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Properties of pellet- and paste-type electrodes of AB_5 hydrogen storage alloy

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Abstract

The discharge capacities of pellet- and paste-type AB_5 alloy electrodes were investigated. The $LmNi_{3.6}Al_{0.4}Co_{0.7}Mn_{0.3}$ alloy was chosen and the alloy powder was coated with various amounts of copper by the electroless plating method. The pellet-type electrodes were fabricated by cold pressing the copper-coated alloy powder into disks of 10 mm diameter without any binding material and the paste-type electrodes were prepared by pasting the bare or the copper-coated alloy powders onto the foamed nickel with some organic binders. The discharge capacities of the electrodes were measured through half cell tests. The experimental results showed that for the pellet-type electrodes, as the amount of copper coat increased the discharge capacity per weight of electrode decreased whereas that per weight of alloy increased. For the paste-type electrodes the copper coated alloy powder showed a much higher discharge capacity than the bare alloy powder. However, the increase of the copper coat over a certain amount did not increase the discharge capacity per weight of alloy while decreasing that per weight of electrode. Considering the discharge capacity and mechanical endurance, the most promising electrode was the paste-type electrode with 2.5 wt.% Cu-coated alloy powder and no carbon black.

Keywords: AB_5 hydrogen storage alloy; Electrodes; Discharge capacity; Copper coating

1. Introduction

The AB_5 type alloy electrodes for commercial use are fabricated by a paste method in which organic binders and carbon black as the electric conducting material are used [1]. In laboratories, the pellet-type electrodes are preferentially prepared because of the simplicity of the fabrication process [2,3]. For the latter case the micro-encapsulation of alloy powders with Cu or Ni and cold pressing have been employed [4,5]. It has often been found that the electrodes prepared by different methods had different discharge capacities and this is true in the pellet- and the paste-type electrodes for which the same alloy power has been used. From our experience the discharge capacity, when estimated per gram of alloy, is higher in the pellet-type electrode compared with that of the paste type. This difference, in spite of being found frequently, has been attributed mostly to the erroneous measurements in experiments. In this work it has been studied more accurately to determine the difference in discharge capacity of the pellet- and the paste-type electrodes and the effect of copper coating of the alloy powder.

2. Experimental

$LmNi_{3.6}Al_{0.4}Co_{0.7}Mn_{0.3}$ alloy was melted by arc furnace and remelted several times for homogeneity. After the removal of surface oxide ingots were pulverized into a powder with particle sizes from 200 to 300 mesh. A part of the alloy powder was coated with copper by electroless plating in an acidic bath. The paste type electrodes were fabricated by mixing together the bare or copper-coated powder, hydroxypropylmethyl cellulose organic binder with or without carbon black, and pasting the resultant slurry onto a foamed nickel gauze. They were dried and cut into 20×20 mm sections. The pellet-type electrodes were prepared by cold pressing the copper-coated alloy powder at 6 tons/cm^2 into disks of 10 mm diameter. The weight of the AB_5 alloy in each electrode was about 0.15 g. The electrochemical measurements were conducted in a Pyrex test cell consisting of alloy electrode, a platinum

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counter electrode, a mercury oxide (Hg–HgO) reference electrode and 6 M KOH electrolyte. The charge and discharge currents were determined by the sample weight and kept at 37.2 mA/g (0.115 C rate) for the first ten cycles and 74.4 mA/g (0.230 C rate) for the subsequent cycles. The charge time was 10 h for the first ten cycles and 5 h for the subsequent cycles. The cut-off voltage for discharge was −650 mV (Hg–HgO).

3. Results

3.1. Pressure–composition isotherms

The pressure–composition isotherms for the copper-coated alloy powders are shown in Fig. 1. The hydrogen storage capacities, when estimated excluding the coated copper, of the alloy powders with different copper coating were nearly equal to each other.

3.2. Discharge capacities of the pellet type electrodes

The discharge capacities of the pellet type electrodes per gram electrode and per gram alloy are shown in Figs. 2 and 3, respectively. The discharge capacity per gram electrode decreased whereas that per gram alloy increased with increasing the amount of copper coating.

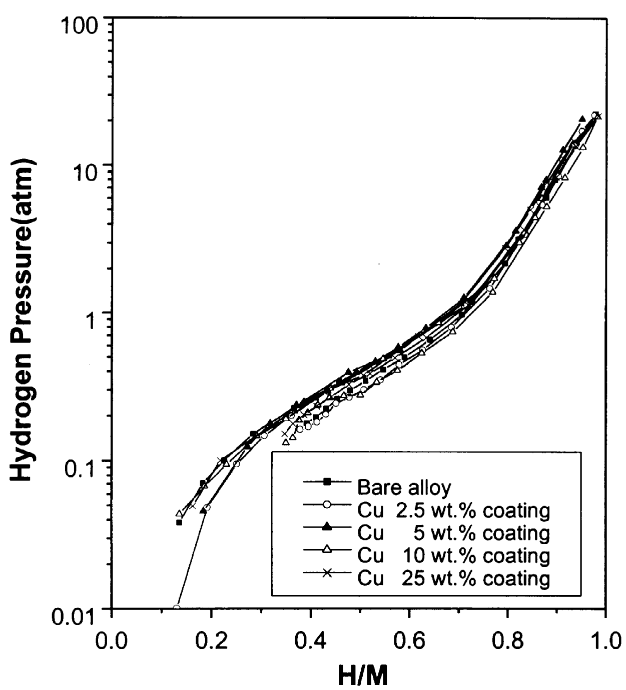

Fig. 1. PCT curves of the Cu-coated $LmNi_{3.6}Al_{0.4}Co_{0.7}Mn_{0.3}$ alloys at 30°C; the weight of the coated copper was excluded for the calculation of H/M.

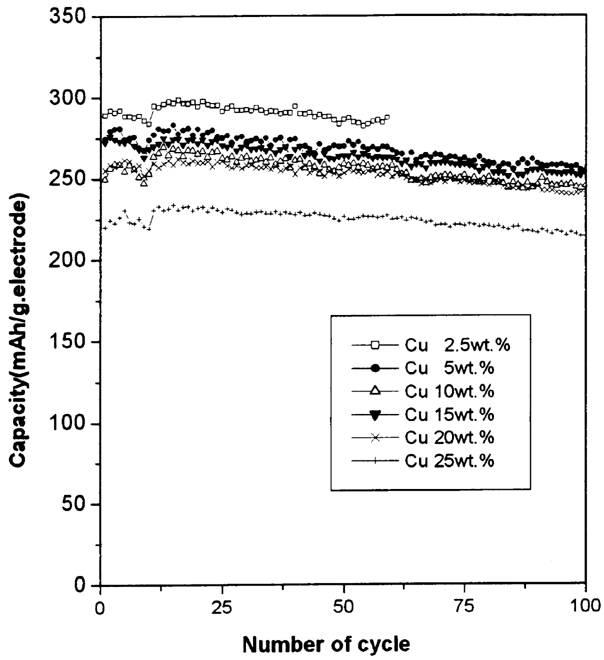

Fig. 2. Discharge capacities (per gram electrode) of the Cu-coated pellet type electrodes.

3.3. Discharge capacities of the paste-type electrodes

The discharge capacities of the paste-type electrodes per gram electrode and per gram alloy are shown in Figs. 4 and 5, respectively. Comparing the discharge capacities of

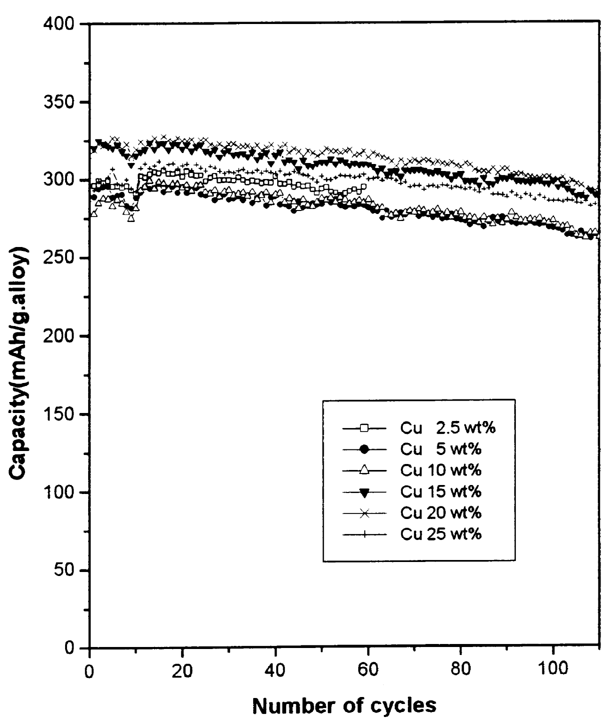

Fig. 3. Discharge capacities (per gram alloy) of the Cu-coated pellet type electrodes.

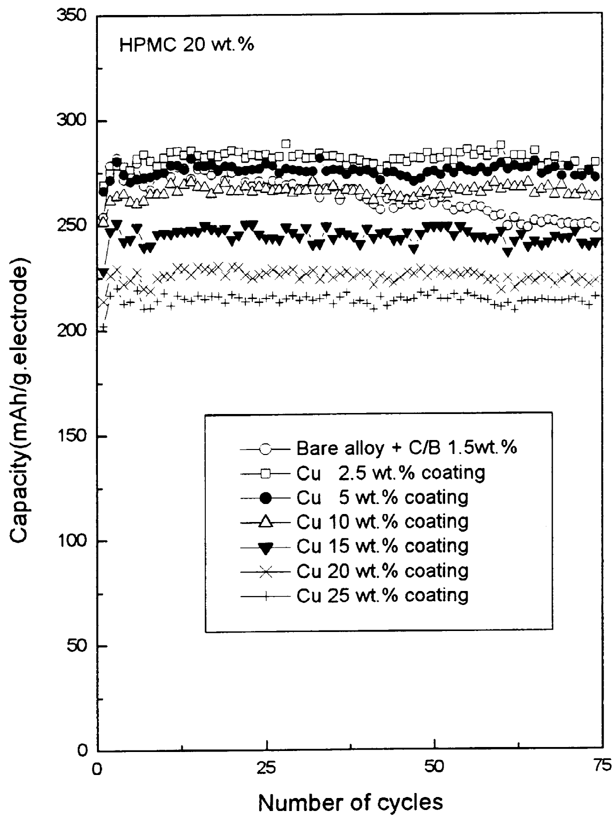

Fig. 4. Discharge capacities (per gram electrode) of the Cu-coated paste type electrodes depending on the amount of Cu coating.

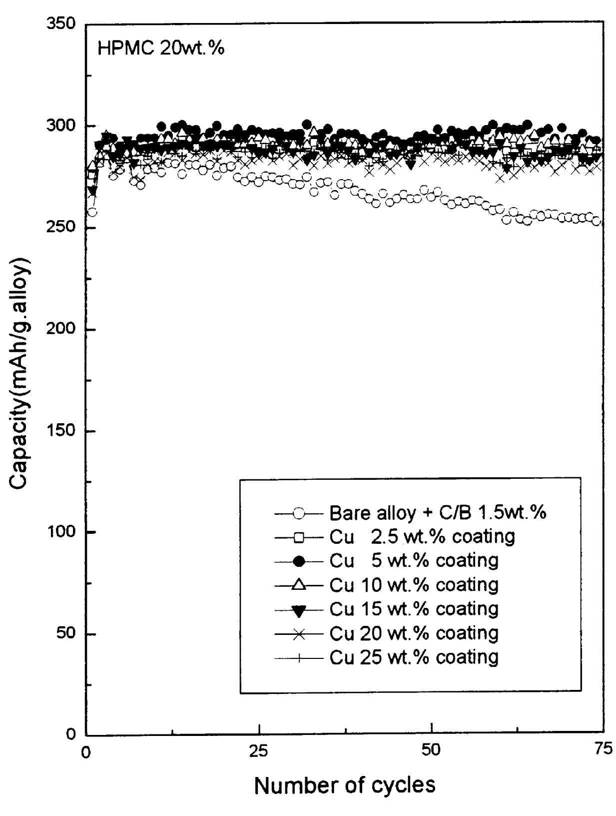

Fig. 5. Discharge capacities (per gram alloy) of the Cu-coated paste type electrodes depending on the amount of Cu coating.

the carbon-black mixed bare alloy electrode and the 2.5 wt.% copper-coated electrode, it can be found that the electrical conducting materials increase the discharge capacity and the copper coating is more effective than the carbon-black. In addition, the copper-coated electrode is more durable against cycling than the carbon-black mixed bare alloy electrode. By comparing Fig. 3 with Fig. 5 it can be seen that when copper-coated alloy powder with a low copper content was used, the paste- and the pellet-type electrodes have an equal amount of discharge capacity per gram alloy. However, for high contents of copper coating the pellet-type electrodes have a higher discharge capacity per gram alloy than that of the paste types.

4. Discussion

The important difference between the commercial paste-type and the laboratory pellet-type electrodes is that the former uses the bare alloy powder and the latter uses the copper-coated alloy powder. But when copper-coated alloy powder was used for both electrodes the discharge capacities per gram alloy for both electrodes were the same. This implies that the difference lies in the copper coating. Copper coating of the alloy powder has two effects: one is to provide a good electrical conductivity to the electrode due to the deposited copper; the other is the removal of the surface oxide film of the alloy powder due to the sulfuric acid etching. Both effects can increase the utilization of the alloy powder and subsequently increase the discharge capacity. Fig. 6 shows the effect of acid treatment on the discharge capacity of the paste-type electrode. The acid

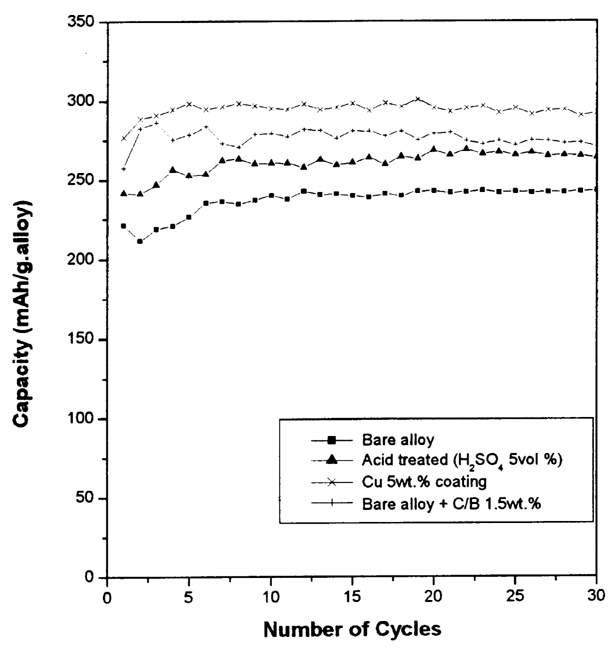

Fig. 6. Discharge capacities of the paste-type electrodes depending on the treatment of alloy powder.

treatment itself increased the discharge capacity. For the paste-type electrodes prepared by using the copper-coated alloy powder the limited increase of the discharge capacity with increasing copper coating can be attributed to the limited increase of electrical conductivity or utilization of alloy powder due to the inherent low density in the paste-type electrodes.

5. Conclusions

1. The pellet-type electrode prepared with the Cu-coated alloy powder has a higher discharge capacity than the paste-type electrode with the bare alloy powder. This can be attributed to the improved utilization of the alloy powder by copper coating in the pellet-type electrode.
2. When Cu-coated alloy powders with <10 wt.% Cu are used, the paste-type electrode has the same discharge capacity as the pellet type.
3. The paste-type electrode prepared with 2.5wt.% Cu-coated alloy powder and no carbon black is promising for practical use due to its high discharge capacity and good mechanical endurance.

Acknowledgements

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