

THERMODYNAMIC AND KINETIC INVESTIGATION OF CARBOTHERMIC REDUCTION OF ELECTRIC ARC FURNACE DUST

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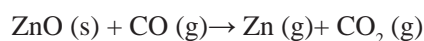
The thermodynamics and kinetics of electric arc furnace dust (EAFD) reduction were studied experimentally. The oxygen potential in the systems was determined by the electromotive force (EMF) method. Experimental equations for $\Delta G = f(T)$ were derived. The CO content at different temperatures was determined. The highest degree of reduction was observed at the ratio EAFD/reducing agent - 1:2 at a temperature of 1 173 K. The changes in the mass during heating, the rate of the processes, and the reduction degree were mathematically modeled. The activation energy is 74,7 kJ/mol for EAFD: reducing agent 1:1 and increased to 95,2 kJ/mol for the ratio EAFD: reducing agent 1:2,5. Analysis of the reaction kinetics showed that the reduction process was mostly chemical kinetics controlled.

Keywords: electric arc furnace dust, thermodynamic, kinetics, EMF method, activation energy

INTRODUCTION

In ferrous metallurgy, Electric Arc Furnace (EAF) generates dust between 10-30 kg/t of liquid steel [1]. The dust is finely dispersed and is formed due to the evaporation of the metal in the area of the activity of the electric arcs and the subsequent condensation and oxidation. The dispersion of the particles depends on the chemical composition of the materials, the technological regime, the period, and the condensation conditions. Steel scrap contains mainly iron as well as some non-ferrous metals. The content of zinc is more significant [2,3]. In the production of stainless steel, the zinc content is between 2-25 %, in high-alloy steel, it is 2 - 15 %, and in low-alloy steel, it is 21 - 43 % Zn.

The reaction of zinc oxide with carbon can be expressed as:



$$\Delta G_1 = \Delta G^0 (RT \ln K_p(T) + RT \ln \frac{P_{\text{CO}}}{P_{\text{Zn}} \cdot P_{\text{CO}_2}}$$

The rate of the heterogeneous reaction is:

$$r = k (P_{\text{CO}} - P_{\text{Zn}} \cdot P_{\text{CO}_2} / K_p)$$

The reduction of EAF dust is mainly controlled by the Boudouard reaction [4].

There are dozens of studies in the literature on the processing of EAFD and the reduction of zinc oxide, but still, only 32 % of the dust is used in the Waelz process, and a significant part of it is deposited. The carbothermal reduction of pure zinc oxide with various additives [5], under nitrogen atmosphere [6], kinetics reduction of zinc oxide [7], selective removal of zinc from EAF dust by microwave [8], etc. were studied.

The present study aims to determine experimentally the thermodynamic and kinetic parameters of carbothermal reduction of real waste dust from electric arc furnace production (waste EAF dust).

EXPERIMENTAL

Materials and equipment

The chemical composition was defined by weight, via ICP-OES analysis. The chemical composition of electric arc furnace dust (EAFD) is presented in Table 1. These elements are presented as oxides and complex minerals such as hematite (Fe_2O_3), magnetite (Fe_3O_4), zinc oxide (ZnO), and franklinite (ZnFe_2O_4).

The sieve analysis was done in a mechanical sieve shaker. The analysis showed a finely divided composition of the waste dust, the basic fraction below 0,06 mm being 34 %. The amount of dust below 0,20 mm was 65 %. There was no fraction over 1,4 mm. The reported bulk density was $0,9228 \text{ g/cm}^3$, and the pycnometric density was $\rho_{np} = 3,49 \text{ g/cm}^3$.

The amount of the reducing agent was determined by the stoichiometrically calculated amount of carbon needed. I studied three mixtures:

Mixture 1 - EAFD and carbon-reducing agent in a ratio of 1 : 1;

Mixture 2 - EAFD and carbon-reducing agent in a ratio of 1 : 2 and

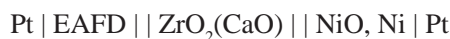
Mixture 3 - EAFD and carbon-reducing agent in a ratio of 1 : 2,5.

Table 1 **Chemical composition of electric arc furnace dust EAFD /wt. %**

| Fe | Zn | Pb | Cu | Cd | Cl |
|-------|-------|------|------|------|------|
| 27,40 | 20,34 | 3,29 | 0,25 | 0,11 | 2,30 |

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Thermodynamic studies of the three mixtures were performed using a galvanic cell with a comparative electrode mixture Ni - NiO in a ratio of 1:1. The test procedure was described in [9].



The $\Delta G^\circ_T(\text{NiO})$ values reported by authors [9, 10] and confirmed by $\Delta G^\circ_T(\text{NiO})$ in this paper



$$\Delta G^\circ(\text{NiO}) = -233\,651 + 84,893 T / \text{J/mol}$$

$$\lg P''_{\text{O}_2} = -12\,225/T + 4,44 \quad (2)$$

Oxygen partial pressure was calculated by the equation:

$$E = \frac{R \cdot T}{n \cdot F} \ln \frac{P''_{\text{O}_2}}{P'_{\text{O}_2}} \quad (3)$$

where E- measured EMF / V; R-gas constant 8,314 / deg K⁻¹mol⁻¹; n-number of the electrons taking part in the reaction; F- Faraday constant 9,6489.10⁴ / C.mol⁻¹; lnP''_{O₂} -oxygen pressure of the reference electrode; lnP'_{O₂} - oxygen pressure of the system under investigation.

A thermogravimetric apparatus was used to study the kinetics of the reduction of waste metallurgical products. The heating rate was 10 °C/min.

The rate of the process was calculated by the expression: $\vartheta = \mp \frac{\Delta m}{\Delta \tau \cdot m_0}$

where- ϑ is the average rate of the process / g/min; Δm is the change in the sample weight / mg; $\Delta \tau$ -the time change /min; m_0 - the initial weight of the sample /g.

The dependence of the rate constant of the reaction on the temperature is expressed by the Arrhenius equation.

$$k = A \cdot e^{-\frac{E_a}{R \cdot T}}$$

where: k-reaction rate constant; A- constant, E_a -activation energy / J/mol; T-temperature / K; R-gas constant. To calculate the apparent activation energy, the following dependence was used $\lg m - 2 \lg T = f(1/T)$.

RESULTS AND DISCUSSION

The thermodynamic results obtained from the galvanic cell measurements of the mixtures in different reducing agent - waste product (EAFD) ratios are presented in Table 2.

Based on the experimental values and the calculations done, Gibbs energy equations were derived $-\Delta G = f(T)$.

Mixture 1 (EAFD): reducing agent 1:1):

$$\Delta G_T = 43\,556 - 43,94 T / \text{J/mol} \quad R^2 = 0,8626.$$

Mixture 2 (EAFD): reducing agent 1:2):

$$\Delta G_T = 82\,634 - 81,78 T / \text{J/mol} \quad R^2 = 0,7482.$$

Mixture 3 (EAFD): reducing agent 1:2,5)

$$\Delta G_T = 50\,351 - 42,75 T / \text{J/mol} \quad R^2 = 0,9906.$$

R^2 – correlation coefficient

The obtained dependencies for $\Delta G = f(T)$ show that the following reactions took place:

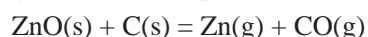


Table 2 Thermodynamic results of the studied mixtures.

| T / K | EMF / V | $\lg P_{\text{O}_2}$ | $\lg \frac{P_{\text{CO}_2}}{P_{\text{CO}}}$ | CO / % |
|--|---------|----------------------|---|--------|
| <i>Mixture 1 (EAFD : reducing agent 1:1)</i> | | | | |
| 1 163 | 0,325 | -17,74 | -0,7286 | 84,26 |
| 1 223 | 0,375 | -17,26 | -1,1115 | 92,82 |
| 1 273 | 0,380 | -16,31 | -1,1128 | 92,84 |
| <i>Mixture 2 (EAFD : reducing agent 1:2)</i> | | | | |
| 973 | 0,160 | -19,51 | 0,865 | 12,01 |
| 1 053 | 0,362 | -21,23 | -1,146 | 93,35 |
| 1 173 | 0,368 | -18,25 | -1,094 | 92,55 |
| <i>Mixture 3 (EAFD : reducing agent 1:2,5)</i> | | | | |
| 923 | 0,240 | -16,05 | 0,008 | 49,56 |
| 973 | 0,132 | -18,93 | 1,156 | 6,53 |
| 1 173 | 0,120 | -20,18 | 1,356 | 4,22 |

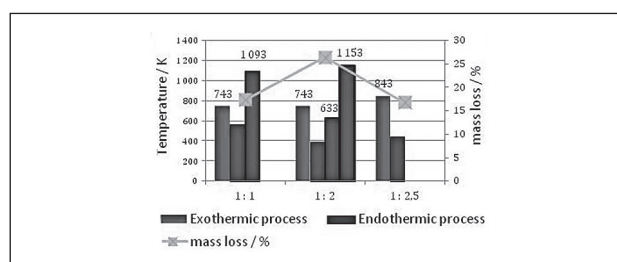


Figure 1 Differential thermal analysis (DTA) data for non-isothermal heating

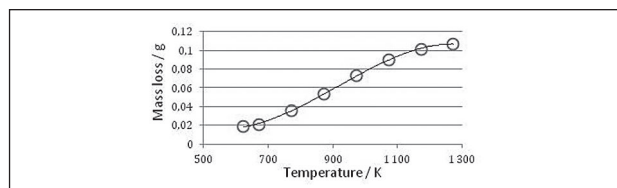
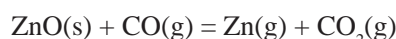
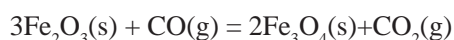


Figure 2 Dependence of the mass loss (m / g) on the temperature

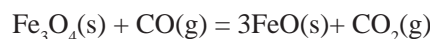
$$\Delta G^0 = 348\,480 - 286,1 T / \text{J/mol}$$



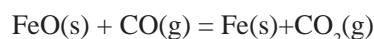
$$\Delta G^0 = 17\,8020 - 111,6 T / \text{J/mol}$$



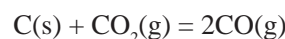
$$\Delta G^0 = -52\,130 - 41,0 T / \text{J/mol}$$



$$\Delta G^0 = 35\,380 - 40,16 T / \text{J/mol}$$



$$\Delta G^0 = -13\,160 + 17,21 T / \text{J/mol}$$



$$\Delta G^0 = 172\,130 - 177,46 T / \text{J/mol}$$

The thermodynamic analysis of the reactions taking place in the studied temperature range 873 K - 1 173 K showed that the reduction of the waste product with solid carbon proceeded mainly according to $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \alpha\text{Fe}$. The reaction $3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2$ was completely irreversible due to the high dissociation pressure of Fe_2O_3 reaching up to 0,01 MPa at 1 725 K resulting in the complete oxidation of CO to CO_2 .

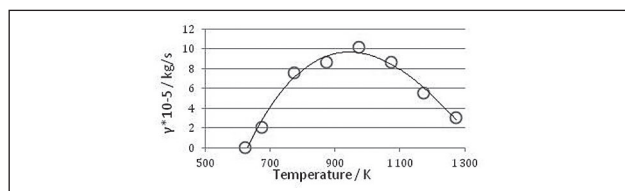


Figure 3 Dependence of the rate ($\gamma \cdot 10^{-5}$ / kg/s) on the temperature

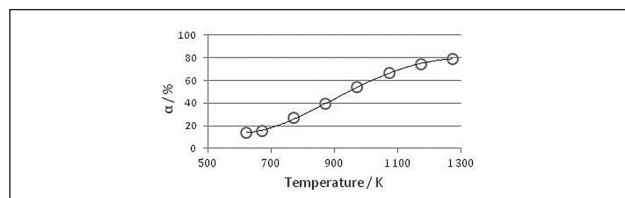


Figure 4 Dependence of the reduction degree (α / %) on the temperature

A high degree of reduction was observed with mixture 2 (EAFD : reducing agent =1:2). The maximum of the ongoing processes moved from 1 223 K for mixture 1 to 973 K for mixture 3. In all samples, iron oxides were reduced to FeO and iron. The reduction of zinc oxide proceeds at a sufficiently high rate at temperatures above 1 273 K – 1 373 K. The rate of reduction of zinc oxide with carbon depends on the rate of the gasification reaction of the solid carbon.

Figure 1 presents the main exothermic and endothermic effects and compares the mass losses of the studied samples during non-isothermal heating. At EAFD: reducing agent ratios of 1:1 and 1:2, the mixtures had an exothermic peak recorded at 743 K. The endothermic peaks of mixture 1 and 2 had a similar character. For mixture 2, the highest mass loss was recorded. The peak at 743 K was due to the reduction of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, and the endothermic effect at 1 153 K of the $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$ transition. The lower degree of reduction for mixture 1 was explained by a deficit of the reducing agent.

The obtained values of the apparent activation energy of the studied mixtures:

Mixture 1 - $E_a = 74,7$ / kJ/mol

Mixture 2 - $E_a = 77,2$ / kJ/mol

Mixture 3 - $E_a = 95,2$ / kJ/mol

Figures 2 to 4 graphically depict the mass loss (m / g), rate ($v \cdot 10^{-5}$ / kg/s), and the degree of reduction (α / %) depending on the temperature of mixture 2 where the highest degree of reduction was recorded.

The kinetic parameters were mathematically modeled based on the regression analysis, which makes a connection between the initial value and the factors $\eta = \eta(x_1, x_2, \dots, x_m)$,

where η is the conditional mathematical expectation of the initial value (y) at given values of the factors.

The mathematical expectation η in the proximity of x_0 is represented by:

$$\eta(x) = \beta_0 + \sum_{i=1}^m \beta_i x_i + \sum_{i=1}^{m-1} \sum_{j=i+1}^m \beta_{ij} x_i x_j + \sum_{i=1}^m \beta_{ii} x_i^2$$

The smallest residual amount of the dispersion was the factor for the appropriate models to be selected. The

Table 3 Dispersion (S) of the studied kintic models

| Order | 1 | 2 | 3 | 4 | 5 |
|-----------------|-------|-------|-------|-------|-------|
| $m = f(T)$ | 0,217 | 0,197 | 0,011 | 0,007 | 0,011 |
| $\gamma = f(T)$ | 13,93 | 0,58 | 0,47 | 0,52 | 0,76 |
| $\alpha = f(T)$ | 11,79 | 3,65 | 0,59 | 0,39 | 0,59 |

obtained dispersion of the models from the first to the fifth order is presented in Table 3.

The change in mass (m / g) as a function of temperature was best described with the third- and fourth-order models, due to the lowest dispersion obtained.

$$m = 0,2798 - 0,0011 T + 1E-06 T^2 - 5E-10 T^3 / g$$

$$\text{at } R^2 = 0,9995$$

$$m = 0,6305 - 0,0027 T + 4E-06 T^2 - 2E-09 T^3 + 5E-13 T^4 / g$$

$$\text{at } R^2 = 0,9998$$

The process rate as a result of the temperature was described by the second-order and third-order models:

$$\gamma = - 65,45 + 0,1548 T - 8E-05 T^2 / \text{kg/s}$$

$$\text{at } R^2 = 0,969$$

$$\gamma = - 106,05 + 0,2918 T - 0,0002 T^2 + 5E-08 T^3$$

$$\text{at } R^2 = 0,9796$$

The degree of reduction process as a function of temperature was described with the third-order and fourth-order models:

$$\alpha = 206,45 - 0,811 T + 0,001 T^2 - 4E-07 T^3 / \%$$

$$\text{at } R^2 = 0,9995$$

$$\alpha = 465,24 - 1,9739 T + 0,003 T^2 - 2E-06 T^3 + 4E-10 T^4 / \%$$

$$\text{at } R^2 = 0,9998$$

Although in Mixture 3, the activation energy was the highest, the degree and rate of reduction had the lowest values. The latter can be explained by the fact that the carbon contained in the mixture was consumed to a lesser amount for reduction, and to a greater amount, it burned. In addition, in Mixture 3 the oxidation potential was the highest, which indicated a higher amount of CO_2 .

According to the literature, the activation energy of the gasification reaction is in the range of 175 kJ/mol – 217 kJ/mol. Bafghi et al. [7] obtained 75,9 kJ/mol. (18,13 kcal/mol) energy when reducing zinc oxide with coke. The average energy value of carbothermic reduction by charcoal calculated from the data of non-isothermal experiments was 222 kJ/mol for zinc oxide [11]. The volatilization reaction rate of lead in the EAF dust was controlled by solid-solid diffusion and had an energy of 175 kJ/mol (41,8 kcal/mol) [12]. The energy for the carbon gasification reaction was estimated to be 38,21 kJ/mol [13].

The results of the kinetic studies of dust from the electric steel production show that with increasing the amount of used reducing agent (coke fines), in the ratios from 1:1 to 1:2.5, the activation energy increases from 74,7 kJ/mol to 95,2 kJ/mol. The bigger amount of reducing agent used compared to the stoichiometrically calculated one adds additional activation energy as the process continues by the carbon gasification reaction.

CONCLUSION

The results of the experiments and the derived equations for $\Delta G = f(T)$ show that the investigated electric arc furnace dust was reduced according to the $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow a\text{Fe}$ reaction sequence. Zinc oxide was reduced and passed into the gas phase at temperatures above 1 300 K. The activation energy for the tested mixtures (the ratio EAFD: coke fines - 1:1, 1:2, and 1:2,5) was in the range of 74,7 kJ/mol – 95,2 kJ/mol, which is typical of the kinetic region.

The derived equations give a mathematical expectation of the studied material but also of materials similar in composition. It has been found that the best thermodynamic and kinetic results of reduction of pelleted dust from electric arc furnace production, including zinc extraction, are achieved at a solid carbon-containing reducing agent content twice above the stoichiometrically calculated amount and temperatures between 1 283 K and 1 423 K. It is not wise to carry out the heating above this temperature, because melting occurs.

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Note: The responsible for English language is PhD Maria Todorova, Sofia, Bulgaria