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RECYCLING OF THE RARE EARTH OXIDES FROM SPENT RECHARGEABLE BATTERIES USING WASTE METALLURGICAL SLAGS

K. Tang[a,*], A. Ciftja[a], C. van der Eijk[a], S. Wilson[a], G. Tranell[b]

[a] SINTEF Materials and Chemistry, N-7465 Trondheim, Norway
[b] Norwegian University of Science and Technology, N-7491 Trondheim, Norway

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Abstract

A high temperature process for recycling spent nickel-metal hydride rechargeable batteries has been recently developed at SINTEF/NTNU. The spent battery modules were first frozen with liquid nitrogen for the de-activation and brittle fracture treatment. The broken steel scraps and plastics were then separated by the mechanical classification and magnetic separation. The remaining positive and negative electrodes, together with the polymer separator, were heated to 600-800°C in order to remove the organic components and further separate the Ni-based negative electrode. XRF analyses indicate that the heat-treated materials consist mainly of nickel, rare earth and cobalt oxides. The valuable rare earth oxides were further recovered by the high-temperature slagging treatment. The waste metallurgical slags, consist mainly of SiO_2 and CaO, were used as the rare earth oxide absorbent. After the high temperature slagging treatment, over 98% of nickel and cobalt oxides were reduced to the metal phase; meanwhile almost all rare earth oxides remain in the molten slags. Furthermore, EPMA and XRF analyses of the slag samples indicate that the rare earth oxides selectively precipitate in the forms of solid $xSiO_2 \cdot yCaO \cdot zRe_2O_3$. The matrix of slag phase is Re_2O_3 deficient, typically being less than 5 wt%. This provides a sound basis to further develop the high-temperature process of concentrating the Re_2O_3 oxides in slags.

Key words: Recycling; Spent rechargeable battery; Waste slag; Rare earth oxide; Nickel-based alloy.

1. Introduction

The increasing popularities of electronic consumer goods, hybrid and electric cars, and wind turbines lead to an unprecedented increase in the demand of rare earths. The rare earths are now considered as the most critical, with the highest supply risk raw materials [1]. Because there exist only few exploitable natural resources of rare earths in Europe, the EU will mainly have to rely on recycling of REEs from pre-consumer scrap and especially End-of-Life products, known as “urban mining”.

Nickel-metal hydride batteries are currently used in many mobile applications: hybrid and electric cars, laptops, mobile phones etc. Because NiMH batteries have about twice the energy density of Ni-Cd batteries and a similar operating voltage as that of Ni-Cd batteries, they are expected to become a mainstay in the current rechargeable batteries. However, sustainable industrial recycling processes for these new types of batteries are still under development. Several hydrometallurgical recycling processes have been reported in the literature for the discarded NiMH batteries. Tzanetakis and Scott [1] used hydrochloric acid to leach the batteries and recover rare earth elements (REEs) by solvent extraction. Similar processes were also proposed by Zhang *et al*. [2], Nan *et al*. [3], Li *et al*. [4] and Rodrigues and Mansur [5]. Kikuta and Sakai [6] reported the process of reuse the components in NiMH batteries for hybrid vehicles. Nickel, rare earths, cobalt alloy, and nickel hydroxide were selective recovered and used again directly for the NiMH battery. Tenorio and Espinosa [7] proposed the process of recycling Ni-based alloys based on mineral processing techniques. A closed loop recycling process for the NiMH batteries was developed by Muller and Friedrich [8]. The CaO-CaF2 slag was proposed to recover the REEs from the NiMH batteries. Similar high temperature process for recycling of Li-ion and NiMH batteries are also published on the Umicore website[2].

In the present study, a pyrometallurgical process for recycling spent NiMH batteries has been developed using the waste metallurgical slags as the rare earth oxides trapping agent. The high temperature process is able to completely separate the valuable nickel based alloys and RE oxides. Furthermore, EPMA and XRF analyses indicate that the rare earth oxides can be selectively enriched from the slag by the precipitation and filtration.

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* *Corresponding author: kai.tang@sintef.no*

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2. Experimental

2.1 Materials

The main parts of a NiMH battery are cathode, anode, electrolyte, separator and the steel case. In cylindrical cells strips of anode, cathode and separator are laminated and are coiled to a helix. The cathode is made of nickel coated with nickel hydroxide whereas the anode consists of a hydrogen storage alloy based on mischmetal (mainly cerium, lanthanum, praseodymium and neodymium) and nickel alloys. The separators are either made of nonwoven fabrics or microporous polymeric films. The assembled battery is fitted into a steel case.

The NiMH batteries used in the present study were cylindrical with dimensions of 32mm and 89mm in height and weight about 250 grams. After mechanical processing, chemical analysis of a typical NiMH battery scrap indicates that it consists of 45–50wt% Ni, 9–11wt% Co and 13–16wt% mischmetal.

2.2 Physical separation of NiHN batteries

In order to separate the steel case from the battery, two types of freezing agents were first tested in the laboratory. The first one, solid carbon dioxide sublimation at -78.5°C, was not able to embrittle the steel case, even cooled the batteries in a polyurethane insulated box for 24 hours. The second freezing agent, liquid nitrogen boils at -196ºC, was then tested in the laboratory. The batteries were put into liquid nitrogen bath for about 15 minutes. Then, they were immediately submitted to a Morse jaw crusher for disassembly. The steel shell cracked and the batteries disassemble into small pieces.

The disassembled batteries were further treated by magnetic separation. A magnetic separator with the max magnetic field of 8000 Gauss was used. In addition to the steel scraps, the Ni-based alloys also show magnetic properties. In order to better separate the steel from the rest of the battery material, two runs were performed. In the first one the applied magnetic field was 5000 Gauss. The magnetic material gained here was used as feed to the second run where a magnetic field of 3000 Gauss was used in the second time. It has been evaluated that the magnetic part makes approximately 27% of the total battery weight. The rest of “non-magnetic” materials will be further used in the high temperature treatments. The magnetic separation has not been optimized yet in the present study.

2.3 Pretreatments

Since the “non-magnetic” materials contain plastic sealing plate and polymer separator, a further separation process is necessary to remove them from the rest of positive and negative electrodes. Heat treatment of the non-magnetic” materials in a muffle furnace were carried out at three different temperatures: 300ºC, 650ºC and 900ºC, respectively. The results are shown in Figure 1.

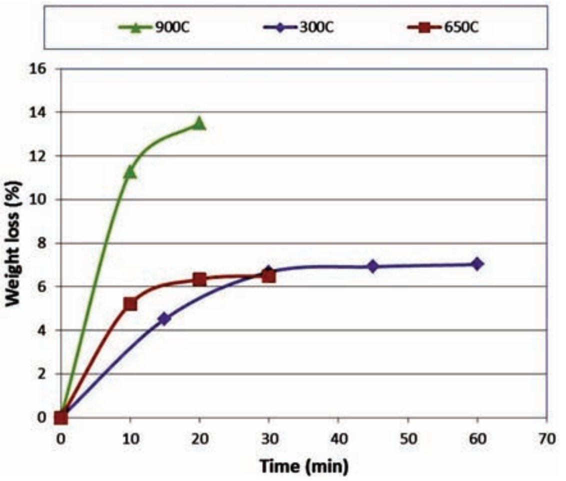


Figure 1. *Results from the heat treatment tests on plastic removal from battery material.*

It takes more than one hour to remove the plastics at 300ºC, whereas only 25 min is required at 650ºC and 900ºC. However, the higher the temperatures, the more the oxidation of the Ni-based alloy plates. Therefore, the midterm temperature 600°C for plastic and polymer removal was chosen.

After heat treatment, the materials were submitted to a sieving procedure in order to separate the black powder (which contains the REEs) from the rest of the material. XRF analysis of the black powder after the sieving procedure was carried out and is shown in Figure 2. It consists of about 22.1 wt% of REE oxides. Cerium, lanthanum, and neodymium oxides are the main part of the REEs. NiO and CoO content are 53.6% and 7.7% respectively.

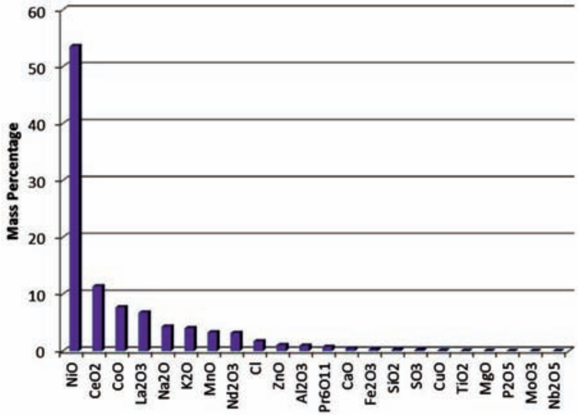


Figure 2. *XRF analysis of the black powder collected from sieving*

2.4 Slagging Tests

The heat treated materials were further separated by slagging process. A waste calcium silicate based slag was used in the present investigation. The smelting tests were conducted in a high temperature vacuum furnace. In all the tests, vacuum of 1×10^{-3} mbar was used. Temperature of sample can be measured by a W/W-Re thermocouple placed inside the crucible, while the heat generating current supplied in the furnace is adjusted manually at the power supply control. The water cooled heating coil was used to heat the graphite crucible.

The crucible was first filled with the heat treated materials. The slag powder was then placed on top of the battery material and mounted to the furnace. After a vacuum of 1×10-3 mbar was reached, the furnace chamber was filled with argon gas up to a pressure of about 700 mbar. The power was then supplied. The slagging process kept at 1700ºC for 60 minutes. After the furnace was totally cooled down, the crucible was taken out for sampling.

3. Results and discussions

A cross section of the sample after the slagging tests is shown in Figure 3. It shows clearly that the metal and slag phases

Since the graphite crucible was employed in the present tests, the reactions of NiO and CoO take place during the smelting process:

$$NiO + C = \underline{Ni} + CO$$

$$CoO + C = \underline{Co} + CO$$

Metal droplets were also found above the slag phase stuck to the graphite crucible or to the graphite shield of the thermocouple.

Figure 3. *Cross section of the crucible after the smelting test.*

Both metal and slag samples from the tests were analysed by EPMA and SEM. The results are shown in Figure 4 and Figure 5 as well as Table 1. The REE oxides are collected in the slag. In these SEM micrographs they appear as bright particles in a slag matrix. Looking at the EPMA data in Table III (see measurement No.1, 2 and 7) we can conclude that they are $REE_xSi_yO_z$ where REE oxides make ca. 70% and 50% of the composition in the first and second slag respectively. They are distributed throughout the slag sample. In Figure 4 they appear to have a needle-like shape, whereas in test No.2 they are more round and sometimes aligned in such a way that they seem to form triangles in the surface area. In both slags they cover a great part of the surface area which indicates that their concentration in the slag is high. In order to prove this XRF analysis of the slag from the first test was carried out. The results are given in Table 1.

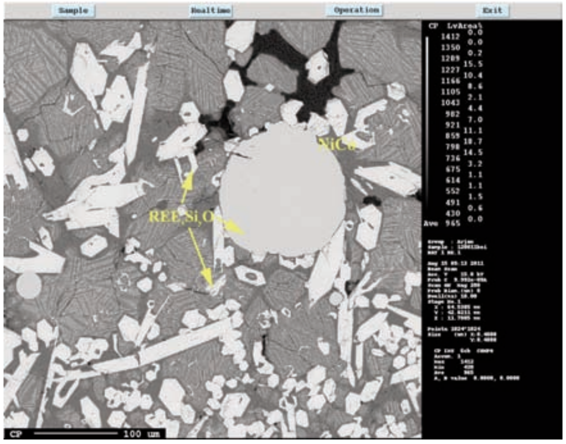


Figure 4. *SEM micrograph of the slag from the first test. The light phase is the REE oxides.*

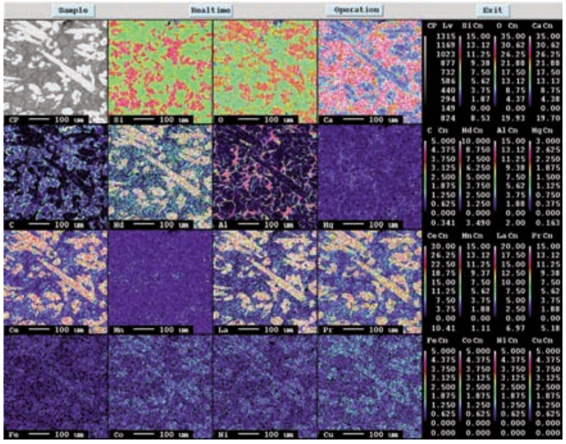


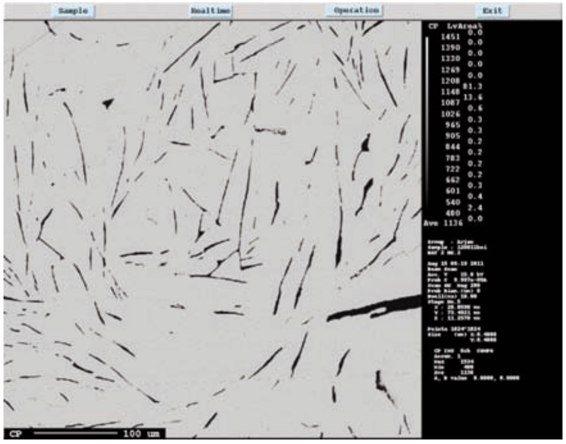
Figure 5. *EPMA mapping area of the slag from the first test.*

XRF analysis, data listed in Table 1, show that the 46wt% of the slag from the first test consists of REE oxides. The concentration of CeO_2 in the slag is 24wt% which makes it the second largest omponent after CaO. The total mass of the slag used in the first test was 64.6 g. Hence, the total mass of the REE oxides present in the slag is about 30g. The total battery material used here was 190.3 g with REE making ca. 22%, which gives about 42 g of REE oxides in the input material. Therefore, ca.71.4wt% of the total REE content of the input battery material is collected in the slag.

Table 1. *XRF analysis of the slag after the first test (normalized to 100%).*

No.	Compound	Concentration	No.	Compound	Concentration
1	CaO	27.81%	12	SO_3	0.12%
2	CeO_2	24.01%	13	K_2O	0.10%
3	SiO_2	19.63%	14	TiO_2	0.07%
4	La_2O_3	13.90%	15	BaO	0.05%
5	Nd_2O_3	6.49%	16	Fe_2O_3	0.02%
6	Al_2O_3	4.73%	17	ZnO	0.01%
7	Pr_6O_{11}	1.49%	18	CuO	0.01%
8	MnO	0.78%	19	Rh	0.01%
9	Na_2O	0.41%	20	Nb_2O_5	98 ppm
10	MgO	0.22%	21	SrO	92 ppm
11	NiO	0.13%			

The EMPA analyses for the NiCo alloy found in the bottom of the crucible were carried out. An SEM micrograph for the metal phase is shown in Figure 6. As the EPMA analysis confirms, the metal phases is mainly consisted of Ni and Co (80wt% Ni and 7-15% Co). However, carbides are also observed inside the metal matrix. The source of this carbon might come from the plastics which were burned in air during the previous step. Another smelting/refining step of the NiCo alloys should be enough to remove the carbon phase and hence, the NiCo alloy could be re-used in the NiMH battery production.



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CP  LvArea%
1451 0.0
1390 0.0
1330 0.0
1269 0.0
1208 0.0
1148 81.3
1087 13.6
1026 0.6
 965 0.3
 905 0.3
 844 0.2
 783 0.2
 722 0.2
 662 0.2
 601 0.3
 540 0.4
 480 2.4
Ave 1136 0.0
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Figure 6. *SEM micrograph of the metal phase from the second test. The dark stripes in the metal matrix consist of carbon.*

4. Conclusions

Recycling of the spend NiMH batteries was tempted here. The developed recycling process aims at recovery of the REE oxides and a NiCo alloy. The recycling process consists of several steps which include:

Mechanical breakage and magnetic separation; through this step the steel shells are separated from the inner part of the battery material.

Heat treatment of the battery material for plastic removal.

Separation of REE oxides from NiCo plates through sieving.

Smelting at 1700ºC under inert atmosphere with a silicate slag.

The resulting products from this procedure are a NiCo alloy which can be re-used as material for new NiMH batteries, and a REE oxide rich slag that can be further processed for extraction of the REEs. An alternative process for extraction of REE oxides from the slag is through filtration with foam or deep bed filters.

References

[1] N. Tzanetakis and K. Scott, J Chem. Tech. Biotech., 79(9) 2004 927-934.

[2] P.W. Zhang, T. Yokoyama, O. Itabashi, Y. Wakui, T.M. Suzuki, and K.Inoue, J. Power Sources, 77(2) 1999 116-122.

[3] J.M. Nan, D. M. Han, M. J. Yang, M. Cui, and X.L. Hou, Hydrometallurgy, 84(1-2) 2006 75-80.

[4] L. Li, S. Xu, Z. Ju, and F. Wu, Hydrometallurgy, 100(1-2) 2009 41-46.

[5] L. Rodrigues and M.B. Mansur, J. Power Sources, 195(11) 2010 3735-3741.

[6] K. Kikuta and M. Sakai, Proc. 8th Intern. Symp. East Asian Resou. Recyc. Tech., 2005, Beijing, China, pp. 378-381.

[7] J.A.S. Tenorio and D.C.R. Espinosa, J. Power Sources, 108(1-2) 2002 70-73.

[8] T. Muller and B. Friedrich, J. Power Sources, 158(2) 2006 1498-1509.

Websites

[1] http://ec.europa.eu/enterprise/policies/raw-materials/critical/index_en.htm

[2] http://www.batteryrecycling.umicore.com/