ELSEVIER

Journal of Alloys and Compounds 253–254 (1997) 570–573

Journal of ALLOYS AND COMPOUNDS

Development of AB_5 type hydrogen storage alloys with low Co content for rechargeable Ni–MH batteries with respect to electric vehicle applications

F. Lichtenberg[a,*], U. Köhler[a], A. Fölzer[b], N.J.E. Adkins[c], A. Züttel[d]

[a]Varta Batterie AG, R and D Center, D-65779 Kelkheim Germany
[b]Treibacher Auermet, A-9330 Treibach Austria
[c]Ceram Research, Stoke-on-Trent, ST4 7LQ UK
[d]University of Fribourg, Physics Institute, Perolles, CH-1700 Fribourg Switzerland

Abstract

Rechargeable alkaline nickel–metal hydride (Ni–MH) batteries have recently started to penetrate the consumer battery market. In contrast to the widely used Ni–Cd batteries they display up to 50% higher storage capacity and, due to the absence of Cd, an improved environmental compatibility. The electrochemically active material at the negative electrode is a hydrogen storage alloy. In most commercial applications so-called AB_5 alloys having a $CaCu_5$ type crystal structure have been used so far. These commercial AB_5 alloys are usually of the type $Mm(Ni,Co,Al,Mn)_5$, containing typically 10 wt% Co. Mm denotes Mischmetal, a cost-effective mixture of the rare earths La, Ce, Pr and Nd. The large amount of Co is added to produce an alloy with a reasonable cycle life, but increases the alloy cost considerably. The Ni–MH system is considered as a promising energy source for pure electric vehicles and hybrid cars. However for this application it is necessary to decrease the Co content in these alloys without diminishing the cycle life endurance. Hydrogen storage alloy production by gas atomisation represents a promising way to achieve this goal.

Keywords: AB_5 alloys; Low Co content; Cycle life; Gas atomisation

1. Introduction

The principle of the alkaline Ni–MH battery using nickel hydroxide as the positive and a hydrogen storage alloy (M) as the negative electrode material is described by the following equation:

$$Ni(OH)_2 + M \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftarrows}} NiOOH + MH$$

.

The practical energy density of this system, ranging from 60–80 Wh kg^{-1}, is attractive for electric traction applications (Pb–acid batteries possess about 30 Wh kg^{-1}). High rate capabilities can also be achieved with Ni–MH cells. Ni–MH batteries are, therefore, not only interesting for pure electric vehicles but also for hybrids, including concepts that require a relatively low capacity but a high power energy source. An alloy of the type $Mm(Ni,Co,Al,Mn)_5$ (Mm denotes Mischmetal) with 10 wt% Co ensures a cycle life of ≈1500 cycles whereas those with only 7 wt% normally hold on for only ≈750 cycles (these values refer to sealed cylindrical cells of AA size as described below at Section 2). The development of AB_5 alloys with low Co content, high cycle life and high rate capability is, therefore, an important task, not only for consumer batteries but also for traction applications where vast quantities are required.

Cycle life in the alkaline electrolyte is limited by the chemical and electrochemical corrosion of the hydrogen storage alloy. The volume expansion–contraction during hydrogenation–dehydrogenation leads to splitting of particles and microcracking at the surface of the particles. This results in a large increase in surface area and, therefore, increased corrosion. Alloys with a small volume expansion tend to have longer cycle lives than those with high volume expansions [1]. However, it is the discrete volume expansion between saturated α-phase and β-phase hydride which is related to the cycle life rather than the total expansion from the unhydrided alloy to the β-phase hydride [2].

---

*Corresponding author.

PII S0925-8388(96)02987-8

Several alloys with low Co content as well as many Co-free materials are known (see e.g. [3,4]). However, in most of these cases, the cycle life was determined in open cells, and not in sealed Ni–MH cells. Compared with the usual flooded experimental setup, sealed Ni–MH cells contain less electrolyte, the negative electrode is oversized and additional corrosion can be caused by the presence of oxygen evolved at the positive nickel hydroxide electrode, when approaching the fully charged state and during overcharging.

We report on the cycle life and rate capability of compositionally different alloys with low Co contents. Each alloy was prepared by two methods, i.e., conventional melting, casting and grinding as well as by gas atomisation.

2. Experimental

The Mischmetal (Mm) composition involving 50% La was fixed. The alloys were prepared by conventional melting and casting at Treibacher Auermet as well as by gas atomisation at Ceram Research. In both cases the alloys were subsequently heat treated [5]. Structural analysis of each alloy was studied using X-ray diffraction (XRD), scanning electron microscopy (SEM) and wavelength or energy dispersive X-ray analysis (WDX or EDX). The discrete volume expansion $\Delta V/V$ was evaluated by XRD determination of the lattice constants of the saturated α-phase and β-phase hydride. For that purpose the hydrides were formed by gas phase hydrogenation (≈ 1 bar) and subsequent exposure to CO gas resulted in a protection of the powder against decomposition in air. The electrochemical performance of the alloys was tested using both sealed cylindrical AA sized cells and also open cells, using nickel plate as the counter electrode. The AA type cells comprised a positive nickel foam and a negative dry rolled electrode using a capacity ratio negative/positive$\approx$ 1,7. Cycle life determination of these AA cells was made by using a constant charge capacity (1.2 h with 1 C rate) and a discharge rate of 1 C/0.97 V. The cycle life is then given by the number of cycles completed until the cell capacity falls below 80% of its initial value. The negative electrodes in the flooded half cell setup were pellets, 7 mm in diameter, made from a mixture of 25 mg of alloy powder and 75 mg of Cu powder, cold pressed using a pressure of 500 MPa. These electrodes were then cycled in 6 M KOH, with a constant charge capacity of 400 mAh g^{-1} and a discharge cut-off potential of $-0{,}6$ V vs. Hg/HgO.

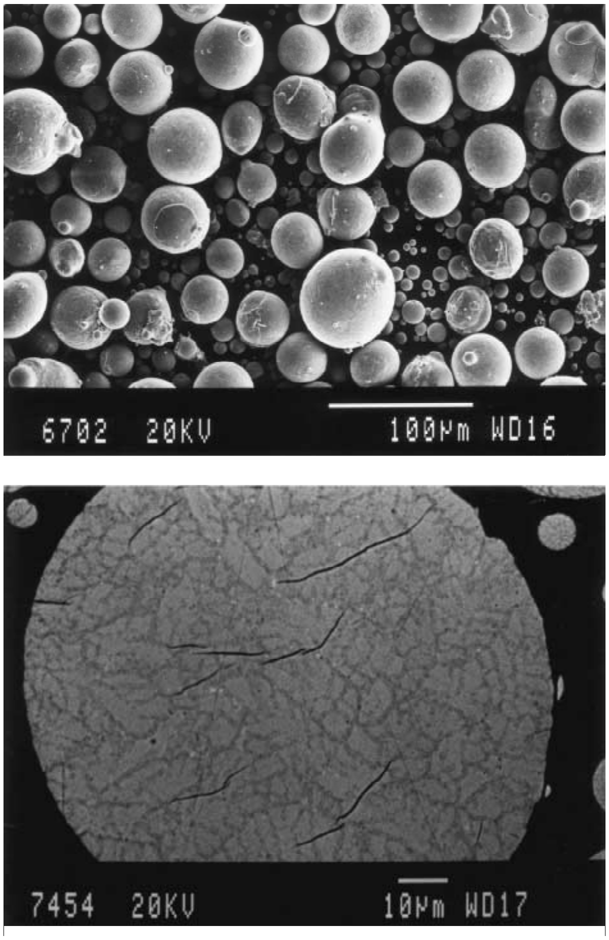

Fig. 1. Representative SEM images of gas atomised AB_5 type alloys (not heat treated).

3. Results and discussion

Fig. 1 shows two representative SEM images of gas atomised AB_5 alloys. At higher magnification a cell-like substructure and cell boundaries (constituting up to 20 vol% of the sample) are clearly visible. The boundary phase (rich in Mn and Al) differs both chemically and structurally from the cell centre. The heat treatment employed homogenises this structure, enabling the alloys to realise their full electrochemical capacity. This suggests that the cell boundaries are capable of storing reduced levels of hydrogen compared to the rest of the sample. SEM, combined with WDX of gas atomised and heat treated material, reveals a more homogeneous elemental distribution and lower levels of additional phase segregation, than their conventionally melted counterparts.

Gas atomised alloys low in Co content displayed a higher cycle life endurance in sealed Ni–MH cells than their conventionally melted counterparts. However, it would seem that there are certain fields of alloy composition, in which the gas atomised material displays an especially pronounced cycle life improvement, of up to 100%. Some examples, including a Co-free alloy, are shown in Fig. 2a and Fig. 3a. In most cases the volume expansion $\Delta V/V$ of the gas atomised materials are sig-

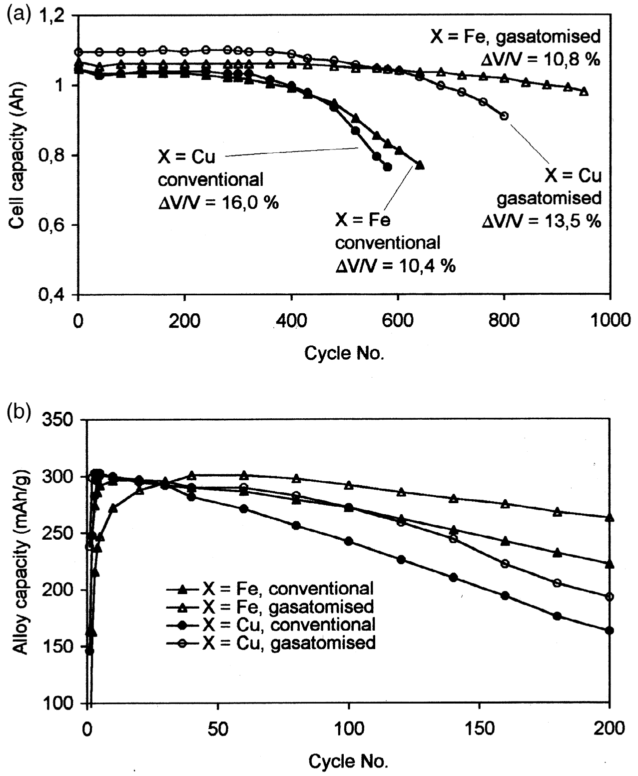

Fig. 2. (a) Cycle life of AA type cells at 21°C using $Mm(Ni,Co,Al,Mn,X)_5$ with 4.2 wt% Co with differing element X and preparation technique. Charge and discharge with 1 C rate. The discrete volume expansion Δ*V*/*V* upon hydrogenation of the alloys is also given. (b) Cycle life in open cells at 40°C of the alloys $Mm(Ni,Co,Al,Mn,X)_5$ with 4.2 wt% Co with differing element X and preparation technique. Charge and discharge with 200 mA g^{-1}.

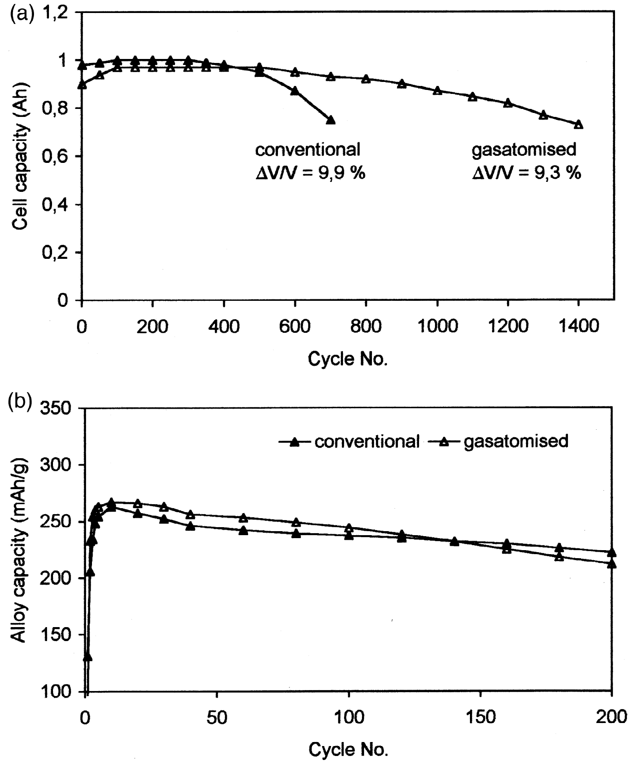

Fig. 3. (a) Cycle life of AA type cells at 21°C using the Co-free alloys $Mm(Ni,Fe,Al,Cu)_5$ with differing preparation technique. Charge and discharge with 1 C rate. The discrete volume expansion Δ*V*/*V* upon hydrogenation of the alloys is also given. (b) Cycle life in open cells at 40°C of the Co-free alloys $Mm(Ni,Fe,Al,Cu)_5$ with differing preparation technique. Charge and discharge with 200 mA g^{-1}.

nificantly smaller than those of their conventionally melted counterparts (see Fig. 2a and Fig. 3a). However, exceptions includes an alloy where X = Fe (see Fig. 2a). The influence of the composition and preparation technique on the cycle life is quite complex. Fig. 2b shows two alloys for which gas atomisation leads to an improved cycling stability in open cells. In contrast, Fig. 3b displays an alloy that exhibits no significant difference between preparation

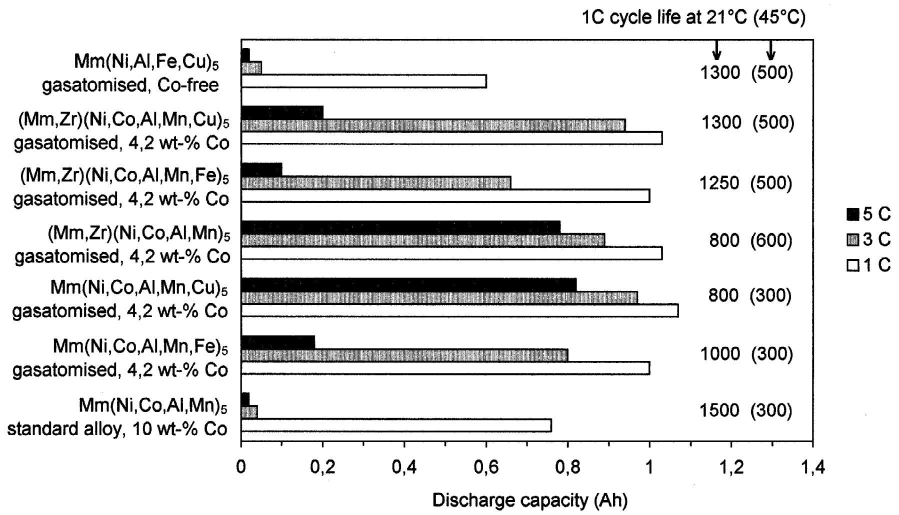

Fig. 4. Rate capability at 0°C and 1 C cycle life of sealed AA type cells using gas atomised low Co content alloys in comparison to a conventionally melted standard alloy with 10 wt% Co.

techniques. Nevertheless, gas atomisation of this alloy does result in a remarkable cycle life enhancement when tested in sealed Ni–MH cells (compare Fig. 2a with Fig. 2b and Fig. 3a with Fig. 3b). Therefore, apart from the smaller discrete volume expansions, the gas atomised materials are in some way more resistant against corrosion, especially with respect to the oxidation by oxygen which appears only at sealed Ni–MH cells but not at flooded cells. It is probably the high level of homogeneity of the gas atomised material that is responsible for this. However, further experimental work is needed to clarify this.

Fig. 4 shows an overview of the achievements of gas atomisation, namely rate capability at 0°C and cycle life of low Co content alloys, as compared to conventionally melted standard type material utilising 10 wt% Co. At low temperatures, the rate capabilities of the low Co content materials are even more pronounced.

4. Conclusion

The results demonstrate that the preparation of AB_5 type hydrogen storage alloys, with low Co content, as well as high cycle life and rate capability, can be achieved by the gas atomisation technique. This is considered to be an important step towards the avoidance of a future shortfall in cobalt.

Acknowledgments

Financial support from the EU project Brite-Euram (contract No. BRE2-CT92-0219) is gratefully acknowledged.

References

[1] T. Sakai, M. Matsuoka and C. Iwakura in K.A. Gschneidner Jr. and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Elsevier, 1995, p. 133–178 (see Fig. 16).
[2] P.H.L. Notten, J.L.C. Daams and R.E.F. Einerhand, *J. Alloys Comp., 210* (1994) 233–241.
[3] F. Meli, *Dissertation*, University of Fribourg, Switzerland, 1993.
[4] F. Meli, A. Züttel and L. Schlapbach, *J. Alloys Comp., 231* (1995) 639–644.
[5] German Patent application P195 12841.9 and P195 27 505.5.