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Research Paper

Experimental and numerical investigation of silicothermic reduction process with detailed chemical kinetics and thermal radiation

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HIGHLIGHTS

- A uniform chemical reaction model of the silicothermic reduction process was investigated by experiments.
- A three-dimensional numerical approach incorporating chemical reaction, radiation and heat conduction models is developed.
- The DTRM radiation model is considered the most reliable and accurate model.
- The effects of radiation model on reduction extent and temperature distribution were investigated.

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ABSTRACT

This paper presents an experimental study on the intrinsic chemical dynamics mechanism of the silicothermic reduction process and a single uniform chemical reaction model which is in accord with Arrhenius' equation under the silicothermic reduction conditions was obtained. The equation of the uniform chemical reaction model can be represented by $1-(1-\alpha)^{1/3} = k_0\exp(-E/RT)\tau$ in the temperature range 1273–1473 K (1000–1200 °C) and the apparent activation energy is a function of reaction time. Then, a three-dimensional unsteady numerical approach incorporating the chemical reaction, radiation and heat conduction models was first developed and verified by industrial production data of the magnesium production enterprises. The most appropriate radiation model was proposed and the simulations of the impact of radiation heat transfer on the magnesium reduction extent and temperature distributions were carried out utilizing this model. The analysis showed that the radiation heat transfer is an important factor in the heat transfer process in the retort. For the intensity of the radiation varies dramatically with temperature, the radiation model must not be ignored or simplified to be a heat conduction mode during the numerical calculation for the purpose of increasing the calculation accuracy. It is also concluded from the numerical results that the heat transfer efficiency is low in the initial stage, so improving the heat conduction rate could increase the magnesium production capacity, especially in the initial phase of the reduction process.

1. Introduction

Magnesium and magnesium alloys now have important application value and broad application prospects because of its advantages such as low density, high specific strength, high specific rigidity and high performance of electromagnetic shielding [1–3]. In China, the current annual primary magnesium production capacity is more than 698,000 metric tons in 2012, accounting for more than 80% total global magnesium metal production. Despite the increased demand for primary magnesium in recent years, the major techniques for producing magnesium did not make great achievements. Almost all of the primary magnesium is produced by the silicothermic reduction (Pidgeon process) [4], which was invented in 1940s in Canada [5].

In the silicothermic reduction process, magnesium vapor is produced from calcined dolomite using ferrosilicon as a reducing agent. Because it is highly endothermic, the reaction environment should be maintained at a high level of about 1473 K (1200 °C), which could be provided by special retorts mounted in the magnesium reducing furnace [6]. In order to protect the magnesium vapor from oxidation during the reduction process, the reaction must be conducted in vacuum of 10 Pa,

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Nomenclature

a	absorption coefficient
c_b	specific heat of briquette (J kg^{-1})
c_r	specific heat of retort (J kg^{-1})
$\frac{d\alpha}{d\tau}$	the change in rate of reduction extent with time
I	total hemispherical intensity (W)
I_0	radiant intensity at the start of the incremental path (W)
k_0	pre-exponential constant (min^{-1})
M_b	maximum magnesium production per unit volume (mol m^{-3})
Mg_c	quantity of magnesium condenser (kg)
Mg_i	initial quantity of magnesium in the experimental briquettes (kg)
Mg_r	quantity of residual magnesium in the unreacted slag (kg)
S_b	magnesium reduction heat source used in Eq. (7) (W m^{-3})
τ	magnesium reduction time in experiment and numerical model (min)
T	local temperature (K)
ϕ_b	thermal energy required per mole of magnesium (J mol^{-1})
ρ_b	density of the briquette (kg m^{-3})
ρ_r	density of the retort (kg m^{-3})
α	extent of magnesium reduction
λ_b	thermal conductivity of briquette (W m^{-1} K^{-1})
λ_r	thermal conductivity of retort (W m^{-1} K^{-1})
σ	Stefan-Boltzmann constant (5.67×10^{-8} W m^{-2} K^{-4})
ε_b	emissivity of briquette
ε_r	emissivity of retort wall

Abbreviations

XRD	X-ray Diffraction
SEM	Scanning Electron Microscope
DO	Discrete Ordinate
DTRM	Discrete Transfer Radiation Model

which is also provided by the retorts. All of the consumption materials including dolomite, ferrosilicon and fluorite are solid, so they must be rubbed to 200 mesh for the purpose of accelerating the reaction rate. These three kinds of mixed powder materials were briquetted by the dry powder pigeonhole ball machine apparatus under a certain pressure to produce briquettes with a shape of walnut. Then the briquettes were placed inside the retorts and were heated to the optimal reaction temperature to conduct the reduction process. The overall reaction of this process took place in the retorts could be expressed as follows:

$$2(CaO{\cdot}MgO)_{(s)} + Si(Fe)_{(s)} \xrightarrow[CaF_2]{1373-1473\ K,\sim 10\ Pa} 2Mg_{(g)} + 2CaO{\cdot}SiO_{2(s)} + Fe_{(s)} \quad (1)$$

Through the past decades, people have done a great deal of experiment research on the chemical dynamics mechanism of the silicothermic reduction [7–9] and the shrinking non-reacted core model [10] was usually applied to describe this process. The physiological data used in the model were obtained from experiments which were conducted on single briquette, the effect of heat conduction in the briquette on the chemical dynamics mechanism of the silicothermic reduction must not be ignored, so the shrinking non-reacted core model cannot be accurately described the intrinsic kinetics of this chemical reaction. As chemical dynamics mechanism of the silicothermic reduction is controversial, the instant endothermic quantity of the chemical reactions took place in the retorts could not be calculated accurately and as a result, the results of the numerical simulation study using existing magnesium reduction models were also not accurate. The reaction heat was treated as a constant by Xia et al. [11] and a function of temperature by Yu et al. [12], respectively. Li et al. [13] calculated the instant endothermic quantity of the chemical reactions according to the experimental data and applied that to a numerical model which was used to simulate the silicothermic reduction process. But since they did not establish a real three-dimensional physical model and they adopted the heat conduction model to replace the real radiation model in order to simplify the numerical simulation model, the simulation results were not sufficiently precise.

Therefore, the aim of this work is to study the intrinsic chemical dynamics mechanism of the silicothermic reduction process and a single uniform chemical reaction model which is in accord with Arrhenius' equation under the silicothermic reduction conditions. Then a real three-dimensional physical model which could simulate the true arrangement of briquettes packed layer in the retort was established and a most appropriate radiation model was applied to simulate the heat transfer between the briquettes under vacuum condition. As an early attempt in considering chemical reaction and radiation heat transfer in the retort, this article first verified the three-dimensional numerical simulation method incorporating the radiation, heat conduction and chemical reaction models, by comparing with the experimental data from metal magnesium enterprises. Moreover, it discussed magnesium reduction extent characteristics and the temperature characteristics in the retort region during the silicothermic reduction process.

2. Experimental procedure

2.1. Materials

For the present study, the materials of qualified dolomite, 75% ferrosilicon alloy and fluorite powder were provided by the Kaitai Magnesium CO. Ltd in China. The chemical compositions of dolomite and 75% ferrosilicon alloy are listed in Tables 1 and 2, respectively.

2.2. Method

Qualified dolomite was calcined at 1373 K for 1 h and the dolime was produced in this calcination process. Then the dolime and 75% ferrosilicon alloy were pulverized to 200 mesh in a ball mill and were mixed with fluorite powder whose grain size was also below 200 mesh. For eliminating the effect of heat conduction on the results of intrinsic chemical dynamics experiments, the thickness of the briquettes which were briquetted in a plunger press at 160 MPa must be controlled within 1 mm. In our experiments, the diameter of the briquettes was set to about 25 mm to make sure each of the experiment subjects has a certain weight. The geometry and size of the briquettes is shown in Fig. 1.

Table 1
Chemical analysis of qualified dolomite (wt%).

MgO	CaO	SiO_2	Fe_2O_3	Al_2O_3	CO_2
20.25	33.81	0.31	0.10	0.04	45.49

Table 2
Chemical analysis of 75% ferrosilicon alloy (wt%).

Si	Fe	Al	Ca	Mn	Cr	C
76.0	21.8	0.8	0.7	0.4	0.2	0.1