Development of a Metal Hydride Electrode Waste Treatment Process

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Manufacturing residues of metal hydride electrodes for nickel− metal hydride batteries were chemically processed to recover the metal part and heat treated for the organic part. Chemical recovery yielded Ni-Co alloy after electrolysis of the solution and hydroxides of other metals, mainly rare earths. The organic part, pyrolyzed at 700°C, led to separation between carbon and fluorinated matter. Infrared coupling at the output of the pyrolysis furnace was used to identify the pyrolysis gases.

Introduction

The manufacturing processes of nickel−metal hydride (Ni−MH) batteries, which are mostly used in microelectronics applications, portable telephony, and video, generate uncycled material waste (England, 1997). The Ni−MH battery is one of the advanced technologies that is likely to see near-term use in electric vehicles (Sabatini et al., 1994; Leonardi and Bouet, 1996). A study of the recovery economics of the materials in this battery has been done and shows that the ratio of reclamation to recycle can be quite profitable (Ruthven, 1997). The development of this waste is significant for mainly two reasons: the reduction of the manufacturing costs, and the protection of the environment (Mortgat, 1998).

The starting material is an alloy of the $LaNi_5$ type, where lanthanum is partially substituted by cerium, neodymium, and praseodymium, and nickel by cobalt, manganese and aluminium (Fetcenko et al., 1988; Yazami et al., 1991). During its manufacture, this metallic alloy is mixed with an organic binder, mainly carbon and polytetrafluoroethylene (PTFE). Development of the metal part has been carried out (Lyman and Palmer, 1994), but does not take into account the organic part. Our development work consisted of separating the organic part from the metal part, extracting the metals for direct development in metallurgy (Kisi et al., 1992). Heat treatment of the organic part by pyrolysis gives a carbonaceous residue that can also undergo beneficial change (Antonini and Gislais, 1995).

Experimental Section

Material

The starting material provided by the SNAM company is a black paste deposited on a nickel grid. It contains an alloy composed of eight metals, but mainly nickel and lanthanum (usual designation, $LaNi_5$). Nickel is partially substituted by two transition metals—cobalt and manganese—and by aluminium. Lanthanum is partially substituted by three other rare earths: cerium, neodymium, and praseodymium. The mass compositions are given in Table 1. The alloy is mixed with an organic binder composed of fine particles of carbon and PTFE filaments. The material is moisture sensitive.

Separation and chemical processing of the metal part

The reaction of 3 M HCl on the alloy dissolves all the metals, while the organic matter is maintained in suspension and then separated by filtration. From 100 g of the initial material and 1 L of HCl, we obtained 80 g of the metal part and 20 g of the organic part. The average mass composition of the metal part, obtained by inductively coupled plasma analysis (ICP, Jobin-Yvon JY24), is reported in Table 2. The extraction of metals was based on precipitation of the rare-earth hydroxides and on the simultaneous complexation of the transition metals Ni and Co in the presence of excess ammonia. We obtained a filtrate containing nickel and cobalt ammonium complexes, and hydroxides of manganese, aluminium, and rare earths. The hydroxides were then purified

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Table 1. Mass Composition of the Alloy Dissolved in HCl

Dissolved metals	Ni	Co	Mn	Al	La	Ce	Nd	Pr
Mass %	54.2	8.1	3.1	2.3	16.6	10	2.1	3.3

Table 2. Metals Repartition after the A Step of the Process

Metals	Ni	Co	Mn, Al, La, Ce, Pr
Filtrate F1	54	63	0
Washing solution	35	6	0

Table 3. Mass % of Metals Recovered at the Different Steps

Metals	Precipitate A	Precipitate B	Filtrate F2	Washing Solution EL2	Precipitate C	Filtrate F3
Ni	10	0.02	8.1	1.9	0.02	0
Co	30	6	17	3	6	0
Mn	3	0.4	2	0	0.4	0
Al	2.3	2.3	0	0	1.3	0.83
La	17	16	0	0.1	14	0
Ce	10	10	0	0	8.5	0
Pr	3.2	3.2	0	0	2.8	0

according to the procedure indicated on the flow chart presented in Figure 1. The evaporation and recondensation of half the ammonia contained in the filtrate lowers the solution pH to 6. Simultaneously, nickel and cobalt were decomplexed. Electrolysis of the remaining solution led to nickel and cobalt being recovered as a metallic alloy deposit.

Processing the organic part

The organic residue from the hydrochloric acid extraction was washed and dried before pyrolysis. A first approach of the composition by EDAX analysis with the MEB shows the presence of the following elements: carbon, fluorine, oxygen, and traces of sulfur, nitrogen, hydrogen and chlorine. To define the pyrolysis conditions (temperature, duration), we used thermogravimetric analysis (SETARAM ATG-ATD 92 equipment) with samples of approximately 10 mg. The vector gas was nitrogen and the temperature rise 7°C per min. The optimal conditions were reached at T = 700°C, this temperature being maintained for 1 h. To identify the gas effluent during pyrolysis, we connected the output of the furnace to the input of an infrared cell with KBr faces placed in a Perkin-Elmer 1760X IR spectrometer. This enabled us to follow the evolution of the gas mixture composition vs. time during pyrolysis. To study the transposition of the process to a higher scale, we carried out pyrolysis in a tubular stainless steel furnace under a flow of nitrogen. The material (approximately 3 g) was placed on a nickel support in the hot part of the furnace, the experimental conditions being identical to those defined by TGA.

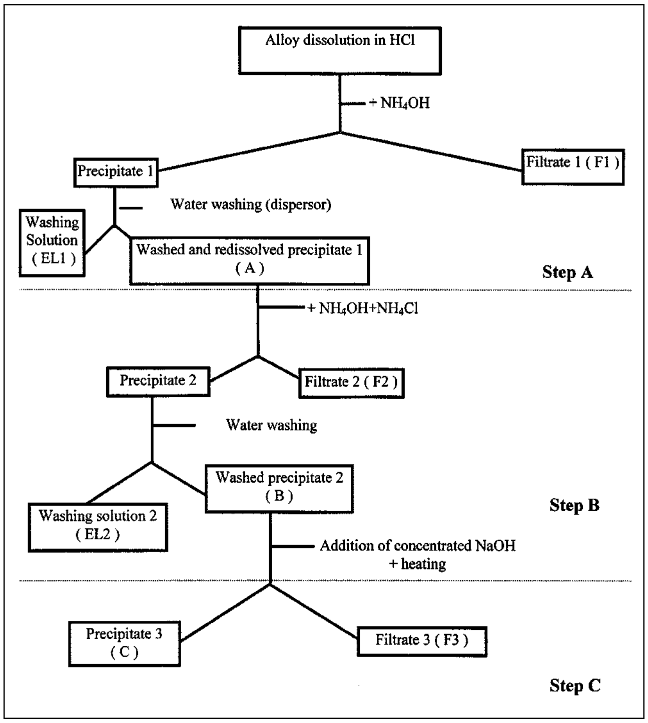


Figure 1. Process flow chart of separation with ammoniac reaction.

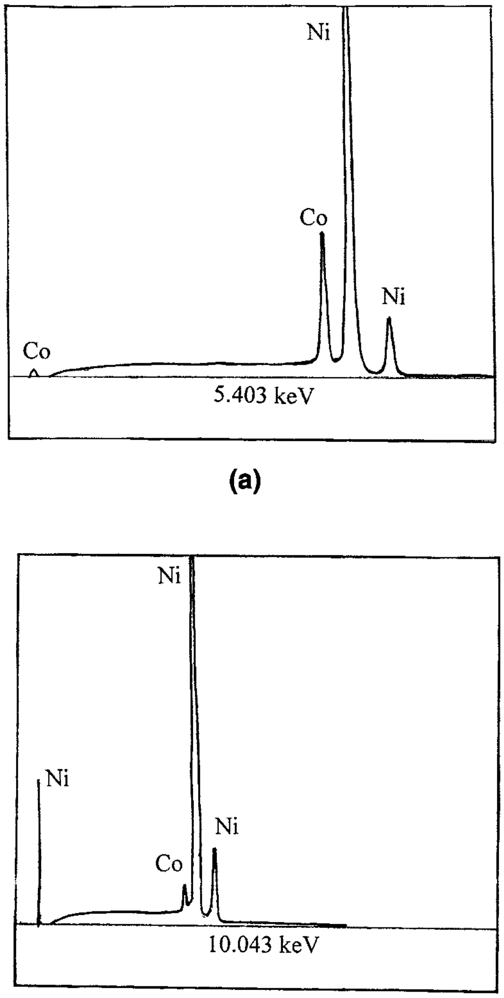
Results

Metal part

The filtrate resulting from the extraction of the hydrochloric acid was treated with approximately 14 M ammonia solution, which has a dual role: the complexation of nickel and cobalt, and the precipitation of other metals as hydroxides. The ICP analyses of the quantitative composition of filtrate F1 and of washing solution EL1 show that the reaction with the ammonia solution is very selective (Table 3). The rare earths are recovered at the end of stage C of the procedure; the mass compositions of the various elements in the precipitate are given in Table 4.

Table 4. ICP Analysis of Cathodes and Solutions after Electrolysis

Metals	Electrode Composition (mg) $P = 16$ W	Solution Concentration after Electrolysis (mg/L)	Electrode Composition (mg) $P = 8$ W	Solution Concentration after Electrolysis (mg/L)
Ni	10,100	56.60	9,270	12.30
Co	947	1.51	970	0.23
Mn	15.60	13.70	20	1.91
Al	0	0.83	0	0.25
La	0.27	4.98	0.12	1.20
Ce	0.63	5.80	0.26	0.84
Nd		1.11	0	0.38
Pr		0.58	1.03	0.26
Grid mass	11.18 g		10.67 g	
Total	11.06 g	85.11 mg/L	10.26 g	17.37 mg/L



(a)

(b)

Figure 2. MEB-EDAX analysis, Ni-Co electrolytic deposit from F1 (a) and EL1 (b).

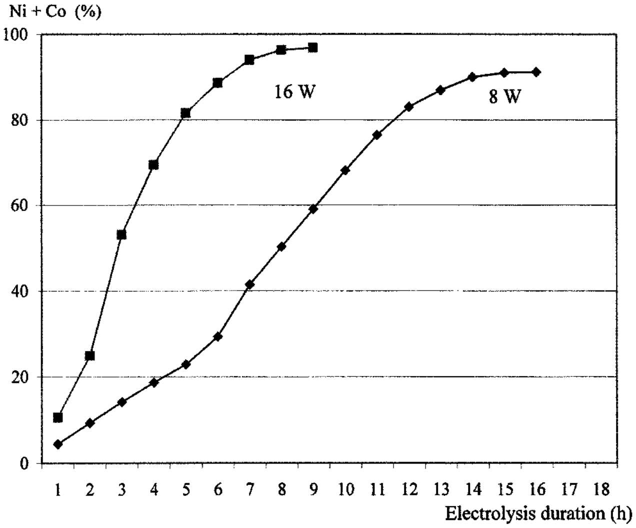


Figure 3. Ni + Co recovering vs. electrolysis duration (pH = 6).

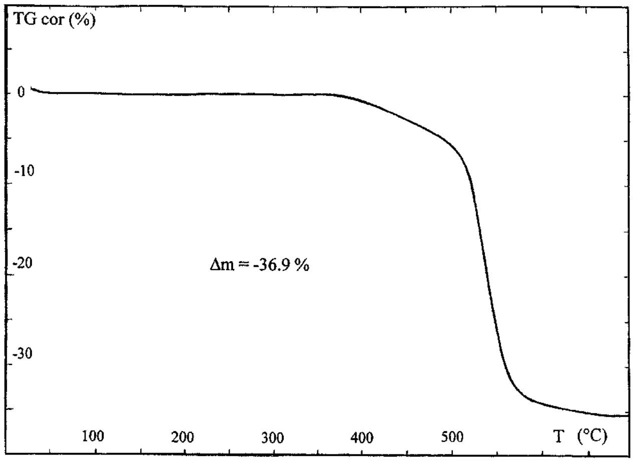


Figure 4. ATG-ATD of organic part.

The analyses having shown that the filtrate and the washing solution of precipitate A only contained nickel and cobalt, we carried out electrolysis at a constant current to recover, on a nickel grid, a mixture of Ni + Co, as shown by MEB-EDAX analyses (Figures 2 and 3). Electrolysis was carried out at 8 and 16 W to optimize the Ni + Co recovery ratio. The curves representing the mass deposited vs. time are reported in Figure 4. The ICP analyses (Table 5) show that no nickel or cobalt ions remained in the solution.

The pH of the solution tends to decrease during electrolysis, so it must be regularly corrected by addition of a base (NH_4OH). Taking into account the selectivity of electrolysis, and in order to decrease the number of processing stages, we tested the electrolysis procedure directly on the solution, before adding the ammonia. The results showed that Ni and Co were not completely extracted from the solution. Moreover, the duration of electrolysis was significantly increased: 25 h to recover 70% of the Ni-Co alloy instead of 9 h to recover 100% in the former procedure, at 16 W. At the end of processing, a mixture of rare-earth hydroxides was also recovered.

Organic part

After extraction of the metals, the resulting residue was analyzed. The results are given in Table 5. A representative example of the thermogravimetric analysis of this organic material is given in Figure 4. It shows that the reaction is en-

Table 5. Analysis of the Organic Part

Elements	C	F	O	H	N	S	Cl
Mass %	65.41	27.01	5.93	0.66	0.49	0.40	0.10
Atom %	68.53	17.88	4.66	8.30	0.44	0.15	0.04

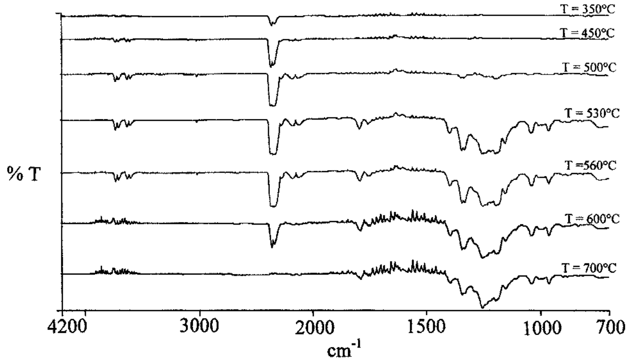


Figure 5. Infrared spectra vs. temperature.

dothermic. The mass loss was 36%, and it mainly occurred in the temperature range 350–700°C. In the tubular furnace, when a 3 g sample was pyrolyzed, the loss of mass was practically identical to that observed with TGA. Transposition to a higher scale is thus possible. The analysis of the solid residue obtained after pyrolysis showed that it was composed of 96% carbon, partially in the form of graphite, as demonstrated by X-ray observation. Coupling the output of the furnace to the IR spectrometer allowed the IR spectra of the gas mixture evolved to be observed at the furnace temperature. The infrared spectra, successively recorded between 450 and 700°C are presented in Figure 5.

For pyrolysis temperatures lower than 500°C, the only gases released were CO and CO_2. When the temperature rose from 500°C to 700°C, characteristic CF_4, C_2F_4, and C_2F_6 bands appeared, while the CO_2 band intensity decreased. At approximately 700°C, the gaseous emission stopped, which is in agreement with the TGA curve, showing that the mass of the sample no longer varies above 700°C. At the end of the pyrolysis process, the organic part was thus partially transformed into graphite carbon and a gas mixture containing fluorocarbons. Rapid cooling of the gas mixture allowed part of the fluorinated gases to be recondensed.

Conclusion

Numerous preliminary tests were carried out in order to recover metals on one side and organic compounds on the other. Regarding the metals, optimization of the different processes has shown that the best selectivity was obtained by electrolysis of the nickel–cobalt-rich leach solutions after precipitation of the rare earth hydroxides.

The recovery ratio of the transition metals reached 95% at 16 W. Therefore, rare-earth hydroxides can be directly developed. Concerning the recovery of the organic part, the study of the pyrolysis conditions shows that 96% of the pure carbon, partially in graphite form, can be separated from the fluorinated compounds.

As a result of our study, we can propose a clean separation process for scrap Ni–MH battery material. For electric vehicle applications, where nickel hydride electrodes are strong candidates, the development of a complete recycling process, including treatment of all residues, is necessary. The present study makes a step in this direction.

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