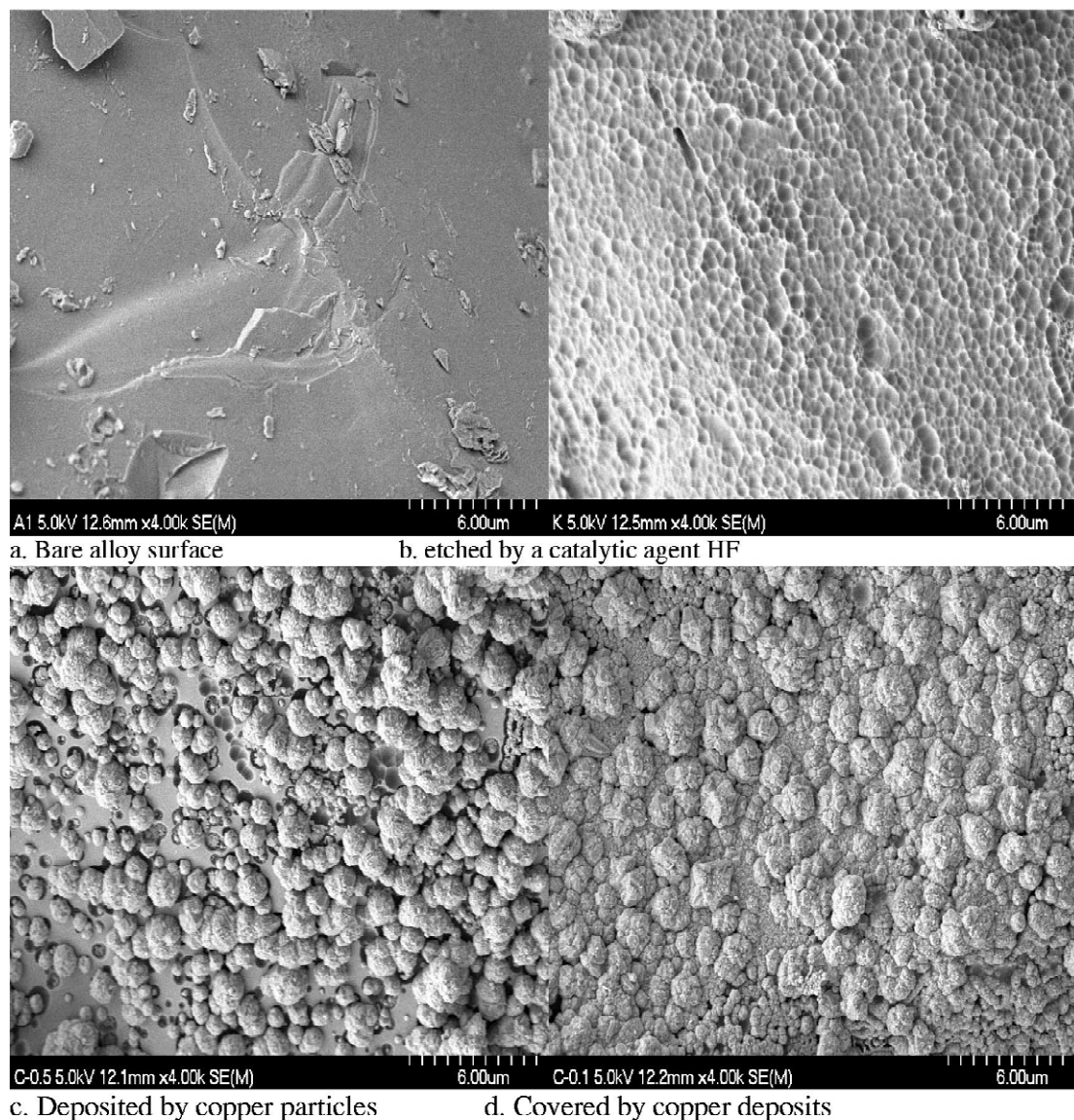| Time | | Element | | | | | | | |
|------|------|------|------|------|------|------|------|------|------|
| | | Ti | V | Cr | Mn | Co | Ni | Zr | Cu |
| Before coating | Alloy | 12.06 | 15.29 | 2.15 | 3.49 | 3.59 | 31.63 | 26.93 | 0.00 |
| | Solution | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 25.00 |
| After coating | Alloy | 10.22 | 11.16 | 3.16 | 5.55 | 5.21 | 21.64 | 19.22 | 23.37 |
| | Solution | 0.11 | 0.13 | 0.04 | 0.06 | 0.06 | 0.24 | 0.23 | 0.00 |

Fig. 2. SEM micrographs of alloy surfaces after copper coating.

to 4.2 and by adding HF it fell to 3.0. When the alloy powder was placed into the solution the pH value decreased quickly to about 2.0 and as coating proceeded it decreased gradually to 1.7.

### 3.2. Electrochemical properties of the copper coated alloy

Fig. 4 shows the activation behavior of $Zr_{0.5}Ti_{0.45}V_{0.54}Ni_{0.87}Cr_{0.15}Co_{0.21}Mn_{0.24}$ alloy with and without copper coating. There is a remarkable difference in initial capacities of the 1st cycle between the copper coated alloy electrode (154 mAh $g^{-1}$ alloy) and the non-coated (7 mAh $g^{-1}$ alloy). The improvement of activation by copper coating can be attributed to a removal of oxide film by HF.

The maximum capacity of the alloy electrode also increased by copper coating from 248 to 352 mAh $g^{-1}$ alloy. This is due to an increase of alloy utilization. The copper coating increases the electrical conductivity and binding force between the alloy particles. The potentiodynamic polarization test was done for the copper-coated and non-coated alloy electrodes and the results are represented in Fig. 5. The copper-coated alloy electrode shows a lower redox potential than the non-coated one. This means an easier oxidation of the copper-coated electrode than the non-coated one. It must be emphasized that the lower redox potential in the copper-coated electrode does not mean an easier corrosion of the alloy, rather it arises from oxidation of the hydrogen that was absorbed during reduction ($<-0.94$ V). The higher current density in the

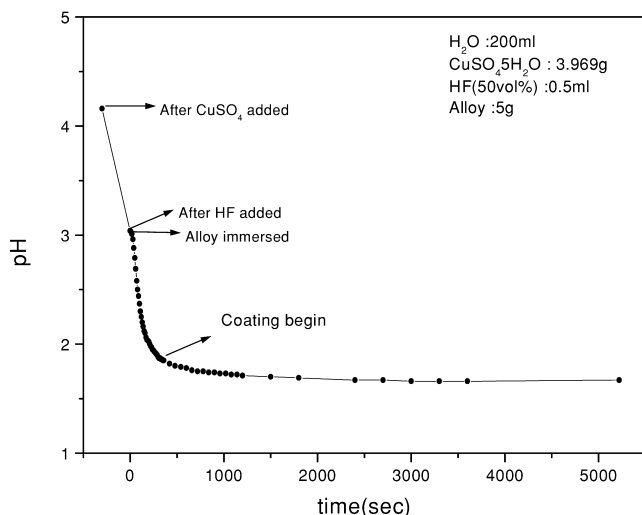Fig. 3. Change of pH value of the coating solution during copper coating.



Fig. 5. The potentiodynamic polarization curves of the non-coated and copper coated electrodes in 6 M KOH at 25 °C.

copper-coated electrode at potentials from −0.75 to −0.3 V was also due to the oxidation of hydrogen. Oxidation of hydrogen in the non-coated electrode can be seen as a very small peak just above its redox potential in Fig. 5. The fact that the copper-coated alloy electrode absorbed hydrogen during the same reduction condition much more than the non-coated one demonstrates that copper-coating improves the activation of the alloy electrode, as shown by the first discharge capacities (Fig. 4). Two peaks, which appear for the copper-coated electrode in Fig. 5 indicated by arrows, are likely to correspond to the following reactions:
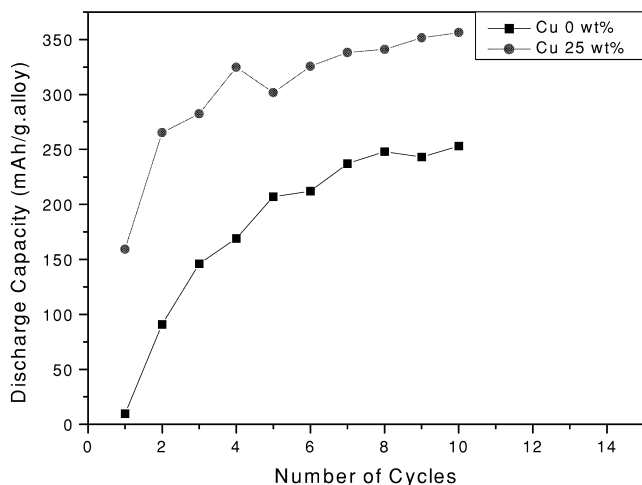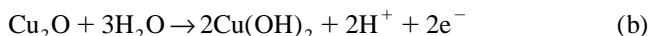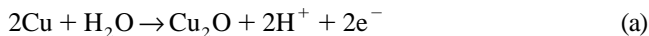
$$2Cu + H_2O \rightarrow Cu_2O + 2H^+ + 2e^- \qquad (a)$$

$$Cu_2O + 3H_2O \rightarrow 2Cu(OH)_2 + 2H^+ + 2e^- \qquad (b)$$

### 3.3. Application to other hydrogen storage alloy electrodes

In order to know whether this copper coating process is applicable to other hydrogen storage alloys, eight $AB_2$-type alloys with different compositions were investigated. The alloy powders were coated by 25 wt% copper and then cold pressed into electrodes without any conducting or binding material. The results of electrochemical tests were shown in Fig. 6. As shown in Fig. 6, all of the $AB_2$-type alloy electrodes showed very fast activation behavior and high discharge capacities.

### 4. Conclusions

An acidic electroless copper plating with HF solution for titanium and zirconium-based hydrogen storage alloys has been developed. HF plays the role of removal of the oxide film which hinders the ion-exchange between copper ion in solution and the alloy elements. The copper coating obtained by this method improved significantly the activation properties and discharge capacities of the Zr(Ti)-based hydrogen storage alloy electrodes for a Ni–MH secondary battery. It can be concluded that the acidic electroless copper plating containing HF as a catalytic agent is a promising method to copper coat the Ti, Zr-based $AB_2$-type hydrogen storage alloy powders and to fabricate electrodes of this type.



Fig. 4. The activation behavior of alloy electrode with and without copper coating.
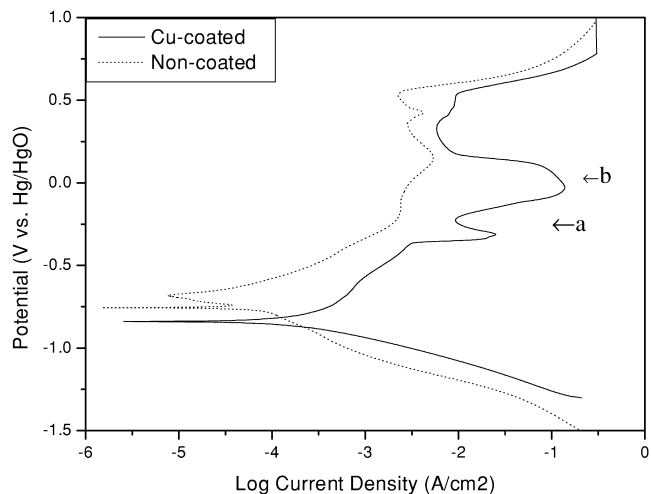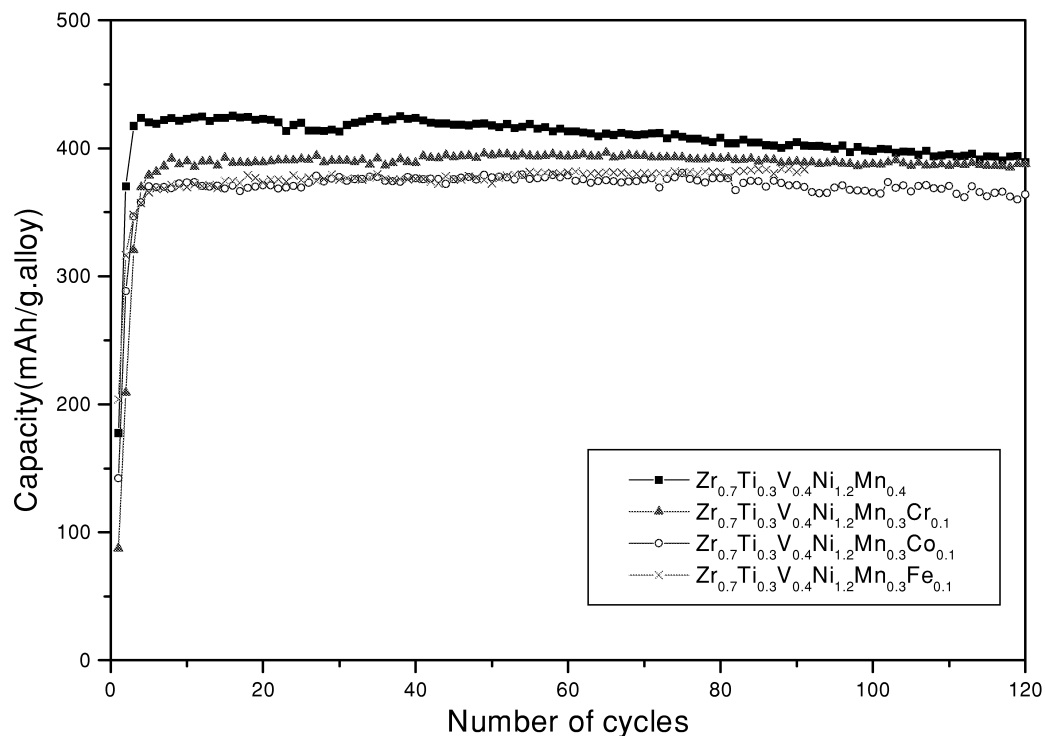
### Acknowledgements

Fig. 6. The discharge capacities of the 25 wt% Cu-coated $Zr_{0.7}Ti_{0.3}V_{0.4}Ni_{1.2}Mn_{0.3}M_{0.1}$ alloy electrodes. The weight of the copper coatings are excluded for the calculation of the capacities.

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