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Thermodynamic Analysis and Experimental Study on Carbothermal Reduction of Zinc Dusts at Vacuum Condition

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The comprehensive recovery of zinc and lead by carbothermal reduction of zinc dusts in vacuum was investigated by XRD, SEM and DTA-TG. Thermodynamics analysis indicates that it can reduce the critical carbothermal reduction temperature of zinc oxides and lead oxides to zinc and lead in vacuum condition. Experimental results demonstrate that pure zinc and lead are obtained with molar ratio of (PbO + ZnO) to C ranging from 1:1 to 1:3 at 850-1000 °C distillation reduction for 40-100 min when the system pressure is 20 Pa.

Keywords: Zinc dusts, Carbothermal reduction, Vacuum, Pyrometallurgy.

INTRODUCTION

The zinc dusts produced as a resulting dusts of smelting lead from Ausmelt furnace process contains considerable amounts of zinc and lead which are of significant economic value. Zinc dusts treatment can be classified into two major categories including hydrometallurgy[1,2] and prometallurgy[3,4]. At present, the traditional method of treating zinc dusts is hydrometallurgical acid leaching process[5,6]. However the hydrometallurgical process has characteristics of high acid consumption, long process flow, complicated subsequent purification process, large equipment investment. So the hydrometallurgical process is eliminated gradually and turning to the hybrid hydrometallurgical and pyrometallurgical process. At present, in overseas this kind of dusts are treated by pyrometallurgical process and recover valuable elements such as Zn, Pb, Fe and so on. Pyrometallurgical process includes the Waelz process[7], the fuming process[8] and the electric furnace smelting process. With the development of the technology, Pickle[9] proposed selective reduction and separation of zinc and lead from electric arc furnace dust with metallic iron. Guo *et al.*[10] reported aluminum bath replacing iron bath to melt reduction bearing Zn-Pb dusts. However, these methods have high production cost, small production scale and difficult to realize industrialization. In this study carbothermal reduction of zinc dusts at vacuum condition was first put forward. According to the report by academician Dai, the vacuum metallurgy technology can not only increase the comprehensive recovery of ores but also reduce the environmental pollution[11]. So far, the vacuum metallurgical technology have been applied widely in materials preparation[12-15] and ores comprehensive recovery fields[16-18].

EXPERIMENTAL

The dusts before mechanical activation were dried at 60 °C for 5 h in the muffle furnace and sieved with 60 mesh. The pretreated material mixed with activated carbon which acting as reductant at different stoichiometric ratio in an agate mortar fully. Then the mixed powders were pressed into blocks of 20 mm in diameter and 10 mm in thickness by uniaxial pressing in a stainless steel die under a pressure of 10 MPa. Then the blocks were removed into graphite crucible and put into the vacuum furnace. When the vacuum degree reducing to 20 Pa the feed was heated to different reaction temperatures at a heating rate of 10 °C/min and keep the temperatures for 60-100 min when the system pressure is about 1-20 Pa.

Phase composition of prepared product was investigated by X-ray diffraction instrument (D/max-3B) using CuK_α radiation in the range of 10°-90° (2θ). The morphology and grain size distribution were studied by scanning electron microscopy (SEM, EPMA-8705) and the thermodynamics stability were detected by thermal analyzer (ZRY-2P).

RESULTS AND DISCUSSION

Thermodynamics analysis: According to the data and formula given by Ye and Hu[19], the Gibbs free energy and reaction enthalpy for carbothermal reduction of zinc dusts can be calcu-

lated. So the initial reaction temperature at different pressure could be obtained. Some potential reactions between PbO, ZnO and C are listed in Table-1. Meanwhile the initial reaction temperature at atmospheric pressure was shown in Table-2.

TABLE-1
REACTIONS FOR ZINC DUSTS WITH C

No.	Reactions
a	$ZnO(s)+C(s)=Zn(g)+CO(g)$
b	$ZnO(s)+CO(g)=Zn(g)+CO_2(g)$
c	$PbO(s)+C(s)=Pb(l)+CO(g)$
d	$PbO(s)+CO(g)=Pb(l)+CO_2(g)$
e	$C(s)+CO_2(g)=2CO(g)$

TABLE-2
INITIAL REACTION TEMPERATURE AT NORMAL PRESSURE

Reactions	a	b	c	d	e
T_0 (K)	1250	1601	555	–	–

Because the experiment was carried out at vacuum condition, the producing CO would be pumped by the vacuum pump. So the main reaction was direct reduction of C. For the reaction (a), the Gibbs free energy is

$$\Delta G = \Delta G^{\theta} + RT\ln\left(\frac{P_{Zn}}{P^{\theta}}\cdot\frac{P_{CO}}{P^{\theta}}\right)$$

for which $\Delta G^{\theta} = 237568 - 189.912T$

if $P_{Zn} = P_{CO}$, $P = P_{Zn} + P_{CO}$, $P = 10^{-m}$ atm, in this case

$$\Delta G = \Delta G^{\theta} + RT\ln\left(\frac{P}{2P^{\theta}}\right)^2$$

$$\Delta G = \Delta G^{\theta} + 2\times 2.303RT\ \log\left(\frac{10^{-m}\text{atm}}{2P^{\theta}}\right)$$

$$\Delta G = 237568 - 201.44T - 38.294mT$$

Hence, the relationship of ΔG and T was calculated at different pressures shown in Fig. 1.

It can be seen from Fig. 1 that the initial reaction temperatures of 1179.35, 990.97, 854.48, 751.03, 669.93 and 604.64 K when the system pressures were 10^5, 10^4, 10^3, 10^2, 10 and 1Pa, respectively. It is apparent that the initial reaction temperature of reaction (a) decreases obviously when the system pressure declines.

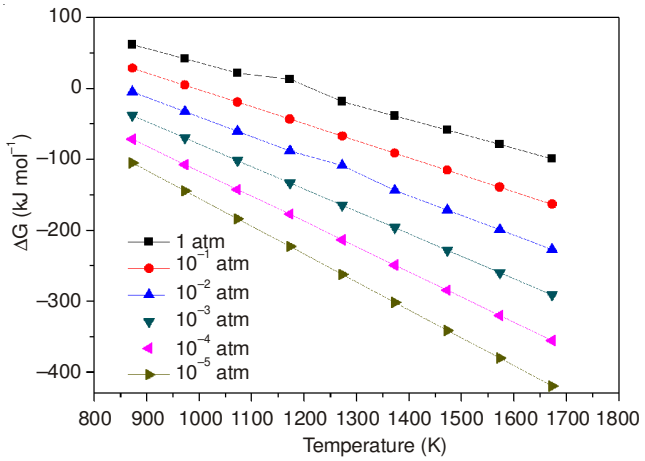

Fig. 1. Gibbs free energy of reaction (a) as function of temperature at different pressures

Meanwhile, in the similar principle the relationship of ΔG and T of reaction (c) were also obtained shown in Fig. 2 which was based on the initial reaction temperature of reaction (c) at 554.92, 529.92, 506.37, 485.15, 465.64 and 447.63 K when the system pressures were 10^5, 10^4, 10^3, 10^2, 10 and 1 Pa, respectively. To sum up, the ZnO and PbO have a more being reduction superiority with vacuum degree decreasing.

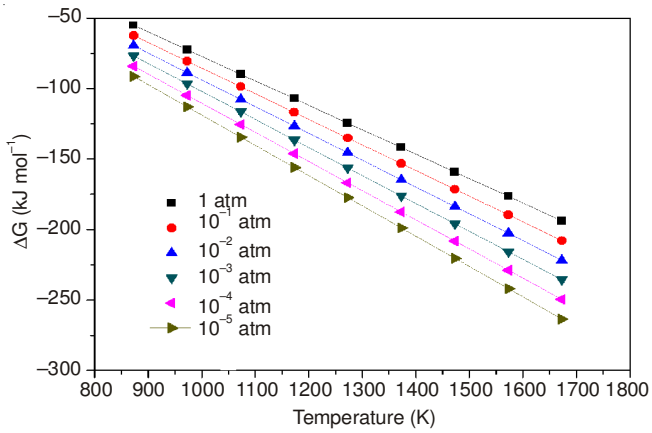

Fig. 2. Gibbs free energy of reaction (c) as function of temperature at different pressures

Thermodynamics stability analysis of zinc dusts: The thermodynamics property of experimental materials were performed and shown in Fig. 3 which reveals that the TG curve keeps constant no mass loss before 800 °C. There is a obvious mass loss after 900 °C. It is because that at 900 °C some chemical components in the dust begin to volatilize or decompose severely. Corresponding with the mass loss, the DTA curve of the materials there is an endothermal peak at about 100 and 800 °C. The first endothermal peak represents phase change, crystal form change or melting reaction without mass loss. The second endothermal peak corresponding with a much mass loss so we can deduce that there is a volatilization or decomposition reaction after 800 °C.

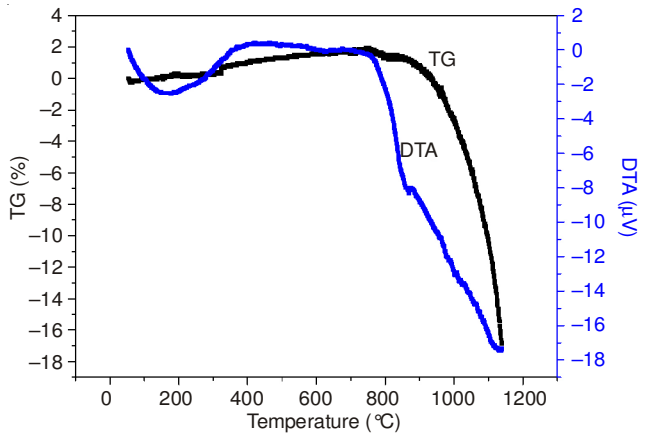

Fig. 3. TG and DTA curves of zinc dusts

XRD analysis of condensation product at different temperatures: The formation phase of carbothermal process was studied at different temperatures. Fig. 4 shows XRD patterns of products prepared at 850, 900, 950 and 1000 °C for 1 h with carbon fitting ratio of 2.5, respectively. It can be seen in Fig. 4 that the reduction product possess pure zinc and lead phases without other impurity phases from 850 to 1000 °C and the diffraction peak intensity is not strong. So we also calculated the average grain size of product with Jade software and the relationship of average grain size and reduction temperature was presented in Fig. 5. It is observed that the average grain size of zinc and lead both decrease with the increasing of temperature between 850 and 950 °C. However, the average grain size begin to increase when the temperature increase to 1000 °C. It may be ascribed to the increase of temperature will lead to the metal vapor quenching and condensing on condenser surface rapidly to form much smaller grains. However when the temperature further increasing to 1000 °C, the average grain size begin to increase attributing to the lateral migration of atoms on the surface of condenser increases with the temperature and the grain start to aggregate and grow.

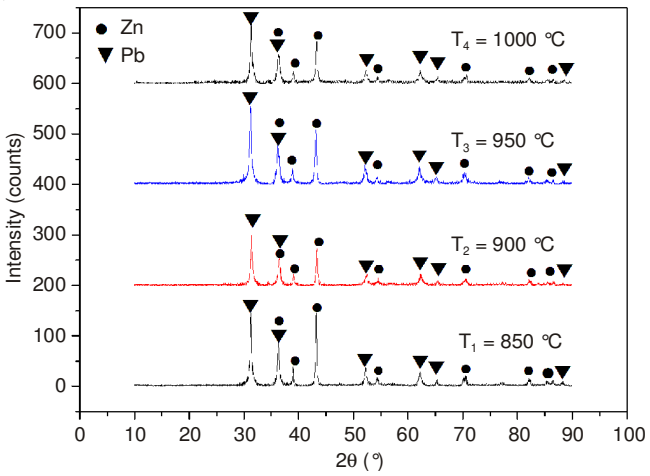

Fig. 4. XRD patterns of products prepared at different temperatures: 850, 900, 950 and 1000 °C

Characterization of product: Fig. 6 shows SEM micrographs of product prepared at 950 °C for 1 h with the carbon fitting ratio of 2.5. Fig. 6 (a) showed that the raw materials have uniform particle distribution and the agglomeration size

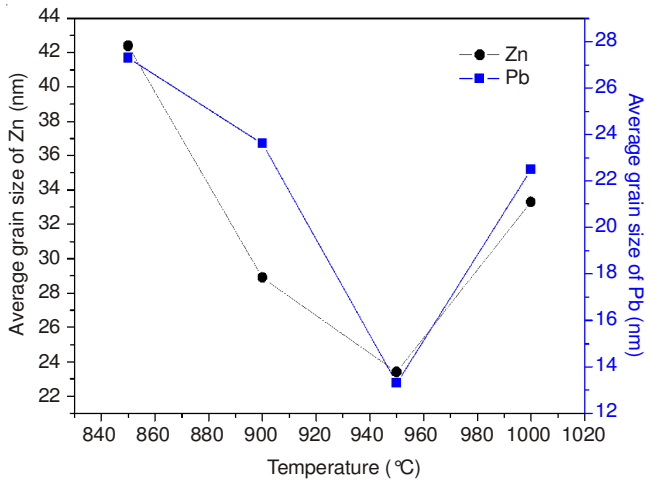

Fig. 5. Relationship diagram of average grain size and reduction temperature

is about 5 μm which is favorable for direct carbon reduction. The loose agglomeration of Zn and Pb metal which is corresponding to the weak peak intensity of XRD patterns (Fig. 4) of reduction product was observed in Fig. 6(b) and the particle size is about 20 μm. Shown in Fig. 6(c), some large long corridors were formed in reduction residue duing to emission of gases such as CO and CO_2.

Effect of carbon fitting ratio on reduction products: Fixing the reduction temperature at 1223 K and the holding time as 1 h, the carbon fitting ratio was changed from 1.5 to 3. The recovery rate of zinc and lead were measured by EDTA titration method. Fig. 7 showed that the recovery of zinc and lead increase with increasing of carbon fitting ratio. The optimum condition is 2.5 which is consistent to experimental results reported by Xiong *et al.*[17].

Effect of reduction temperature on reduction products: Fig. 8 represents the relationship curve of recovery rate with reduction temperature. As shown, the recovery rate of zinc and lead increased with the reduction temperatures. When the temperature increased from 1123 to 1173 K the recovery rate of zinc increased from 45.55 to 74.99 % and the recovery rate of lead increased from 23.48 to 42.28 %. But the trend of augment weakened with further increment of temperature to 1273 K. In view of taking both the recovery and energy utilization efficiency into consideration, the optimum reduction temperature is 1173 K.

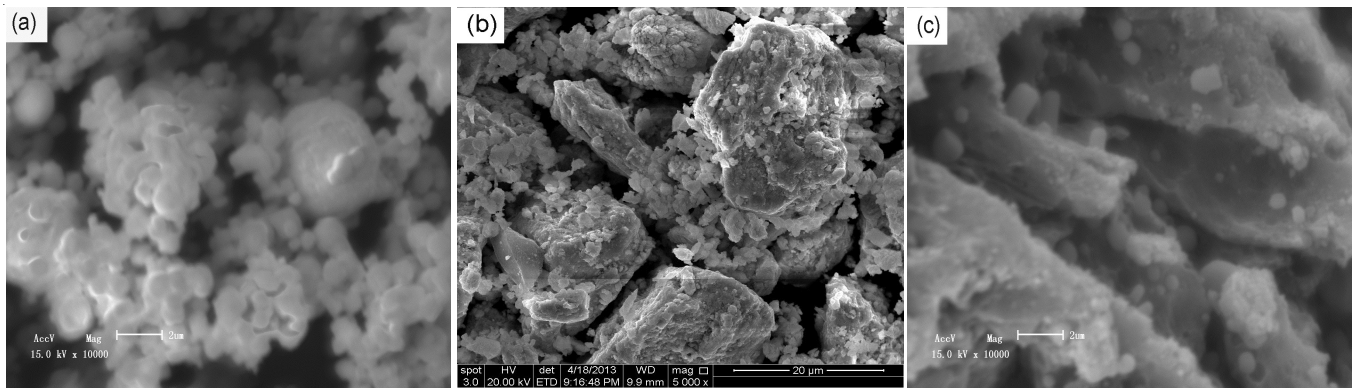

Fig. 6. SEM micrographs of materials: (a) raw materials, (b) reduction product, (c) reduction residue

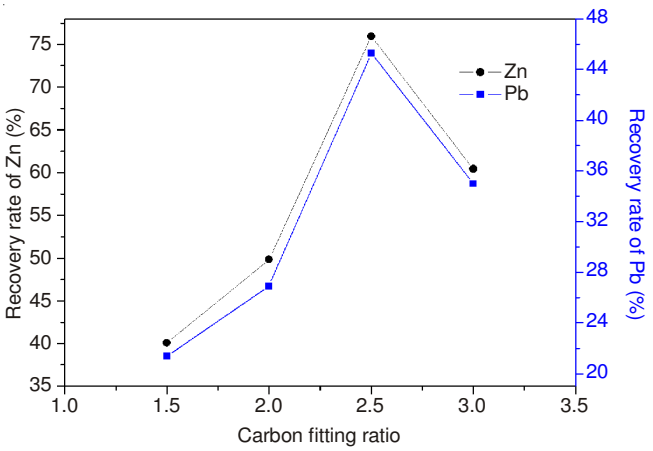

Fig. 7. Relationship curve of recovery rate with carbon fitting ratio

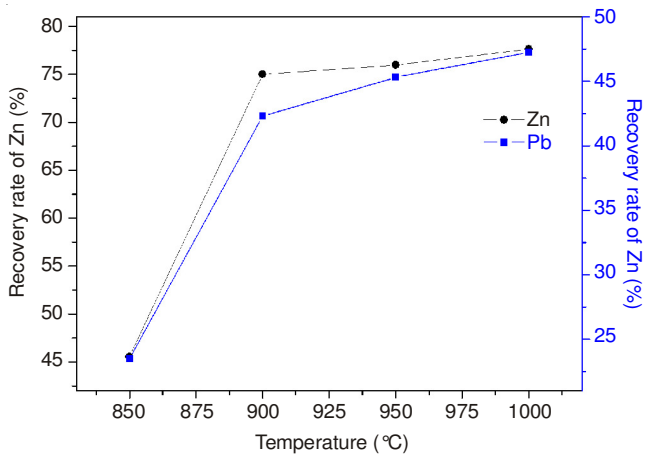

Fig. 8. Relationship curve of recovery rate with reduction temperature

Effect of holding time on reduction products: Fixing the reduction temperature as 1173 K, the carbon fitting ratio as 2.5 and the holding time was changed from 40 to 100 min. The relationship curve of recovery rate with holding time is displayed in Fig. 9. When the holding time increased from 40 to 60 min, the recovery of zinc increases from 69.82 to 75.96 % and that of lead from 39.30 to 45.30 %. While when the holding time further prolonged to 100 min the recovery of zinc increased to 79.28 % while that of lead decrease to 32.17 %. So the optimal holding time is 60 min.

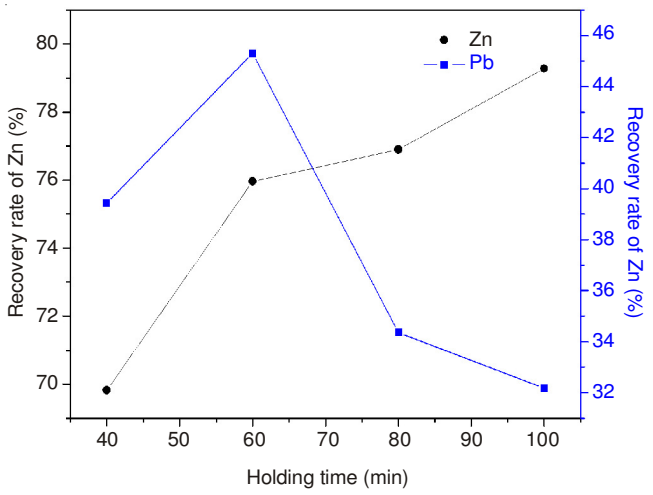

Fig. 9. Relationship curve of recovery rate with holding time

Conclusion

Based on the thermodynamics analysis, the initial reaction temperature of zinc dusts with carbothermal reduction method decreases with the reducing of system pressure. XRD analysis shows that large quantity of pure zinc and lead with the grain size of about 20 nm can be obtained at 850 °C which is lower 100-150 °C than at atmospheric pressure. Several important process parameters for carbothermal reduction zinc dusts and their effects on the recovery rate of zinc and lead were investigated and optimized: the carbon fitting ratio = 2.5, the reduction temperature = 1173 K and the holding time = 60 min. At the optimum technical parameter the recovery of zinc and lead are 74.99 and 42.28 %, respectively.

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