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Recovery of cadmium by high-temperature vaccum evaporation from Ni-Cd batteries ①

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Abstract: High-temperature vaccum evaporation is a recycling technology that includes a selective material recovering process. The fundamental research on a process of disassembling and recovering selected materials from Ni-Cd batteries was conducted using self-designed experimental apparatus. An effective recycling technology based on the evaporation phenomenon of batteries and the elements of cadmium under the laboratory condition was studied. The results show that: (1) Ni/Cd can be effectively recovered by vacuum distillation at appropriate temperature, pressure and time, and high purity cadmium (> 99%) can be obtained through the process; (2) the effective distillatory temperature should be at the range of 573 - 1 173 K; (3) the higher the evaporation temperature, the lower the purity of cadmium in condensate metal

Key words: vacuum evaporation; recycling; waste battery; Ni-Cd batteries
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1 INTRODUCTION

Portable electricity has become a part of daily living. Batteries empower many kinds of portable electric and electronic devices to be used, but on the contrary at their end-of-life they can harm to us. Every year 400 million pieces of spent Ni-Cd batteries produced in China[1, 2]. If the spent batteries are discarded directly into the environment, soil and water are potentially polluted. At the same time, large quantities of useful substances are disposed without recycling. Therefore, the recovery and treatment technologies of Ni-Cd batteries are very important, especially in China, which is a cadmium-poor country.

The technologies of recycling Ni-Cd batteries can be classified into two categories: hydrometallurgical and pyrometallurgical processes. Hydrometallurgical process has the advantages of low device-cost, many kinds of technologies can be selected and high flexibility, but this kind of process has the disadvantages of complex pre-treatment, long technological process and the cadmium contaminate can't be controlled effectively. As to the pyrometallurgical process, owing to the using of vacuum evaporation technologies, it has the advantages of simple operation, high recovery ratio, low operating-cost and friendly to environment. Obviously the later has a better future[3-7], yet there are no reports of pyrometallurgical processes for Ni-Cd recycling of batteries in China.

In this work the disassembling and materials recovering process of Ni-Cd batteries are studied in laboratory by self-designed vacuum evaporation recycling systems.

2 EXPERIMENTAL

2.1 Ni-Cd batteries

The Ni-Cd batteries used in experiments are AA-NiCd batteries supplied by Motorola, which come from Ni-Cd battery pack of Motorola TalkAbout Distance. The contents of the Ni-Cd batteries are listed in Table 1.

Table 1 Contents of Ni-Cd batteries (mass fraction, %)

Active mixture*	Metallic shell	Anode	Insulating plate	Total
24.33	4.80	1.40	0.35	30.97

* Including negative plate, positive plate, diaphragm paper and nickel net.

The positive electrode substances in a Ni-Cd battery are $Ni(OH)_2$, NiOOH powdered graphite, while the negative electrode substances are Cd, $Cd(OH)_2$, Fe_3O_4, $NiSO_4$ and powdered graphite. The depleted electrolyte consists of potassium hydroxide and distilled water. So a key technology for the recovery and treatment of spent Ni-Cd batteries is to separate cadmium or nickel from the active mixture.

2.2 Vacuum-evaporation recycling system

A number of zone melting and distillation appa-

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ratus for cadmium purification are studied carefully[8]. An apparatus for distillation and condensation of Ni-Cd batteies is designed as Fig. 1[9].

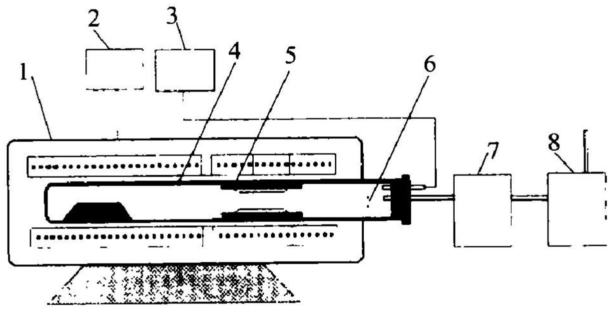

Fig. 1 Experimental apparatus for vacuum-aided recycling of batteries
1 —Furnace; 2 —Temperature controlling unit;
3 —Pressure controlling unit; 4 —Quartz tube;
5 —Slip condensator; 6 —Screen; 7 —Vacuum pump;
8 —Exhaust gas handling unit

3 RESULTS AND DISCUSSION

3.1 Vacuum evaporation behavior of Ni-Cd battery

The relationship between the pressure and temperature with the heating speed of 2.5 K/min is shown in Fig. 2. With increasing temperature, the pressure changes sharply. There are three peaks at 380, 460 and 750 K during the process.

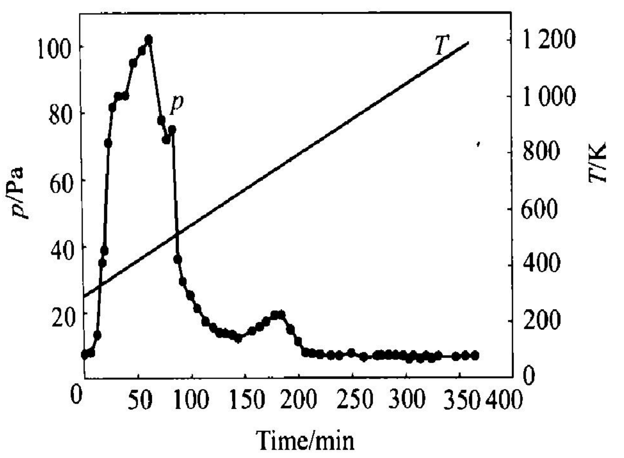

Fig. 2 Vacuum evaporation phenomenon of Ni-Cd battery during heating

The pressure peaks indicates there is a great deal of gas produced at that time. In Fig. 2, the three pressure peaks are the corresponding points of evaporation of water, organic substances (diaphragm paper and other addition agents) and cadmium.

During the early heating-up, the evaporation of water lifts the pressure rapidly. At about 390 K, the organic substances in the battery evaporate too. Both of the evaporation of water and organic substances produce much gas, so the maximum pressure appears at that time. With increasing heat, the depreciation of water and organic substances in the battery decreases the pressure sharply. The evaporation of cadmium at about 660 K brings another pressure peak. Above 900 K, the pressure is constant when the vaporizing speed of cadmium is invariable.

3.2 Evaporation of cadmium during vacuum evaporation

The operating temperature was respectively set at 373, 473, 573, 673, 773, 873, 973, 1 073 and 1 173 K. And each of them be held for 10 h. After the vacuum evaporation of Ni-Cd batteries, the mass values of residue and cadmium condensate were recorded as shown in Fig. 3.

Put AA-NiCd batteries weighed into the furnace, set the pressure at 3 Pa, temperature at 373 K for 12 h; cool down the furnace to room temperature, and take out the residue and metal condensates, weigh them. Then repeat the process, set the temperature at 473, 573, 673, 773, 873, 973 and 1 173 K, respectively. The results were shown in Fig. 3.

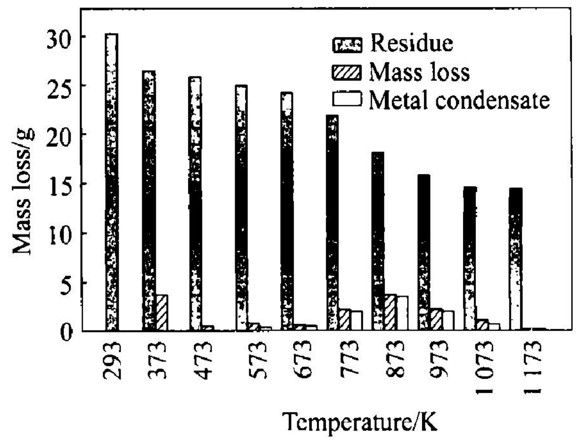

Fig. 3 Masses of residue and metal condensates at different temperatures

Fig. 3 shows that with the increase of temperature, the residue mass decreases all along. But during each of the temperature intervals, the value of mass loss and metal condensates show fluctuations. From 293 K to 373 K, the mass loss is big. But during 373 and 473 K the loss value decreases. Then it increases again from 573 K, and reaches a peak of 873 K. From 873 K it begins to decrease continuously and is about zero at 1 173 K.

From 293 K to 373 K, most of the water in the battery becomes vapor, so the pressure is high. Then there is few water in the battery so the pressure decreases. During 373 – 473 K, there may be some organic material becomes gases. When the temperature reaches 573 K, the evaporation of cadmium begins. And the pressure increases quickly with the increment of the temperature. With the continuous evaporation of cadmium, the mass of the volatile content in the battery decreases largely. So the mass loss also decreases.

From the results it can be inferred that the effective distillatory temperature should be at the interval from 573 K to 1 173 K. The condensed materials at the temperature intervals were analyzed by ICP-AES. The cadmium contents are listed in Table 2.

Table 2 shows that with the increase of the temperature the purity of the cadmium contents in the condensed materials decrease. And in order to distill the cadmium completely, the temperature must be higher than 1 173 K. It is a contradiction between the surplus cadmium and the distillation efficiency. If we want a very low surplus cadmium contents the distillation will be very low because of the decrease of the distillate.

Table 2 Cadmium contents in condensed materials at temperature intervals

Temperature/K	Cadmium contents in condensate/%
673	99.601
773	99.538
873	99.393
973	97.279
1 073	96.926
1 173	90.725

For a relatively higher efficiency, the following experiment was done at 1 173 K and 10 Pa for 10 h. Fig. 4 shows the XRD pattern of the condensates metals, which shows there is no nickel or iron in the condensate cadmium.

The elements contents of condensates metals and residue were analyzed by ICP-AES. Table 3 shows the results.

3.3 Mechanism

Fig. 5 shows the XRD pattern of active mixture of AA-NiCd batteries.

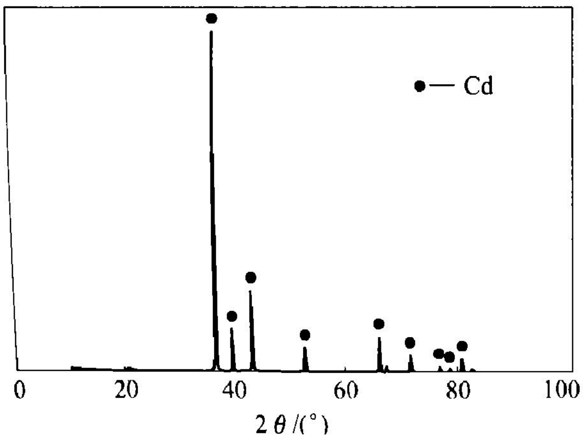

Fig. 4 XRD pattern of distillate at 1 173 K

From Fig. 5, it can be seen that the active mixture of AA-NiCd batteries mainly contain CdO, NiO, $Cd(OH)_2$, $Ni(OH)_2$ and H_2O. Carbon element is also existing in the system, which comes from the current-conducting carbon powders and distillation residue of diaphragm paper. The possible reactions in the system are shown as following:

Table 3 Elements contents of condensate metals and residue (%)

Condensate metals		Residua			
Cd	Others	Cd	Ni	Fe	Others
99.45	0.55	0.22	63.12	27.51	9.15

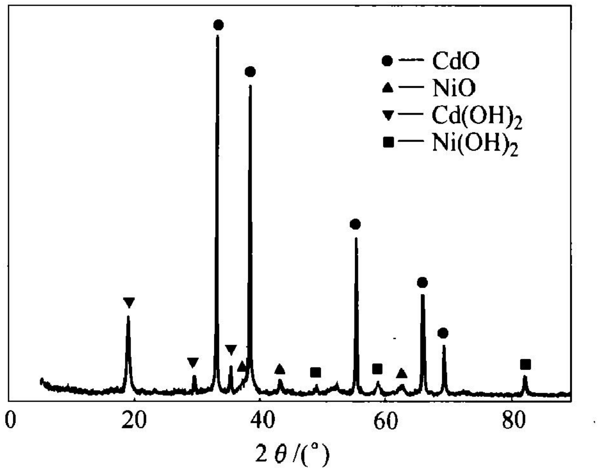

Fig. 5 Typical XRD analyses of active mixture of AA-NiCd batteries

$$Cd(OH)_2 = CdO + H_2O \quad (1)$$

$$Ni(OH)_2 = NiO + H_2O \quad (2)$$

$$H_2O\,(l) = H_2O\,(g) \quad (3)$$

$$CdO + C = Cd\,(g) + CO \quad (4)$$

$$NiO + C = Ni\,(s) + CO \quad (5)$$

$$Cd\,(s) = Cd\,(g) \quad (6)$$

$$Ni\,(s) = Ni\,(g) \quad (7)$$

$$Fe\,(s) = Fe\,(g) \quad (8)$$

In order to simplify the calculation, the potassium element was excluded. At high temperature and low pressure reactions (1), (2) and (3) will proceed completely. For reactions (4) and (5), the pressure is a very important factor. Table 4 shows the reduction temperatures of CdO and NiO under different pressures[10].

Results in Table 4 show that the reduction temperature is between 600 − 700 K under about 80 Pa. The nickel and cadmium are metallic in the system when the pressure is lower than 80 Pa. Whether the separation of cadmium and nickel can achieve or not depend on their volatility.

Table 4 Reduction temperatures of CdO and NiO at different pressures

p / Pa	T_{CdO} / K	T_{NiO} / K
6.70×10^{-2}	604.96	421.16
10.00	673.08	491.39
20.00	683.74	503.00
40.00	694.75	515.18
80.00	706.11	527.96
100.00	709.85	532.21
1.00×10^{5}	849.31	709.35

Table 5 shows the vapor pressures of metallic cadmium, nickel and iron at different temperatures[11, 12]. It can be seen that the vapor pressures of metallic cadmium are high at relatively low temperature, but of the metallic nickel and iron are so low that it can be ignored at 1 273 K. The obvious difference of cadmium, nickel and iron makes it possible to separate metallic cadmium by vacuum distillation.

Table 5 Vapor pressures of Cd, Ni and Fe at different temperatures

T / K	p_{Cd} / Pa	p_{Ni} / Pa	p_{Fe} / Pa
773.15	1.799×10^{3}	1.982×10^{-16}	1.713×10^{-14}
873.15	1.124×10^{4}	3.230×10^{-13}	1.220×10^{-11}
973.15	4.746×10^{4}	1.124×10^{-10}	2.219×10^{-9}
1 073.15	1.514×10^{5}	1.289×10^{-8}	1.512×10^{-7}
1 173.15	3.923×10^{5}	6.482×10^{-7}	4.966×10^{-6}
1 273.15	8.682×10^{5}	1.738×10^{-5}	9.344×10^{-5}

4 CONCLUSIONS

1) Ni-Cd batteries can be effectively recovered by vacuum distillation at appropriate temperature, pressure and time. The high purity cadmium (> 99%) can be obtained through the process.

2) The effective distillatory temperature should be within the range from 573 K to 1 173 K.

3) When temperature is higher than 1 073 K, with the increase of temperature the purity of the cadmium in condensate materials decreases distinctly.

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