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Thermochimica Acta 278 (1996) 129–134

thermochimica
acta

Dependence of zinc oxide reduction rate on the CO concentration in CO/CO₂ mixtures

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Received 27 June 1995; accepted 15 October 1995

Abstract

A combined experimental and theoretical approach presents the kinetics of ZnO reduction as a function of CO content and temperature. The equation that gives the dependence between these variables is developed. The rate constant values are verified with the topochemical model. The Arrhenius activation energy value of 60.15 kcal mol⁻¹ identifies the reaction as being chemically controlled. The study of the temperature effect is conducted within the 1183–1497 K temperature range, and the CO concentration is maintained at selected constant values between 17% and 100% CO.

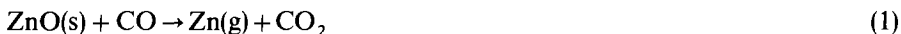
Keywords: Kinetics; Modeling; Reduction; Zinc oxide

1. Introduction

A series of experiments was conducted to determine the kinetics of ZnO reduction by CO as a function of temperature and CO content. This reaction plays an important role in several metallurgical processes and has been investigated by a number of authors, resulting in different models due to the strong kinetic dependence on the solid oxide properties. Refs. [1–3] reported chemically controlled kinetics. Refs. [4] and [5] concluded mixed kinetics control. Somewhat more detailed experiments were done in Refs. [6] and [7], where the structure and disorder of the ZnO dependence in the reaction ZnO + CO was investigated. The present experimental work was done to analyze and interpret the topochemical model. The relation between measured mass change and maximum possible degree of mass change was used to measure the progress

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of the reaction [8]. The process chemistry is based on the reaction



where gaseous zinc is produced. In this case, the maximum degree of mass change of the sample ΔM_0 is equal to 100%. The expression for the rate constant as a function of temperature and CO concentration is developed using these parameters and according to the topochemical model [8, 9]. The first derivative of mass loss versus time is plotted according to the model and experiments were carried out to determine how closely the model prediction fits the measured data during the initial stages of the process.

2. Model equations

The ZnO reduction process can be simulated by a topochemical model using known formulae [9] for spherical particles. The general rate equation is

$$\frac{dM}{dt} = -S\bar{k}_i f(x_i) \quad (2)$$

where $f(x_i)$ is a function of gas composition and the constant \bar{k}_i depends only on the CO concentration.

The subsequent expressions are $S = S^0(r/r_0)^2$ and $S^0 = M^0 S^*$, where the terms M^0 , S^0 , S and S^* represent initial mass, initial surface, surface of unreacted particle and specific surface, respectively. The surface area change during the process can be represented by

$$r = r_0 \left(1 - \frac{\Delta M}{\Delta M_0}\right)^{1/3} \quad (3)$$

where $\Delta M_0 = M^0 - M_{\text{final}}$ represents the maximum possible degree of mass change. The relation $\Delta M/\Delta M_0$ expresses the extent of reaction progress and can be expressed

$$\frac{\Delta M}{\Delta M_0} = x$$

Then Eqs. (2) and (3) are modified to

$$S = S^0(1 - x)^{2/3} \quad (4)$$

$$\frac{dM}{dt} = -M^0 S^* \bar{k}(1 - x)^{2/3} \quad (5)$$

Moreover, the rate derivatives $\dot{x} = d(\Delta M/\Delta M_0)/dt$ and $\dot{x}\Delta M_0 = dM/dt$ give the following expression

$$\dot{x} = -M^0/\Delta M_0 k(1 - \Delta M/\Delta M_0)^{2/3} \quad (6)$$

where $k = \bar{k}S^*$. Integrating Eq. (6) once, with respect to mass M and time t , results in

$$k = \frac{3\Delta M_0}{M^0 t} \left[1 - \left(\frac{\Delta M}{\Delta M_0}\right)^{1/3}\right] \quad (7)$$

$$\Delta M = \Delta M_0 \left[1 - \left(\frac{k M^0 t}{3\Delta M_0}\right)^3\right] \quad (8)$$

The dependence of the constant \bar{k} on the CO concentration is usually found to fit an expression of the form

$$\ln \bar{k} = C + n \ln X_{\text{CO}} \quad (9)$$

where n is the power law exponent for the reaction with respect to CO.

3. Experimental results and discussion

A gravimetric technique was applied to determine the isothermal weight loss of each 100-mg reactant sample, using pure analytical grade zinc oxide (Baker reagent). The process was carried out with a gas flow rate of 8 l h⁻¹ and six different CO/CO₂ mixtures were used. The comparison between experimental data and calculated weight loss values is satisfactory, but some measurements show more scatter. For all the gas mixtures studied, the Arrhenius activation energies were evaluated using regression analysis. Within the scattered experimental points, the results are in good agreement with a linear dependence of the rate constant versus the reciprocal temperature. This interpretation, which uses the expression $\ln k = a + bT^{-1}$, is presented in Table 1.

Small variations of the activation energies with regard to CO contents were observed. The mean value $E = 60.15 \text{ kcal mol}^{-1}$ has the standard deviation $\pm 3.25 \text{ kcal mol}^{-1}$. To unify the kinetic description, this average value is applied, and the expression for the rate constant is reasonably well expressed as

$$k = \bar{k} e^{-60150/RT} \quad (10)$$

The activation energies and rate constant values \bar{k} are listed in Table 1. The proposed unification does not cause noticeable deviation from the original description. The dependence of the constant \bar{k} on CO concentration, calculated by Eq. (9), is given by

$$\ln \bar{k} = 21.733 + 3.08 \ln X_{\text{CO}} \quad (11)$$

Finally, the rate constant is expressed according to

$$k = e^{-60150/RT} e^{21.733} X_{\text{CO}}^{3.08} \quad (12)$$

Table 1
Rate constant characterization done with the expression $\ln k = a + bT^{-1}$

| %CO | a | b | $E(\text{kcal mol}^{-1})$ | $\ln \bar{k}$ | R^2 |
|-----|--------|----------|---------------------------|---------------|-------|
| 17 | 15.600 | -29359.3 | 58.30 | 16.261 | 0.977 |
| 27 | 18.645 | -31211.3 | 61.98 | 17.945 | 0.990 |
| 50 | 19.440 | -31106.5 | 61.70 | 18.836 | 0.959 |
| 62 | 22.218 | -32184.0 | 63.85 | 20.689 | 0.987 |
| 83 | 19.290 | -27941.4 | 55.49 | 21.180 | 0.983 |
| 100 | 21.536 | -29972.0 | 59.52 | 21.797 | 0.983 |

The factor $e^{21.733}$, which corresponds to $\ln \bar{k} = 21.733$, is very close to the value of the constant $\ln \bar{k} = 21.797$, determined for the experimental condition of 100% CO. The model predicted represents the weight loss results fairly well (Fig. 1).

To know how close the model predictions compare to the process real conditions at its initial stage, the first mass derivatives versus time for $t=0$ are calculated,

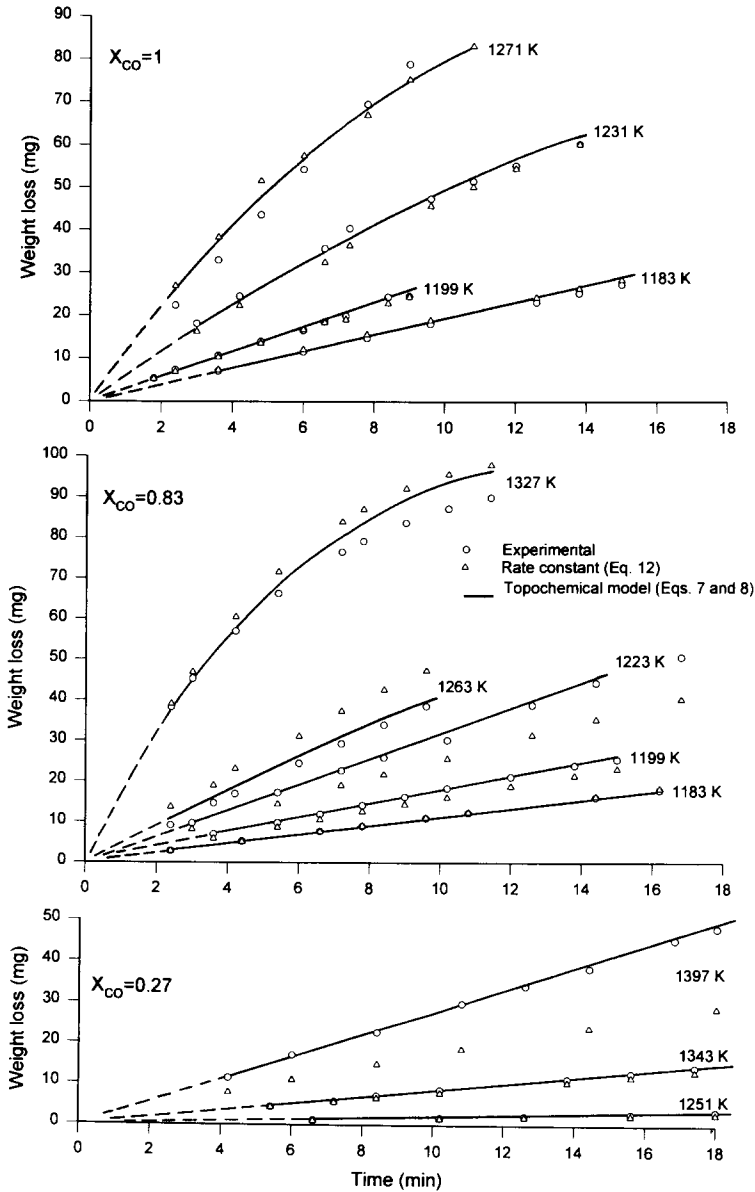


Fig. 1. Experimental and calculated sample isothermal weight losses (100 mg samples) during ZnO reduction.

and the expression

$$\left. \frac{dM}{dt} \right|_{t=0} = -kM^0 \quad (13)$$

represents the maximum rate of the reaction.

The measured weight loss data show a linear tendency within the initial period of time, and the experimental initial derivative is calculated by

$$\left. \frac{dM}{dt} \right|_{t=0} = \frac{M(t_1) - M(t_0)}{t_1 - t_0} \quad (14)$$

Fig. 2 confirms that the model predictions fit the measured data for ZnO reduction during the initial stage. Although some experimental scatter is present for the CO concentrations, the general reaction trend is established.

It can be seen clearly from the results in Figs. 1 and 2 that the value of the CO/CO₂ ratio strongly affects the reaction rate and that this rate is sensitive to temperature for constant CO concentration. The weight loss versus time was registered for six CO/CO₂

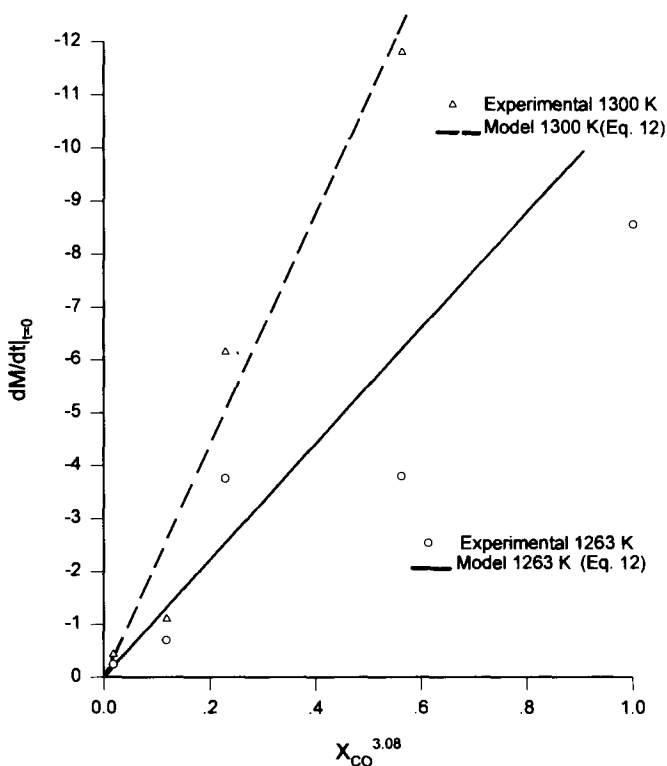


Fig. 2. Relation between mass derivative during the initial stages of the process and CO concentration (mass derivative calculated from experimental data and Eq. 12)

mixtures, each of them in six separate tests at six different temperatures. For a small X_{CO} value, the temperature interval had to be higher and, for example, for $X_{\text{CO}} = 0.17$ at 1498 K, the weight loss data obtained was approximately 36% after 17 min. However, the reduction was complete after 12 min at 1271 K in pure CO.

It can be observed (Fig. 1) that the isothermal weight loss of the sample, which was calculated using the rate constants from Eq. (7), provides a good fit with the experimental data. However, a broad scattering occurs when the rate constant interpretation is made using Eq. (12). Fig. 1 shows some points calculated for this interpretation based on the equation with the power law exponent for the reaction with respect to CO. Under some conditions, less agreement occurs with the topochemical model for this case.

4. Conclusions

ZnO reduction by CO is chemically controlled and the activation energy value of $60.15 \text{ kcal mol}^{-1}$ is consistent with this model. This assertion is confirmed since the activation energy does not depend noticeably on CO concentration and the gaseous products Zn(g) and CO_2 are removed from the interface. The ZnO reduction rate shows a strong temperature dependence, which also supports the kinetic control. A reasonable agreement between the contracting volume topochemical model and experimental results was found.

Acknowledgments

The authors would like to express their sincere gratitude to Prof. M. Sukiennik, University of Mining and Metallurgy of Cracow, Poland, for the valuable information provided. Financial support from National Science and Technology Council (CONACyT), México, is greatly appreciated.

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