Electrode stability of La–Ni–Mn hydride-forming materials prepared by conventional and rapid quenching techniques

Tang Weizhong and Sun Guangfei
Department of Materials Science and Engineering, Beijing University of Science and Technology, Beijing 100083 (China)

Abstract

Electrochemical charge–discharge-cycling measurements are made on electrode samples prepared from alloy powders of composition $LaNi_{4.5}Mn_{0.5}$. It is observed that by using the rapid quenching technique, the electrode durability of this hydride-forming compound can be improved. X-Ray diffraction energy-dispersive X-ray analysis as well as charge–discharge curves of the electrodes show that this improvement in electrode properties is accompanied by an improvement in material homogeneity as well as changes in atomic order of the crystal structure.

1. Introduction

Rechargeable nickel/metal hydride batteries based on the AB_5 (A denotes rare earth elements R, especially La, and B transition metals, primarily Ni) intermetallic compounds have undergone rapid development since Willems reported in 1984 that the long-term stability of electrodes made of $LaNi_5$ can be improved by replacing part of the La and Ni by other alloying elements, especially Co [1]. Since then a breakthrough has been made which has resulted in multicomponent alloys being employed nowadays in producing this kind of material [2, 3]. On the other hand, with multicomponent substitutions the kinetic properties and electrical capacities of $LaNi_5$-type materials may be severely damaged, leading to a sharp rise in raw material costs.

Recently it was shown that by using non-stoichiometric $AB_{5.5}$ compositions, good long-term stability may be obtained compared with that of the corresponding stoichiometric $AB_{5.0}$ material [4, 5]. Such non-stoichiometry may be achieved either by rapidly quenching the master alloy or by properly selecting the substitution elements. In another work it was indicated that the cooling condition of the AB_5 alloy is important in determining the stability of the material, which revealed that in addition to the composition of the alloy, the microstructure of the electrode material may affect its stability [6].

Rare earth compounds can be prepared by various techniques. For example, rapidly quenching the alloy melt may produce a microstructure very different from that of the corresponding alloy prepared by conventional techniques. Both amorphous and ultrafine crystalline microstructures may be employed depending on the final properties required. It is the aim of this paper to investigate the possibility of improving the long-term stability of electrode materials of simple composition by using the rapid quenching technique.

2. Experimental details

A master alloy of composition $LaNi_{4.5}Mn_{0.5}$ was prepared by induction melting the commercial metal materials La, Ni and Mn (purity 99%). After induction melting, the melt was rapidly cooled by pouring it into a copper mould which was cooled by water. The alloy was then divided into two parts: one was used directly for electrode preparation and the other was first melt quenched in an argon atmosphere. A linear velocity of the copper wheel of about 30 m s^{-1} was used for the rapid quenching process.

Fractions of both materials which passed a 200 mesh sieve were used for preparation of the electrodes. The alloy powders were mixed with fine Cu powder in a weight ratio of 1:4 and then pressed at about 4×10 N m^{-2} to produce pellets 12 mm in diameter. Every pellet contained 200 mg of hydride-forming material without so-called microencapsulations [3].

The electrochemical capacity and long-term stability properties were measured by charging the pellets at a current density of 300 mA g^{-1} for 1.5 h and then discharging them at a current density of 300 mA g^{-1} to -0.74 V with respect to an Hg/HgO reference

electrode. NiOOH plates and 6 M KOH solution were
used as the counterelectrodes and electrolyte respec-
tively.

3. Results and discussion

Figure 1 shows the results of the long-term stability
study of both the master and rapidly quenched
$LaNi_{4.5}Mn_{0.5}$ electrode materials. It is seen that com-
pared with that of the master alloy, the activation of
the quenched material is somewhat slower. The master
alloy absorbs hydrogen more rapidly, which is char-
acteristic of the simple AB_5 composition.

More striking is the difference in long-term stability
between the two materials. A rapid decrease in capacity
was observed for the electrode made of the master
alloy, while the electrode made of the rapidly quenched
material showed a slower decrease in capacity. After
100 cycles a capacity decrease of about 40% was observed
for the rapidly quenched material compared with about
60% for the corresponding master alloy. Although this
improvement in electrode stability is insufficient for
practical applications, it indicates that further improve-
ment may be possible by optimizing the alloy composition
as well as the preparation process.

The maximum capacities of the two electrodes were
almost the same, reaching about 315 mA g^{-1} at a
discharge current density of 300 mA g^{-1}. This result
may indicate that the primary phase for hydrogen
absorption in both materials is the same AB_5 phase.

Figure 2 shows the powder diffraction patterns of
both the master and rapidly quenched materials. At
first glance it can be seen from the diffraction patterns
at low angles that in both materials the primary phase
is the AB_5 compound. However, a striking difference
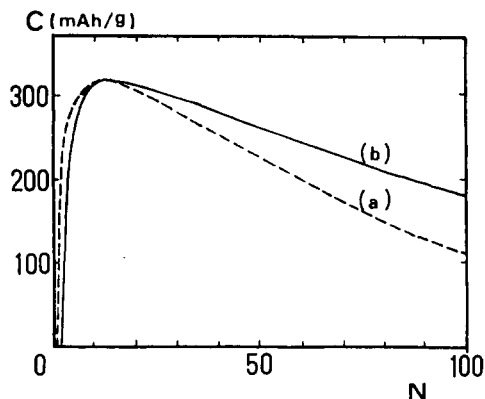in diffraction patterns can also be observed. First, for

Fig. 1. Curves of capacity C vs. cycle number N for conventionally
prepared (a) and rapidly quenched (b) $LaNi_{4.5}Mn_{0.5}$ electrodes
at 25 °C. The electrodes were charged at 300 mA g^{-1} for 1.5
h, kept at rest for 30 s and then discharged to -0.74 V with
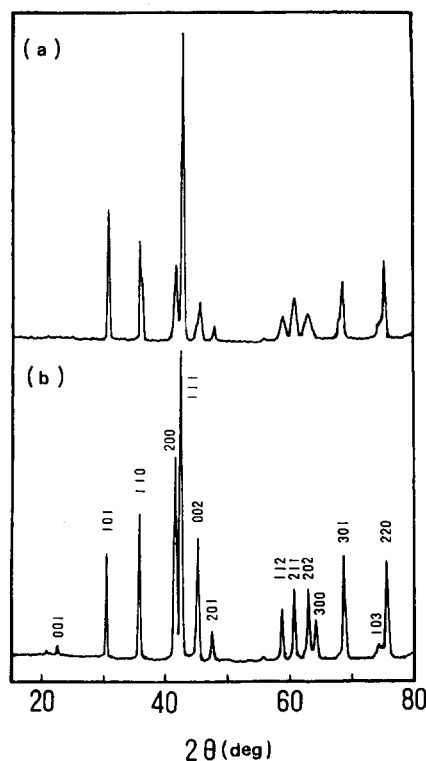respect to Hg/HgO.

Fig. 2. Powder diffraction curves of conventionally prepared (a)
and rapidly quenched (b) $LaNi_{4.5}Mn_{0.5}$ materials.

the rapidly quenched material the well-defined dif-
fraction peaks can easily be indexed to the AB_5 structure,
while for the master alloy smeared diffraction peaks
were encountered at high diffraction angles and these
cannot easily be indexed. This latter phenomenon has
also been observed in $MmNi_{3.5}Co_{0.8}Mn_{0.4}Al_{0.3}$ alloy
(Mm, misch metal) and has been attributed to a dis-
ordered distribution of Mn atoms within the crystal
structure. It was argued that such a disordered Mn
distribution was a result of a high rate of nucleation
of the Mn-containing alloy [3]. However, according to
the results of the present study, the even higher nu-
cleation rate of the rapidly quenched alloy brought
about a well-defined pattern of X-ray diffraction, sug-
gesting that disorder on the atomic scale may not be
responsible for the smeared X-ray peaks observed for
the Mn-containing alloy. An alternative explanation
might be that Mn-containing alloys are inhomogeneous
in chemical composition and hence have a spectrum
in their lattice constants, as will be discussed later in
this paper. Secondly, it is noticeable from Fig. 2 that
the two materials show very different intensities in their
X-ray diffraction patterns, even taking into consideration
the broadened X-ray peaks of the master alloy. For
example, in contrast with the situation in the master
alloy, the relative diffraction intensities of the rapidly
quenched material are in the order (101), (110) and
(200). This should be taken as an indication that both

materials have AB$_5$-type structures but with somewhat different atomic disorders. Such a phenomenon has also been observed in La(Ni,Si)$_5$ compositions and further investigation is under way [7].

Figure 3 shows the potential–time curves of both the master and rapidly quenched materials measured by charging the electrodes at a current density of 1000 mA g^{-1} for 0.5 h and then discharging them at a current density of 200 mA g^{-1} to -0.74 V. For the rapidly quenched material a potential plateau is recognizable in the charge curve and the discharge curve is flat. This is in accordance with a somewhat well-defined AB$_5$ crystallinity. On the other hand, both the charge and discharge curves of the master alloy are slightly more sloped, also in accordance with the X-ray diffraction result showing material inhomogeneity.

A scanning electron microscope (SEM) was employed to investigate the microstructures of the electrode materials. Figure 4 shows SEM photographs of both material powders embedded in a Cu matrix. Generally speaking, the AB$_5$ phase is always the primary phase within the LaNi$_{4.5}$Mn$_{0.5}$ powders, but with a difference in morphology between the two materials. Furthermore, in the master alloy powder, chemical inhomogeneity is detected by using the energy-dispersive X-ray analysis (EDXA) technique. Figure 5 shows photographs of the microstructures of the master alloy and the rapidly quenched material, together with representative EDXA results from three areas within these alloys. It is seen that in the master alloy two kinds of regions can be distinguished by their white and dark colours. A significant difference in composition, especially in Mn content, is detected between the two regions. In contrast, a very homogeneous composition is characteristic of the rapidly quenched material.

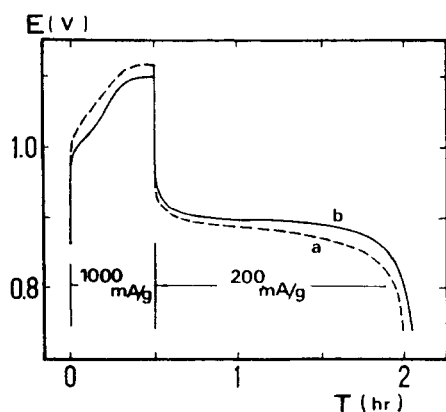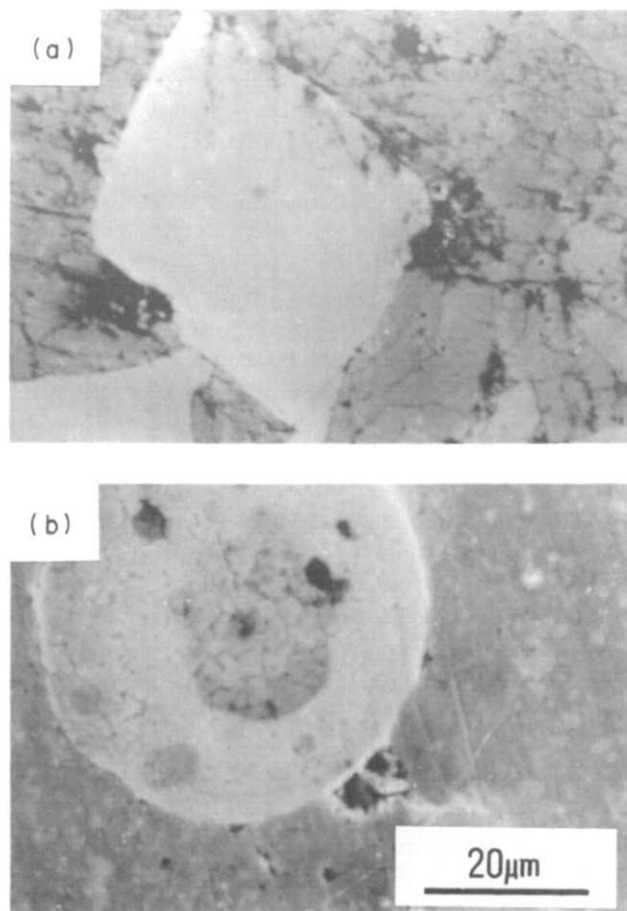Mn is an element which is often used in producing LaNi$_5$-type hydride-forming materials, because it is ef-

Fig. 4. SEM photographs of conventionally prepared (a) and rapidly quenched (b) LaNi$_{4.5}$Mn$_{0.5}$ powders embedded in a Cu matrix.

Fig. 3. Electrochemical potential curves of conventionally prepared (a) and rapidly quenched (b) LaNi$_{4.5}$Mn$_{0.5}$ electrodes. The electrodes were charged at 1000 mA g^{-1} for 0.5 h and then discharged at 200 mA g^{-1} to -0.74 V.
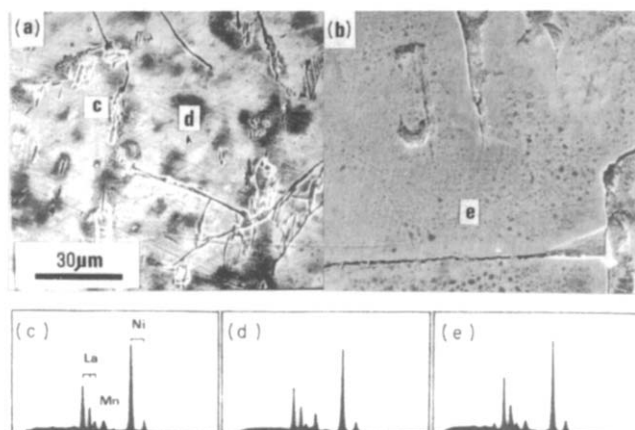

Fig. 5. SEM images of microstructures of conventionally prepared (a) and rapidly quenched (b) LaNi$_{4.5}$Mn$_{0.5}$ alloys and EDXA spectra of three areas (c–e) within the alloys (corresponding letters are used to label the places where the EDXA spectra were taken).

fective at adjusting the equilibrium pressure but does not affect the hydrogen absorption capacity of the compound. Unfortunately, Mn has been found to deteriorate the long-term stability of $LaNi_5$ electrodes. The reason for this has been ascribed to the rapid transportation of Mn atoms to the surfaces of alloy particles [8], thus accelerating the decomposition of the AB_5-type compound to rare earth and Mn hydroxides and metallic Ni and leading to the degradation of the electrodes during the charge–discharge cycling [9].

As we have noted, conventionally prepared $LaNi_{4.5}Mn_{0.5}$ material is inhomogeneous in composition in addition to being disordered in atomic structure. This may be the origin of the instability of the Mn compound, because differences in Mn content may result in differences in corrosion resistance and fast degradation of the electrodes may originate from the less corrosion-resistant regions in the alloy (probably the Mn-rich regions in Fig. 5(a)). This chemical inhomogeneity is present because substitution of Mn in the AB_5 composition should result in the consequence that under ordinary casting conditions the solidification process of the melt is initiated from an Mn-poor composition at high temperatures and then ends up with an Mn-rich composition, because we know that the melting point of $LaNi_5$ should be higher than that of $La(Ni,Mn)_5$. Rapid quenching of the alloy would greatly depress the log-distance diffusion of atoms, resulting in an improvement in chemical homogeneity and bringing about a beneficial effect on the electrode properties.

Regarding the atomic order differences observed by X-ray diffraction analysis, there seems to be no simple explanation. It is known that rare earth–transition metal intermetallic compounds display many variations in crystalline structure types. For example, on the basis of the so-called AB_5 structure, we can derive in the B-rich direction the A_2B_{17} structure (with two polymorphs showing minor atomic order differences) and in the A-rich direction the A_2B_7, AB_3 and AB_2 structures. Furthermore, these structure types are so closely related that substitution of B atom pairs at A atom positions produces structure types one after another. These two facts may be responsible for the atomic order differences observed by X-ray diffraction between the master and

rapidly quenched $La(Ni,Mn)_5$ materials. Changes in the atomic order in the same AB_5 crystal structure may also have a fundamental influence on the degradation behaviour of the material, as was observed in the $AB_{5.5}$ non-stoichiometric compounds [4, 10], but the detailed mechanism remains to be clarified.

4. Conclusions

The electrode properties and microstructures of conventionally prepared and rapidly quenched $LaNi_{4.5}Mn_{0.5}$ alloys have been investigated. It is found that the electrode capacities of the two materials are almost the same, but the long-term stability of the rapidly quenched material is better than that of the conventionally prepared material. By X-ray diffraction and the SEM technique, differences in atomic order and compositional homogeneity are observed between the two materials. It is suggested that the improvement in electrode stability of Mn-containing materials is associated with these microstructure differences and that rapid quenching may depress chemical inhomogeneity and bring about changes in atomic order, resulting in an improvement in electrode durability.

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