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A Novel Technology for Recycling Waste Dry-battery

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Abstract: A novel technology for recycling valuable metals contained in waste dry-battery by vacuum metallurgy was devised by theoretical analysis. On the condition of the total chamber pressure of 1.013×10^1Pa, Hg, Cd and Zn are distilled in the temperature range of 773~973K, Pb is volatilized in the range of 1173~1273K while Mn, Cu, Fe and C are remained in residual. MnO_2 and ZnO are reduced by carbon in waste dry-battery in 773~1273K. Pure metals including Zn, Cd, Hg and Pb can be recovered respectively from their mixed vapor by fractional condensation. Metal Cu and MnO_2 can be obtained from the residual by hydrometallguical method. The technology can eliminate the pollution of Cd, Hg and Pb to environment.
Key Words: waste dry-battery, recycling, vacuum metallurgy

1. Introduction

The Zinc-Manganese dry-battery is widely used and its yield is the most in the world because of its low cost. However, dry-battery is usually discarded as waste after being used in which contained metals, such as Zn, Mn, Cu, Pb, Cd, Hg, Fe etc, and their compounds. The valuable metal resource is wasted and Pb, Cd and Hg also cause serious environment pollution. Therefore, recycling of waste batteries has paid attention widely in the world.

The main methods for recyling waste batteries include roasting-leaching method, hydro-based leaching method and reducing-smelting method. These methods, however exist some disadvantages, such as long technological process, more pollution sources, high invest cost, high consumption of energy and raw material, which result in lower benefit in the process of recycling waste dry-batteries. Because the differences in saturation vapor pressure of Zn, Mn, Cu, Pb, Cd, Hg and Fe contained in waste dry-batteries at specific temperature are rather great, it is feasible to recycle these metals respectively by vacuum metallurgical method[1]. The disintegrated waste dry-batteries are heated to certain temperature in vacuum, the metal with high vapor pressure is evaporated into gas phase while that with low vapor pressure is remained in residual liquid or residue. The metals in the mixed vapor can be separated from each other by condensing at different temperature, which can recycle various valuable metals. This paper is aimed at investigating the technological conditions in theoretics for recycling waste dry-battery by vacuum metallurgical method.

2. Behaviors of Components in Waste Dry-battery in Vacuum

2.1 Relationships between vapor pressure of *components in waste dry-battery and temperature*

The components in waste Zinc-Manganese dry-battery include Zn, $ZnCl_2$, MnO_2, Cu, Pb, Cd, Hg, Fe, C and so on, in which Zn and MnO_2 are the main components. Relation-ships between saturation vapor pressure of these substances (p*/Pa) and temperature (T/K) are listed as following Equations[2]:

$$lgp^*_{Zn} = -6850T^{-1} - 0.755lgT + 10.365 \quad (298\sim699K) \qquad (1)$$

$$lgp^*_{Zn} = -6620T^{-1} - 1.255lgT + 14.465 \quad (699\sim1180K) \qquad (2)$$

$$lgp^*_{ZnCl_2} = -8500T^{-1} - 1.50lgT + 18.735 \quad (298\sim599K) \qquad (3)$$

$$lgp^*_{ZnCl_2} = -8415T^{-1} - 5.035lgT + 28.545 \quad (599\sim1005K) \qquad (4)$$

$$lgp^*_{Mn} = -14920T^{-1} - 1.96lgT + 18.315 \quad (298\sim1519K) \qquad (5)$$

$$lgp^*_{Pb} = -10130T^{-1} - 0.985lgT + 13.285 \quad (600\sim2013K) \qquad (6)$$

$$lgp^*_{Cd} = -5908T^{-1} - 0.232lgT - 2.84\times10^{-4}T + 11.842 \quad (298\sim594K) \qquad (7)$$

$$lgp^*_{Cd} = -5819T^{-1} - 1.257lgT + 14.407 \quad (594\sim1050K) \qquad (8)$$

$$lgp^*_{Hg} = -3305T^{-1} - 0.795lgT + 12.475 \quad (298\sim630K) \qquad (9)$$

$$lgp^*_{Cu} = -17770T^{-1} - 0.86lgT + 14.415 \quad (873\sim1356K) \qquad (10)$$

$$lgp^*_{Cu} = -17520T^{-1} - 1.21lgT + 15.335 \quad (1356\sim2843K) \qquad (11)$$

$$lgp^*_{Fe} = -21080T^{-1} - 2.14lgT + 19.015 \quad (298\sim1808K) \qquad (12)$$

The saturation vapor pressure values of substances were calculated in the temperature range of 573~1473K according to Eqs. 1~12, as listed in Table1.

It can be seen from Table 1 that the differences of the saturation vapor pressure values of the components contained in waste dry-battery are obvious. Because the values of p^*_{Hg} are in the range of 3.27×10^4~8.88×10^4Pa in 573~623K and the values of p^* of Cd, Zn and $ZnCl_2$ are 1.89×10^2~7.10×10^4Pa in 773~973K, these four components would volatilize easily in vacuum at lower temperature (≤973K). Metal Mn, Cu and Fe volatilize little when the temperature is less than 1273K because their saturation vapor pressure values are less than 3.20Pa at 1273K. The values of p^*_{Pb} are $4.22υ10^1$~$1.86υ10^2$Pa in 1173~1273K, so it would evaporate remarkably in that temperature range. Therefore, a fractional vacuum evaporation should be taken. Metal Hg, Cd, Zn and $ZnCl_2$ can be volatilized in the range of 773~973K and pure substance can be obtained by condensing the mixed gas fractionally. Metal Pb can be distilled in 1173~1273K and the other metal are remained in the residual because of their lower vapor pressure. The recovered Hg, Cd, Zn and Pb can be reused as materials to manufacture Zn-Mn dry-battery.

Table 1 Relationships between vapor pressure of substances (p*/Pa) and temperature (T/K)

T(K)	p^*_{Hg}(Pa)	$p^*_{ZnCl_2}$(Pa)	p^*_{Cd}(Pa)	p^*_{Zn}(Pa)	p^*_{Pb}(Pa)
573	$3.27υ10^4$	0.58	5.35	0.21	-
623	$8.88υ10^4$	9.28	$3.58υ10^1$	1.82	-
673	-	$6.34υ10^1$	$1.61υ10^2$	$1.13υ10^1$	-
773	-	$1.31υ10^3$	$1.77υ10^3$	$1.89υ10^2$	-
873	-	$1.25υ10^4$	$1.11υ10^4$	$1.55υ10^3$	$6.09υ10^{-2}$
973	-	$7.10υ10^4$	$4.68υ10^4$	$8.15υ10^3$	0.85
T(K)	p^*_{Mn}(Pa)	p^*_{Cu}(Pa)	p^*_{Fe}(Pa)	p^*_{Zn}(Pa)	p^*_{Pb}(Pa)
1073	$2.95υ10^{-2}$	$1.77υ10^{-5}$	$7.65υ10^{-8}$	$3.10υ10^4$	7.23
1173	0.380	$4.23υ10^{-4}$	$2.99υ10^{-6}$	$9.32υ10^4$	$4.22υ10^1$
1273	3.230	$6.11υ10^{-3}$	$6.48υ10^{-5}$	-	$1.86υ10^2$
1373	$1.99υ10^1$	$6.00υ10^{-2}$	$8.85υ10^{-4}$	-	$6.55υ10^2$
1473	$9.47υ10^1$	0.40	$8.40υ10^{-3}$	-	$1.94υ10^3$

2.2 Relationships between maximum evaporation rate and temperature

The production efficiency for treating waste dry-battery in vacuum, namely the evaporation rate, is affected mainly by temperature. The evaporation rate can be described as Equation 13[3]:

$$Z_{max} = 2.623\times10^{-2}\Delta p^*_i\,(M/T)^{1/2} \quad (\text{g cm}^{-2}\ \text{min}^{-1}) \qquad (13)$$

where Z_{max} stands for the maximum evaporation rate, Δ is the distillation coefficient, M is molecular weight of the distilled substance. The saturation vapor pressure of the distilled substance is p^*_i (Pa) when the temperature is T (K).

Supposing that the distillation coefficient Δ is 1, the maximum evaporation rates of substances in waste dry-battery were calculated in the temperature range of 573~1273K according to Eqs. 13 and Table 1, as presented in Table 2.

It is shown from Table 2 that the maximum evaporation rate is affected remarkably by temperature. Metal Cd, Zn and $ZnCl_2$ are volatilized quickly in 773~973K at maximum evaporation rates of $1.77υ10^1$~$4.17υ10^2$ g cm^{-2} min^{-1}, 1.44~5.54 $υ10^1$g cm^{-2} min^{-1} and $1.44υ10^1$~$6.97υ10^2$ g cm^{-2} min^{-1}, respec-tively. Because the value of $Z_{max,Hg}$ is $1.32υ10^3$ g cm^{-2} min^{-1} at 623K, metal Hg would be volatilized into vapor when Cd, Zn and $ZnCl_2$ are evaporated. The maximum evaporation rates of Pb are $4.66υ10^{-1}$~1.97 g cm^{-2} min^{-1}, are 10^2 times more than that of Mn, Cu and Fe in the range of 1173 ~ 1273K, respectively. Thus, these three metals are remained in the residual while Pb is concentrated in vapor in the temperature range.

Table 2 Relationships between the maximum evaporation rate Z_{max} (g·cm^{-2}·min^{-1}) and temperature T (K)

T(K)	$Z_{max,Hg}$	$Z_{max,ZnCl_2}$	$Z_{max,Cd}$	$Z_{max,Zn}$
573	$5.07υ10^2$	$7.42υ10^{-3}$	$6.22υ10^{-2}$	$1.89υ10^{-3}$
623	$1.32υ10^3$	$1.14υ10^{-1}$	$3.99υ10^{-1}$	$1.55υ10^{-2}$
673	-	$7.49υ10^{-1}$	1.72	$9.21υ10^{-2}$
773	-	$1.44υ10^1$	$1.77υ10^1$	1.44
873	-	$1.30υ10^2$	$1.04υ10^2$	$1.11υ10^1$
973	-	$6.97υ10^2$	$4.17υ10^2$	$5.54υ10^1$
1073	-	-	-	$2.01υ10^2$
1173	-	-	-	$5.77υ10^2$
T(K)	$Z_{max,Pb}$	$Z_{max,Mn}$	$Z_{max,Cu}$	$Z_{max,Fe}$
1073	$8.33υ10^{-2}$	$1.75υ10^{-4}$	$1.13υ10^{-7}$	$4.58υ10^{-10}$
1173	$4.66υ10^{-1}$	$2.16υ10^{-3}$	$2.58υ10^{-6}$	$1.71υ10^{-8}$
1273	1.97	$1.76υ10^{-2}$	$3.58υ10^{-5}$	$3.56υ10^{-7}$
1373	6.67	$1.04υ10^{-1}$	$3.38υ10^{-4}$	$4.68υ10^{-6}$
1473	$1.91υ10^1$	$4.80υ10^{-1}$	$2.21υ10^{-3}$	$4.29υ10^{-5}$

2.3 Behavior of $ZnCl_2$ in vacuum

It can be known from Table 1 that the value of $p^*_{ZnCl_2}$ is 1.29×10^3Pa at 773K. Thus, $ZnCl_2$ will volatilize in abundance inevitably and reduce the purity of Hg, Zn and Cd. Adding certain amount of CaO in the charge can solve the problem and the reaction is followed as Equation 15:

$$ZnCl_2 + CaO = CaCl_2 + ZnO \qquad (15)$$

According to the thermodynamical data[4], the value $∋G_m\theta$ of the reaction (15) is -89.81 kJ/mol at 800K and -85.07 kJ/mol at 1000K. Therefore, the reaction has a great trend to proceed to the right from thermodynamic view. When Hg, Zn and Cd are distilled at 773~973K, $ZnCl_2$ with higher vapor pressure is turn into ZnO with lower vapor pressure. Thus, the influence of $ZnCl_2$ on the purity of Hg, Zn and Cd can be eliminated. In addition, the effects of chlorine and gaseous sulfur can also be eliminated[5].

As mentioned above that carbon is contained in waste dry-battery. Metal Zn can be reduced by carbon from ZnO at high temperature in vacuum and the reaction is shown as Equation 16[6]:

$$ZnO_{(s)} + C_{(s)} = Zn_{(g)} + CO_{(g)}$$

$$∋G_m\theta = 371204 + 43.3TlgT - 432.33T \quad \text{J/mol} \qquad (16)$$

Supposing that p stands for the total pressure of the vacuum chamber, p_{Zn} and p_{CO} stands for the partial pressure of Zn and CO, respectively. In general, $p_{Zn}=p_{CO}$ and $p_{Zn}+p_{CO}=p$. As a result, Equation 16 can be described as Equation 17:

$$∋G = ∋G_m\theta + RTln(p_{Zn}\cdot p_{CO})$$

$$= 371204 + 43.3TlgT - 432.33T + 2RTln(p/2) \ \text{J} \qquad (17)$$

The Gibbs Free Energy values of the reducing reaction of ZnO were calculated in the range of 773~1273K when the total pressure is 1.013υ10^{5}~1.013Pa, as depicted in Fig.1.

It can be seen from Fig.1 that the initial reaction temperature decreases with reducing the total chamber pressure in vacuum. The reaction will proceed at 787K when the value of p is 1.013υ10^{1}Pa. In order to ensure that the reduction of ZnO proceeds at great trend possibly, it can be carried out in the temperature of 1173~1273K and 1.013υ10^{1} Pa. Metal Zn is reduced into vapor and mixed with gaseous Pb. Pure Zn and Pb can be obtained after the mixed gas is condensed fractionally.

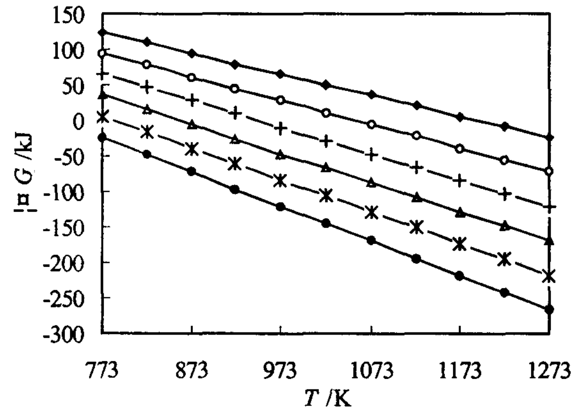

Fig. 1 Relationship of Gibbs Free Energy of $ZnO_{(s)}$+$C_{(s)}$=$Zn_{(g)}$+$CO_{(g)}$ and temperature

ι 1.013×10^{5}Pa; P 1.013×10^{4}Pa; 1.013×10^{3}Pa; ϶ 1.013×10^{2}Pa; 1.013×10^{1}Pa; ξ 1.013Pa

2.4 Behavior of MnO_2 in vacuum

Manganese exists as MnO_2 in waste dry-battery. Metal Mn can be reduced by carbon from MnO_2 at an elevated temperature in vacuum and the reaction is followed as Equation 18[4]:

$MnO_{2\,(s)} + 2C_{(s)} = Mn_{(s)} + 2CO_{(g)}$

϶G_mθ= 290900 - 352.37T J/mol (298~1000K) (18)

Supposing that p and p_{CO} stands for the total pressure of the vacuum chamber and the partial pressure of CO, respectively. In general, p_{CO}=p. As a result, Equation 18 can be described as Equation 19:

϶G = 290900 - 352.37T + 2RTln$p$ J/mol (298~1000K) (19)

The Gibbs Free Energy values of the reducing reaction of MnO_2 were calculated in the range of 773~973K when the total pressure is 1.013υ10^{5}~ 1.013Pa, as shown in Fig.2.

It can be seen from Fig.2 that the initial reaction temperature decreases with decreasing the total chamber pressure in vacuum. The reaction proceeds automatically at a high trend in the range of 773~973K when the total pressure is 1.013υ10^{1}Pa. Therefore, MnO_2 will be reduced by carbon in the process of distilling Hg, Zn and Cd at 1.013υ10^{1}Pa. It can be also known from Table 1 and Table 2 that the value of p^*_{Mn} and $Z_{max,Mn}$ at 1273K is 3.230Pa and 1.76υ10^{-2} g cm^{-2} min^{-1}, respectively, which is c.a. 10^{-2} times as that of Pb. Thus, the reduced Mn will be remained in the residual with C, Cu and Fe if the distillation temperature does not exceed 1273K. And MnO_2 and Cu can be obtained from the residual by hydrometallurgical method, which can be directly reused to manufacture Zn-Mn dry-battery.

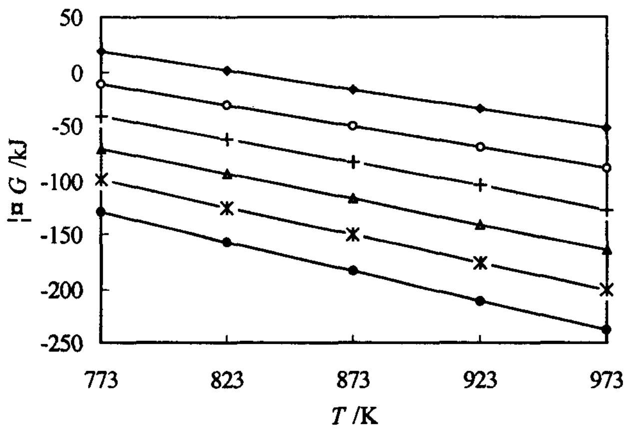

Fig. 2 Relationship of Gibbs Free Energy of $MnO_{2(s)}$+2$C_{(s)}$=$Mn_{(g)}$+2$CO_{(g)}$ and temperature

ι 1.013×10^{5}Pa; P 1.013×10^{4}Pa; 1.013×10^{3}Pa; ϶ 1.013×10^{2}Pa; 1.013×10^{1}Pa; ξ 1.013Pa

3. Conclusions

(1) The valuable metals in waste dry-battery, such as Zn, Mn, Cu, Pb, Cd and Hg, can be recycled by vacuum metallurgical method in the total chamber pressure of 1.013υ10^{1}Pa.

(2) A fractional vacuum distillation and condensation should be taken to obtain metals with high purity. Metal Hg, Cd and Zn are volatilized in the temperature range of 773~973K. MnO_2 and ZnO are reduced by carbon in waste dry-battery in 773~1273K. Metal Pb evaporates in the range of 1173~1273K while Mn, Cu, Fe and C are remained in residual. Metal Cu and MnO_2 can be gained from the residual by hydrometallguical method.

Referrences

[1] Chen Weiliang. 1999a. Comprehensive Recycle and Utilization of Waste Dry-Battery. *Renewable Resources Research* (1):30~35

[2] Kubaschewski,O., Alcock,C. B. eds. 1985. *Metallurgical Thermochemistry*. Beijing: Metallurgical Industry Press

[3] Dai Yonnian, Zhao Zhong eds. 1988. *Vacuum Metallurgy*. Beijing: Metallurgical Industry Press

[4] Liang Yingjiao. Ju Yinchang eds. 1993. *Thermo-dynamical Handbook of Inorganic Substances*. Shenyang: Northeasten University Press

[5] Koch Walter, Tuerke Wolfgang, Pietsch Hartmut. 1985. DE342196

[6] Dai Yongnian eds. 1998. *Vacuum Metallurgy of Non-ferrous Metals*. Beijing: Metallurgical Industry Press