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A simple method of electroless copper plating for the preparation of metal hydride electrodes

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Abstract

The simple method of electroless copper plating using an acidic bath containing only $CuSO_4$ and H_2SO_4 has been applied to rare earth–nickel-based hydrogen storage alloy powders for the preparation of a hydride electrode. The coating characteristics and electrode properties were investigated. The coating was very easy and fast being performed within 5 min without any pretreatment for air-exposed samples. The results of chemical analyses showed a coating mechanism of an ion exchange between Cu^{2+} and alloy constituents. It could be suggested from the electrochemical measurements that this copper plating method is very promising for electrode preparation in hydride batteries.

1. Introduction

Recently metal hydride electrodes have been studied very extensively [1–10] because they can be used as a substitute for the $Cd(OH)_2$ electrode which constitutes together with a $Ni(OH)_2$ electrode an Ni–Cd rechargeable battery. Because of the cadmium, this battery is highly toxic, causing environmental problems. Compared with Ni–Cd rechargeable batteries, the Ni–metal hydride rechargeable battery has many superior properties such as higher energy density, faster charging–discharging rate and higher energy efficiency.

There are many methods to produce the metal hydride electrode for practical applications [8–12]. With the exception of amorphous materials, however, the active alloy (hydrogen storage alloy) powder should be compacted densely in order to obtain good electrical conductivity and mechanical endurance. For this purpose, fine metallic (copper, nickel, platinum) powders have been used [9, 12]. The active alloy powder and the metal powder were mixed with or without organic binder and compacted on current-collecting nickel grids and often sintered afterwards. A more promising method to increase the electrical conductivity and compactability of the alloy powder is to coat the alloy powder with copper by employing an electroless plating

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ıethod. The process of electroless copper plating which has been used by shikawa and coworkers [7, 10] consists of pretreating the alloy powder with dCl$_2$–HCl and SnCl$_2$–HCl aqueous solutions and coating in an alkaline olution containing Cu^{2+}, CH$_2$O, ethylene diamine tetraacetic acid (EDTA) nd NaOH. This electroless copper plating allows the fraction of copper to e reduced very much compared with copper powder mixing and has many dvantages in the preparation and properties. The advantages are (1) the lloy powder is easy to compact and preserve in the electrode, (2) the lectrical and thermal conductivities are increased, (3) the cycle life is xtended, (4) copper acts as a microcurrent collector, (5) the chargıg–discharging rate is high and (6) self-discharging is suppressed. The rawbacks of this method are: the relatively high costs, the rather complicated ature of the process and the use of highly toxic chemicals such as PdCl$_2$, H$_2$O and NaOH.

In this study we have attempted to apply another electroless copper lating method in order to coat a rare earth–nickel-based hydrogen storage lloy by using an acid solution. This technique is very simple, inexpensive nd uses less toxic chemicals. The coating characteristics were examined s well as some properties of the metal hydride electrode prepared by this ıethod.

. Experimental details

(LM)Ni$_{4.49}$Co$_{0.1}$Mn$_{0.205}$Al$_{0.205}$ alloy powder (where (LM) refers to lanıanum-rich mischmetal provided by JMC Company, Japan) was chosen as ıe hydrogen storage material to be coated with copper. This powder has particle size below 100 μm, the hydrogen desorption plateau pressure was .6 atm at 25 °C and an effective hydrogen storage capacity of about 0.9 M^{-1} corresponding to an electrode capacity of 340 mA h g^{-1}.

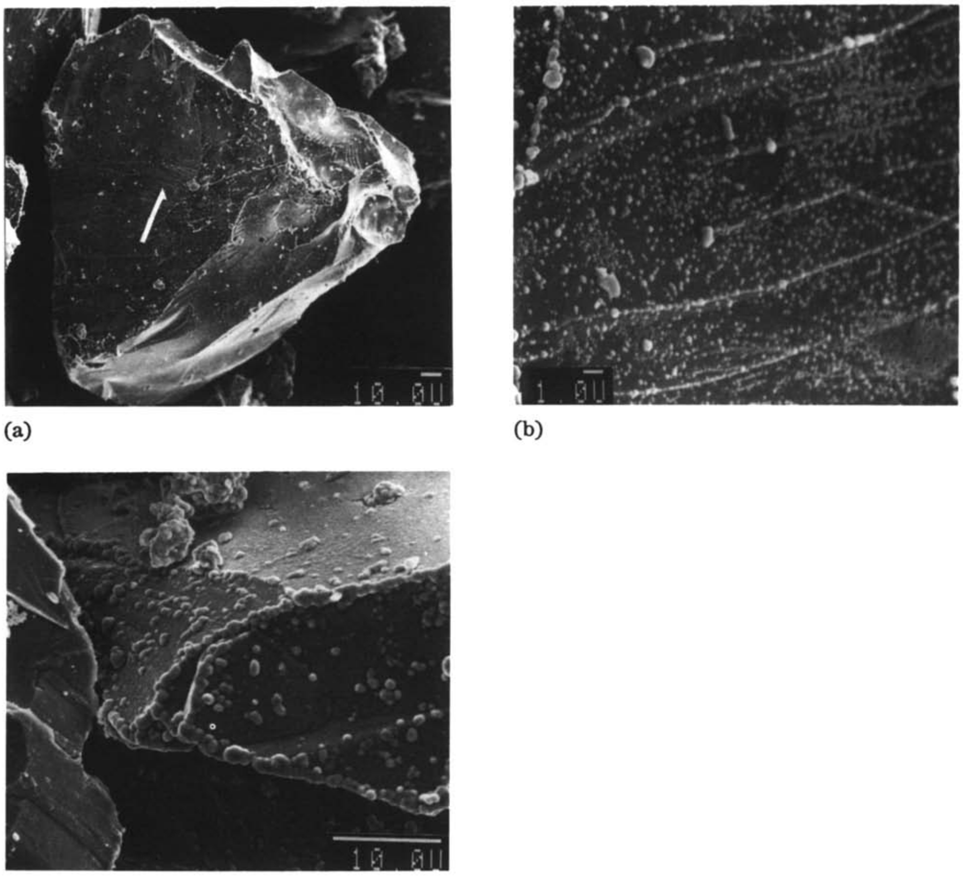
2.4 g of the alloy powder as received were immersed in 100 ml of the opper plating solution containing 1.5 g CuSO$_4$ (about 0.6 g Cu) and 0.8 ıl H$_2$SO$_4$ at room temperature for a given time between 1 and 5 min. After eing rinsed with distilled water, part of the dried powder was subjected to canning electron microscopy (SEM) and X-ray photoelectron spectroscopy XPS) investigations. Chemical analyses of the plating solution and alloy owder before and after coating were also performed. About 0.12 g of the owder was cold compacted by 5 ton cm^{-2} into a disk with 10 mm diameter nd about 0.24 mm thickness. The disk was connected to a holder made f nickel grid and used for the electrode testing procedure.

The electrochemical measurements were conducted in a Teflon cell which ontained the metal hydride electrode, a platinum counterelectrode, a saturated alomel electrode (SCE) as a reference electrode and 6 M KOH as electrolyte. harging–discharging cycles were carried out automatically up to 100 cycles. he charging and discharging currents were of equal magnitude and changed rom 10 mA for the first 10 cycles to 15 mA for the following cycles. The charging time was 200 min for 10 mA and 130 min for 15 mA. Discharging was interrupted at -850 mV (*vs.* SCE) to avoid any oxidation of copper. A rest time of 20 s was allowed for every change of the current direction.

3. Results

3.1. *Morphology of the coating*

The SEM photographs of the alloy powder coated for 1 min and 5 min are shown in Fig. 1 and Fig. 2 respectively. As can be seen in Fig. 1, copper was deposited preferentially on the sharp edges, cleavage steps and river patterns of the larger particles. On small alloy particles the coverage by copper was close to 100%. The copper deposits had spherical shape with

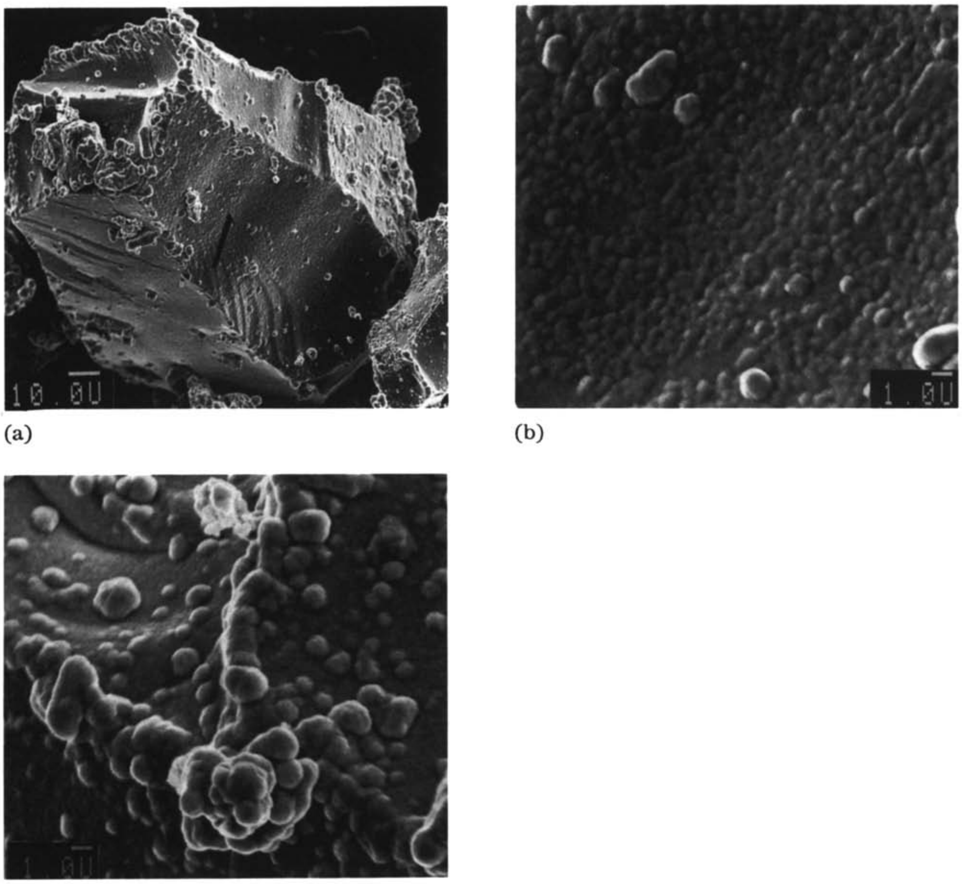


(a)

(b)

(c)

Fig. 1. Scanning electron micrographs of the copper-coated alloy powder (coating time, 1 min) with high magnifications for the flat surface (b) marked by an arrow in (a) and an edge (c). On the left-hand side in (c) a fracture surface is shown.



(a) (b)

2. Scanning electron micrographs of the copper-coated alloy powder (coating time, 5 with high magnifications for the flat surface (b) marked by an arrow in (a) and an edge

ameter of about 0.1–0.2 μm on flat surfaces and about 0.5–1.0 μm on s. The surface coverage by copper deposits was very low. When coating gressed for 5 min, the coverage increased and the particle size of the osits was about 0.5–1.0 μm on the flat surfaces and 1–2 μm on the s. In addition, some copper clusters were seen on edges. As the copper ing was non-uniform depending on the particle size and surface roughness, alloy surfaces were not completely covered by copper although the entire unt of copper in solution was transferred onto the surface. Energy-ersive X-ray point analysis showed considerable variations of copper centration on the surfaces.

Chemical analysis of the plating solutions and the coated alloys

Before and after coating for 1 and 5 min the plating solutions and the y powder were subjected to chemical analysis. The results are summarized in Table 1. From Table 1 it can be seen that the results of chemical analyses of the plating solutions and the alloy powder were very consistent with each other. Coating had progressed about 50% after 1 min and was finished almost completely after 5 min. The total amount of copper coated was 24 wt.% with respect to the weight of the alloy powder which means that 96% of copper in the solution was transferred to the alloy powder. The fact that the gains for all components were opposite to that of copper and had nearly the same value implies that the coating mechanism was an ion exchange between Cu^{2+} and the elements in the alloy, and that all constituents of the alloy participated in the ion-exchanging process according to the given composition of the alloy. By assuming that the electrochemical valences of all the elements in the alloy were the same and equal to two (with the exception of aluminium being assumed to go into solution as Al^{3+}), the charge transfer between copper and the elements of the alloy is about the same as can be calculated from the values in Table 1, *i.e.* the charge necessary for the reduction of Cu^{2+} (24% of 2.4 g) is about 1760 C which has to balance the charge necessary to oxidize about 26 wt.% of 2.4 g of the alloy. The latter charge is calculated to be 1670 C (assuming a molecular weight of 430 g per formula unit of the alloy) in good agreement with the charge obtained for copper.

During plating, copper is replacing elements in the alloy which on the average have a higher atomic weight, and therefore a weight loss after 5 min of 1.5–2% has been observed experimentally, which is slightly lower than the calculated value of 2% (calculated from the reduced amount of copper). The fact that all the elements of the alloy are replaced by copper is in agreement with thermodynamics, because all of them are less noble

TABLE 1

Chemical composition of the plating solutions and alloy powder as weight/weight of alloy powder before coating

Element	Content in samples (%)						Gain[a] (%)	
	L0	L1	L5	S0	S1	S5	L	S
Cu	24.7	13.0	0.07	<0.01	8.53	24.0	−24.0[b]	24.0[b]
Ni	<0.02	7.38	16.0	62.3	57.6	48.0	25.7	−23.0
La	<0.02	1.79	3.83	14.6	13.3	10.9	26.2	−25.3
Ce	<0.02	0.29	0.58	2.28	2.06	1.69	25.4	−25.9
Mn	<0.004	0.32	0.71	2.71	2.46	2.04	26.2	−24.7
Al	<0.02	0.16	0.35	1.49	1.35	1.11	23.5	−25.5
Co	<0.004	0.16	0.34	1.36	1.23	1.02	25.0	−25.0
Fe	<0.004	0.03	0.04	0.14	0.13	0.10	28.6	−30.8

L0, L1 and L5 are plating solutions before and after coating for 1 min and 5 min respectively. S0, S1 and S5 denote the alloy powder before and after coating for 1 min and 5 min respectively.

[a] Weight obtained for each element after coating for 5 min, divided by the weight of all the elements in the alloy powder before coating.

[b] (Weight after 5 min coating)/(alloy powder weight before coating).

than copper. Usually pure aluminium is not plated with copper because of a dense protecting oxide film.

3.3. *XPS analysis*

XPS measurements were performed on the surface of the coated and compacted sample and after argon sputtering. The sputtering times were 10 and 40 min with a sputtering rate of about 5 Å min^{-1}. The results are shown in Fig. 3. From the copper-coated surface the peaks of copper, nickel, oxygen, lanthanum and carbon appeared whereas after sputtering for 10 or 40 min only peaks of copper, nickel and oxygen were left. The Cu $2p^3$ peak in Fig. 4 reveals that copper on the outermost layers was in the metallic and hydroxide state, but after sputtering only metallic copper remained. The

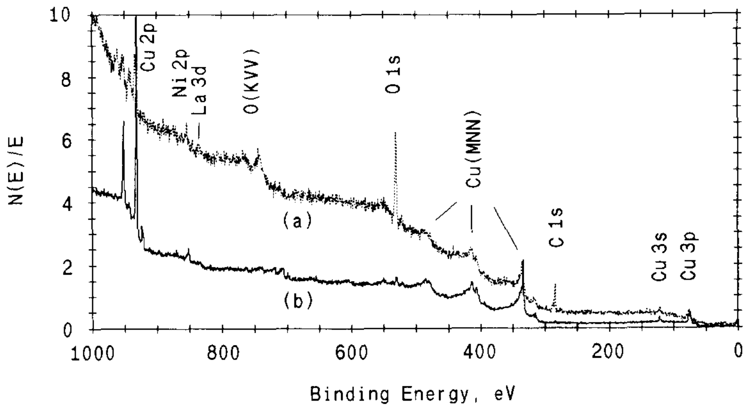


Fig. 3. XPS spectra from the copper-coated surfaces: curve a, as coated; curve b, sputtered for 10 min.

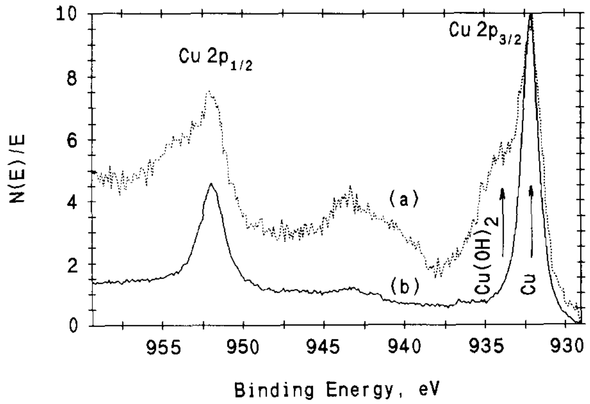


Fig. 4. XPS spectra of copper from the copper-coated surfaces: curve a, as coated; curve b, sputtered for 10 min.

presence of nickel and lanthanum on the coated surface implies the incomplete coverage of the surface by copper deposits. The Ni $2p^3$ peak in Fig. 5 shows that nickel on the coated surface is mostly $Ni(OH)_2$ changing to NiO below the surface. This NiO layer was so thick that it appeared even after sputtering for 40 min, whereas the La_2O_3 peak disappeared after sputtering for 40 min (Fig. 5). The O 1s peak in Fig. 6 is revealing two chemical states of oxygen: OH^- and O^{2-}. The intensity of the former decreased drastically and continuously with sputtering and that of the latter increased after 10 min sputtering and then decreased after 40 min sputtering. Similar to passive films on metals the oxide/hydroxide film consists of an outermost hydroxide and an inner oxide layer [13].

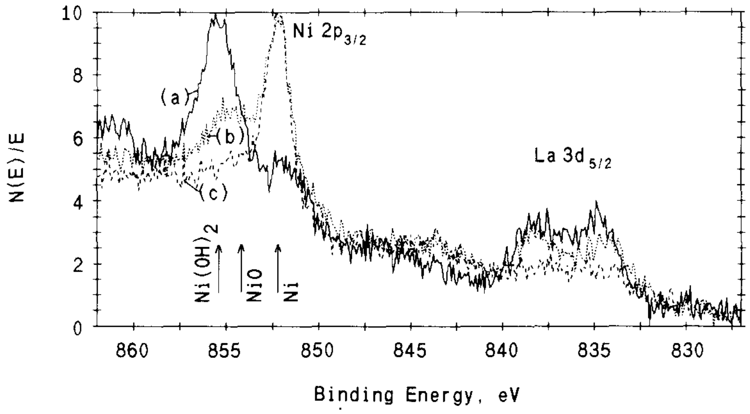


Fig. 5. XPS spectra of nickel and lanthanum from the copper-coated surfaces: curve a, as coated; curve b, sputtered for 10 min; curve c, sputtered for 40 min.

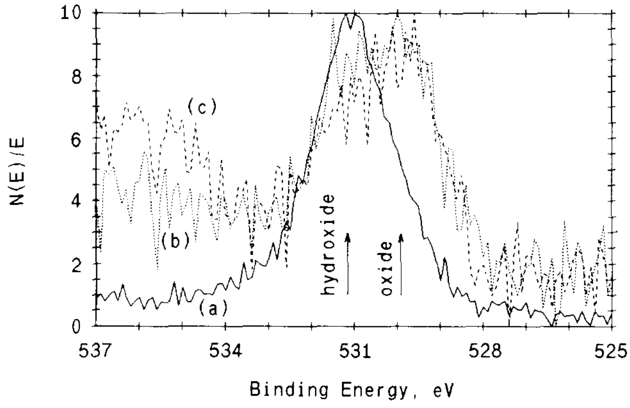


Fig. 6. XPS spectra of O 1s from the copper-coated surfaces: curve a, as coated; curve b, sputtered for 10 min; curve c, sputtered for 40 min.

3.4. Electrochemical measurements of the electrode

The variation of the discharge capacity with charging–discharging cycles is presented in Fig. 7. Similar to other metal hydride electrodes this electrode also showed a considerable degradation in discharge capacity with increasing number of cycles. the maximum discharge capacity, appearing at about 20–30 cycles, was about 247 mA h per gram of coated alloy or 325 mA h per gram of alloy. The decrease of the discharge capacity after 100 cycles was about 15%, which was smaller than that of $LaNi_5$ and larger than that of $LaNi_{2.5}CoAlSi$. This somewhat large amount of degradation could be attributed to the high content of manganese in this alloy as indicated by Sakai *et al.* [7]. They have suggested that manganese in the $LaNi_{5-x}Mn_x$ system has the effect of increasing pulverization of the alloy and, in turn, increasing the alloy surface and its oxidation, resulting in a short cycle life of the alloy electrode.

4. Discussion

The electroless method of copper plating using an acid solution containing $CuSO_4$ and H_2SO_4 is very promising for application during the preparation of metal hydride electrodes. This method, contrary to the existing method using an alkaline bath, is very simple and inexpensive and is not time

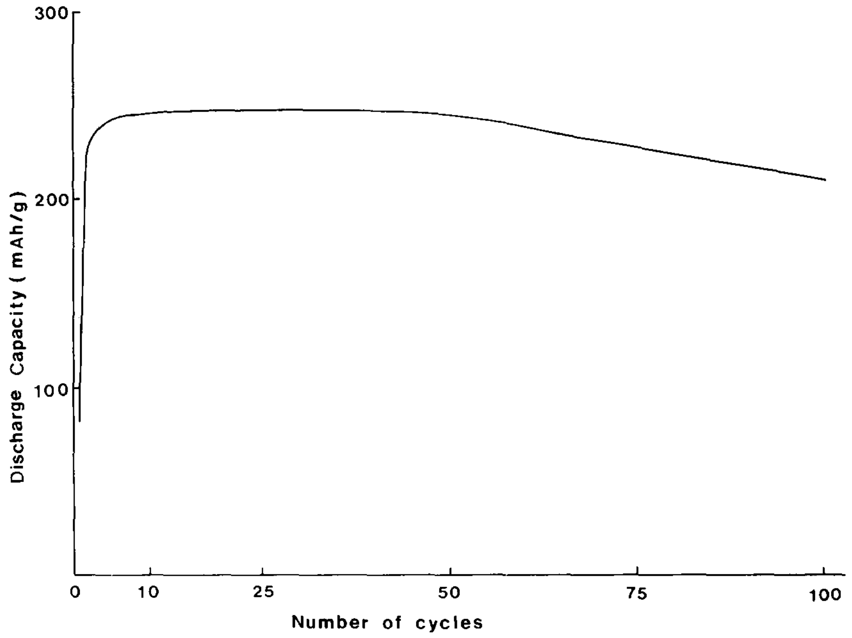


Fig. 7. Variation of the discharging capacity on the number of cycles for the copper-coated $(LM)Ni_{4.49}Co_{0.1}Mn_{0.205}Al_{0.205}$ alloy electrode.

consuming. In addition, it does not use highly toxic chemicals such as $PdCl_2$, CH_2O, NaOH etc.; pretreating of the storage alloy is not necessary because the ion exchange itself has a surface cleaning effect. Besides the application in batteries the high thermal conductivity and deformability of the compact prepared by this method make it suitable to be used as a metal hydride in heat pumps. The measurements of thermal conductivity of this type of compact have been performed by Ishikawa *et al.* [14] and Josephy *et al.* [15]. The proposed method can be applied to rare earth–nickel-based hydrogen storage alloys only but not to other alloys such as TiFe and Laves phases which might also be promising materials for metal hydride electrodes. This is due to their inability to dissolve and reduce copper ions in solution. We have checked some hydrogen storage alloys and metallic elements as to whether they could be copper coated by our method. The results are shown in Table 2.

From Table 2 it could be suggested that, in order to be copper coated by the solution, the alloy should contain as the main constituents those elements which can be coated with copper. For example, titanium is inert but iron reacts with the copper solution; however, the TiFe was inert in the solution. Another problem of our method is the loss of storage material because the ion exchange takes place by sacrificing that part of the alloy which is electrochemically equivalent to the amount of the copper coating. The weight loss of the alloy used in this study was calculated to be about 108 wt.% of the copper deposited. It should be noticed that in methods using alkaline baths there could be also a loss of material during the pretreatment due to the reaction between alloy and HCl.

TABLE 2

Examination of copper coating of some alloys and elements in $CuSO_4$ acid solution

$(RE)Ni_5$	○	Sn	●
Mg_2Ni	○	Ga	●
TiFe	×	Zr	×
$Zr(Cr, Fe, Ni)_2$	×	Ti	×
Ni	○	Al	×
Co	○	Cr	×
Fe	○	W	×
In	○	Mo	×
Cd	○	Ta	×
RE	●	Ag	×
Mg	●	Nb	×
Mn	●	Ge	×
Zn	●	Si	×
		B	×

○, Copper coated.

●, Rapid reaction but copper coating was not observed or was very poor.

×, Apparently no copper coating nor reaction.

5. Conclusion

It has been attempted to coat a rare earth–nickel hydrogen storage alloy with copper by a new electroless plating method using an acid solution containing $CuSO_4$ and H_2SO_4. Examining the coating characteristics and electrochemical properties of the electrode prepared by this method we have found that coating occurs by a homogeneous ion exchange between Cu^{2+} and the constituent elements of the alloy and that this coating method could be utilized in the preparation of rare earth–nickel-based alloy electrodes. The process was very simple and inexpensive, was not time consuming and did not use highly toxic chemicals nor a pretreatment for air-exposed samples.

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