Article ID: 1003－6326(2004)03－0593－06

Kinetics of isothermal reduction of stainless steelmaking dust pellets①

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Abstract: The stainless steelmaking dust pellets were reduced in isothermal temperature condition simulating the direct recycling practice in the stainless steel production and the kinetics of the reduction process was investigated. The pellets were formed after mixing the dust with carbon as the reducing agent and dolomite as the binder and smelting flux. An electric furnace was used to heat the pellets and an electrical microbalance was used to check the mass of the pellets in the reduction process. The reduction rate was calculated according to the data of pellet mass change in consideration of the evaporation of moisture, zinc and lead at high temperature. The results of the experiments show that the reduction process is in two consecutive stages. The reduction kinetic models were set up for each stage and the kinetic parameters such as activation energy and frequency factor were determined. The apparent activation energy of the first stage is 21.69 kJ/mol, and this stage is controlled by chemical reaction. The apparent activation energy of the second stage is 17.35 kJ/mol, and this stage is controlled by the diffusion of carbon monoxide through the resultants of reaction.

Key words: stainless steelmaking dust; isothermal reduction kinetics; pellets; direct recycling

CLC number: TF 741.5 **Document code:** A

1 INTRODUCTION

The flue dust is a by-product of steelmaking process. This steelmaking dust has been assigned as a hazardous waste and banned from landfills by various government regulatory agencies because it contains a lot of heavy metals which will be leached into groundwater or rainwater when stockpiled[1]. Many dust treatment methods were developed in the past[2-4], but most of them only dealt with the recycling of zinc and lead[5, 6]. Vitrification of the dust lost the valuable metal resources in it[7] and plasma treatment of the dust consumed too much electric power[8]. A new technology of direct recycling of stainless steelmaking dust was developed[9-12] and it was a self-reduction process. In the process, the dust was mixed with a reducing agent carbon and formed into pellets that were subsequently fed to the smelting furnace. Under the high isothermal temperature conditions that prevailed in the furnace, the carbon was expected to reduce the metal oxides in the dust and the reduced metals were recovered directly to the steel bath in the form of metallic elements. This study focused on the kinetics of the direct reduction process. There was few kinetic studies on the direct recycling on the stainless steelmaking dust even though some of them have been undertaken on the iron composites and chromite fines[13, 14].

2 EXPERIMENTAL

2.1 Materials and method

The stainless steelmaking dust used in the experiment was taken from a stockpile located in the open air. As it was exposed to the atmosphere, the dust contained a large amount of moisture that caused particles to agglomerate over time. The range of particle sizes in the dust samples was very wide from less than 38 μm to approximately 5 mm. Elemental analysis of the dust samples was performed using X-ray fluorescence(XRF) for Al, Ca, Cr, Fe, K, Mg, Mn, Na, P, Si and Ti, and inductively coupled plasma(ICP) for Ni, Pb and Zn. The compositions of the samples are given in Table 1. Most of the elements within the dust were oxidized since it was formed in air at high temperature. X-ray diffraction(XRD) observations indicated that the main phases present in the dust were Fe_2O_3, CrO, CaO and NiO and the phase compositions are given in Table 2.

① **Foundation item:** Project (50274073) supported by the National Natural Science Foundation of China; project (Metallurgy, 2003) supported by Natural Sciences and Engineering Research Council of Canada

Received date: 2003－07－14; **Accepted date:** 2003－11－07

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Table 1 Compositions of stainless steelmaking dusts(mass fraction, %)

Si	Al	Ca	Cr	Fe
2.55	0.35	6.53	10.33	40.57
Mn	**Ni**	**Pb**	**Zn**	**Mg**
2.95	5.42	0.15	0.75	2.10

Table 2 Main phases of stainless steelmaking dust(mass fraction, %)

SiO_2	Al_2O_3	CaO	CrO	Fe_2O_3
5.45	0.66	9.14	13.51	56.00
MnO_2	NiO	PbO	ZnO	MgO
4.67	6.70	0.16	0.93	3.48

The dust was crushed in a ball miller for about 20 min and then screened to below 0.45 mm in order to be suitable for pelletization. The carbon particles used as the reducing agent in the pellets were very fine. Four types of pellets containing 10%, 15%, 20% and 25% (mass fraction) carbon were formed. In each case the dolomite content was 5% and the other content was the dust. Fig. 1 shows the cross-section morphology of a pellet, observed using a scanning electron microscope(SEM). The different particles of the cross-section were identified using energy dispersive spectroscopy (EDS). It can be seen from the figure that each dust particle was surrounded by carbon so that the area of contact between dust and carbon was very large. The pellets formed were about 10 mm in diameter and were dried at 100 ℃ for 3 h to remove the moisture.

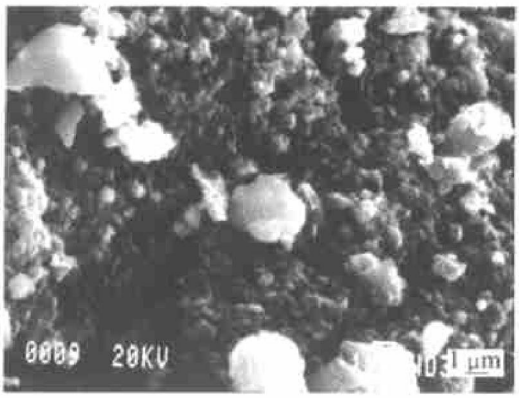

Fig. 1 SEM morphology of pellet

An electric furnace was used to heat the pellets in the experiments. The furnace was heated to a certain temperature first. The pellets were put into the alumina crucibles and then sent to the furnace. The pellets and the crucibles were taken out of the furnace in an assigned period of time. An electrical microbalance was used to check the initial mass of the pellets and crucibles and the mass of them after the thermal treatment. The mass changes of pellets with the time of reduction in the treatment were recorded in this way and the data were used to set up the isothermal kinetic model of the reduction.

2.2 Experimental results

The composition of stainless steelmaking dust is much more complex than that of pure metal oxides. There exist various metal oxides within the dust and they are reduced simultaneously in the isothermal temperature condition. The oxides and reduced metals formed at different stages of reduction may affect the next reduction process. The evaporation of reduced zinc and lead should be considered in order to calculate a degree of reduction correctly based on the data of mass change. Typically, the gasification temperature of zinc is 906 ℃ and that of lead is 1 525 ℃ after being reduced from the oxides. But the evaporation processes begin before arriving at these typical temperatures. The rate of metal evaporation can be expressed as[15]

$$\frac{dm}{dt} = p_i \sqrt{\frac{M}{2\pi RT}} \tag{1}$$

where m represents the mass of evaporated metal; t is time; p_i is the partial pressure of the evaporated metal and $\ln(p_i) = A/T + B$[16] (A and B are constants); M is the molecular mass of the metal; R is the gas constant; T is the temperature. Therefore, the mass of evaporated metal can be calculated by integrating Eqn. (1).

$$\Delta m_E = \int_0 dm = \int_0 e^{\frac{A}{T}+B} \sqrt{\frac{M}{2\pi RT}}\, dt = e^{\frac{A}{T}+B} \sqrt{\frac{M}{2\pi RT}} \cdot t \tag{2}$$

The total mass loss of the pellets Δm_Σ in the isothermal reduction process can be expressed as

$$\Delta m_\Sigma = \Delta m_O + \Delta m_C + \Delta m_E \tag{3}$$

where Δm_O corresponds to mass loss of oxygen in metal oxides; Δm_C considers the mass loss of carbon and Δm_E represents mass loss by metal evaporation at high temperature. Thus, the degree of reduction $g(t)$ can be determined as

$$g(t) = \frac{m_i - m_t - \Delta m_E}{\Delta m_\Sigma}$$

In Eqn. (4), m_i is the initial mass of the pellets; m_t is the pellet mass at time t. The isothermal reduction degrees $g(t)$ based on the calculation of the experimental data at 1 200 ℃, 1 300 ℃, 1 400 ℃ and 1 500 ℃ are given in Fig. 2. It can be seen from the figure that the reduction degree increases with the increase of temperature and carbon content in the pellets. The rate of the reduction is much fast in the beginning of the reduction. It slows down after the formation of reduced product and the consumption of the reducing agent.

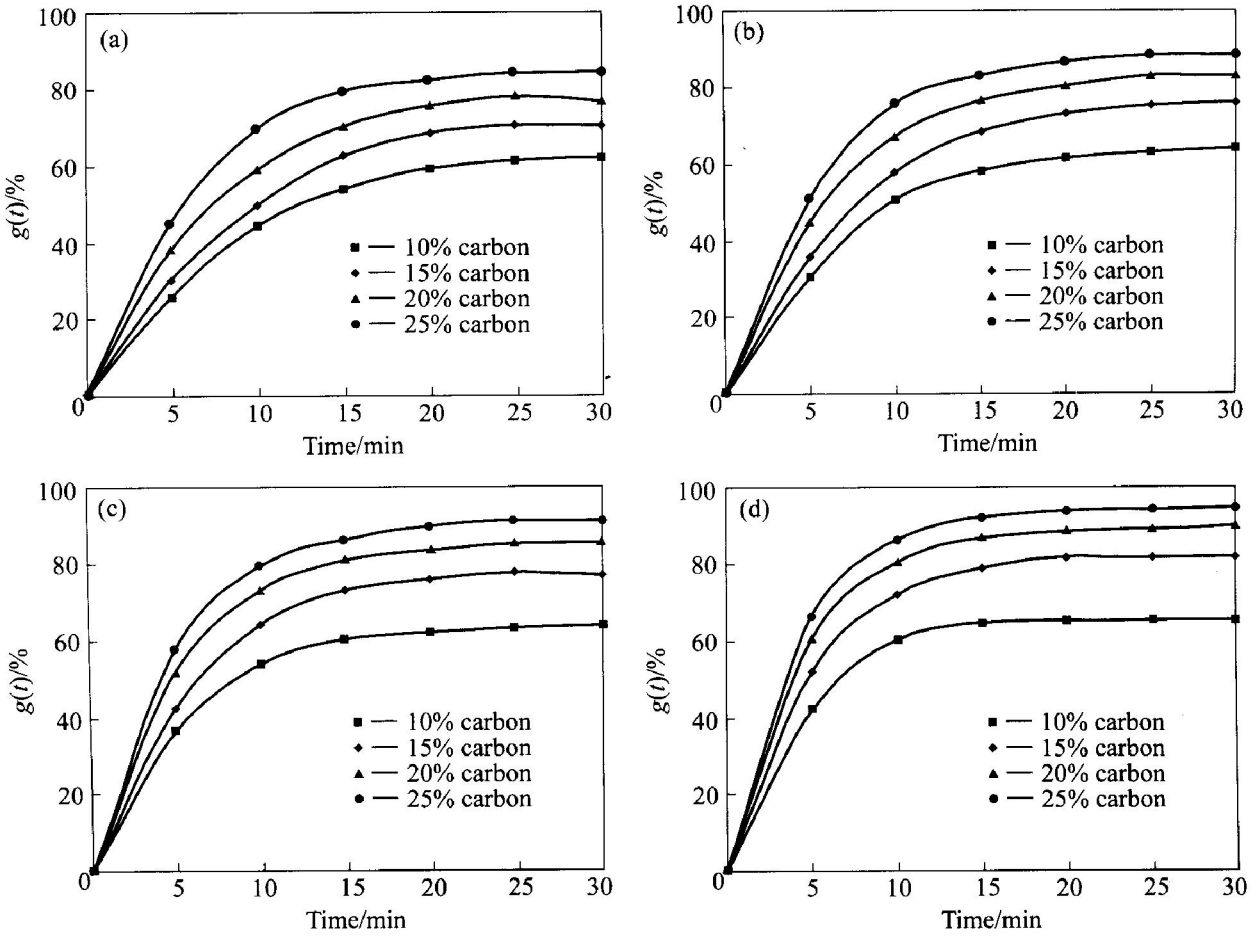

Fig. 2 Profiles of reduction degree at different temperature and content of carbon (a) —1 200 ℃; (b) —1 300 ℃; (c) —1 400 ℃; (d) —1 500 ℃

3 KINETICS OF ISOTHERMAL REDUCTION

3.1 Reactions in isothermal reduction

Some metal oxides can be reduced but some cannot in the isothermal reduction process. The possible reactions taking place during the reduction are mainly as follows:

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

$$NiO + CO = Ni + CO_2 \quad (6)$$

$$3Fe_2O_3 + C = 2Fe_3O_4 + CO \quad (7)$$

$$3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2 \quad (8)$$

$$Fe_3O_4 + C = 3FeO + CO \quad (9)$$

$$Fe_3O_4 + CO = 3FeO + CO_2 \quad (10)$$

$$FeO + C = Fe + CO \quad (11)$$

$$FeO + CO = Fe + CO_2 \quad (12)$$

$$CrO + C = Cr + CO \quad (13)$$

$$CrO + CO = Cr + CO_2 \quad (14)$$

$$PbO + C = Pb + CO \quad (15)$$

$$PbO + CO = Pb + CO_2 \quad (16)$$

$$ZnO + C = Zn + CO \quad (17)$$

$$ZnO + CO = Zn + CO_2 \quad (18)$$

In the initial stage of isothermal reduction, the reactions happen in the way of direct contact between the metal oxides and reducing agent carbon as the odd number equations above because there is not enough carbon monoxide present in the pellets at this time. In the later stage of isothermal reduction, the reduced products are formed on the surface of the dust and baffle the contact between carbon and the oxides. It is so hard to make the solids pass through the product layer to continue the reactions. The carbon monoxide, from the reaction between the carbon and carbon dioxide produced in the initial stage, acts as the reducing agent instead of carbon in this condition. The reactions take place in the even number equations above. In these consideration, the reduction process can be classified into two stages, the first stage and the second stage. The reduction condition of the first stage is better than that of the second stage and the reduction rate of the first stage is much fast, which has been confirmed in Fig. 2.

3.2 Kinetic equation in first stage of reduction

In the first stage of reduction, the reaction rate depends on the contact area between the metal oxides and the carbon in the pellets. The kinetic equation of this stage can be expressed as

$$-\frac{dm}{dt} = K \times S \quad (19)$$

where K is a rate constant; t represents the time of

reaction; m is the mass of the dust in pellets ($m = \frac{4}{3}\pi r^3 \rho n$, ρ is the density of the dust, r is the radius of the dust particles and suppose there are n dust particles in the pellet); S is the surface area of the dust ($S = 4\pi r^2 n$). So, Eqn. (19) can be expressed as

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[\frac{4}{3}\pi r^3 \rho n\right] = K \times [4\pi r^2 n]$$

or

$$-\mathrm{d}r = \frac{K}{\rho}\mathrm{d}t \tag{20}$$

Integrate Eqn. (20) in the time range from 0 to t and dust radius from initial r_0 to r, the following equation can be got:

$$r_0 - r = \frac{K}{\rho}t \tag{21}$$

The degree of the reduction g equals to ($1 - r^3/r_0^3$), so $r = r_0(1-g)^{1/3}$ and take this expression into Eqn. (21) we get the function of reduction degree as follows:

$$F(g) = 1-(1-g)^{1/3} = \left(\frac{K}{r_0\rho}\right)t$$

or

$$F(g) = 1-(1-g)^{1/3} = A\,\mathrm{e}^{-\frac{E}{RT}}t \tag{22}$$

In Eqn. (22), $F(g)$ is the function only related to the reduction degree g, A is the frequency factor, E is the apparent activation energy, R is gas constant and T is the reduction temperature. Differentiate Eqn. (22) to the time t, get the following expression:

$$F'(g)\frac{\mathrm{d}g}{\mathrm{d}t} = A\,\mathrm{e}^{-\frac{E}{RT}} \tag{23}$$

Take logarithm to two side of Eqn. (23) and get

$$\ln\left[F'(g)\frac{\mathrm{d}g}{\mathrm{d}t}\right] = \ln A - \frac{E}{RT} \tag{24}$$

The relationship of $\ln\left[F'(g)\frac{\mathrm{d}g}{\mathrm{d}t}\right]$ and temperature is given in Fig. 3. The apparent activation energy of the reduction process is determined as 21.69 kJ/mol according to the line slope of this figure. It is found that the frequency factor A changes with the carbon content w(C) (mass fraction, %) in the pellets, which is shown in Fig. 4 and $A = 0.4w(\mathrm{C}) + 10$. The kinetic model of isothermal reduction process in the first stage can be given in the following form:

$$1-(1-g)^{1/3} = (0.4w(\mathrm{C}) + 10)\,\mathrm{e}^{-\frac{21\,690}{RT}}t \tag{25}$$

3.3 Kinetic equation in second stage of reduction

In the second stage of reduction, the rate of reaction depends on the carbon monoxide passing through the reduced metal layer. According to the Fick law, the diffusion quantity J can be expressed as

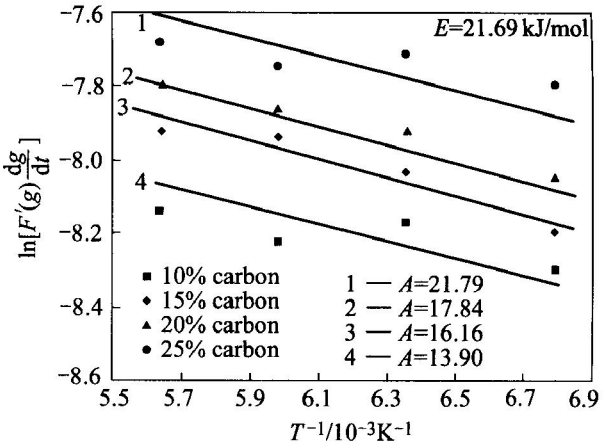

Fig. 3 Kinetics parameters of first stage reduction

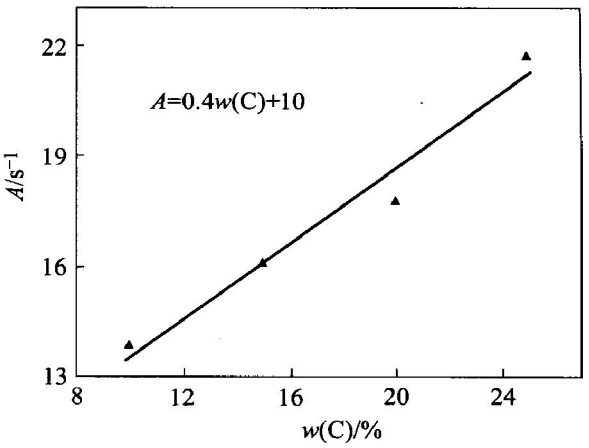

Fig. 4 Relationship between frequency factor A and carbon content w(C)

$$J = SD\frac{\mathrm{d}c}{\mathrm{d}r} = 4\pi r^2 D\frac{\mathrm{d}c}{\mathrm{d}r} \tag{26}$$

where c stands for the content of carbon monoxide, r for the radius of particles and D for the diffusion constant. The form of Eqn. (26) can be exchanged into Eqn. (27) as follows

$$\mathrm{d}c = \frac{J}{4\pi D}\frac{\mathrm{d}r}{r^2} \tag{27}$$

Integrate the Eqn. (27) in the range of carbon monoxide from initial content c_0 to c and radius of particle from initial size r_0 to r. In other word, by the way of $\int_0 \mathrm{d}c = \frac{J}{4\pi D}\int_0 \frac{\mathrm{d}r}{r^2}$, we can get

$$\Delta c = c_0 - c = \frac{J}{4\pi D}\frac{r_0 - r}{r_0 r}$$

or

$$J = \frac{4\pi D\,\Delta c r_0 r}{r_0 - r} \tag{28}$$

It is a steady diffusion in the second reduction stage so that Δc is a constant. The reactions of the reduction are in the form of $n\mathrm{Me}_x\mathrm{O}_y + m\mathrm{CO} =$ reduced products. Let $\alpha = m/n$, the diffusion quantity has the form of $J = -\mathrm{d}m/\mathrm{d}t = -\alpha\mathrm{d}n/\mathrm{d}t$ and

$n = \frac{4}{3}\pi r^3 \frac{\rho}{M}$ (M is the molar mass of metal oxide).

Differentiate n to time, get the following expressions:

$$\frac{dn}{dt} = \frac{dn}{dr}\frac{dr}{dt} = \frac{4\pi\rho dr^3}{3M\ dr}\frac{dr}{dt} = \frac{4\pi\rho r^2}{M}\frac{dr}{dt} \quad (29)$$

$$J = -\alpha\frac{4\pi\rho r^2}{M}\frac{dr}{dt} \quad (30)$$

According to Eqns. (28) and (30),

$$4\pi D\Delta c\frac{r_0 r}{r_0 - r} = -\alpha\frac{4\pi\rho r^2}{M}\frac{dr}{dt}$$

or

$$-\frac{MD\Delta c}{\alpha\rho}dt = (r - \frac{r^2}{r_0})dr$$

Integrate this equation in the time range from 0 to t and radius from r_0 to r, we get

$$\int_0 -\frac{MD\Delta c}{\alpha\rho}dt = \int_0 (r - \frac{r^2}{r_0})dr$$

or

$$-\frac{MD\Delta c}{\alpha\rho}t = \frac{1}{2}r^2 - \frac{1}{6}r_0^2 - \frac{1}{3}\frac{r^3}{r_0} \quad (31)$$

The relationship between particle radius r and reduction degree has the form of $r = r_0(1-g)^{1/3}$. Get this relationship into Eqn. (31), we have the function:

$$F(g) = 1 - \frac{2}{3}g - (1-g)^{2/3} = \frac{2MD\Delta c}{\alpha\rho r_0^2}t \quad (32)$$

Let

$$k = \frac{2MD\Delta c}{\alpha\rho r_0^2}$$

and it is a constant. So, we get

$$F(g) = 1 - \frac{2}{3}g - (1-g)^{2/3} = kt \quad (33)$$

The method for the determination of kinetic parameters of the second stage is in the same way as that of the first stage(see Fig. 5). The apparent activation energy of this stage is determined as 17.35 kJ/mol and frequency factor as 8.99. In this stage of reduction, the frequncy factor is not affected by the carbon content in the pellets. The kinetic

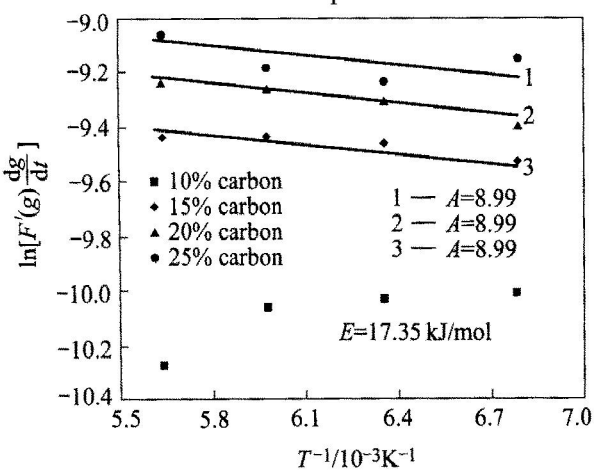

Fig. 5 Kinetics parameters of second stage of reduction

model of isothermal reduction process in the second stage is given in the form as follows:

$$1 - \frac{2}{3}g - (1-g)^{\frac{2}{3}} = 8.99e^{-\frac{17350}{RT}}t \quad (34)$$

4 CONCLUSIONS

1) The reduction process of stainless steelmaking dust pellets in the isothermal temperature condition is classified as consecutive two stages. The first stage of the reduction is dependent on the contact between the metal oxides in the dust and the carbon. The rate of reduction in this stage is controlled by the chemical reactions. The second stage of the reduction is dependent on the carbon monoxide passing through the reduced layer and the kinetics accords with a standard shrinking core model.

2) The activation energies of the first and second stage of the reduction processes are 21.69 kJ/mol and 17.35 kJ/mol respectively. They are smaller than that of the reduction of iron composites or chromite fines.

3) The kinetic model for the first stage reduction is $1-(1-g)^{\frac{1}{3}} = (0.4w(C) + 10)e^{-\frac{21690}{RT}}t$ and the model for the second stage reduction is $1 - \frac{2}{3}g - (1-g)^{\frac{2}{3}} = 8.99e^{-\frac{17350}{RT}}t$.

4) The reduction rate of the stainless steelmaking dust can be speeded up at higher temperature conditions.

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(Edited by YUAN Sai-qian)