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Electrode stabilities of copper-containing misch metal–nickel-based hydride forming alloys

T. WEIZHONG, G. YINGXIN, Z. HAOYU

Department of Materials Science and Engineering, Beijing University of Science and Technology, Beijing 100083, Peoples's Republic of China

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Electrochemical charge–discharge cycling measurements were conducted on electrode samples prepared from alloy powders of a series of Cu-containing Ce- and La-rich misch metal (Mm and Ml, respectively)–Ni-based stoichiometric multicomponent alloys. A severe decrease in the electrochemical capacity was observed for Mm–Ni–Al electrodes, which was believed to be related to the deterioration of electrical contact within the electrodes, in addition to the decomposition of the active materials. Although the addition of cobalt powders to these electrodes improved the electrical contact within the electrodes, it had no effect on retarding the decomposition of the active materials. The substitution of copper into the Mm–Ni–Al composition improved the stability of this electrode material, but brought about a decrease in its electrochemical capacity. As a compromise, partial substitutions of copper for cobalt in Mm–Ni–Co–Al, Mm–Ni–Co–Mn–Al as well as Ml–Ni–Co–Al alloys were proved to be possible without remarkable changes in electrode properties, but too much of this substitution brought about decreases in material stability, which was observed to be accompanied by an increase in tendency of the materials to pulverize during electrochemical cycling.

1. Introduction

Rechargeable Ni/metal hydride batteries based on the AB_5 (A denotes rare earth elements, especially La or misch metal Mm and Ml, and B transition metals, primarily Ni) intermetallic compounds have achieved rapid development since, in 1984, Willems reported that the long term stability of electrodes made from $LaNi_5$ can be markedly improved by Co substitution for part of the Ni [1]. This breakthrough has led to the multicomponent alloys currently employed in producing such materials, for example, Mm–Ni–Co–Mn–Al [2, 3] and La–Nd–Ni–Co–Si [4] series. But since the price of Co is relatively high, this Co substitution is always accompanied by a sharp rise in the raw material costs.

A recent study showed that by using simple nonstoichiometric $AB_{5.5}$ compositions, the long term stability of electrode materials could be improved, compared with that of the corresponding stoichiometric AB_5 materials [5]. Furthermore, it has been shown that such nonstoichiometry could be obtained by properly selecting substitution elements, such as copper, though it has been well established by earlier investigations that substitutions of copper had no beneficial effect on the electrochemical properties of simple binary AB_5 compositions [1, 6]. Therefore, it is interesting to have a closer look at the effect of copper on the electrode stability property of various compositions, especially those of normal stoichiometric, but multicomponent, AB_5 materials, though preliminary studies revealed that multicomponent Cu-containing alloys showed low kinetics and slow activation [7].

2. Experimental details

Alloys of nominal compositions were prepared by arc melting commercially pure metal materials including two kinds of misch metals Mm (22.47% La, 53.74% Ce, 5.88% Pr and 18.13% Nd) or Ml (78.8% La, 4.85% Ce, 12.1% Nd and 4.02% Pr) in an Ar atmosphere. No annealing treatment was applied to the alloys. Alloy powders of 200 mesh, mechanically ground in the air, were mixed with fine copper powders in the weight ratio 1:4, and then mechanically pressed to pellets of 12 mm in diameter. Each pellet contained hydride forming alloys of 200 mg, without the so-called microencapsulation treatment [3].

Discharge capacity and long term stability properties of the alloys were automatically measured by charging the pellets with a current density of $150\,mA\,g^{-1}$ for 2 h, followed by discharging them with the same current density to 0.65 V with respect to Hg/HgO reference electrodes. Nickel plates and 6 M KOH solution were used as the counter electrodes and electrolyte, respectively.

The morphologies of alloy powders in cycled electrodes were observed by using a JSM-35CF scanning electron microscope (SEM), and magnetic moments of the same samples were measured by using a PAR-155 vibrating sample magnetometer (VSM) with the maximal magnetic field of 1.5 T.

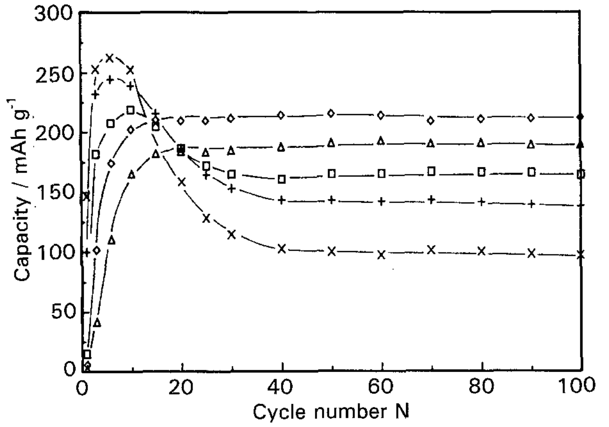

Fig. 1. Curves of discharge capacity against cycle number for $MmNi_{4.2-x}Cu_xAl_{0.8}$ alloy electrodes. x values: (×) 0, (+) 0.25, (□) 0.5, (◇) 0.75 and (△) 1.0.

3. Results and discussion

3.1. *Mm–Ni–Cu–Al compositions*

Figure 1 shows the results of long term stability measurement of the Co-free alloy series $MmNi_{4.2-x}Cu_xAl_{0.8}$. It can be seen that within this alloy series two fundamental characteristics can be inferred. First, the Cu-free composition showed the highest maximum electrochemical capacity and the highest electrode activity, but it showed also a severe decrease in electrochemical capacity within the initial tens of charge–discharge cycles. Second, as the copper content in the alloys increased, the maximum capacity decreased and the cycle number needed for the electrochemical activation increased, accompanied by an improvement in the electrochemical stability of the materials.

It was notable that in the earlier experiments for the Cu-free microencapsulated Mm–Ni–Al compositions, no severe decrease in electrochemical capacity had been observed within the initial tens of cycles [2]. Noticing that for unmicroencapsulated materials, severe decreases in the electrochemical capacity appeared when the electrodes were held in a discharged state and that cobalt powder addition to the electrodes was effective in retarding such decreases [8], we also conducted an experiment in which different amounts of $MmNi_{3.9}Cu_{0.4}Al_{0.7}$ powders were substituted by using corresponding amounts (up to 5 wt%) of cobalt powder in the preparation of the electrodes. The result of such an experiment is shown in Fig. 2. It was seen that with the increase in the amount of cobalt powder substitution, an improvement in cycle life behaviour of the electrodes appeared, in addition to a very slight increase in the maximum electrochemical capacity due to the reaction of cobalt in the charge and discharge cycling [9]

$$Co + 2OH^- = Co(OH)_2 + 2e^- \qquad (1)$$

This was observed to occur at about 0.7 V relative to the Hg/HgO electrode potential. For cobalt powder substitution of 5 wt %, no severe decrease in electrochemical capacity was observed. Only a relatively gradual decay in electrochemical capacity occurred, the appearance of which could be attributed to the gradual decomposition of the active materials during the electrochemical cycling, as discussed later.

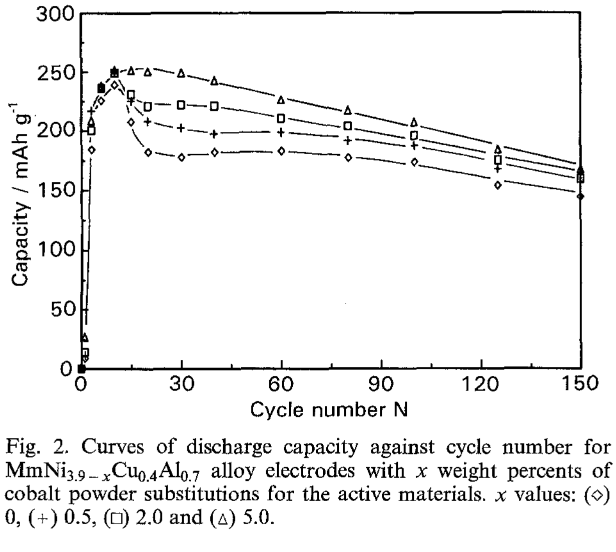

Fig. 2. Curves of discharge capacity against cycle number for $MmNi_{3.9-x}Cu_{0.4}Al_{0.7}$ alloy electrodes with x weight percents of cobalt powder substitutions for the active materials. x values: (◇) 0, (+) 0.5, (□) 2.0 and (△) 5.0.

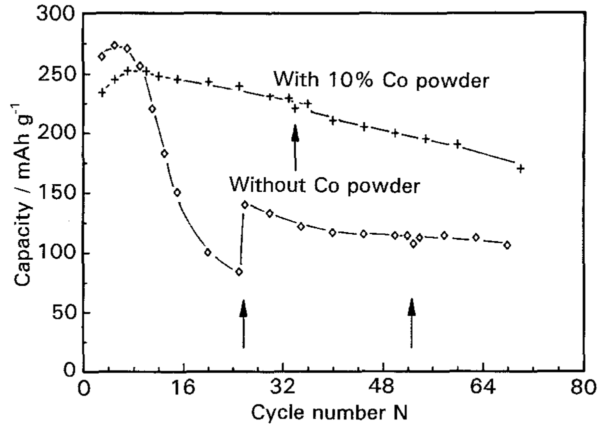

Fig. 3. Curves of discharge capacity against cycle number for $MmNi_{4.2-x}Al_{0.8}$ alloy electrodes with and without cobalt powder substitutions. The arrows show the cycles at which the corresponding electrodes were mechanically repressed.

The possible reason for the severe decrease in capacity observed for the electrodes of Cu-poor compositions (see Fig. 1) is believed to be related to the rapid deterioration in electrical contact between alloy powders within the electrodes due to the formation of poorly conductive rare earth hydroxide on the powder surface as well as the severe pulverization of the alloy powders, when the electrodes were electrochemically cycled [10]. An improvement in this electrical contact might be affected by cobalt powder additions which dissolved partially into the electrolyte and then precipitated on the surface of the alloy powders [9, 11] when the electrodes were electrochemically cycled. It has been suggested that these precipitates may have the effect of improving the electrical conductivity between alloy particles [11]. Such an assumption was further proved by an experiment, in which the discharge capacities of electrodes containing $MmNi_{4.2}Al_{0.8}$ alloy powders with and without cobalt powder substitutions were measured. At certain cycle numbers the cycling was interrupted and the electrodes mechanically repressed. Fig. 3 shows the result of such a comparison experiment.

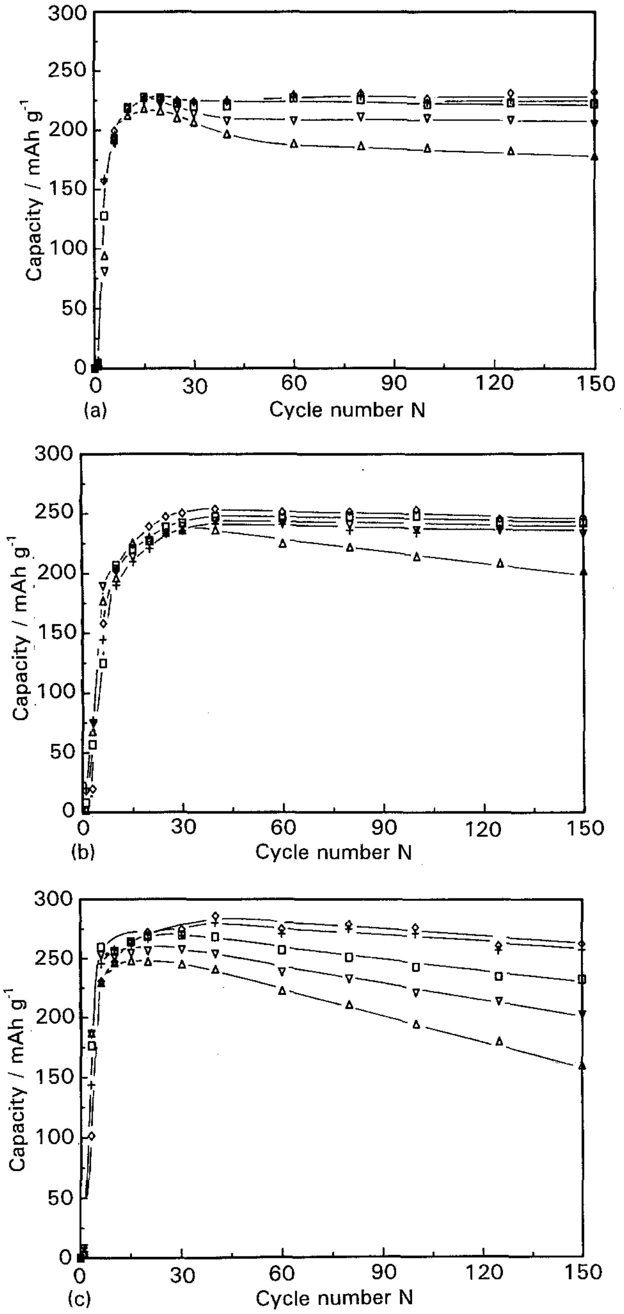

Fig. 4. Curves of discharge capacity against cycle number for (a) $MmNi_{3.5}Co_{0.7-7x}Cu_{8x}Al_{0.8-x}$, and (b) $MlNi_{3.5}Co_{0.7-7x}Cu_{8x}Al_{0.8-x}$. x values for (a) and (b): (+) 0, (◇) 0.025, (□) 0.05, (▽) 0.075 and (△) 0.10. (c) $MmNi_{3.5}Co_{0.8-x}Cu_xMn_{0.4}Al_{0.3}$ alloy electrodes. x values for (c): (+) 0, (◇) 0.2, (□) 0.4, (▽) 0.6 and (△) 0.8.

It is noticeable that for the cobalt powder containing electrode there was no discontinuity in the discharge capacity curve, but for the cobalt powder free electrode an increase in discharge capacity was observed immediately after the first repressing. A later repressing had no effect on the properties of the same electrode. This phenomenon can be understood when it is considered that the electrochemical cycling is a process in which the hydride forming alloy powders in the electrodes pulverize and are oxidised when they are repeatedly charged and discharged [1] and a poorly conductive rare earth hydroxide layer deposits on the surface of the alloy powders [10]. This causes the alloy powders to lose their electrical contact to the rest of the electrodes when they are severely pulverized and/or only partially oxidized. The mechanical repressing partly restores the lost electrical contact and increases the active volume fraction of the electrode. This results in restoration of part of the lost electrochemical capacity. On the other hand, the cobalt powder addition to the electrode may result in the formation of a conductive layer of precipitates which ensures good electrical contact of alloy powders from the beginning of the cycling and no improvement can be expected when the electrode is repressed. That is, both the formation of a conductive precipitated surface layer on the alloy powders caused by the cobalt powder addition and the repressing of the cycled electrode have the same effect of improving the electrical contact and increasing the utilizable fraction of the materials, though to different degrees, as can be seen from Fig. 3.

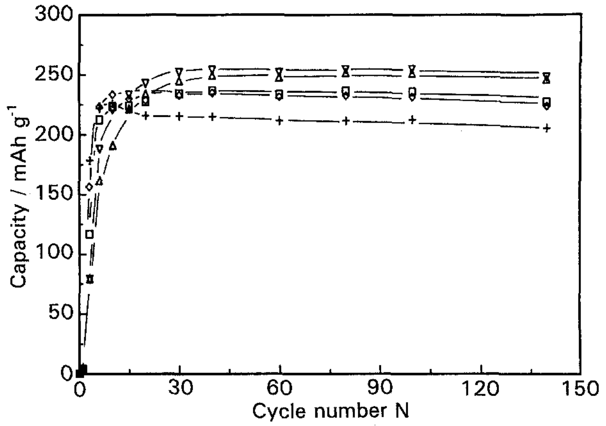

Fig. 5. Curves of discharge capacity against cycle number for $La_xCe_{1-x}Ni_{3.5}Co_{0.35}Cu_{0.4}Al_{0.75}$ alloy electrodes. x values: (+) 0, (◇) 0.25, (□) 0.50, (▽) 0.75 and (△) 1.0.

3.2. *Mm–Ni–Co–Cu–Al, Ml–Ni–Co–Cu–Al and Mm–Ni–Co–Cu–Mn–Al compositions*

The copper substitution in the Mm–Ni–Al alloy was seen to be effective in improving the stability of the electrodes, but at the same time it resulted in a decrease in the electrochemical capacity. Similar

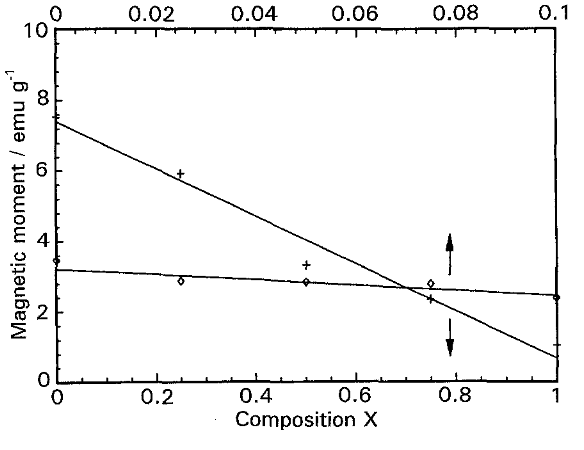

Fig. 6. Magnetic moments measured for electrochemically cycled $MmNi_{4.2-x}Cu_xAl_{0.8}$ after 55 cycles (+) and $MlNi_{3.5}Co_{0.7-7x}Cu_{8x}Al_{0.8-x}$ after 125 cycles (◇) alloy electrodes.

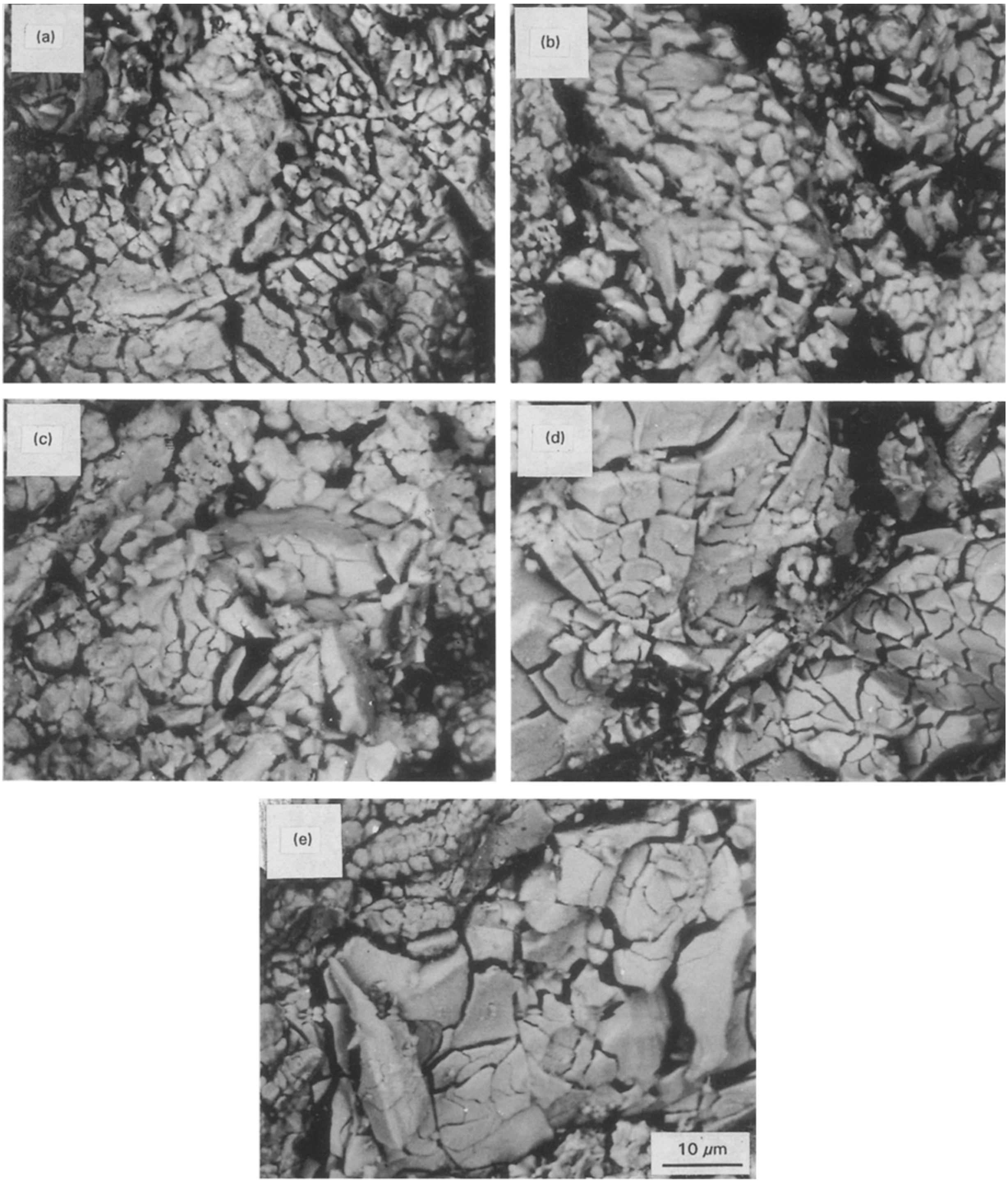

Fig. 7. SEM photographs of electrochemically cycled $MmNi_{4.2-x}Cu_xAl_{0.8}$ electrodes showing the differences in the alloy powder pulverization after 55 cycles. x values: (a) 0, (b) 0.25, (c) 0.5, (d) 0.75 and (e) 1.0.

results were reported by Meli *et al.* [7]. So further investigations of the effect of copper substitution in a series of cobalt-containing alloy systems were made. Figure 4 shows the results of three alloy systems in which the effect of copper substitution for cobalt was investigated. A certain amount of copper substitution had almost no effect on the properties of the electrodes, including electrochemical capacity, activation behaviour and long cycle stability, but a further increase in the amount of substitution brought about a deterioration in the material stability. For the system $MmNi_{3.5}Co_{0.8-x}Cu_xMn_{0.4}Al_{0.3}$ (Fig. 4(c)) the amount of substitution can be as high as $x = 0.2$, that is, 25% of the cobalt content in the alloy can be replaced by copper, while for the other two alloy systems, higher amounts of substitution may be possible before the long cycle stability of the materials severely deteriorates. It was noticed that both of the Mn-free material systems had lower discharge capacities compared with the Mn-containing one, consistent with the result of Sakai *et al.* [3]. The reason for the comparatively low capacity of $MmNi_{3.5}Co_{0.7-7x}Cu_{8x}Al_{0.8-x}$ is, on the one hand, a result of the open-cell effect observed by Yagi *et al.* [12] and, on the other hand, may be related to the high cerium and neodymium contents in the misch

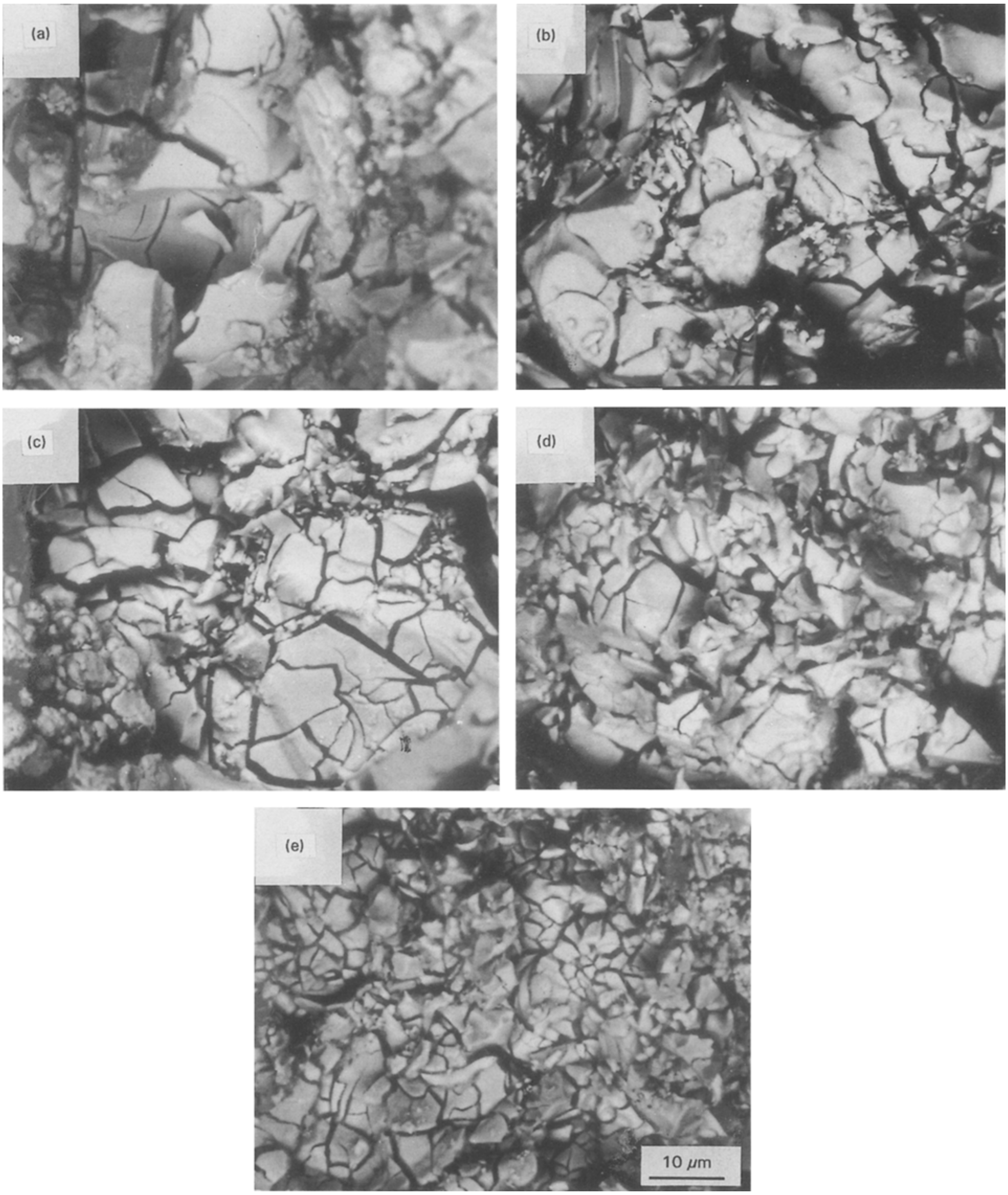

Fig. 8. SEM photographs of electrochemically cycled $\mathrm{MlNi_{3.5-x}Co_{0.7-7x}Cu_{8x}Al_{0.8-x}}$ electrodes after 125 cycles. x values: (a) 0, (b) 0.025, (c) 0.05, (d) 0.075 and (e) 0.1.

metal raw material. The latter assumption was supported by Fig. 5, in which the discharge capacity is shown as a function of cycle number for the $\mathrm{La_xCe_{1-x}Ni_{3.5}Co_{0.35}Cu_{0.4}Al_{0.75}}$ alloy system. It can be inferred from a comparison between the results of this figure and Fig. 4 (a and b) that, by decreasing the cerium and neodymium contents, the discharge capacity may be increased. The La-rich compositions showed relatively higher material stability than the Ce-rich ones. In Fig. 5, for example, a slight decrease in discharge capacity was observed for the composition $\mathrm{CeNi_{3.5}Co_{0.35}Cu_{0.4}Al_{0.75}}$ at the initial tens of cycles, suggesting that such a phenomenon may be related to the presence of elemental cerium in the alloys.

It is interesting to note that, although complete substitution of copper for cobalt leads to a deterioration in the stability properties of these stoichiometric materials, as was revealed in Fig. 1 and Fig. 4, partial substitution of copper for cobalt in the above mentioned multi-component alloy systems was possible, at least to an extent, without deterioration of the cycle life properties. This is of benefit in decreasing raw material costs in production. It also shows a strong contrast when the result is compared with those of simple compositions such as La(Ni, Cu)$_5$ where a rapid capacity decay was encountered [1, 6]. This suggests that a multicomponent substitution may have effects very different from those of respective substitutions of the same elements, a phenomenon already observed for La–Ni–Co–Al and La–Ni–Co–Si systems in the early work by Willems [1].

3.3. *Decomposition of hydride forming compounds*

It has been demonstrated that when hydride forming compounds were electrochemically cycled, their hydrogen absorbing abilities decreased as a result of the decomposition of the compounds into rare earth hydroxide R(OH)$_3$ and metallic Ni [6], though Boonstra *et al.* [10] reported that the decomposition products were R(OH)$_3$ and Ni(OH)$_2$. If metallic nickel forms as a result of the decomposition, then the measurement of magnetic moments of the cycled electrodes can be employed to trace the decomposition process of the alloys, since nickel is ferromagnetic at room temperature.

Figure 6 shows the magnetic moments of electrodes of two alloy systems, measured with VSM, after electrochemical cycling. For both the $\mathrm{MmNi_{4.2-x}Cu_xAl_{0.8}}$ and the $\mathrm{MlNi_{3.5}Co_{0.7-7x}Cu_{8x}Al_{0.8-x}}$ composition series an appearance of ferromagnetic moments was observed, indicating that metallic nickel has been formed during cycling. The magnetic moment of cycled $\mathrm{MmNi_{4.2-x}Cu_xAl_{0.8}}$ electrodes decreased as the copper content increased, in accordance with the fact that in this alloy series the Cu-rich alloys were electrochemically more stable than the Cu-poor ones (see Fig. 1). That is, though the decrease in the magnetic moment in the cycled electrodes as a function of increasing copper content in the alloys may have another cause (the decomposition product nickel of the Cu-containing alloys may have lower magnetic moments due to the nonzero solubility of elemental copper in the formed nickel precipitates), the rapid decrease in the magnetic moments for the $\mathrm{MmNi_{4.2-x}Cu_xAl_{0.8}}$ alloy system as a function of increasing copper content can be taken as a result of the stabilization of the alloys by the copper substitution. For the series $\mathrm{MlNi_{3.5}Co_{0.7-7x}Cu_{8x}Al_{0.8-x}}$, both increase in the copper and decrease in the cobalt solubility in the decomposition product nickel may influence the value of magnetic moment and so result in relatively small values in the magnetic moments for copper-containing compositions, though based on the results of Fig. 4, a decrease in the material stability and higher amounts of decomposition products in the alloys may be expected when the amount of copper substitution is increased.

Scanning electron microscopy (SEM) can be used to observe the pulverization of the alloy powders in the cycled electrodes [1]. Figures 7 and 8 show the SEM photographs of such observations. These show that, for the $\mathrm{Mm_{4.2-x}Cu_xAl_{0.8}}$ compositions (Fig. 7), the alloy powders showed less tendency to pulverization, as the copper content in the alloys increased. The Cu-free alloy powders were the most seriously pulverized (Fig. 7(a)), corresponding to a severe drop in electrochemical capacity of the electrodes, as has been discussed earlier (see Fig. 1). As to the $\mathrm{MlNi_{3.5}Co_{0.7-7x}Cu_{8x}Al_{0.8-x}}$ compositions, the tendency for the alloy powders to pulverize increased, with increase in the copper content. It is notable that the alloys with limited copper substitutions showed moderate increases in the pulverization tendency but meanwhile had relatively good stabilities (see Fig. 4(b)). This corresponds to the fact that, although it has been proved that alloy powder pulverization processes are important in determining the stability of electrode materials [13] and complete copper substitution for cobalt may result in the deterioration in the cycling properties of the stoichiometric alloys, a partial substitution with limited increase in the tendency to pulverize may have limited deteriorating effect on the electrochemical properties.

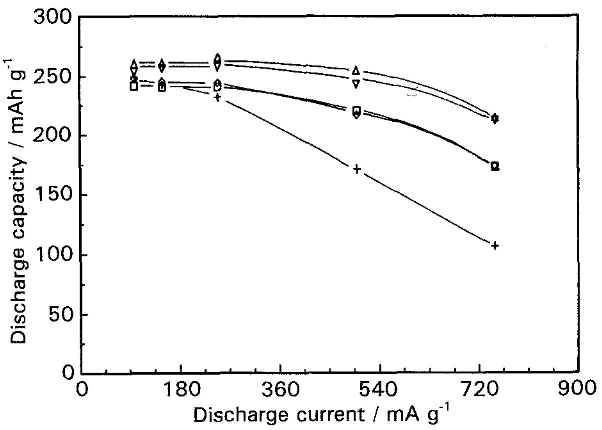

Fig. 9. Current dependencies of discharge capacity for a series of Cu-free and Cu-containing alloys. Key: (+) $\mathrm{MlNi_{3.5}Co_{0.7}Al_{0.8}}$; (◇) $\mathrm{MlNi_{3.5}Co_{0.525}Cu_{0.2}Al_{0.775}}$; (□) $\mathrm{MlNi_{3.5}Co_{0.35}Cu_{0.4}Al_{0.75}}$; (▽) $\mathrm{MmNi_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3}}$; (△) $\mathrm{MmNi_{3.5}Co_{0.6}Cu_{0.2}Mn_{0.4}Al_{0.3}}$.

Figure 9 shows the current dependencies of the discharge capacity of some Cu-free and Cu-containing electrodes measured after 120 cycles. For these non-microencapsulated alloy electrodes, the high rate discharge property of Mn-containing alloys was generally better than that of the Mn-free ones. Furthermore, small amounts of copper substitution for cobalt in Mn-free compositions brought about beneficial effects to the high rate discharge properties. This may be a result of the fact that copper substitution has, to some extent, increased the pulverization tendency of the alloy powders, and may have the side-effect of increasing the effective surface area of the alloy powders within the electrodes.

4. Conclusions

Electrochemical experiments were conducted to investigate the electrode properties of copper containing misch metal-based stoichiometric alloys. It was shown that copper has some beneficial effect in improving the cycle properties of cobalt-free alloys, but may result in a decrease in their electrochemical capacity. Partial copper substitutions for cobalt are possible with little or no deterioration in electrochemical properties, accompanied by a moderate increase in the tendency of alloy powder pulverization and an improvement in the high rate discharge properties of the electrodes.

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