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The optimal condition of acidic electroless copper plating method for Ti, Zr-based hydrogen storage alloys for electrode use

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Abstract

An acidic electroless copper plating using HF for titanium and zirconium-based hydrogen storage alloys shows a significant improvement in activation and discharge capacity of the alloy electrodes even though the plating process is simple. In this paper, the optimal conditions of this acidic electroless copper plating have been investigated for Ti, Zr-based AB_2-type alloy powders for a negative electrode of a Ni–MH secondary battery. $Zr_{0.5}Ti_{0.45}V_{0.54}Ni_{0.87}Cr_{0.15}Co_{0.21}Mn_{0.24}$ alloy powder was coated by copper under various coating conditions (amount of catalytic agent, stirring speed and temperature of coating bath, and amount of coated copper) and the coatings were examined by S.E.M. The electrodes prepared by the copper coated alloy powders were electrochemically tested. Considering the electrode properties and economics, it is suggested that the optimal coating conditions are: 0.2 ml as an amount of agent (HF), 400 rpm as a stirring speed, 25 °C as a coating temperature and 2 wt% as an amount of coated copper for 0.3 g of alloy in 50 ml of distilled water.

Keywords: Electrochemical reactions; Metal hydrides

1. Introduction

A Ti, Zr-based hydrogen storage alloy as a negative electrode of Ni–MH secondary battery has been studied intensively because it has a large hydrogen storage capacity, good cycle life and low cost [1–4]. It is, however, more difficult to activate than AB5-type hydrogen storage alloys, and therefore many studies to improve the activation property have been undertaken [5–10]. Recently authors [11] have reported that a microencapsulation of the Ti, Zr-based AB_2-type alloy powders with copper by an electroless copper plating using HF acid as a catalytic agent is a promising method to improve the activation and discharge capacity of the alloy electrode. The plating method is very simple requiring a few minutes to complete whereas a conventional reduction-type electroless copper plating method requires 30–60 min. The HF removed the oxide film layer on the alloy surface during the coating process and the coated copper had a good electrical conductivity and formability.

The purpose of this research is to determine the optimal conditions of the electroless copper plating for Ti, Zr-based AB_2-type alloy powders for use as negative electrodes of Ni–MH secondary batteries.

2. Experimental

The hydrogen storage material used in this experiment was a $Zr_{0.5}Ti_{0.45}V_{0.54}Ni_{0.87}Cr_{0.15}Co_{0.21}Mn_{0.24}$ alloy powder with particle size below 75 μm. For a copper coating, 0.3 g of the alloy powder was immersed in the copper plating solution (50 ml). The variables of coating were amounts of $CuSO_4$ (2–25 wt% in copper with respect to copper coated alloy weight), amounts of HF (0.05–0.5 ml), coating temperatures (0, 25 and 50 °C) and stirring speeds (400–800 rpm). For simplicity and convenience all other variables were fixed as standard condition (25 wt% Cu, 0.2 ml HF, 25 °C and 800 rpm, respectively) except the variable whose optimal conditions were to be de-

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termined. A coating completion time was determined by measuring the saturation time of pH change during coating. After Cu plating, the alloy powder was washed in distilled water and methanol and dried in vacuum to avoid oxidation. Some alloy powders were examined by S.E.M. to observe the morphologies of the copper coatings. About 0.2 g of the copper coated alloy powder was cold compacted (6 ton/cm^2) into a disk electrode with 10 mm diameter. The disk was connected to a holder made of nickel grid and used for electrochemical measurements which were conducted in a half-cell containing the metal hydride electrode, a platinum counter electrode, a Hg/HgO reference electrode and 6 M KOH solution as electrolyte. Charging–discharging cycles were carried out automatically up to 10 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 was allowed for every change of current direction.

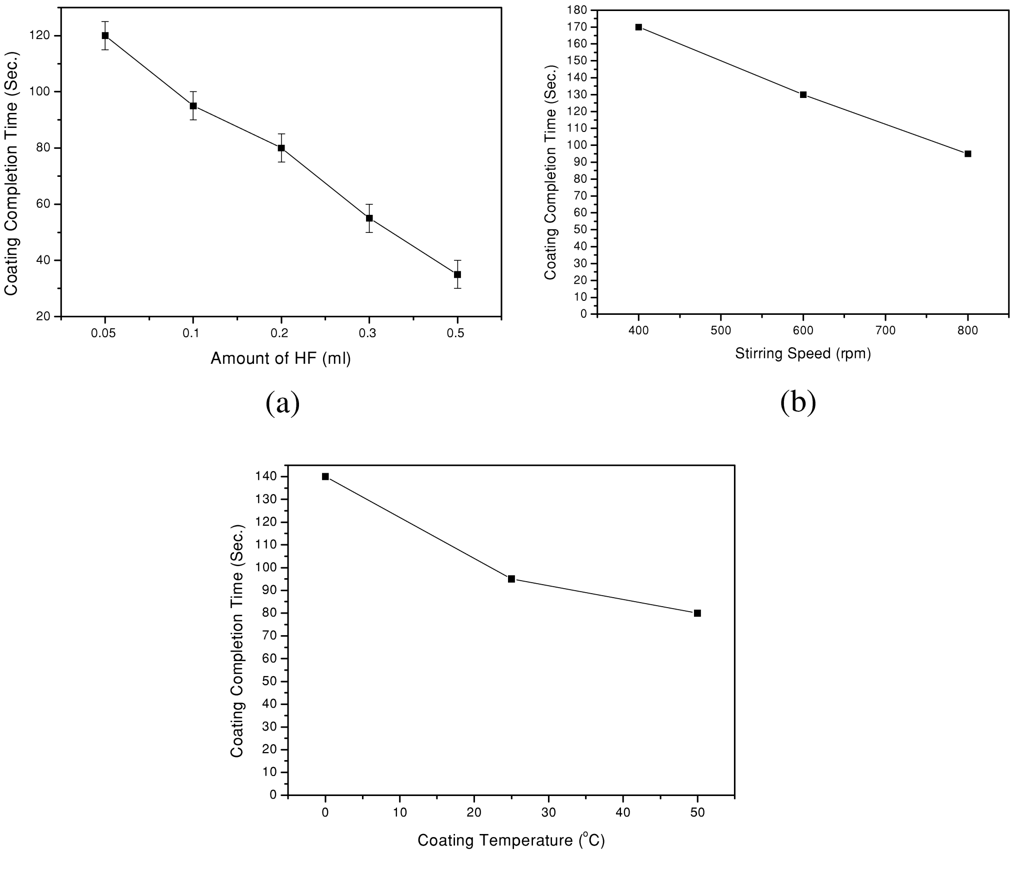
3. Result

3.1. Amount of HF

Fig. 1 shows the coating completion times as a function of the amount of HF (a), stirring speed (b) and coating temperature (c). As shown in Fig. 1(a), the coating completion time decreased from 120 s at 0.05 ml to 40 s at 0.5 ml with increasing amount of HF. The surface morphologies change with amounts of HF and shown in Fig. 2 where it can be seen that when the amount of HF was too small, nucleation of the copper deposit was limited to high energy sites such as sharp edges and grain boundaries, resulting in a severely non-uniform copper coating. On the other hand, if too much HF was added the coating layer easily peeled off the alloy. The reason for this was that an eroding of the alloy surface by the HF acid continued even after completion of the copper coating. Thus an optimal amount of HF must be added to the solution. In the cases of 0.1 or 0.2 ml HF, it was found that the alloy surface was covered with copper relatively uniformly. The discharge capacities of the electrodes prepared by the alloy powders with different amount of HF are shown in Fig. 3 where it is seen that the electrode of 0.2 ml HF has the best discharge capacity. Thus it is suggested that an optimal amount of HF for 50 ml distilled water and 0.3 g alloy is 0.2 ml.

3.2. Amount of copper coating

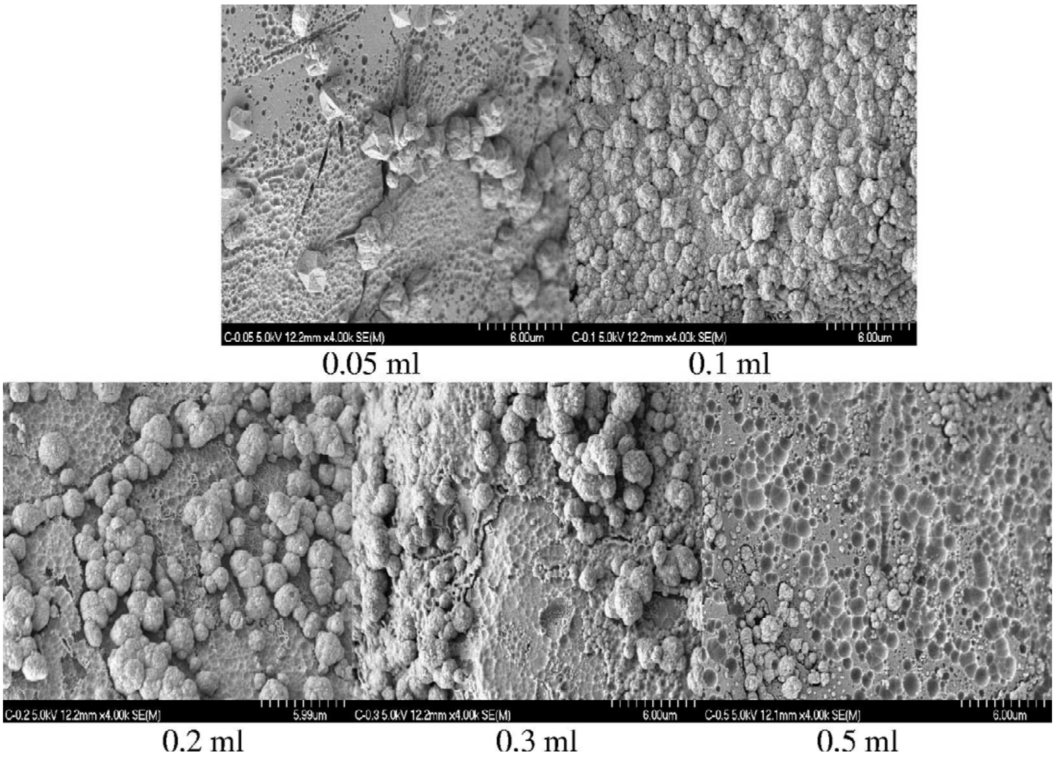
Fig. 4 shows the surface morphologies of the copper



(a) (b)

(c)

Fig. 1. Coating completion time with the change of coating conditions.



0.05 ml 0.1 ml

0.2 ml 0.3 ml 0.5 ml

Fig. 2. S.E.M. photographs of the alloy particles Cu-coated with various amounts of HF.

coated alloy powders with different amounts of copper. Even if the coating was only 2 wt% copper, the alloy surfaces were covered uniformly and it was possible to compact the powders into a pellet without adding any other conducting or binding material. As the amount of copper increased the copper coating became thicker and non-uniform. The discharge capacities of electrodes prepared with these alloy powders are shown in Fig. 5. It can be seen from Fig. 5(a) that the activation and discharge capacity were improved significantly with copper coating, but these improvements do not correlate with the amount of copper coating. The discharge capacity of a 2 wt% copper coating was the best. The discharge capacities estimated per alloy weight, excluding weight of copper, are shown in Fig. 5(b). As the amount of copper coating increased, the discharge capacity per alloy weight increased significantly. It means that the efficiency of alloy utilization of electrodes increases with increasing copper coating and this is reasonable because the copper coating increases the electrical conductivity and binding force between particles. It is concluded that the optimal amount of copper coating is 2 wt%, considering economics and electrode properties.

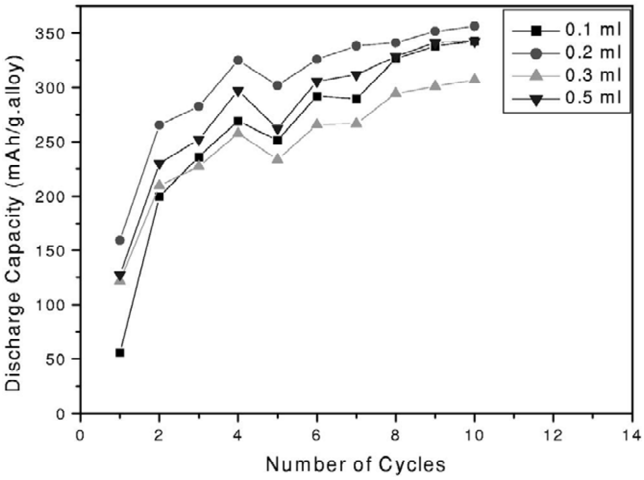
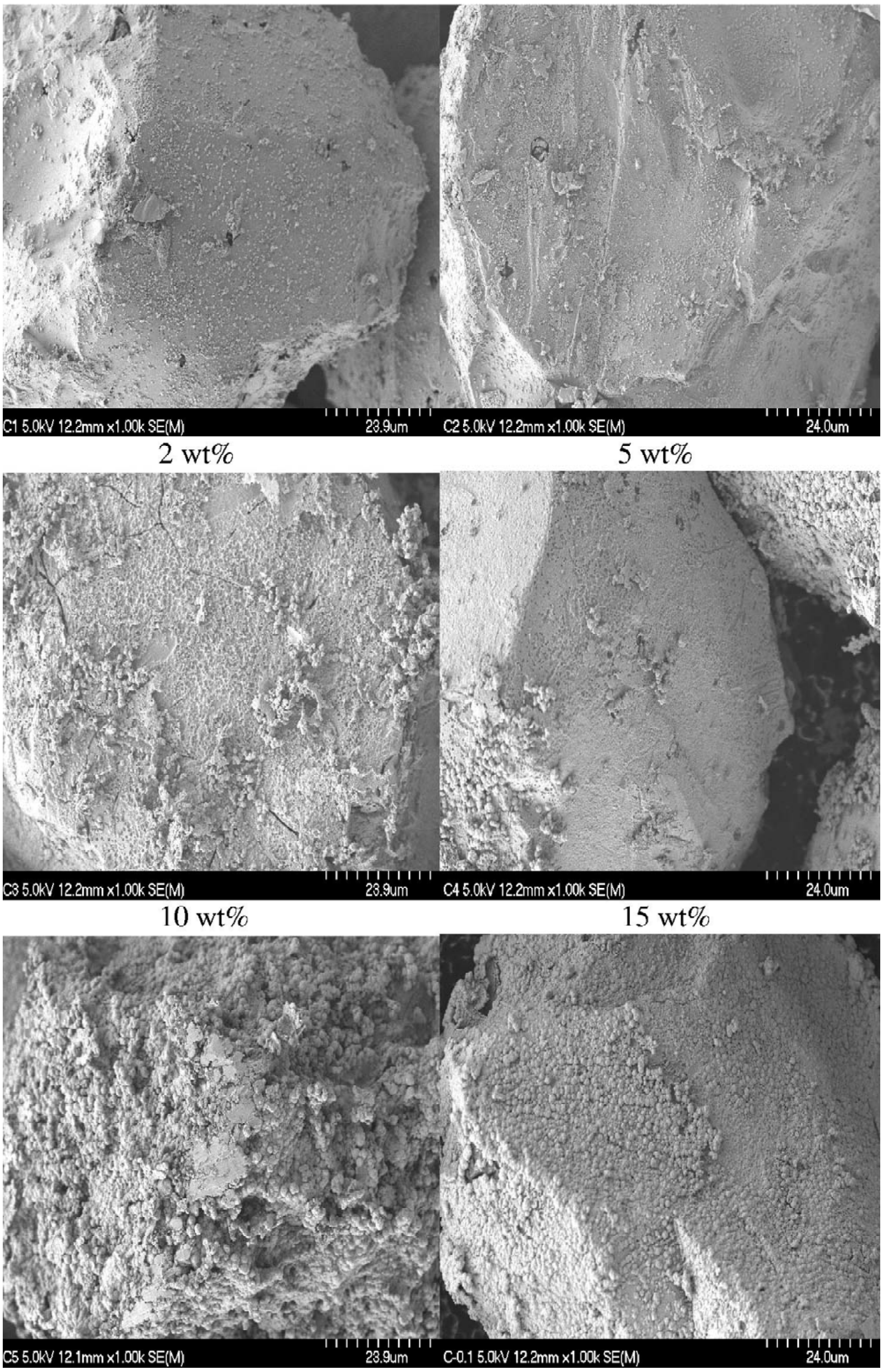


Fig. 3. The discharge capacities of the alloy electrodes 25 wt% Cu-coated with various amount of HF.

3.3. Stirring speed and coating temperature

It was shown in Fig. 1(b) that if the stirring speed increases, the coating completion time decreases. The S.E.M. micrographs of the copper coating on the alloy surfaces showed that the copper deposits are slightly more uniform with increasing stirring speed. The discharge capacities prepared with these powders also did not show a significant difference. Therefore the stirring speed in the range of a few hundreds rpm is appropriate. A speed of 400 rpm was chosen as the optimal because of less energy consumption.

The coating temperature did not affect the surface morphologies nor discharge capacities and therefore the coating temperature was chosen as 25 °C because of its convenience.



2 wt% 5 wt%

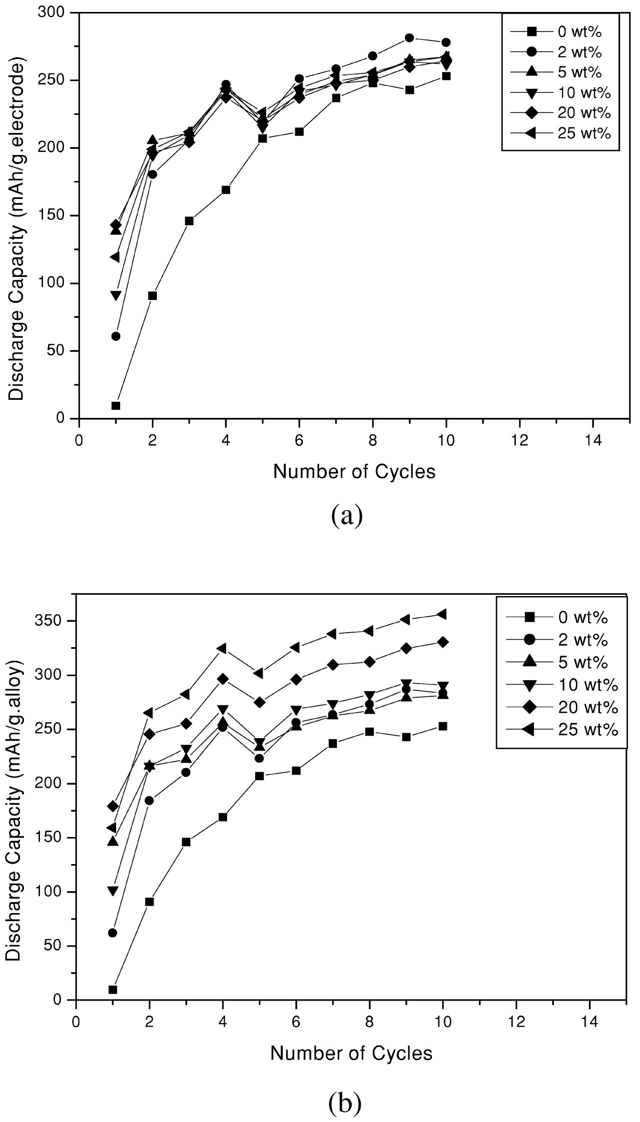
10 wt% 15 wt%

20 wt% 25 wt%

Fig. 4. S.E.M. photographs of the Cu-coated alloy particles with various amounts of copper.

4. Conclusions

The optimal condition of the acidic electroless copper plating using HF as a catalytic agent for the $Zr_{0.5}Ti_{0.45}V_{0.54}Ni_{0.87}Cr_{0.15}Co_{0.21}Mn_{0.24}$ alloy powder as a negative electrode for a Ni–MH secondary battery has been investigated. From the experimental results obtained, it is recommended that the optimal coating conditions are: 0.2 ml as an amount of catalytic agent (HF), 400 rpm as a stirring speed, 25 °C as a coating temperature and 2 wt%



(a)

(b)

Fig. 5. The discharge capacities of the alloy electrodes with various amount of copper: (a) discharge capacity per electrode weight (alloy + Cu); (b) discharge capacity per alloy weight.

as an amount of copper coating for 0.3 g of alloy in 50 ml of distilled water.

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