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Isothermal oxidation kinetics of ilmenite concentrate powder from Panzhihua in air

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ABSTRACT

The objective of this study was to establish the kinetics of oxidation of ilmenite concentrate powders, which promotes reduction via the oxidation process. In this paper, the kinetics of the oxidation of ilmenite concentrate powders from low temperature to high temperature was studied comprehensively using the thermal gravity method. The reaction mechanism and model function were studied using two different classical methods, and then the results were compared. The results showed that, when the oxidation temperature was below 973 K (700 °C), the reaction mechanism is the three-dimensional diffusion, and the model function was $G(\alpha) = (1-\frac{2}{3}\alpha)-(1-\alpha)^{2/3}$ (α, reaction degree). When the temperature was above 1273 K (1000 °C), the reaction mechanism is random nucleation and subsequent growth, and the model function was $G(\alpha) = [-\ln(1-\alpha)]^{1/3}$. No single model function can fit well the oxidation process at 1023 K (750 °C), 1073 K (800 °C), 1123 K (850 °C), and 1173 K (900 °C); thus, a multistage mechanism was proposed to explain the reaction process; this mechanism includes three-dimensional diffusion, random nucleation and subsequent growth in the order of increasing reaction degree. The apparent activation energies for the oxidation were also studied using two different methods: 199.43 and 194.01 kJ/mol at 873 K (600 °C), 923 K (650 °C), and 973 K (700 °C); 4.11 and 3.96 kJ/mol at 1273 K (1000 °C), 1373 K (1100 °C), and 1473 K (1200 °C). The relationship of oxidation degree with time and temperature is also discussed, which is helpful for the selection of the parameters of the oxidation process.

1. Introduction

A mineral of ilmenite type is a common raw material to produce titanium dioxide and titanium metal. The ilmenite concentrate from Panzhihua, which is mainly composed of $FeTiO_3$, $MgTiO_3$ and Fe_3O_4, is an important mineral resource for TiO_2 pigment production in China [1,2]. The reduction and smelting of ilmenite in an electric arc furnace (EAF) is necessary for the subsequent enrichment or extraction process. However, the ilmenite is difficult for reduction because of the formation of stable phase between FeO and TiO_2 with the existence of high MgO [3]. As a result, a significant amount of electivity energy is consumed during the EAF process. The oxidization of ilmenite can change the crystal structure and form new phases, such as Fe_2TiO_5, Fe_2O_3 and TiO_2, which can easily be reduced [4]. The oxidation of ilmenite concentrate process converts the lower oxides of iron to higher oxides and enhances the subsequent rate of reduction to metallic iron [5]. Therefore, an oxidization pretreatment before the reducing and smelting process is recommended for the Panzhihua ilmenite concentrate [6,7]. There are many researchers who have studied the effect of pre-oxidation on ilmenite concentrate. Some researchers have found that pre-oxidation destroyed the crystal lattice of raw titanomagnetite concentrates and increased the specific surface area, which can accelerate the reduction process [1,8]. Others have also recognized that pre-oxidation can enhance the rate of the reduction [9–12]. Although pre-oxidation is beneficial to the subsequent reduction process, the pre-oxidation process also consume some energy, and whether the energy consumed for the oxidation process is worth or not should be better studied and make it operate in an optimization condition.

There are many researchers have studied the oxidation of ilmenite powders. Rao and Rigaud [13], Fu et al. [14] and Lu et al. [15] found that the oxidation products of ilmenite concentrate change with oxidation temperature. The products can be divided into three parts corresponding to three different temperature levels. At the relative low temperature (below 1043 K/770 °C), the oxidation products are TiO_2 and Fe_2O_3. At intermediate temperatures (1043 K/770 °C-1273 K/1000 °C), the products are TiO_2 and $Fe_2Ti_3O_9$. When temperature is above 1273 K (1000 °C), Fe_2TiO_5 is the only stable phase product. Mozammel et al. [16] studied the kinetics of the isothermal oxidation of Iranian ilmenite concentrate powder found that below 973 K (700 °C) chemical reaction

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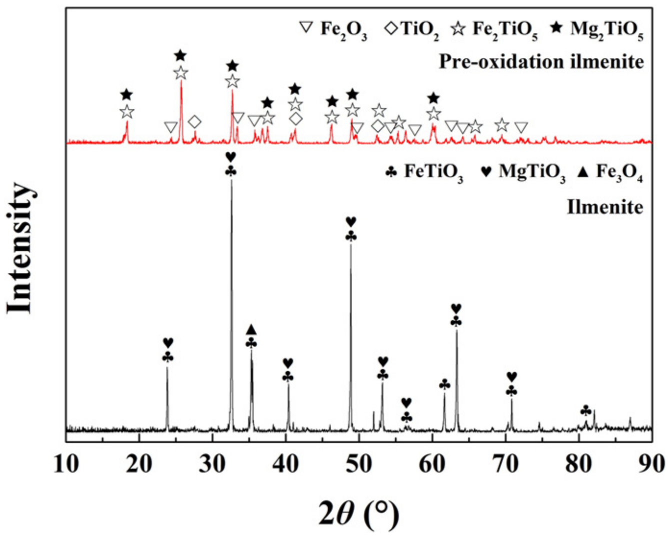

Fig. 1. XRD pattern of ilmenite and oxidized ilmenite concentrate powders.

was rate controlling step and above 1073 K (800 °C) diffusion through the product layer controlled the oxidation reaction. Gillot et al. [17] studied the phase transformation-related kinetic in the oxidation of a manganese mixed oxide powder with a spinel structure, they found that below 723 K (450 °C), the oxidation kinetics are controlled by a diffusion, and above 723 K (450 °C), the kinetic mechanism is nucleation-growth mechanism. Jablonski and Prezepiera [18,19] have focused on non-isothermal oxidation kinetics (293 K/20 °C–1273 K/1000 °C) of Norwegian ilmenite concentrate and Canadian titanium slag. They found that the oxidation of titanium slag can be divided into two stages, and the activation energy for the first oxidation stage is in average 55.42 kJ/mol and for second stage is about three times higher and its mean value is 144.27 kJ/mol. They also found that the contracting interfacial surface with activation energy of 30.88 kJ/mol has the main influence on the oxidation kinetics of the Norwegian ilmenite concentrate. Sun [20] studied the oxidation kinetics of ilmenite powder in a fluidized bed and found that the oxidation rate was mainly controlled by the intrinsic chemical reaction at 1053–1153 K (780–880 °C). They also studied the oxidation kinetics of pellet-shaped cement-bonded ilmenite in temperature range 1073–1273 K (800–1000 °C), the reaction was controlled by the intraparticle diffusion and the intrinsic chemical reaction [21,22]. Han et al. [23] investigated the high-temperature oxidation behavior of vanadium titanium-bearing magnetite pellet, they found that oxidation process of pellet is controlled by chemical reaction from temperature 1073 (800) to 1223 K (950 °C) and mixed-controlled by chemical reaction and diffusion between temperature 1223 (950) and 1273 K (1000 °C). When oxidation temperature exceeds 1273 K (1000 °C), the limited link of oxidation reaction is the diffusion. D. Papanastassiou and Bitsianes [24] investigated the mechanisms and kinetics underlying the oxidation of magnetite in the induration of iron ore pellets, the results showed that below 693 K (420 °C) chemical reaction was the controlling step of the overall reaction. Above 693 K (420 °C), mass transfer through the gaseous boundary layer dominated the reaction rate and was the controlling step. All in all, mineral species, particle size (pellet or powder) and temperature play remarkable role in mechanisms of oxidation. According to the literature, the oxidation rate can be controlled by diffusion, chemical reaction or nucleation-growth.

From the situation mentioned above, it has become obvious that temperature range in the previous research about oxidation of ilmenite concentrate powder is relatively narrow, and the reaction mechanism transformation and restriction factors are not clearly understood at different temperature levels. There are different mechanisms of transformation over a very wide range of temperature, and there is even a temperature interval controlled collectively by several mechanisms. Identification of these mechanisms for the Panzhihua ilmenite concentrate is deficient, especially the reactions at high temperature (above 1273 K/1000 °C). Therefore, in this paper, the isothermal kinetics of the Panzhihua ilmenite concentrate in air at a very wide range of temperatures was studied using the Thermal Gravity (TG) technique. The classic methods are used to study the mechanism and the model function of the reaction mechanism can be established.

2. Material and methods

The ilmenite concentrate powder used in this study was obtained from Panzhihua Steel Company. An X-ray diffraction (XRD) experiment and a chemical component analysis were performed on the samples. The XRD pattern of the ilmenite concentrate and its oxidation product are shown in Fig. 1, the chemical composition analysis results (pure oxides) are shown in Table 1. Both Fig. 1 and Table 1 indicate that $FeTiO_3$ and Fe_2TiO_5 were the main component of the ilmenite concentrate and oxidized ilmenite concentrate, respectively. The SEM morphology images of both the ilmenite and oxidized ilmenite concentrate are shown in Fig. 2(a) and (b), respectively. From Fig. 2, the surface of the ilmenite concentrate is observed to be smooth and compact. However, there are many protuberances and cracks on the surface of the oxidized ilmenite concentrate, which can increase the specific surface area and can be of great benefit to the reduction.

The TG experiments were conducted using a Setaram Evo TG-DTA 1750 thermal analyzer. The heating rate adopted in all the experiments was 20 K/min; the isothermal temperatures were 873 K, 923 K, 973 K, 1023 K, 1073 K, 1123 K, 1173 K, 1273 K, 1373 K, and 1473 K. The size of the particles for ilmenite concentrate was 100–200 mesh. All test samples were placed in alumina crucibles, each of which is 8 mm in height and 6 mm in diameter. The weight of each of the samples was 191 ± 0.5 mg. Before the heating process, the reaction vessel was initially pumped down to vacuum level and subsequently filled with Ar. During the heating process, the flowing rate of Ar that filled the reactor was 20 mL/min to eliminate the interference of other reactions. After the temperature reached a fixed value, air was filled into the reactor instead of Ar at a flow rate of 20 mL/min until the completion of the oxidation reaction.

3. Results and calculation

3.1. TG analysis

Fig. 3 shows the TG curves of ilmenite concentrate powder samples reacting in air at temperatures ranging from 873 K (600 °C) to 1473 K (1200 °C). Over time, the weight of each sample increases because of oxidization. The reaction rate, which is reflected in the slope of the weight increase curves, significantly increases with increasing temperature. For all the samples, the oxidization rate decreases with time, in other words, oxygen diffusion decelerates from the outside to the

Table 1
Experiment of ilmenite and oxidized ilmenite concentrate sample chemical composition analysis (wt%).

	TiO_2	FeO	Fe_2O_3	MgO	SiO_2	Al_2O_3	CaO	MnO	V_2O_5	S	P
Ilmenite	46.82	34.52	6.10	5.66	3.23	1.00	0.842	0.635	0.058	0.14	<0.005
Oxidation ilmenite	45.17	0.772	42.76	4.78	2.95	1.25	0.761	0.745	0.063	0.09	<0.005