Recycling of the rare earth oxides from spent NiMH batteries using waste metallurgical slag

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Abstract: A high temperature process for recycling spent nickel-metal hydride batteries has been recently developed at SINTEF/NTNU. The spent battery modules were first frozen with liquid nitrogen for the deactivation and brittle fracture treatment. The broken steel scraps and plastics were then separated by 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 process. The waste calcium silicate slags 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 calcium cerite ($x\mathrm{SiO_2}\cdot y\mathrm{CaO}\cdot z\mathrm{RE_2O_3}$). The matrix of slag phases are therefore RE_2O_3 deficient, typically being less than 15wt%. This provides a sound basis to further develop the high temperature process of concentrating the RE_2O_3 oxides from the slag phase.

Keywords: Recycling, spent NiMH battery, rare earth oxide, nickel-based alloy, waste slag

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] in European Union. Because there exist only few exploitable natural resources of rare earths in Europe, the EU will mainly have to rely on recycling of rare earth elements (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, the sustainable industrial recycling processes for these new types of batteries are still under developing. For example, several hydrometallurgical recycling processes have been reported in the literature for the

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

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-CaF_2 slag was used to recover the REEs from the NiMH batteries. Similar high temperature process for recycling of Li-ion and NiMH batteries was also reported in 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 REEs 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.

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 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 of diameter 32 mm and height of 89 mm. Its weight is around 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 Mechanical Disassembly and Magnetic Separation

In order to separate the steel case from the battery, two types of freezing agents have been 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 the primary disassembly. The steel shell was cracked and the batteries were disassembled into small pieces.

The disassembled batteries were further classified by the magnetic separation. A magnetic separator with the max magnetic field of 8000 Gauss was used in the work. 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.

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

In the first one the applied magnetic field was 5000 Gauss. The first separated magnetic material was then fed to the magnetic machine again where a magnetic field of 3000 Gauss was applied. It has been estimated that the magnetic materials make approximately 27% of the total battery weight. The rest of "non-magnetic" materials will be further used in the high temperature treatments.

2.3 Heating Treatment

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

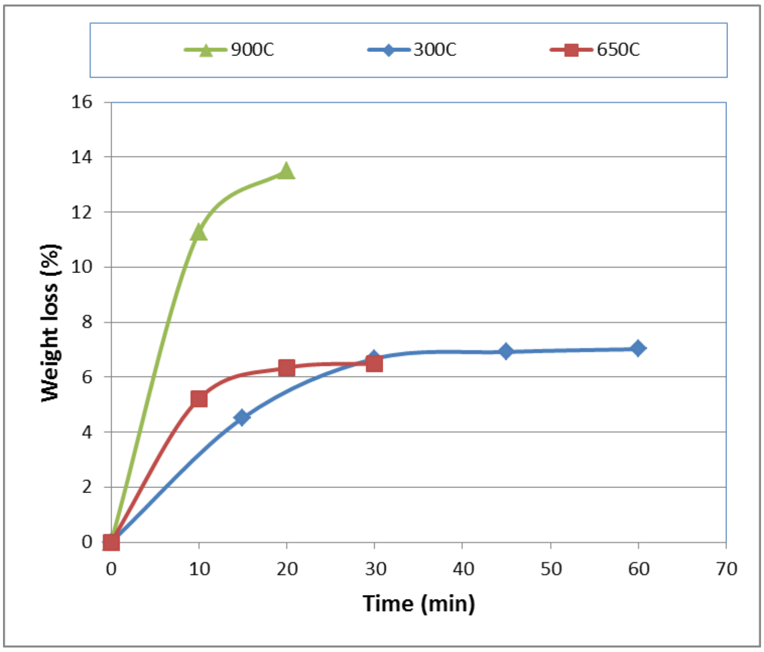


Figure 1 Results from the heat treatment tests on plastic removal from battery material.

It takes more than one hour to remove the plastics and polymers at 300ºC, whereas only 25 minute is required at 650ºC and 900ºC. However, the higher the temperatures, the more the oxidation of the Ni-based alloy plates. It is therefore to choose the middle temperature, 600ºC, for plastic and polymer removal in the present study.

The materials after heat treatment were further submitted to a sieving procedure in order to separate the black powder (which contains the RE oxides) 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 rare earth oxides. Cerium, lanthanum, and neodymium oxides are the main part of the RE oxides. The contents of nickel and cobalt oxides are, respectively, 53.6 wt.% and 7.7 wt.%.

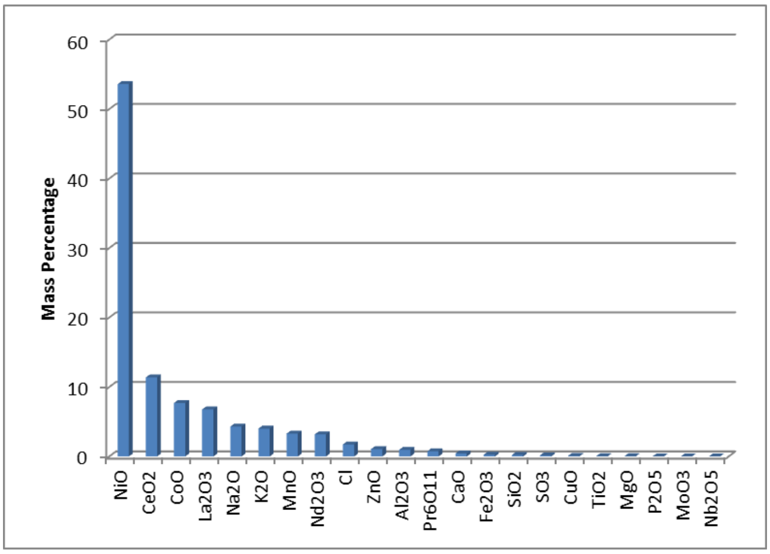


Figure 2 XRF analysis of the black powder collected from sieving

2.4 Slagging Tests

The heat treated materials were further separated by the high temperature slagging process. The waste calcium silicate slag was used in the present investigation. The smelting tests were conducted in an high temperature vacuum furnace. In all the tests, vacuum of 1×10^{-3} mbar was applied. 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 crucible was first filled with the heat treated battery materials. The slag powder was then placed on top of the battery materials. The crucible was then 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 began to supply. The slagging processes were run at 1700ºC for 60 minutes. After the furnace was 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 is obviously that a metal phase coexists with the slag at high temperature. From Figure 2 one may obtain that the pre-treated battery materials were mainly oxides and no metal remains in the heat treated materials. However, since the graphite crucible was employed in the present tests, the reactions between NiO, CoO and carbon take place in the smelting process:

$$(NiO) + C_{(gr)} = [Ni] + CO_{(g)} \qquad (1)$$

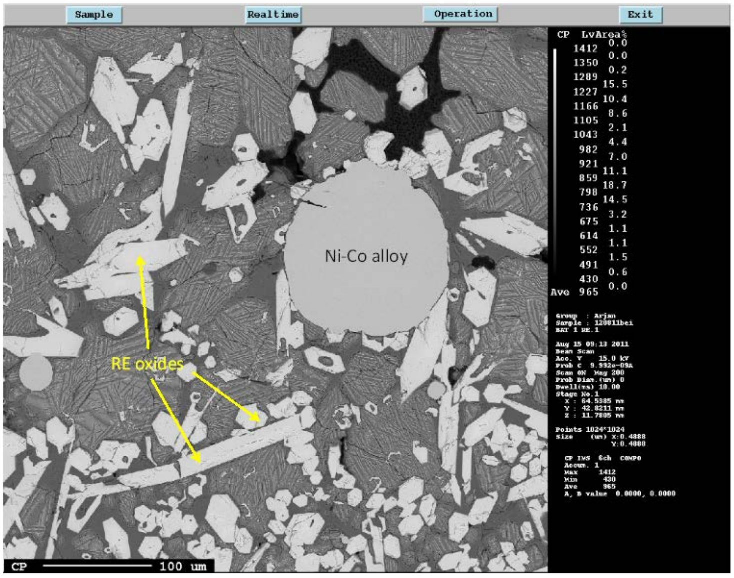
$$(CoO) + C_{(gr)} = [Co] + CO_{(g)} \qquad (2)$$

where parentheses denote slag phase, square brackets the liquid metal.

Both the metal and slag samples were examined by electron probe micro analysis (EPMA) and scanning electron microscopy (SEM) analyses. The concentrations of components in slag samples were also determined semi-quantitatively by the X-ray fluorescence (XRF) spectrometer. The results are shown in Figure 4, Figure 5, Table 1 and **Table 2**, respectively.

Figure 3 Cross section of the crucible after the smelting test

Metal droplets are found in the slag phase (Figure 4) and on the wall of graphite crucible. The EPMA analyses confirm that the metal phase is mainly consisted of Ni, Co and Mn (70-80 wt.% Ni, 7-15 wt.% Co and 5-7 wt.% Mn). The sums of REEs content in all 12 EPMA analyses for the metal phase are less than 0.2wt%, which indicates that almost all REE oxides stay in the slag phase.



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    982  7.0
    921 11.1
    859 18.7
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Ave 965

Group  : Arjan
Sample : 120811bei
BAT 1 RE.1

Aug 15 09:13 2011
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Figure 4 Typical SEM micrograph of the slag phase

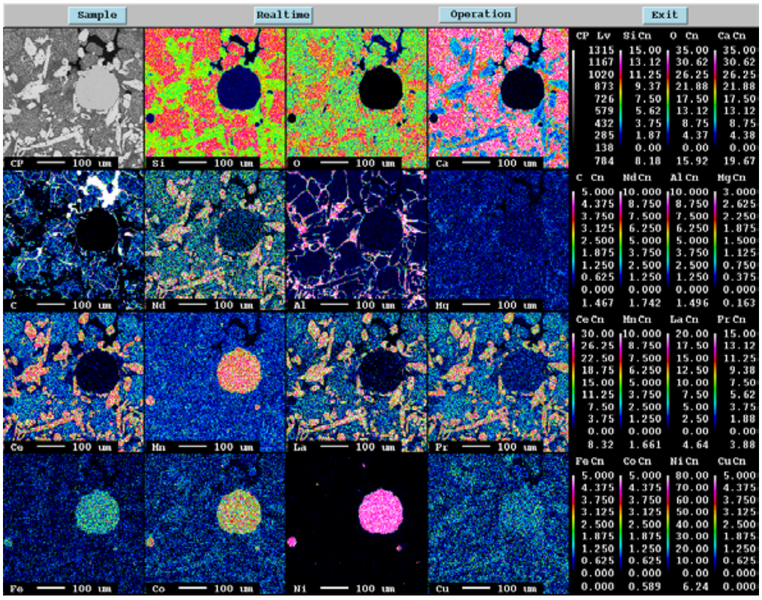


Figure 5 Typical EPMA mapping area of the slag in Figure 4

Figure 4 shows that the RE oxides precipitate as acicular and polygon crystals from the slag matrix (the light phases). According to the EPMA (Table 1) and XRF (Table 2) analyses, the light phases are stoichiometrically closed to the $RE_2O_3{\cdot}2SiO_2{\cdot}CaO$ and the $RE_2O_3{\cdot}2SiO_2{\cdot}2CaO$. The average rare earth oxide composition is in the range of 51-69 wt.%. The contents of RE_2O_3 in the gray phases are approximately 13-16 wt.%. The dark phase contains the lowest RE_2O_3 contents, being around 3-6 wt.%. The present observations are similar to those found in the PhD thesis of Li[9], who studied the precipitation behavior of rare earth oxides from the Bayan Obo blast furnace slags. It has been found by Li[9] that the most rare earth elements in the RE-bearing blast furnace slag are concentrated in to the calcium cerite during slow-cooling process. The nucleation and growth of calcium cerite is based primary on the cooling rate. In the present study, the samples were cooled rapidly from 1700°C to room temperature within about 60 minutes. The sizes of light phases are in the range of few μm to 100 μm. The average crystal size of calcium cerite was able to achieve in 150-180 μm when the cooling rate is controlled to be 0.5°C/min. This provides the sound basis to develop the high temperature filtration process for the production of the RE oxide concentrates.

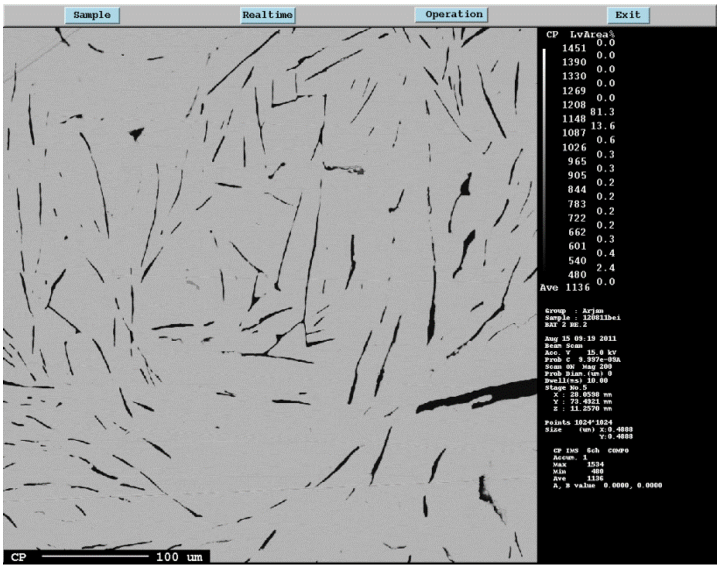
Table 1 EPMA analysis data of the slag phases from the first and second smelting tests (wt%)

No.	SiO_2	CaO	Ce_2O_3	Al_2O_3	La_2O_3	Pr_2O_3	Nd_2O_3	Nb_2O_5	MnO	CoO	NiO	Comments
1	21.8	9.7	33.5	0.3	23.8	3.3	8.7	0	0	0	0	Light phase
2	21.7	9.5	33.1	0.2	24.7	3.3	8.7	0	0	0	0	Light phase
3	30.5	45.9	7.7	0.4	4.7	0.7	2.5	0	1.4	0	0	Grey phase
4	29.7	47.7	7	0.4	4.2	0.6	2	0	1	0	0.1	Grey phase
5	23.7	36	3	26.5	2	0.3	0.7	0	1.6	0	0.2	Dark phase
6	43.5	43.3	1.8	5	1.3	0.2	0.4	0.1	1	0	0	Dark phase
7	28.2	20.8	24.8	0.6	17.2	2.4	6.6	0.1	0	0.2	0	Light phase

Figure 6 shows the SEM image for the metal phase. The black needle-like phase is the carbides which contains only small amount of Ni (1.5-2.5 wt.% Ni). Neither REEs nor Fe/Mn was found in this phase. The source of this carbon might come from the plastics/polymer separators, which were burned in the heat treatment. Although the EPMA analyses for this phase cover more than 18 common elements in the battery materials (Si, Mg, Ca, C, Ce, La, Pr, Nd, Nb, Al, Ti, Mo, Mn, Fe, Co, Ni, Cu, and Zn), the rest of element(s) in this phase still remain unknown. A detail examination on this phase may be necessary in the future.

Table 2 Typical XRF analysis results of the slag sample (normalized to 100%)

CaO	CeO_2	SiO_2	La_2O_3	Nd_2O_3	Al_2O_3	Pr_6O_{11}
27.81	24.01	19.63	13.9	6.49	4.73	1.49
SO_3	K_2O	TiO_2	BaO	Fe_2O_3	ZnO	CuO
0.12	0.1	0.07	0.05	0.02	0.01	0.01
MnO	Rh	Na_2O	MgO	NiO	Nb_2O_5	SrO
0.78	0.01	0.41	0.22	0.13	98 ppm	92 ppm



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          0.0
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          0.0
    1269
          0.0
    1208
         81.3
    1148
         13.6
    1087
          0.6
    1026
          0.3
     965
          0.3
     905
          0.2
     844
          0.2
     783
          0.2
     722
          0.2
     662
          0.3
     601
          0.4
     540
          2.4
     480
          0.0
Ave 1136

Group  : Arjan
Sample : 120811bei
BAT 2 BE.2

Aug 15 09:19 2011
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Prob C  9.997e-09A
Scan ON  Mag 200
Prob Diam.(um) 0
Dwell(ms) 10.00
Stage No.5
  X : 28.0598 mm
  Y : 73.4921 mm
  Z : 11.2570 mm

Points 1024*1024
Size     (um) X:0.4888
              Y:0.4888

  CP IMS  6ch  COMPO
  Accum. 1
  Max     1534
  Min      480
  Ave     1136
  A, B value  0.0000, 0.0000
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Figure 6 SEM image of the metal phase

4. Conclusion

A high temperature process for recycling spent nickel-metal hydride batteries has been developed in the laboratory at SINTEF/NTNU. After mechanical dissembling, magnetic separating and heating treatments, a pre-treated battery materials consists mainly of nickel, rare earth, cobalt, alkaline and manganese oxides, has been obtained. The waste calcium silicate slag was then used to further separate the rare earth elements from the battery materials. Most of nickel and cobalt oxides were reduced to the metal phase. Almost all rare earth oxides remain in the molten slags. EPMA and XRF analyses of the slag samples indicate that the rare earth oxides selectively precipitate in the forms of solid rare earth silicates, stoichiometrically closed to the $RE_2O_3{\cdot}2SiO_2{\cdot}CaO$ and the $RE_2O_3{\cdot}2SiO_2{\cdot}2CaO$. This provides a sound basis to further develop the high temperature process of concentrating the REEs from slag phase.

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