Journal of Alloys and Compounds 253–254 (1997) 621–625

Effects of the materials processing on the hydrogen absorption properties of $MmNi_5$ type alloys

K. Yasuda

Corporate R&D Center, Mitsui Mining and Smelting Co., Saitama, Japan

Abstract

The effects of heat treating conditions on the hydrogen absorption characteristics of low-cost cobalt-free $Mm(Al–Mn–Fe–Ni–Cu)_{5+x}$ alloys were investigated. The alloys were prepared by induction melting and water cooling and thermally treated at temperatures between 1153 and 1353 K in vacuo. For the stoichiometric alloy of $Mm(Al–Mn–Fe–Ni–Cu)_5$, brittleness was increased abruptly by heat treatment at temperatures above 1300 K; however, electrochemical deterioration was not much influenced by the thermal treatment conditions. For over-stoichiometric alloys a segregation into an iron-rich secondary phase could be seen after a heat treatment at 1153 K. The segregation disappeared and a single phase was attained in an alloy prepared at 1353 K. The hydrogen absorption characteristics were, therefore, strongly dependent on the thermal treatment conditions.

Keywords: AB_5; Thermal treatment; Hydrogen absorption segregation

1. Introduction

Most of the work on $MmNi_5$ type alloys concerns the partial substitution of the host elements. Partial replacement of lanthanum by other lanthanides or nickel substitution by cobalt was very effective in improving the long-term cycling stability of AB_5-type alloys [1–3]. Nowadays it is well known that cobalt influences positively the charge–discharge cycling stability in alkaline solutions and suppresses the decrepitation of the alloys [4]. The $MmNi_5$ type alloys for battery applications contain about 10% Co and constitute about 40% of the raw material cost of the alloys. More cost-effective alloys with high reliability are demanded for application to electric vehicles. Iron is one of the candidates for cobalt substitution. The use of iron is not only cost-effective, but is also reasonable for the purpose of recycling.

Meanwhile, it was shown that electrochemical stability could also be improved by employing over-stoichiometric materials [5–8]. Several works have been performed regarding the casting conditions and the deviation from the stoichiometry in cobalt containing $MmNi_5$ alloys [9,10]. Several cobalt-free alloys have been proposed [11–14]; however, they were checked only in half-cell geometry and their hydrogen absorption capacities are much lower than that of cobalt containing battery alloys. No detailed information is available on the hydrogenation characteristics of cobalt-free Fe-containing alloys. This report describes the influence of thermal treatment on the metallurgical structures and hydrogenation properties of $Mm(Al–Mn–Fe–Ni–Cu)_{5+x}$ alloys.

2. Experimental details

The nominal compositions of the sample alloys are listed in Table 1. The alloy ingots were melted by induction heating from the constitutional elements in an alumina crucible under an atmosphere of purified argon and solidified by pouring into a water-cooled copper mold with a cooling rate of about 10^2 K s^{-1}. Thereafter, the water-cooled alloys were heat-treated at temperatures between 1153 and 1353 K for 6 h in vacuo.

The alloys were mechanically pulverized to an average grain size of 45 μm. The crystal structures and lattice constants of the alloys were determined by X-ray diffraction. The microstructures were investigated by a scanning

Table 1
Chemical compositions of the cobalt-free Fe including $Mm(Al–Mn–Fe–Ni–Cu)_{5+x}$ alloys

	Composition	B/Mm
A	$MmAl_{0.3}Mn_{0.4}Fe_{0.38}Cu_{0.02}Ni_{3.9}$	5.0
B	$MmAl_{0.3}Mn_{0.4}Fe_{0.38}Cu_{0.22}Ni_{3.9}$	5.2
C	$MmAl_{0.3}Mn_{0.4}Fe_{0.38}Cu_{0.42}Ni_{3.9}$	5.4

0925-8388/97/$17.00
PII S0925-8388(96)03045-9

electron microscope (SEM) equipped with an electron probe microanalyzer (EPMA).

Cyclic hydrogenation–dehydrogenation tests were performed by use of a fully automatic PCI monitor (Suzuki Shokan, Japan) to obtain information on the decrepitation behaviour of the powders. The alloy powders of 32–63 μm were exposed to 4 MPa hydrogen at 573 K for 0.5 h and cooled down to room temperature. This was repeated 3 times for activation. The powders were exposed to 3 MPa hydrogen for 0.5 h and then evacuated to about 10 Pa for 0.5 h at 313 K. These absorption–desorption processes were repeated 10 times. After that, the particle size and the powder distributions were measured before and after cycling tests with a Microtrac II particle size analyzer (Leeds & Northrup, PA, USA).

Electrodes were made by pressing a mixture of the alloy powders of 22–53 μm and fine nickel powder at a weight ratio of 1 to 3, with a slight amount of polyethylene powder as binder onto porous nickel matrices at a pressure of 3.7 MPa for 1 min. The pellets were heat-treated at 423 K for 1 h. The weight of the alloys was 0.18 g and the pellets measured 10 mm in diameter. Electrochemical tests were performed in an electrochemical cell at room temperature containing a 6 M KOH solution, an MH electrode and two $Ni(OH)_2$ counter electrodes. The following activation process was repeated for the first 10 cycles. The cells were charged with a current of 55 mA g^{-1} for 7 h, followed by 0.5 h rest, and then discharged until the working terminal voltage reached at 0.7 V. Afterwards, a galvanostatic accelerated cycling test was performed by charging with a current of 220 mA g^{-1} for 1 h and discharging with the same current rate until a working voltage of 0.7 V was reached. The discharge capacities were checked at a rate of 55 mA g^{-1} at every 50 cycles.

3. Results and discussion

Back-scattering electron images are shown in Fig. 1, in which the elements indicated by arrows were determined by EPMA measurements. For the stoichiometric alloy A, small amounts of Mischmetal were found to concentrate in the as-cast alloy as usually seen in stoichiometric alloys, which tended to become homogeneous by the heat treatment. For the over-stoichiometric alloy B, a slight Mischmetal deficient part occurred in as-cast alloys and a segregation into iron-rich secondary phase could be seen after a heat treatment at 1153 K. Eventually, the segregation totally disappeared in the alloy prepared at 1353 K. Almost the same behaviour was observed for alloy C.

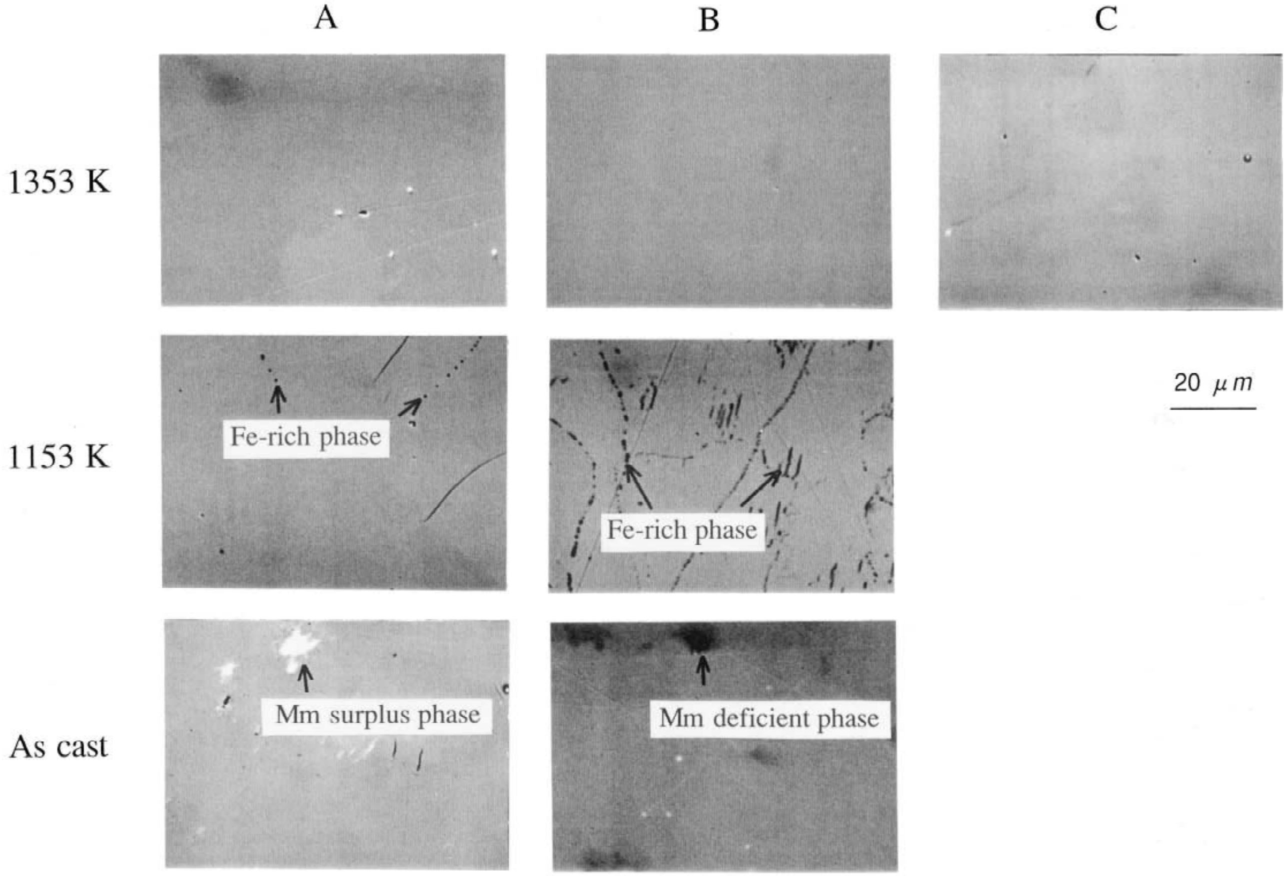

Fig. 1. SEM photographs with a backscattered electron image for $Mm(Al–Mn–Fe–Ni–Cu)_{5+x}$ alloys.

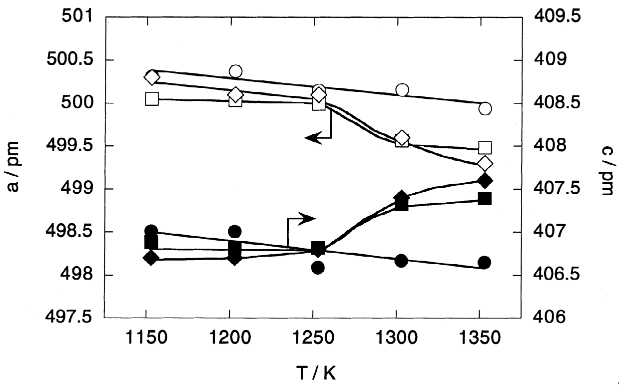

Fig. 2. Lattice constants, a and c, for the hexagonal AB_5 type alloys prepared at different heat treatment temperatures (A: ○, B: □, and C: ◊).

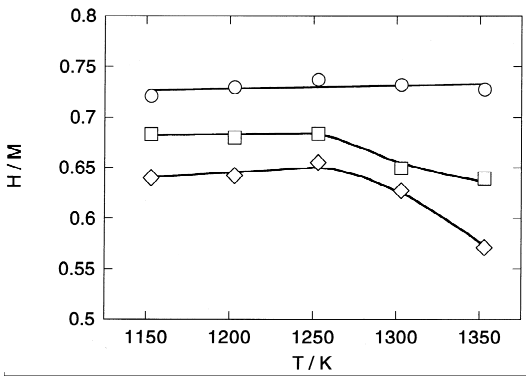

Fig. 4. Influence of heat treatment on the hydrogen capacities of $Mm(Al\text{–}Mn\text{–}Fe\text{–}Ni\text{–}Cu)_{5+x}$ alloys calculated between 0.01 and 0.5 MPa for absorption isotherms measured at 313 K (A: ○, B: □, and C: ◊).

Fig. 2 shows the change of lattice constants a and c of the alloys as a function of heat-treating temperature. All of the alloys have the hexagonal $CaCu_5$ type structure. For alloy A, neither a nor c change much as a function of heat-treating conditions. On the other hand, for the non-stoichiometric alloys B and C, a decreases and c increases significantly with an increase in the annealing temperature, suggesting a partial substitution of Mischmetal A atoms by two B atoms, as suggested by Notten et al. [7,8]. The atomic diffusion and rearrangement occurred at an annealing temperature above 1253 K in alloys B and C.

Figs. 3 and 4 show the dependence of the plateau pressures (evaluated at hydrogen to metal ratio H/M of 0.4 on heat treatment) and the effective hydrogen absorption capacities calculated between 0.01 and 0.5 MPa for the absorption isotherms as measured at 313 K. For alloy A, the plateau pressure and hydrogen concentration do not change much with heat-treating conditions. In the case of alloys B and C, PCT properties are strongly dependent upon heat treatment conditions, i.e. the plateau pressure gradually increases with increasing annealing temperature and the hydrogen capacity decreases at temperatures above 1253 K. The hydrogen atoms in the structure occupy the 3f and 6m sites in space group P6/mmm (in reality, the 3f sites leaves little space for hydrogen occupation, and the 6i and 12n sites are preferentially occupied [15]; however, all these sites are lumped together under the name ‘3f sites’ for simplicity here). Incidentally, if Mischmetal atoms are replaced by dumb-bell B-type atoms in MmB_5 [7], some 3f and 6m sites for hydrogen atoms around the dumb-bell atoms are blocked by the Coulomb potential barrier of the latter (Fig. 5). Theoretical considerations of the blocking of hydrogen sites in the $CaCu_5$ type structure, show that three of the 6m hydrogen sites are totally blocked and that the 3f sites are not strongly affected by the dumb-bell atoms since they provide more space for hydrogen occupation [16]. This causes a decrease in hydrogen storage capacity for over-stoichiometric alloys, as shown in Figs. 3 and 4.

The decrepitation behaviour as measured by the cyclic hydrogenation–dehydrogenation tests is plotted in Fig. 6. The decrepitation factor D was evaluated as the ratio of mean particle sizes after and before cycling. It is clearly seen that alloys A prepared at temperatures above 1253 K progress in their decrepitation behaviour when exposed to hydrogen gas. This can be attributed to the better homogeneity and the larger crystal grain size of the alloy. For alloy B, the decrepitation improves with increasing heat-

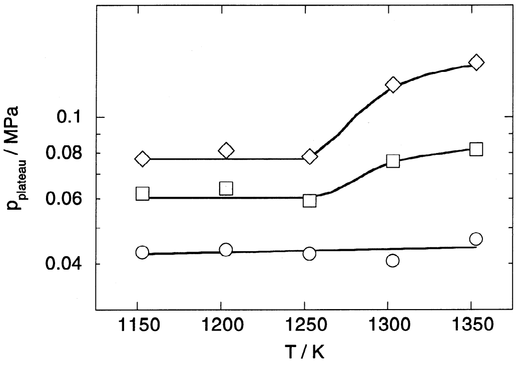

Fig. 3. Influence of heat treatment on the plateau pressures of $Mm(Al\text{–}Mn\text{–}Fe\text{–}Ni\text{–}Cu)_{5+x}$ alloys evaluated at H/M=0.4 for absorption isotherms measured at 313 K (A: ○, B: □, and C: ◊).

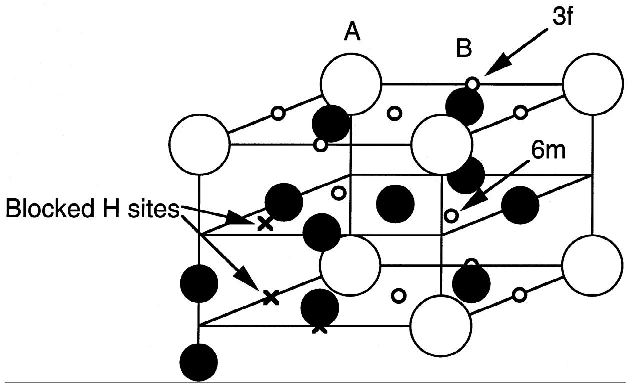

Fig. 5. Schematic description of the blocking of some hydrogen sites by the dumb-bell atoms for the hexagonal AB_5 structure.

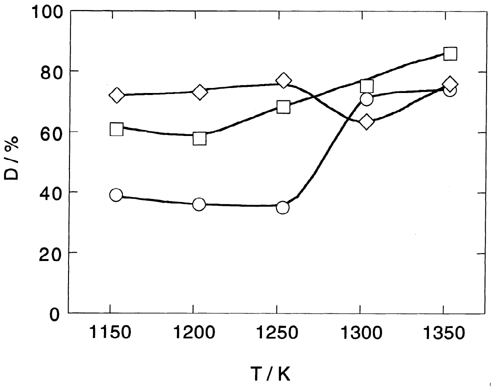

Fig. 6. Decrepitation behaviour D of the Mm(Al–Mn–Fe–Ni–Cu)$_{5+x}$ alloys prepared at different temperatures: (A: ○, B: □, and C: ◊).

treating temperature. For alloy C which was prepared at 1303 K it is only 63%, which is presumably due to its transitional morphology towards a single phase. For the alloy prepared at 1353 K D is 76%, which is smaller than the value of alloy B (D=86%). The melting points of alloys A, B and C are 1380 K, 1399 K and 1413 K, respectively. Therefore, it is reasonable to assume that long times and high temperatures of annealing are necessary for producing a homogeneous single-phase sample for the over-stoichiometric alloy C.

The lifecycle plots of the alloy electrodes are shown in Fig. 7, where the ratio between the remaining discharge capacity after 500 cycles and the maximum capacity is taken as a measure for cycle stability, H. The maximum discharge capacities were 288, 263 and 226 mAh g^{-1} for alloys A, B and C, respectively. For alloy A, the cycle stabilities are practically independent of the heat-treating conditions on the scale of this investigation, despite the fact that alloy A which was prepared at a higher temperature is well homogenized and has a better decrepitation property, as discussed above. Alloys B and C have an excellent stability, i.e. 97% for alloy C annealed at 1353 K. From the observations one can conclude that morphological structure and stoichiometry strongly affect the electrochemical deterioration.

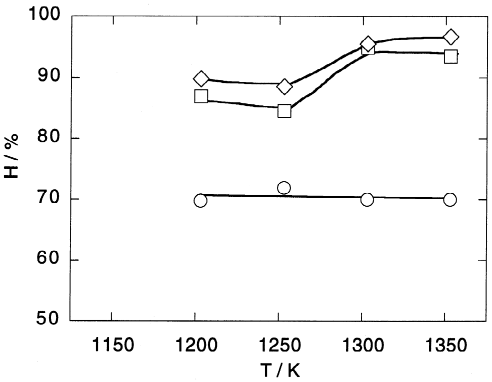

Fig. 7. Electrochemical deterioration H of the Mm(Al–Mn–Fe–Ni–Cu)$_{5+x}$ alloys prepared at different temperatures: (A: ○, B: □, and C: ◊).

By comparison, the 10% Co including Mm(Al–Mn–Co–Ni)$_5$ alloy, that is commonly used in Ni–MH batteries, has characteristics with a capacity of 280 mAh g^{-1}, D of 80% and H of 93%. Therefore, the iron-including alloys without cobalt show a better cyclic stability with reasonable capacity and low cost and could be utilized as battery materials used in electric vehicles.

4. Conclusions

The effects of stoichiometry and heat treatment on the decrepitation by hydrogen and on the electrochemical deterioration for cobalt-free Fe-including alloys were investigated. A segregation into iron-rich phases occurred in alloys which underwent heat treatment at lower temperatures, but disappeared in alloys treated at higher temperatures. The decrepitation of the stoichiometric alloy was abruptly improved by heat treatment at 1303–1353 K; however, the electrochemical life was independent from heat-treatment conditions. Alloys having over-stoichiometric compositions presumably undergo an atomic rearrangement to maintain the hexagonal single-phase structure. This leads to a decrease of hydrogen capacity and a better decrepitation behaviour at increasing annealing temperature.

Acknowledgments

The author gratefully appreciates Mr. Nakayama for his help in the experimental work.

References

[1] J.R.G.C.M van Beek, J.J.G. Willems and H.C. Donkersloot, in L.J. Pearce (ed.), *Proc. 14th Int. Power Sources Symp.*, Brighton, *Power Sources, 10* (1985) 317.
[2] J.J.G. Willems, *Philips J. Res., 39, Suppl. No. 1* (1984) 1.
[3] J.J.G. Willems and K.H.J. Buschow, *J. Less-Common Met., 129* (1987) 13.
[4] T. Sakai, K. Oguro, H. Miyamura, N. Kuriyama, A. Kato, H. Ishikawa and C. Iwakura, *J. Less-Common Met., 161* (1990) 193.
[5] K.H.J. Buschow and H.H. van Mal, *J. Less-Common Met., 29* (1972) 203.
[6] M. Nogami, M. Tadokoro, M. Kimoto, Y. Tikano, T. Ise and N. Furukawa, *Denkikagaku, 61* (1993) 1088.
[7] P.H.L. Notten, R.E.F. Einerhand and J.L.C. Daams, *J. Alloys and Comp., 210* (1994) 221.
[8] P.H.L. Notten, R.E.F. Einerhand and J.L.C. Daams, *Z. Phys. Chem., 183* (1994) 267.
[9] T. Sakai, T. Hazama, H. Miyamura, N. Kuriyama, A. Kato and H. Ishikawa, *J. Less-Common Met., 172/174* (1991) 1175.
[10] T. Sakai, H. Yoshinaga, H. Miyamura, N. Kuriyama and H. Ishikawa, *J. Less-Common Met., 180* (1991) 37.

[11] T. Sakai, H. Miyamura, N. Kuriyama, A. Kato, K. Oguro and H. Ishikawa, *J. Electrochem. Soc., 137* (1990) 795.

[12] T. Hazama, T. Sakai, H. Miyamura, N. Kuriyama, A. Kato and H. Ishikawa, *57th Meeting of Electrochemical Society*, Japan, 1991, p. 245.

[13] K. Hasegawa, H. Mori and M. Oshitani, *Yuasa-Jiho, 71* (1991) 13.

[14] F. Meli, A. Zuettel and L. Schlapbach, *Z. Phys. Chem. NF, 183* (1994) 371.

[15] A. Percheron-Guegan, G. Latigue, J.C. Achard, G. Germin and F. Tasset, *J. Less-Common Met., 74* (1980).

[16] H. Brodowsky, K. Yasuda and K. Itagaki, *Z. Phys. Chem., 179* (1993) 45.