Volatilization of zinc and lead in direct recycling of stainless steel making dust [①]

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Abstract: The volatilization of zinc and lead from the stainless steel making dust pellets in the direct recycling procedure was conducted by using a thermo-gravimetric analyzer and a Tamman furnace in the nitrogen atmosphere respectively. The results show that the temperature has a significant effect on the volatilization rates of zinc and lead, and the carbon content in the pellets has no effect on the volatilization process. The volatilization of zinc is controlled by the chemical re- action between zinc oxide and carbon monoxide, while the volatilization of lead is controlled by the evaporation from liquid phase to the atmosphere. The volatilization of zinc and lead mainly happen at about 1 000 ℃ according to non-isothermal experiment.

Key words: volatilization of zinc and lead; stainless steel making dust; reduction; recycling

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1 INTRODUCTION

The smelting temperature of stainless steel mak- ing operation generally reaches 1 600 ℃ or higher. Approximately 1% − 2% (mass fraction) of the scrap charged into the furnace are converted into dust under this condition[1]. And further more dusts are generat- ed in the argon-oxygen decarburization(AOD) or vac- uum-oxygen decarburization (VOD) vessels. All of the zinc and lead present in the charging process enter into the gas phase. At the same time, the high tem- peratures and turbulence in the smelting furnace cause a lot of iron, chromium and nickel to volatilize. As the metal vapors exit from the furnace and the tem- perature drops, the fumes are oxidized and con- densed. Complex microscopic agglomerates form physically and chemically on condensed nuclei such as fugitive dust particles and then are collected as partic- ulate matter in the bag-house. This dust is considered as a by-product of steel making process. When being stockpiled, the dust leaches heavy metals to the groundwater or rainwater in concentrations that ex- ceed the environmental guidelines. This makes the dust be assigned as a hazardous waste and banned from landfills by government. In addition, the dust is also an economical factor for stainless steel makers as it contains large amount of valuable metals such as chromium and nickel. There were many different re- cycling methods[2−5] developed for the dust but most of them are not commercially available. One of the e- conomical ways to recover the metals present in the dust seems to be a direct self-reduction and self-recy- cling method during the smelting of stainless steels.

Direct recycling is an improved method which aims at recovering the metallic elements from the dust directly to the steel bath. In this method, the dust is mixed with a reducing agent(carbon) and formed into pellets that are subsequently fed to the steelmaking furnace. Under the thermal conditions, the carbon reduces the metal oxides in the dust. The characteris- tics of the dust were investigated[6] as well as the isothermal[7] and non-isothermal[8, 9] kinetics models of the reduction. However, it was found that a lot of zinc and lead emitted out by volatilization and accu- mulated in the secondary dust. It is not a suitable way to treat this secondary dust by the direct recy- cling again because zinc and lead will circulate in the smelting system.

Inmetco process[10, 11] by International Metal Reclamation Company or Fastmet process[12−14] by Midrex Direct Reduction Corporation is a representa- tive of the direct reduction method. The dust was mixed with carbon-bearing materials and formed into pellets. Then the pellets were directly reduced into

alloyed sponge iron or directly reduced iron in the rotary hearth furnace and volatile metal oxides were concentrated to secondary zinc and lead products. The alloyed sponge iron or directly reduced iron was then charged in primary melting system such as electric arc furnaces. Alternatively, the pellets were directly reduced in submerged arc furnace. The direct recycling process mentioned above is different from Inmetco process and Fastmet process in that the rotary hearth furnace is not required and the temperature of reduction is much higher. Two stage recycling of Inmetco process or Fastmet process is changed into one step in the direct recycling process. In this study the volatilization of zinc and lead in the direct recycling of stainless steel making dust was investigated.

2   EXPERIMENTAL

2.1   Samples preparation

The stainless steel making dust used in this study was taken from a stockpile located in the open air. A large amount of moisture existed in the dust. This caused the dust particles to agglomerate and the diameter of the particles ranged from less than 38 μm to approximately 5 cm. The composition of the dust is listed in Table 1(Inductively coupled plasma(ICP) for nickel, zinc, lead and X-ray fluorescence(XRF) for other elements). It indicated that the primary composition of the dust is iron, chromium and other alloying elements, such as silicon, calcium, nickel, manganese, magnesium, sodium, zinc and lead. Most of the elements in the dust were oxidized since it was formed in air at high temperature. XRD analysis indicated that the main phases present in the dust were Fe_2O_3, CrO and Al_2O_3 and the calculation result of phase composition is listed in Table 2. The dust was crushed in a ball miller for about 20 min and then

Table 1   Element composition of stainless steel making dust(mass fraction, %)

Fe	C	Ca	Cr	Al	K	Mg	Mn
39.12	1.96	6.13	10.60	0.41	0.15	15.96	8.36

Na	Ni	P	Ti	Si	Pb	Zn	Others
0.17	3.92	0.02	0.14	2.64	0.12	0.59	9.71

Table 2   Phase composition of stainless steel making dust(mass fraction, %)

Fe_2O_3	CaO	CrO	Al_2O_3	K_2O	MgO	MnO_2
56.00	9.14	13.51	0.66	0.36	3.48	4.67

Na_2O	NiO	P_2O_5	TiO_2	SiO_2	PbO	ZnO
0.26	6.70	0.05	0.23	5.45	0.16	0.93

screened to below 0.45 mm. The carbon particles used as the reducing agent in the pellets were finer than 0.04 mm.

The pellets were made from the mixtures of stainless steel making dust with carbon and dolomite binder. They were agglomerated by hand using a semi-ball shaped ceramic bowl. A water droplet was added to the 1 g dust/carbon/dolomite mixture. The nucleus of pellet is created by rotating the bowl in a clock-work manner. The addition of more water droplets and continuing rotating of the bowl allowed the pellet to grow in size. The ball was rolled for about 1 min after the pellet was completely formed. Four types of carbon content 5%, 10%, 15% and 35% were chosen. In each case the dolomite content was 5%. The pellets agglomerated were about 10 mm in diameter and dried in air at room temperature for 4 d.

2.2   Experimental procedure

The thermal process of stainless steel making pellets was investigated by using a Cahn-171 thermogravimetric analyzer(TGA). A heating rate of 40 ℃/min was chosen up to 1 190 ℃ and it was progressively slowed down above 1 190 ℃ so as not to exceed furnace capacity. The maximum temperature was 1 500 ℃, which is a typical operating temperature in metallurgical operations. Holding time at maximum temperature was 30 min to ensure that chemical equilibrium was reached. A flow of nitrogen with the rate of 140 mL/min was introduced to the furnace during the thermal process to prevent the oxidation of carbon. The pellets were put in the alumina crucible, which was connected to the microbalance. The temperature was detected by a thermocouple set under the crucible in TGA furnace. The data of mass, temperature and time of the thermal process were recorded automatically for analysis.

The experiment for the same pellet as above mentioned was carried out in a Tamman furnace with a corundum tube inside. The pellets were put in the crucible and lowed down into the uniform temperature zone of the tube. A flow of nitrogen with the rate of 120 mL/min was maintained to purge the tube. The pellets were taken out of the furnace in predetermined period and quenched in water or liquefied nitrogen. The cold pellets were dried and the contents of zinc and lead were determined by the chemical analysis.

3   RESULTS

Fig. 1 shows the TGA results. It can be seen that all the pellets containing different contents of

carbon have the same tendency of mass loss in the beginning of the thermal treatment. And this tendency keeps exactly the same before 1 200 ℃. The mass loss comes from the reduction of metal oxides present in the dust and gasification of some reduced metals. The reduction process stops earlier for the pellets containing 5% and 10% carbon because all the carbon in the pellets are consumed, which keeps the mass of the pellets unchanged in the late period of the reduction process.
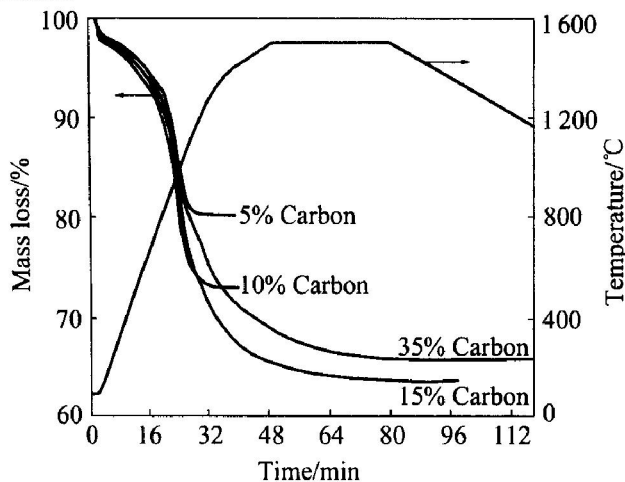

Fig. 1　TGA curves of steelmaking pellets

It is not so easy to check the information about the rate of mass loss of the pellets from Fig. 1. The differential values of mass loss are calculated by a computer program and the results are shown in Fig. 2. There are two sharp peaks in the figure. One results from the fast evaporation of moisture and the other from the volatilization of zinc and lead and the removal of oxygen from the dust by the reduction. The peak of mass loss rate happened in the time range of 2 – 4 min at the temperature below 200 ℃ is related to the evaporation of water from the pellet. The peak of mass loss rate happened in the time period of 20 – 28 min at the temperature range of 800 – 1 200 ℃ is related to the volatilization of zinc and lead. The rate peak only existing in the pellets containing 15% or 35% carbon illuminates that 10% carbon in the pellets is not enough for reduction and recovery of the valuable metals in the dust.

The reduction and volatilization of zinc and lead happen at the temperature around 1 050 ℃ based on TGA test(Fig. 2). In the standard condition, the evaporation temperatures of zinc and lead are 906 ℃ and 1 525 ℃ respectively after being reduced from the oxides. Tamman furnace tests under the isothermal condition are taken at the temperature range of 1 100 – 1 400 ℃. The experimental results are shown in Figs. 3 and 4.

Fig. 3 shows the profile of zinc volatilization. The percentage of zinc volatilization is dependent on the temperature. The volatilization can be accelerated
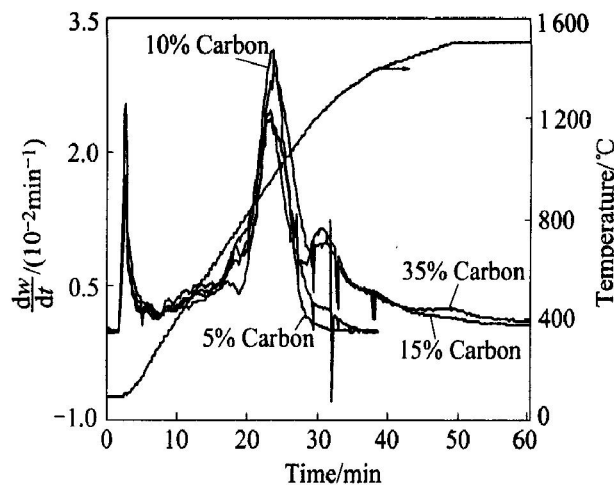

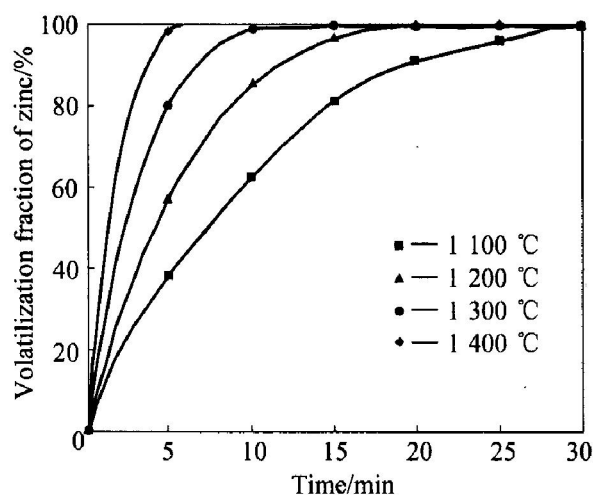**Fig. 2**　Profile of mass loss rate during TGA test

Fig. 3　Profile of zinc volatilization in Tamman furnace test under isothermal condition
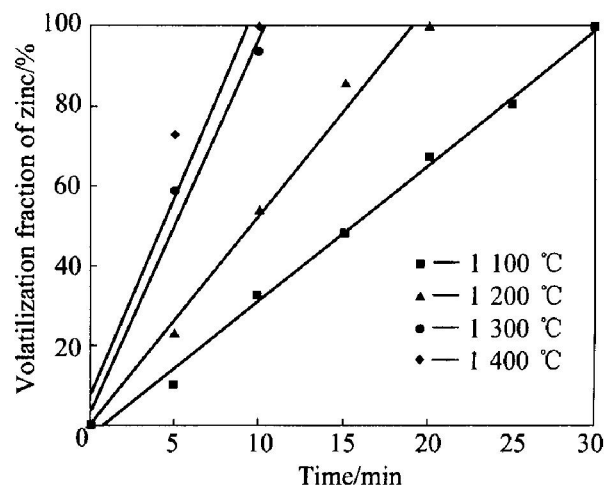

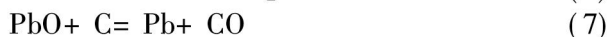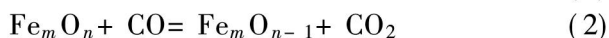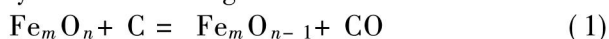**Fig. 4**　Profile of lead volatilization in Tamman furnace test under isothermal condition

as the temperature increases. All the reduced zinc can be volatilized in 5 min at 1 400 ℃. It needs about 30 min to volatilize all the zinc at 1 100 ℃. Fig. 4 shows the profile of lead volatilization. The percentage of lead volatilization depends on the temperature too. All the reduced lead can be volatilized in 10 min

and this reveals the rate differences of lead reduction and volatilization between the standard condition and the experimental condition. The figure also shows that 30 min is needed to reduce and volatilize all the lead at 1 100 ℃.

Furthermore, it is found that the particle size of the dust and the carbon content of the pellet do not influence the volatilization of zinc and lead. So, the effects of particle size and carbon content on the volatilization are not given in this study and the carbon content in all Tamman furnace tests is 15%.

4　MODELLING OF VOLATILIZATION OF ZINC AND LEAD

In thermal treatment of the pellets, the metal oxides CrO, Fe_2O_3/Fe_3O_4, NiO, PbO and ZnO can be reduced by the carbon or carbon monoxide. The possible reactions during the reduction process are mainly as the following:

$$Fe_mO_n + C = Fe_mO_{n-1} + CO \qquad (1)$$
$$Fe_mO_n + CO = Fe_mO_{n-1} + CO_2 \qquad (2)$$
$$NiO + C = Ni + CO \qquad (3)$$
$$NiO + CO = Ni + CO_2 \qquad (4)$$
$$ZnO + C = Zn + CO \qquad (5)$$
$$ZnO + CO = Zn + CO_2 \qquad (6)$$
$$PbO + C = Pb + CO \qquad (7)$$
$$PbO + CO = Pb + CO_2 \qquad (8)$$
$$CrO + C = Cr + CO \qquad (9)$$
$$CrO + CO = Cr + CO_2 \qquad (10)$$
$$C + CO_2 = 2CO \qquad (11)$$

The reactions of the zinc oxide or lead oxide with carbon depend on the contact between the oxides and carbon. Some reduced metals can cumber the contact so that the reactions between the oxides and solid carbon proceed in an indirect manner, in which the metal oxides are reduced by carbon monoxide instead of carbon. Furthermore, the volatilization processes of zinc and lead are different. The gasification temperature of zinc is 906 ℃ based on the calculation with HSC-chemistry[15]. This temperature is lower than that of experiment so that all the reduced zinc can be volatilized into gas phase quickly. The resistance of zinc volatilization is the reaction between zinc oxide and carbon monoxide. The lead gasification temperature is 1 525 ℃ based on the calculation with HSC-chemistry, which is much higher than the experimental temperature. The reduced lead can exist in a liquid form in the pellets and can not be volatilized directly into zinc. The volatilization of lead can be involved in the reduction process. The amount of lead reduced in the pellets is much less than that of zinc according to Table 1. It is impossible to melt the lead into the steel based on the previous study[16] and this makes the reduced lead exist in the form of pure metal. The resistance of lead volatilization is the diffusion of

gaseous lead through the gas/liquid boundary. Under these considerations, the rate of zinc volatilization is dependent on the reaction between zinc oxide and carbon monoxide, and the rate of lead volatilization is dependent on the evaporation of liquid lead.

According to Szekely[17], the relationship between the volatilization fraction of zinc($V(Zn)$) and time(t) can be expressed as follows:

$$1 - (1 - V(Zn))^{1/3} = k(Zn) t \qquad (12)$$

where $k(Zn)$ represents the rate constant and is a function of temperature. This rate constant can be determined by the experimental data regression according to Eqn.(12). The relationship between $k(Zn)$ and temperature is shown in Fig. 5. The rate constant increases with increasing temperature. It needs longer time to achieve the same amount of volatilized zinc at low temperature. The calculated volatilization fraction of zinc and the experimental data are shown in Fig. 6. The good consistence of the calculated with experimental results shown in Fig. 6 indicates that the process of zinc volatilization is controlled by the reaction between zinc oxide and carbon monoxide.

It can be seen from Fig. 4 that the volatilization fraction of lead ($V(Pb)$) increases with the

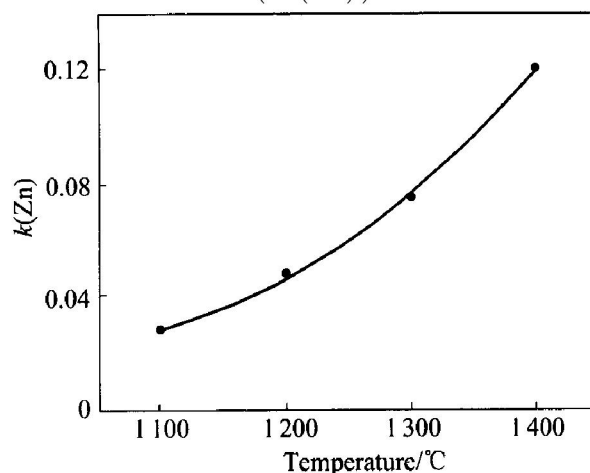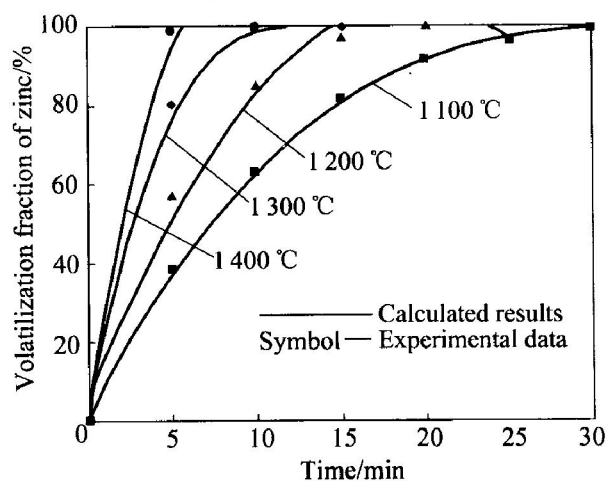**Fig. 5**　Effect of temperature on $k(Zn)$ during volatilization of Zn

Fig. 6　Comparison of calculated results with experimental data of Zn volatilization

time(t). The relationship between them is linear and it can be expressed as

$$V(Pb) = k(Pb) \cdot t \qquad (13)$$

where $k(Pb)$ is a rate constant of lead volatilization and it varies with the temperature. The effect of temperature on $k(Pb)$ is shown in Fig. 7. The $k(Pb)$ increases with increasing temperature. In other words, the rate of the lead volatilization can be speeded up at high temperature. The linear relationship between the volatilization fraction of lead and the time indicates an important conclusion that the process of lead volatilization is controlled by the evaporation of liquid lead to gas atmosphere.
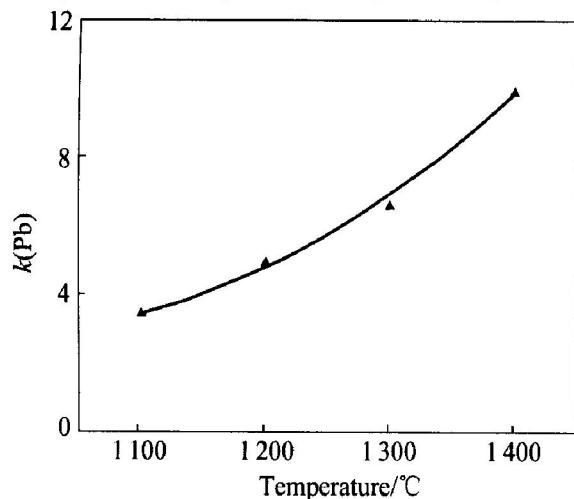

Fig. 7 Effect of temperature on $k(Pb)$ during volatilization of Pb

The volatilization of lead is speeded up much faster than that of zinc with the increase of temperature based on the comparison of Fig. 5 with Fig. 7. This indicates that the volatilization of lead requires higher temperature than that of zinc does.

5 CONCLUSIONS

1) The volatilization of zinc and lead present in the stainless steel making dust happens in the temperature range of 8 00 ~ 1 200 ℃, mainly around 1 000 ℃, according to the differential analysis of the mass loss rate.

2) The rate of zinc volatilization from the pellets in the direct recycling procedure of stainless steel making dust is controlled by the chemical reaction between zinc oxide and carbon monoxide.

3) The rate of lead volatilization from the pellets in the direct recycling procedure of stainless steel making dust is controlled by the evaporation process of liquid lead.

4) The volatilization of zinc and lead can be speeded up from the pellets in the direct recycling procedure of stainless steel making dust at higher temperature. The volatilization of lead favors much higher temperature than that of zinc does.

5) The carbon content in the pellets does not influence the volatilization process of zinc and lead.

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