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Deterioration of copper-containing mischmetal–nickel-based hydrogen absorption electrode materials

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Abstract

The deterioration process of a series of Cu-containing mischmetal (Mm)–nickel-based multi-component alloy electrodes was investigated by electrochemical measurements, X-ray diffraction, magnetic measurements, scanning electron microscopy and microhardness measurement techniques. It was noted that this deterioration process was accompanied by decomposition of the materials into rare earth hydroxide and metallic Ni, and marked differences in the tendency for pulverization on hydrogenation for alloy powders of different compositions were observed, in spite of the fact that there was no significant difference in the volume expansion rates of the alloys during hydrogen absorption. It is suggested that the differences in the alloy pulverization could be attributed to differences in the microhardness of the alloys. With respect to decreasing microhardness properties of the materials, Cu had a beneficial effect on the Mm–Ni–Al system, although its effects were not as good as those of Co.

Keywords: Rare earth intermetallic compounds; Hydrides; Electrode materials

1. Introduction

Intermetallic compounds of the type $LaNi_5$ have been extensively investigated for application in many technical fields owing to their excellent hydrogen absorption properties [1]. For the preparation of Ni–metal hydride rechargeable batteries, an irreversible deterioration of negative electrodes made from the simple $LaNi_5$ composition was observed to occur when the electrodes were electrochemically cycled, although with this compound a theoretical discharge capacity of as high as 372 mA h g^{-1} had been expected [2]. It was observed that alloy powders of $LaNi_5$ pulverized during the charge–discharge cycling and decomposition of the compound into rare earth hydroxide and metallic Ni [2,3] or $Ni(OH)_2$ [4] could be detected. The very large volume expansion, as high as 24%, of the compound on hydrogenation was proved to be responsible for the alloy powder pulverization [2].

Since then, multi-component alloys that have higher cycle stabilities than the simple $LaNi_5$ compound (but inevitably containing elemental Co) have been developed. Examples are the series La–Nd–Ni–Co–Si and Mm–Ni–Co–Mn–Al, where Mm denotes mischmetal [2,5,6]. The Co substitution in the alloys has been believed to have the effect of lowering the volume expansion rate of the compound on hydrogenation, which in turn was believed to be crucial for success in improving the electrochemical stability of the materials [2].

A recent investigation showed that by using a simple non-stoichiometric $La(Ni, Cu)_{5.5}$ composition, good long-term stability of the materials may be obtained without using the expensive element Co [7]. In our investigations, we also found that partial substitution of Cu for Co in Mm–Ni–Co–Mn–Al alloys was possible without deterioration of the stability of the materials, although complete substitution always led to a decrease in stability [8]. This gives rise to the question of what effects Cu and Co have on the electrochemical stability properties. With this question in mind, we conducted experiments in which the deterioration process of some Cu-containing alloy electrode materials was investigated and factors influencing the stability properties of the materials were explored.

2. Experimental

The preparations of the alloys and electrodes has been described elsewhere [8]. Alloys of nominal compositions were prepared by arc-melting commercial pure

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metal materials and two kinds of mischmetals, Mm (22.47% La, 53.74% Ce, 5.88% Pr and 18.13% Nd) and Ml (78.8% La, 4.85% Ce, 4.02% Pr and 12.1% Nd). Alloy powders of 200 mesh were mixed with fine Cu powders in the weight ratio (active material/copper powder) 1:4, and then pressed into pellets 12 mm in diameter. Every pellet contained hydride-forming materials of 200 mg, without the so-called microencapsulations [9]. Electrochemical capacity and long-term stability properties 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. Ni plates and 6 M KOH solution were used as the counter electrodes and electrolyte, respectively.

Powder X-ray diffraction and scanning electron microscopy (SEM) experiments were performed by using a DMX-RB X-ray diffractometer and a JSM-35CF scanning electron microscope, respectively. In the X-ray diffraction experiments to measure the lattice parameters of the compounds and their corresponding hydrides, Cu powder was added to the samples and its diffraction peaks were used for the calibration of the diffraction angles. For the purpose of measuring the lattice parameters of the hydrides, the alloy powders were activated by three hydrogen gas absorption–desorption cycles with a maximum hydrogen pressure of 40 atm before they were kept under this hydrogen pressure for 16 h. After the hydrides had been removed from the hydrogen atmosphere, powder X-ray diffraction patterns were taken within 6 h, without taking special measures to prevent the evolution of the absorbed hydrogen from the materials. Magnetic moments of both as-prepared and cycled electrodes were measured by using a PAR-155 vibrating sample magnetometer (VSM) with a maximum magnetic field of 1.5 T. For the microhardness measurements, a MOB-1-15 apparatus with a load of 50 g was used. Twenty measurements were made and evaluated for each alloy sample.

3. Results and discussion

3.1. Electrochemical stability of Cu-containing alloys

A series of Cu-containing alloys were prepared and electrochemically studied; detailed results will be published elsewhere [8]. Fig. 1 shows the results for two representative alloy systems investigated.

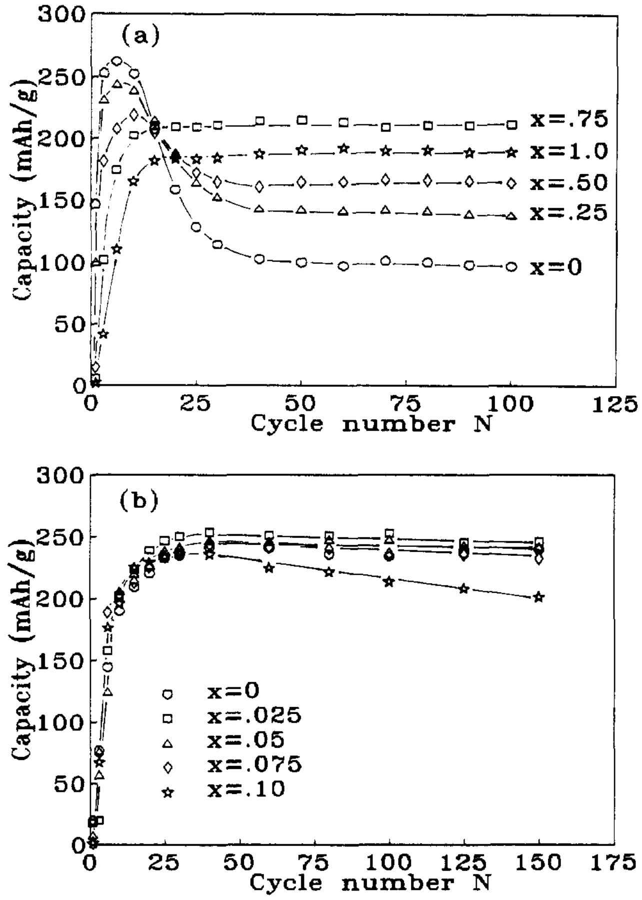

Fig. 1. Curves of discharge capacity vs. cycle number for (a) MmNi$_{4.2-x}$Cu$_x$Al$_{0.8}$ and (b) MlNi$_{3.5}$Co$_{0.7-7x}$Cu$_{8x}$Al$_{0.8-x}$ alloy electrodes.

In the Co-free multi-component system MmNi$_{4.2-x}$Cu$_x$Al$_{0.8}$ (Fig. 1(a)), the effect of Cu substitution on the electrochemical properties of Co-free alloys was investigated. It was observed that the Cu-free alloy showed the highest maximum discharge capacity and the highest electrode activity, but it also showed a severe decrease in discharge capacity within the initial tens of charge–discharge cycles, the reason for which has been proved to be related to the deterioration of the electrical contact of alloy powders with the rest of the electrodes when these alloy powders were severely pulverized and/or partially oxidized [8]. As the Cu content in the alloys increased, the maximum discharge capacity decreased and the cycle number needed for the electrochemical activation increased, accompanied by an improvement in the electrochemical stability of the materials.

In the MlNi$_{3.5}$Co$_{0.7-7x}$Cu$_{8x}$Al$_{0.8-x}$ alloy system (Fig. 1(b)), we investigated the effect of Cu substitution for Co on the properties of electrodes. It is clear that for this alloy system, a certain amount of Cu substitution, e.g. 50% of the Co content, is possible without deteriorating the electrochemical properties, including discharge capacity, activation behaviour and long-term stability, but too much Cu substitution would result in a decrease in the long-term stability.

It can be seen from Fig. 1(a) that Cu has beneficial effects in improving the long-term stability of the Co-free multi-component alloy, and in this respect its function is somewhat similar to that of Co, which has long been believed to be crucial in improving material stabilities. On the other hand, when we compare the functions of Cu and Co, we see from the results in Fig. 1(b) that with respect to improving the stabilities of materials, Co is superior to Cu, that is, complete Cu substitution for Co in this alloy system will bring about a decrease in stability. Similar results have also been obtained for Mm-Ni-Co-Cu-Al and Mm-Ni-Co-Cu-Mn-Al systems [8].

3.2. X-ray diffraction, VSM and SEM investigations of cycled electrodes

Decomposition of electrode materials into rare earth hydroxide and metallic Ni or nickel hydroxide has been observed to occur when the electrodes were electrochemically cycled [2–4]. Fig. 2 shows the powder X-ray diffraction patterns of the $MmNi_{4.2-x}Cu_xAl_{0.8}$ series of cycled electrodes. It can be seen that for the $MmNi_{4.2}Al_{0.8}$ alloy, rare earth hydroxide $Mm(OH)_3$ was formed after the alloy electrode was electrochemically cycled for 55 cycles, but the diffracted X-ray line intensities of the rare earth hydroxide seemed to be insufficiently high to account for the large decrease in the discharge capacity of the electrode (about 60% at 55 cycles, as can be seen from Fig. 1(a)), although a quantitative estimation of the extent of decomposition has not been attempted owing to the relatively weak intensities of the diffracted lines from the mischmetal hydroxide compared with those from the alloy powders and the Cu matrix. As will be discussed later, the actual decomposition ratio of the active material in this electrode was much lower than the value which would be deduced from the decrease in the discharge capacity of the electrode.

It is seen from Fig. 2 that as the content of Cu in the $MmNi_{4.2-x}Cu_xAl_{0.8}$ alloys increased, the amount of the rare earth hydroxide formed during electrochemical cycling decreased (although a quantitative analysis based on the results in this figure has not been attempted), corresponding to stabilization of the materials by the Cu substitution for Ni in the alloys.

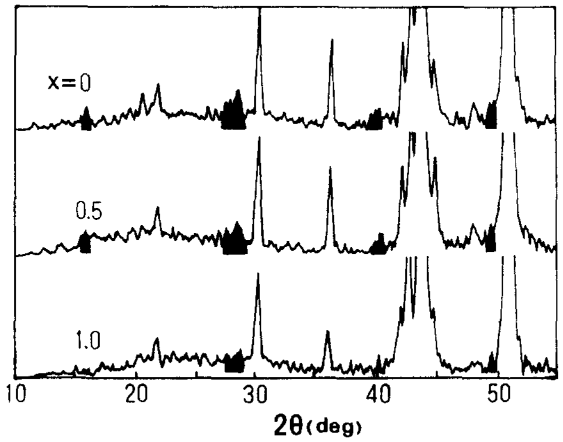

Fig. 2. Powder X-ray diffraction patterns for $MmNi_{4.2-x}Cu_xAl_{0.8}$ electrodes after 55 electrochemical cycles (Cu Kα). The shaded areas show the diffraction peaks of the rare earth hydroxide. The diffraction peaks of the metallic Ni-based phase could not be identified because they coincide with those of the Cu powder (at about 43.5° and 50.7°).

To estimate the actual decomposition ratios of the active materials within the above electrodes, magnetic moments of the electrodes were measured by the VSM technique both before and after the electrochemical cycling experiments. Fig. 3 shows the net magnetic moment increases of the electrodes after they had been electrochemically cycled. For as-prepared electrodes, the magnetic moments were very small, but they increased markedly after electrochemical cycling for only 55 cycles, indicating that ferromagnetic metallic Ni (or Ni-based solid solution) has formed as a result of the decomposition of the materials, in addition to the rare earth hydroxide [3]. As the Cu content in the alloys increased, the net increase in magnetic moments decreased, consistent with the result that the Cu substitution for Ni into the alloys improved the stability of the alloys.

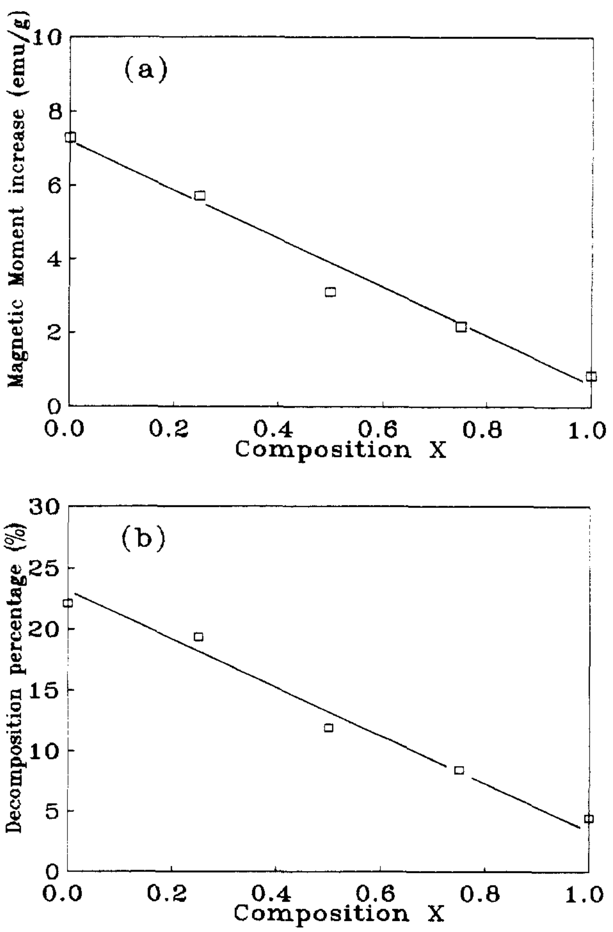

Fig. 3. (a) Magnetic moment increase and (b) estimated decomposition percentages of active materials in electrochemically cycled $MmNi_{4.2-x}Cu_xAl_{0.8}$ alloy electrodes (after 55 cycles) calibrated for the weight of the original active materials.

From the net increases in magnetic moment in the cycled electrodes, the ratios of decomposition of the active materials could be estimated by assuming that the Ni-based solid solution as one of the decomposition products would have the same Ni/Cu ratios (without Mm or Al solubility) as the as-received alloys and that this solid solution would possess the same ferromagnetic moment values as those of normal Ni–Cu alloys of corresponding compositions [10,11]. These estimated decomposition ratios are also shown in Fig. 3. We see that a decomposition ratio of about 22% has been estimated for the 55-cycled MmNi$_{4.2}$Al$_{0.8}$ electrode, a value which is much lower than the capacity decrease of about 60% (Fig. 1(a)). This large difference can be accounted for by the explanation that the electrochemical capacity decrease for this electrode was partially caused by deterioration of the electrical contact within the electrode when the alloy powders were pulverized and oxidized during the electrochemical cycling, in addition to the capacity decrease caused by the intrinsic deterioration of the electrode materials via the decomposition process.

From the estimations shown in Fig. 3, the decomposition ratios of the active materials decreased as the Cu substitution for Ni in the alloy system increased, that is, the substitution of Cu into the alloy system brought about an improvement in stability.

For the alloy series MlNi$_{3.5}$Co$_{0.7-7x}$Cu$_{8x}$Al$_{0.8-x}$, we see also the formation of the rare earth hydroxide, but its amount increased gradually with increasing substitution of Cu for Co, consistent with the result that substantial substitution of Cu for Co would result in a decrease in stability (Fig. 1(b)).

The decomposition of the electrode materials into hydroxide and metallic Ni has been observed to accompany the process of alloy powder pulverization which would take place when the alloy electrodes were electrochemically cycled. Higher degrees of powder pulverization would result in higher degrees of deterioration in the discharge capacities [2,3].

Figs. 4 and 5 show SEM observations of the cycled Cu-containing alloy electrodes. For the MmNi$_{4.2-x}$Cu$_x$Al$_{0.8}$ series, the degree of alloy powder pulverization decreased as the Cu content in the alloys increased, as is revealed in Fig. 4. The sequence of the tendency for alloy pulverization was in accordance with the results of the electrochemical experiments discussed above: the greater the extent of Cu substitution, the more stable the alloys. For the MlNi$_{3.5}$Co$_{0.7-7x}$Cu$_{8x}$Al$_{0.8-x}$ series, the tendency for alloy pulverization increased as the extent of Cu substitution for Co increased. This is again consistent with the results in Fig. 1(b), but this time the greater the extent of Cu substitution, the more liable the alloy powders are to pulverize (see Fig. 5).

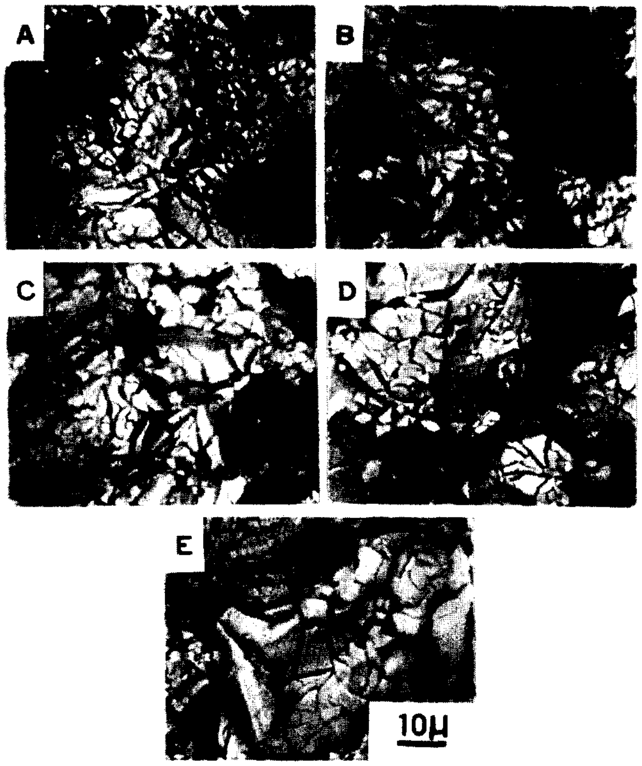

Fig. 4. SEM photographs of electrochemically cycled MmNi$_{4.2-x}$Cu$_x$Al$_{0.8}$ electrodes showing the differences in alloy powder pulverizations after 55 cycles. x=(A) 0, (B) 0.25, (C) 0.5, (D) 0.75 and (E) 1.0.

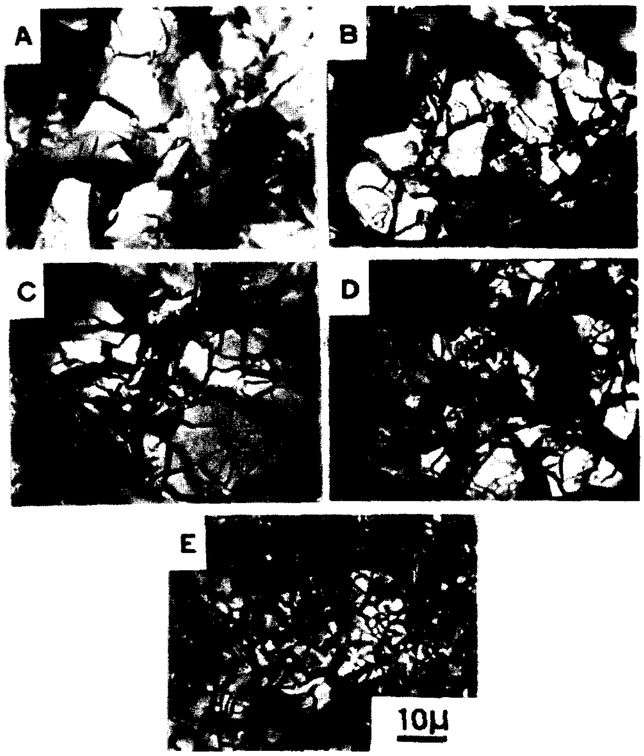

Fig. 5. SEM photographs of electrochemically cycled MlNi$_{3.5}$Co$_{0.7-7x}$Cu$_{8x}$Al$_{0.8-x}$ electrodes after 125 cycles. x=(A) 0, (B) 0.025, (C) 0.05, (D) 0.075 and (E) 0.1.

3.3. Volume expansion on hydrogenation and microhardness of the compounds

The tendency for alloy powder pulverization in the Cu-containing materials has been shown to possess considerable differences. It has been suggested that such a pulverization was the result of the very high rate of lattice expansion of the alloys when they absorbed large amounts of hydrogen [2].

Co has been proved to have the effect of considerably decreasing the rate of lattice expansion, and this knowledge had led to the development of a series of stable electrode materials, e.g. $La_{0.8}Nd_{0.2}Ni_{2.5}Co_{2.4}Si_{0.1}$ [2] and $MmNi_{3.5}Co_{0.7}Al_{0.8}$ [5,6]. On the other hand, it has long been observed that a series of Cu-substituted $CeNi_5$-based compounds also had relatively low lattice expansion rates [12,13], although no electrochemical characterization was carried out.

Table 1 and Figs. 6 and 7 summarize the lattice parameters of the Cu-containing compounds before and after hydrogenation, lattice parameter expansion rates and cell volume expansion rates on hydrogenation. For the unhydrogenated compounds, the lattice parameters a and c did not change very much. This result was difficult since it has been shown that for the $LaNi_5$-type hydride-forming compounds there existed a relationship between the unit-cell volume of the unhydrogenated compounds and the plateau pressure of hydride formation [14] and we have chosen the compositions of the alloys so that their plateau pressure of hydride formation did not change very much from that of the composition $MmNi_{3.5}Co_{0.7}Al_{0.8}$ [3].

However, it was surprising to note that for the 10 alloys investigated, no remarkable differences in the volume expansion rate were observed as the compositions changed. The lattice parameters a and c expanded by about 5.5% and 2.5–4.3%, respectively, with a cell volume expansion of about 15%. Although it was not known under our experiment conditions how much hydrogen was absorbed into the alloys and to what hydrogen pressure these volume expansion rates would correspond, it is noticeable that a volume expansion of about 15% was comparable to the values for Cu-

Table 1
Lattice parameters a and c and unit-cell volume V for two series of Cu-containing compounds and their hydrides

Alloy composition	Before hydrogenation			After hydrogenation		
	a (Å)	c (Å)	V (Å^3)	a (Å)	c (Å)	V (Å^3)
$MmNi_{4.2-x}Cu_xAl_{0.8}$ series						
$x=0$	4.98	4.07	87.3	5.24	4.17	99.2
$x=0.25$	4.97	4.06	86.9	5.25	4.19	99.9
$x=0.5$	4.98	4.06	87.4	5.25	4.20	100.4
$x=0.75$	5.00	4.09	88.6	5.26	4.22	101.2
$x=1.0$	5.00	4.08	88.3	5.28	4.23	102.0
$MlNi_{3.5}Co_{0.7-7x}Cu_{8x}Al_{0.8-x}$ series						
$x=0$	5.03	4.07	89.1	5.30	4.24	103.3
$x=0.025$	5.04	4.06	89.2	5.30	4.24	103.2
$x=0.05$	5.03	4.06	89.1	5.31	4.23	103.3
$x=0.075$	5.03	4.06	89.1	5.31	4.24	103.3
$x=0.10$	5.04	4.06	89.2	5.31	4.22	102.9

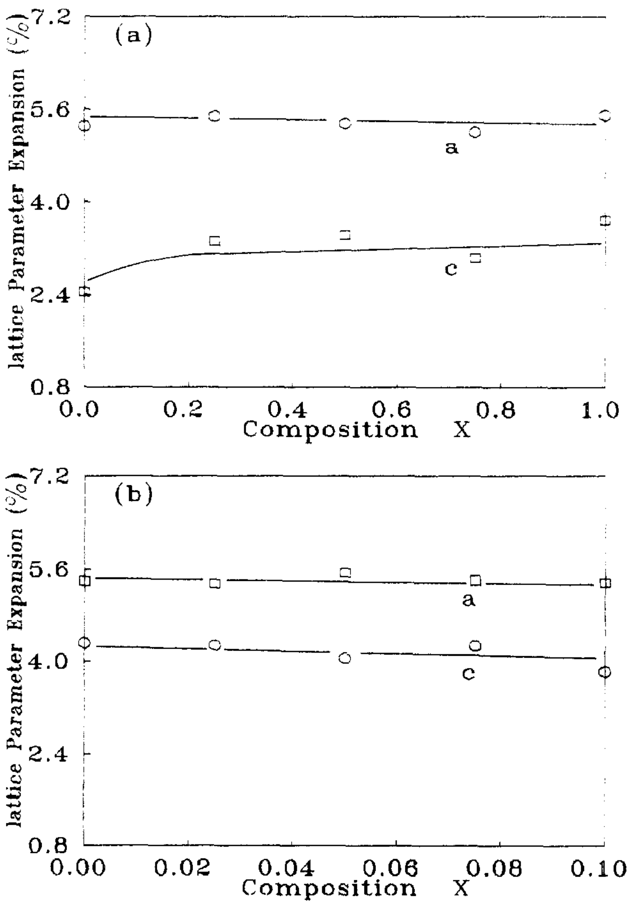

Fig. 6. Lattice parameter expansion rates on hydrogenation for (a) $MmNi_{4.2-x}Cu_xAl_{0.8}$ and (b) $MlNi_{3.5}Co_{0.7-7x}Cu_{8x}Al_{0.8-x}$ compounds.

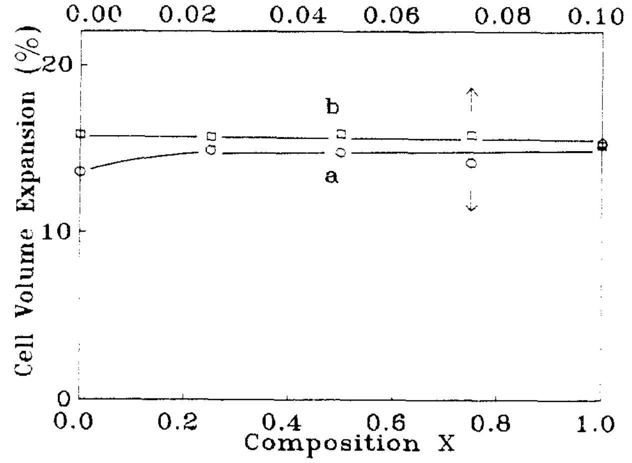

Fig. 7. Cell volume expansion rate on hydrogenation for (a) $MmNi_{4.2-x}Cu_xAl_{0.8}$ and (b) $MlNi_{3.5}Co_{0.7-7x}Cu_{8x}Al_{0.8-x}$ compounds.

substituted $CeNi_5$ alloys [12,13], but was considerably lower than that of the compound $LaNi_5$, which showed a volume expansion as high as 24% [2].

Since no remarkable differences in volume expansion rate could be found between the Cu-containing materials investigated, the differences in the tendency for pulverization (Figs. 4 and 5) and the stability properties (Fig. 1) of these materials could not be simply attributed to the volume expansion properties of the materials. Such a result proved that a lower lattice expansion rate could not ensure the stabilization of the electrode materials, and that material compositions, for example, Co or Cu substitutions into the alloys, should lead to other effects which are also important in influencing the stability of the materials.

Fig. 8 shows the results of microhardness measurements on the Cu-containing materials. It can be seen that large uncertainties were present in the measurements, and these uncertainties may be a result of the fact that the grain size of these alloys was not large enough for an accurate determination of the microhardness, although attention was paid to ensure that no measurement was made near grain boundaries. On the other hand, tendencies in the microhardness change of these materials could be observed as the composition was changed. For the composition series $MmNi_{4.2-x}Cu_xAl_{0.8}$ the microhardness decreased as the Cu content increased; however, for the composition series $MlNi_{3.5}Co_{0.7-7x}Cu_{8x}Al_{0.8-x}$, it increased as a result of the Cu substitution.

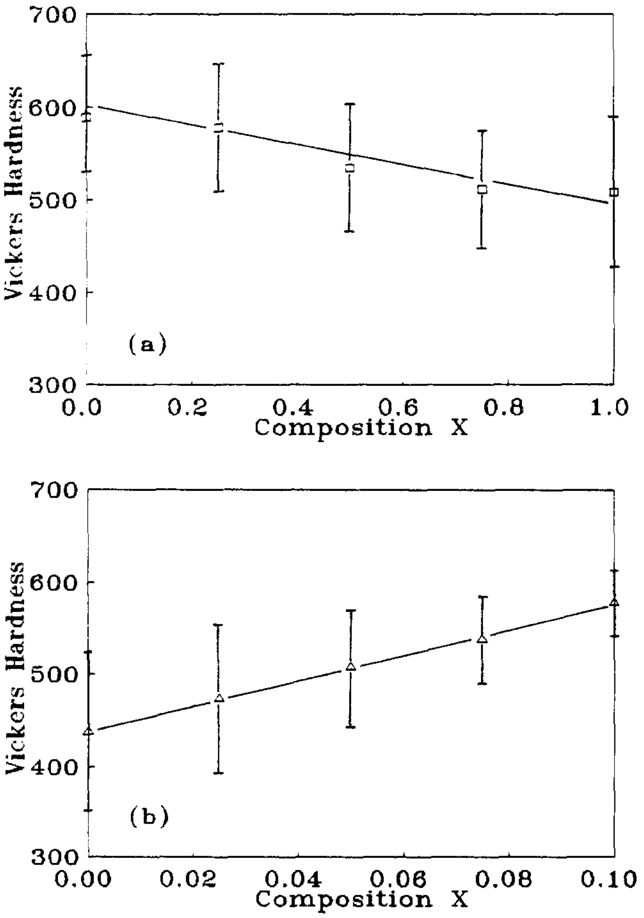

Fig. 8. Vickers microhardness of (a) $MmNi_{4.2-x}Cu_xAl_{0.8}$ and (b) $MlNi_{3.5}Co_{0.7-7x}Cu_{8x}Al_{0.8-x}$ materials.

Furthermore, these tendencies were found to be consistent with the results of both electrochemical measurements and the SEM observations: in the $MmNi_{4.2-x}Cu_xAl_{0.8}$ series, a higher Cu content with a lower value of microhardness led to better electrochemical stability and a lower tendency to pulverize the materials. In the $MlNi_{3.5}Co_{0.7-7x}Cu_{8x}Al_{0.8-x}$ series, higher Cu substitution would result in a higher microhardness, which corresponded to a higher tendency for material pulverization, and, when the Cu content was high enough, a deterioration in the cycle stability. These results suggest that the microhardness of the materials is very important in determining the stability properties of the hydrogen absorption materials for electrode applications, and the favourable effect of both Co and Cu in improving material stabilities may be a result of their effect in decreasing the microhardness. Comparing the results in Fig. 8 and those of Sakai et al. [3], it seems that a microhardness value lower than HV = 500 should be a criterion for the selection of such materials, although the mechanical properties of the hydrides may be very different from those of the original compounds and therefore should also be investigated.

4. Conclusions

Copper has favourable effects in improving the stability properties of Co-free multi-component electrode materials. Partial Cu substitutions for Co are possible without deterioration of the material properties, but complete substitution leads to deterioration of the stability. Decomposition of the materials into rare earth hydroxide and metallic Ni was observed by X-ray diffraction and magnetic measurements, and differences in the pulverization of material powders during electrochemical cycling were observed by SEM. A volume expansion of about 15% was found for all the materials investigated under our experimental conditions, although the material stabilities differed markedly, as was revealed in the electrochemical cycling experiments. Microhardness measurements showed that Co and Cu had the effect of decreasing the hardness of the materials, and in this respect the effect of Co was superior to Cu. It is suggested that in selecting hydrogen-absorbing electrode materials, the microhardness may be an important property affecting the stability.

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