Journal of Power Sources 108 (2002) 70–73

www.elsevier.com/locate/jpowsour

Recovery of Ni-based alloys from spent NiMH batteries

Jorge Alberto Soares Tenório*, Denise Crocce Romano Espinosa

Department of Metallurgical and Materials Engineering, Polytechnic School, University of São Paulo, Av. Prof. Mello Moraes 2463, CEP 05508-900 São Paulo SP, Brazil

Received 6 October 2001; accepted 14 December 2001

Abstract

Although spent nickel metal-hydride (NiMH) batteries are not considered hazardous waste, there are valuable materials that could be recovered; therefore the recycling of these batteries should be considered. This paper discusses spent NiMH batteries characterization and describes a simple process to recover valuable materials based on mineral processing techniques, hence the specific objective of this work is to study a process for the recovery of valuable metals from spent NiMH batteries. Batteries were manually dismantled in order to classify their components. The electrodes could be separated during the manual dismantling and were characterized through X-ray diffraction (XRD) analysis. A significant fraction of the batteries, around 37 wt.%, is composed of Ni-based alloy. The spent batteries were treated using laboratory equipment. The treatment that produced the best results was hammer milling, magnetic separation, knife milling, magnetic separation and size separation. The overall metal yield was in the order of 86%. A preliminary economic study is presented to show the feasibility of the process.

Keywords: Recycling; Batteries; Nickel alloys

1. Introduction

Although the use of nickel metal-hydride (NiMH) is growing, very little research exists on their recycling, Generally, batteries are complex systems containing a great number of materials inside a small volume, but NiMH and lithium ion batteries contains more valuable materials than primary cells and nickel–cadmium (NiCd) batteries. Even though much work has been done to improve the performance of this system in the last years, a remarkable lack of information still exist on the development of a recycling facility.

The use of portable devices is increasing nowadays and along with it, the use of batteries. The disposal of an increasing amount of spent batteries created a necessity to study ways to recover or recycle the materials that exist inside these batteries. The main primary accumulator used is Zn–MnO_2 alkaline. The most significant secondary energy accumulator systems are NiCd, NiMH, sulfuric lead acid and lithium ion (Li ion).

In the southern hemisphere primary batteries are still preponderant over secondary ones. Zn–MnO_2 alkaline is the most popular household battery. It is used for applications that require low cost and low energy. It has also low life cycle.

The lead acid battery is the cheapest secondary battery, and the process for its recycling is well-known in many countries around the world. It is specially used where the weight has little importance.

In appliances where the weight is important, NiCd, NiMH and Li ion batteries compete. Although NiCd batteries are still very popular, their use tends to decrease because of environmental problems. However, NiCd batteries are cheap, have a long life cycle and high discharge rates. Cadmium is a toxic metal, so NiCd batteries must be properly treated before being disposed off. NiMH and Li ion batteries were developed to replace NiCd batteries. These two new types of batteries have less environmental impact.

Comparing NiMH batteries to NiCd, NiMH batteries have a higher capacity, but a lower life cycle and lower charge current. NiMH batteries are also more expensive than NiCd ones. Li ion batteries are used when high density of energy is required, but its cost is still high compared to NiCd and NiMH batteries.

In addition to these features, it is important to highlight that NiMH and Li ion batteries were designed to replace NiCd due to the environmental aspects related to Cd disposal. NiCd and NiMH batteries have similar charge and discharge features. Li ion and NiMH batteries exhibit no memory effect.

* Corresponding author. Tel.: +55-11-3818-5546; fax: +55-11-3818-5243.
E-mail address: jtenorio@usp.br (J.A.S. Tenório).

0378-7753/02/$ – see front matter
PII: S0378-7753(02)00007-1

1.1. NiMH batteries for cellular phones

A NiMH battery for cell phones is basically composed of four–five cells connected in series inside a plastic case. Each cell has nine parts [1]: positive electrode, separator, negative electrode, gasket, release vent mechanism, isolating PVC disc, positive terminal, protection seal and metallic case.

The positive electrode is composed of a porous blade made of a nickel-based alloy and a paste basically composed of nickel hydroxide. The negative electrode is composed of a porous nickel-based alloy blade and the metallic case is essentially a nickel coated steel plate cup that gives the structural shape of battery and also acts as a negative pole [2].

NiMH batteries were developed based on the Ni–H_2 system. In fact, the hydrides replace the hydrogen and this avoids the risks involved in working with gas at high pressures. A great part of NiMH batteries are based on $LaNi_5$ and $MnNi_5$ [3] combined with rare earth elements such as Ce, Pr, Nd and also Al, Zn, and Co [4].

According to Yoshida et al. [5], the cup is made of a Fe–Ni alloy (91.1 and 7.3 wt.% Fe and Ni, respectively) and the metallic screen is composed of a Ni–Fe–Co alloy (80.5, 3.4 and 1.6 wt.% Ni, Co, Fe, respectively). Since the cup is made of a ferritic stainless steel and the screen is composed of a nickel alloy, both materials exhibit ferromagnetic behavior.

The following general equations show the main processes in a NiMH battery [3]

$$\text{anode}: \quad Ni(OH)_2 + OH^- = NiOOH + H_2O + e^-$$

$$\text{cathode}: \quad M + H_2O + e^- = MH + OH^-$$

$$\text{overall}: \quad Ni(OH)_2 + M = NiOOH + MH$$

2. Objectives

The goals of the present work are to characterize the main components of a NiMH battery, and to define a process to recover the Ni-containing materials from spent NiMH batteries.

3. Methodology

To reach the described objectives, the study was divided in two distinct steps. The first step was the characterization of spent batteries, and in the second was a test of the unit operations of mineral processing. The unit operations of mineral processing were used, essentially due to their low intrinsic cost.

3.1. Characterization of spent batteries

Dismantling of batteries and X-ray diffraction (XRD) were the two techniques used to characterize the spent batteries. A great number of batteries were disassembled through the use of scissors, saws, knife, and a set of hand devices. Each component was classified, separated and weighted.

The inner part of the accumulator is a three-layered bobbin. The layers were composed of positive electrode, separator and negative electrode. The electrodes were composed of a metallic screen and a paste. The pastes were scratched off and were submitted to XRD tests to identify their components.

The separated components were classified according to the following classes: metallic components, plastics and remaining components. Thus, the proportion of these materials in the batteries was determined, and based on these figures the steps for recovering of Ni-containing metallic parts were selected.

3.2. Process to recover the Ni-containing metallic parts

All of the tests were performed on a laboratory scale, e.g. the amount of material processed each time was around 5 kg. Mineral processing operations were studied to separate the Ni-containing parts of NiMH spent batteries. The following sequence of operations were performed: hammer milling of spent batteries, magnetic separation to separate the NiMH accumulators released in the hammer milling, knife milling of the accumulators, magnetic separation of the Ni-containing parts of the accumulators and size separation.

The hammer mill was used to open the plastic case releasing the accumulators and circuits, which could be easily separated. A double hammer mill grinding was necessary to liberate all accumulators. The final product was a pile of accumulators free from circuits and almost all intact, that means that after grinding the accumulators do not open and most did not change their shapes.

The first magnetic separation was done to separate the accumulators from circuits and plastic cases, as the Ni-based alloy inside the accumulator was attracted by the magnet.

The knife mill was used to grind the accumulators. The sieve used in this equipment was a 5 mm one, and this grinding was enough to liberate the metallic parts from separators and pastes.

The second magnetic separation was used to separate the metallic cup and screen from pastes and separators, since the magnet attracts the first ones.

After this treatment some paste held by the metallic parts contaminated the metallic fraction, and it was necessary to isolate the metallic part. To release the contamination the size classification equipment was used. The sieve used was of around 2 mm. During this operation the pastes left the metallic parts and also desegregated into fine powder.

4. Results and discussion

4.1. Characterization

Almost all spent NiMH batteries that were opened were composed of five 1.2 V cells connected in series. Through

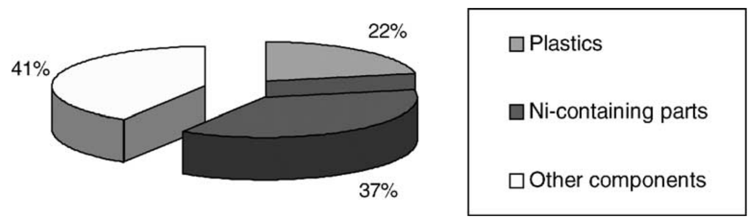

Fig. 1. Weight distribution of NiMH battery's components.

the careful use of hand equipment described previously it was possible to make an assured separation of the inner components of the cells.

The classification and weight of each part provide the data shown in Fig. 1. The results showed that around 37% of total weight of a NiMH battery contains a valuable Ni-bearing alloy, the recovery of which is the goal of the next step of this research.

XRD was performed to identify the compounds present in the pastes from negative and positive electrodes, and the results showed the presence of the phases presented in Table 1.

Basically, these results confirm the data from the literature [3,6]. XRD typically identifies phases with concentrations above 5%, minor constituents may not be identified. Therefore, the phases showed in Table 1 are the main phases of the electrodes. The pastes are essentially composed of La, Nd, Co, Ce and Ni, which are also valuable metals. Thus, the recovery of these materials can be profitable.

4.2. Process to recover the Ni-containing metallic parts

The treatment of spent NiMH batteries was carried out using mineral processing operations. A flow sheet of the process with the main separated materials in each step is presented in Fig. 2.

The outputs of the process are the plastic cases, the pastes and the Ni alloys. The cases are made of a thermoplastic material and consequently can be recycled, and the Ni alloys can also be recycled. As mentioned before, the electrodes contain valuable materials that may be recycled probably by a hydrometallurgical process. Zhang et al. [7] developed a hydrometallurgical process that recovers cobalt, nickel and rare earth metals through the leaching and solvent extraction of the material of the electrodes of spent NiMH batteries.

The process developed by the authors and described in this paper recovers the metal parts of the batteries. One output of the process is composed of pastes (electrodes) and fabric. The process of Zhang et al. recovers metal values from the electrodes, so the process presented in this paper could be considered a complementary approach to the work of Zhang et al.

Using the results reached in the laboratory scale study it is possible to do the mass balance presented in Fig. 3.

One can notice that about 33% of the total burden was recovered material containing valuable Ni. According to the characterization step, the amount of this material is 37%; thus, it indicates an overall yield of 86%. Nevertheless, these data were obtained in batch laboratory scale probably under industrial conditions the recovery would be even higher.

4.3. Economic benefits

A forecast for the NiMH worldwide use in 2001 predicts a production of around 1700 million units. In 1995 the production was about 300 million units. This big increase in the consumption was due to a strong decrease in the market for NiCd batteries, mainly because of the environmental restrictions on the Cd dissipation. Estimating a unit weight average

Table 1
Phases identified in the pastes of negative and positive electrodes of spent NiMH batteries

Electrode	Phases identified
Negative electrode	Ni, AlLaNi, Al_2Nd, AlNiCo, Ce
Positive electrode	Ni, $Ni(OH)_2$

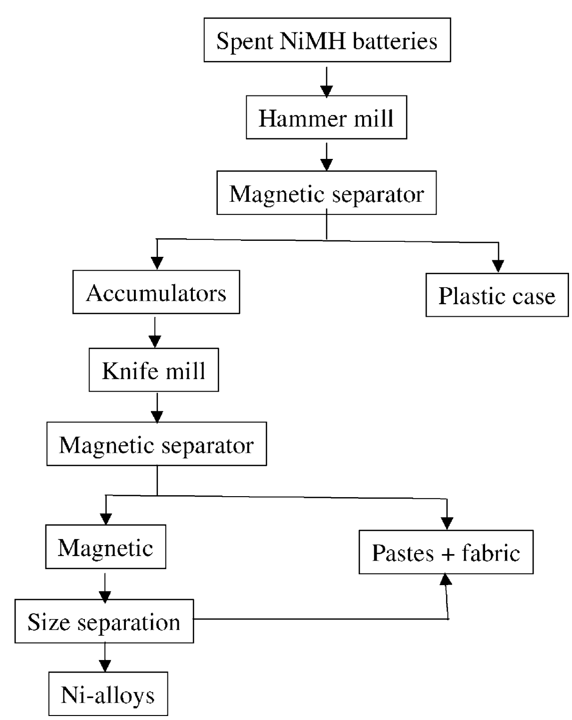

Fig. 2. Flow sheet of the Ni-containing metals recycling process.

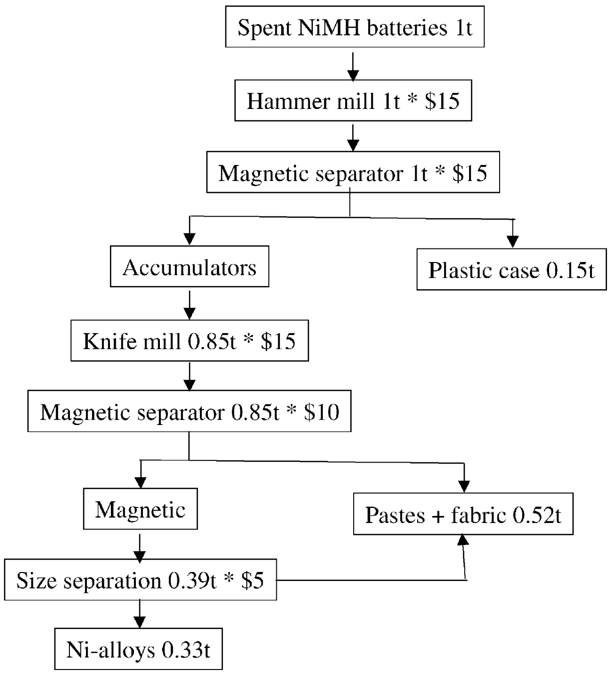

Fig. 3. Flow sheet considering operational cost and mass balance.

Table 2
Data used for the estimate of the costs for recycling

Operation	Estimated cost
Hammer mill	US$ 15.00 t^{-1}
Knife mill	US$ 15.00 t^{-1}
Magnetic separation	US$ 10.00 t^{-1}
Size classification	US$ 5.00 t^{-1}

of 20 g, and assuming 37% of Ni-containing alloys are present, the total amount of metal discharged will be 12,600 metric tons. The nickel concentration in the metallic magnetic parts is around 50%, and also using a US$ 5000.00 per metric ton as a low estimate price for the cost of the scrap, the total Ni lost is low estimate in 27 million dollars in 2001. At a yield of 86% the recovery achieved will be in the order of 23 million dollars.

The data presented in Table 2 and Fig. 3 were considered in order to evaluate the economic feasibility of the process. All data were estimated based on previous experience. Although these data are not precise, because there are many variables that should be considered, these data can give an initial idea about the costs and benefits.

According to a steel making industry the material is suitable for charging in electric furnaces without any kind of melting or briquetting process, so the costs of packaging are negligible. Consequently, the overall cost to process 1 t of NiMH batteries is at maximum US$ 50.00, and this produces 316 kg of a Ni-containing scrap that worth at least US$ 680.00.

5. Conclusions

Battery recycling is motivated for environmental reasons. NiMH battery does not present any environmental problems related to its disposal. On the other hand, NiCd battery must be collected and recycled; although the recycling is not profitable. Generally the applications of these two types of batteries are similar and most of time they are disposed off together. Hence, NiMH batteries are collected along with spent NiCd batteries. Consequently, there exists a necessity for a process to treat NiMH batteries, and this paper demonstrates that the recovery of metal parts can be profitable.

Around 37 wt.% of a recycling burden of NiMH batteries is composed of Ni-containing metals. A simple and cheap process developed to recover the Ni-containing materials, based on unit operations of mineral processing, gives a overall yield of about 86%.

References

[1] Fritz Beck, Paul Rüetschi, Rechargeable batteries with aqueous electrolytes, Electrochim. Acta 45 (2000) 2467–2482.
[2] Toshiba Battery Company S.A, Sealed-type nickel metal hydride batteries, Original equipment manufacturer, Available from world wide web: http://www.tbcl.co.jp/TB_e/ni_const.htm (1997).
[3] R.E. Kirk, D.F. Othmer, Batteries, Encyclopedia Chem. Technol. 3 (1984) 963–1079.
[4] MingMing Geng, Dereck O. Northwood, The characteristics of the negative electrode of a nickel metal hydride cell, Int. J. Hydrogen Energy 21 (10) (1996) 887–890.
[5] T. Yoshida, H. Ono, R. Shirai, Recycling of Used NiMH Rechargeable Batteries, in: Proceedings of the 3rd International Symposium on Recycling of Metals and Engineered Materials. Warrendale, TMS, 1995. p. 1995.
[6] F. Haschka, W. Warthmann, G. Benczúk-Ürmössy, Alkaline batteries for hybrids and electric vehicles, J. Power Sources, 1998, 32–36.
[7] P. Zhang, T. Yokoyama, O. Itabashi, Y. Wakui, T.M. Suzuki, K. Inoue, Hydrometallurgical process for recovery of metal values from spent nickel metal hydride secondary batteries, Hydrometallurgy 50 (1998) 61–75.