Oxidation kinetics of ilmenite concentrate by non-isothermal thermogravimetric analysis

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ARTICLE INFO

ABSTRACT

The non-isothermal oxidation experiments of ilmenite concentrate were carried out at various heating rates under air atmosphere by thermogravimetry. The oxidation kinetic model function and kinetic parameters of apparent activation energy (E_a) were evaluated by Málek and Starink methods. The results show that under air atmosphere, the oxidation process of ilmenite concentrate is composed of three stages, and the chemical reaction ($G(\alpha)=1-(1-\alpha)^2$, where α is the conversion degree) plays an important role in the whole oxidation process. At the first stage ($\alpha=0.05-0.30$), the oxidation process is controlled gradually by secondary chemical reaction with increasing conversion degree. At the second stage ($\alpha=0.30-0.50$), the oxidation process is completely controlled by the secondary chemical reaction ($G(\alpha)=1-(1-\alpha)^2$). At the third stage ($\alpha=0.50-0.95$), the secondary chemical reaction weakens gradually with increasing conversion degree, and the oxidation process is controlled gradually by a variety of functions; the kinetic equations are $G(\alpha)=(1-\alpha)^{-1}$ ($\beta=10$ K·min^{-1}, where β is heating rate), $G(\alpha)=(1-\alpha)^{-1/2}$ ($\beta=15-20$ K·min^{-1}), and $G(\alpha)=(1-\alpha)^{-2}$ ($\beta=25$ K·min^{-1}), respectively. For the whole oxidation process, the activation energies follow a parabolic law with increasing conversion degree, and the average activation energy is 160.56 kJ·mol^{-1}.

1. Introduction

Panzhihua ilmenite, located in Sichuan Province of China, is one of the largest ilmenite reserves over the world, with an estimated ilmenite reserve of about 870 Mt, which accounts for more than 92% of the total reserve of China and is greater than 35% of world reserves[1-3]. Efficient utilization of the ilmenite resources is very important for the development of the titanium industry. However, the TiO$_2$ content in ilmenite is lower than 52.6% owing to the high impurity contents (MgO, CaO, SiO$_2$, MnO, etc.). It is difficult to upgrade the ilmenite to titanium-rich slag, which limits the development and utilization of ilmenite deposit in Panzhihua region[4]. Moreover, the ilmenite concentrate has a complicated mineral composition including ilmenite, geikielite, gangue and other minerals. Ilmenite is more stable than ordinary iron oxides because of the solid solution of iron (II) oxide with titanium dioxide.

The reduction of ilmenite concentrate is more complicated than that of other common ores, because of the high percentage of impurities like magnesium and silicone oxides and a small quantity of manganese oxide[5]. It requires higher temperature and longer reduction time to achieve a relatively high metallization ratio[6]. However, pre-oxidation of ilmenite is a broadly adopted practice in the production process of ilmenite ore to TiO$_2$ pigment and metallic titanium[7-10]. It is regarded as an effective method to increase the reduction and leaching rate by changing the structure and composition of iron oxide[11-13]. The oxidizing roasting leads to the breakage of complex mineral structure, and the formation of porous simple oxides[14].

Over the past several decades, many studies have been carried out on the isothermal oxidation mechanism of ilmenite. One of the main oxidation products was usually pseudobrookite when oxidation temperature was higher than 900 ℃, which was a

stable phase at high temperatures[15]. When the temperatures ranged from 400 to 800 ℃, the rutile, hematite, and crystallographic shear (CS) structure phases formed simultaneously during the oxidation of ilmenite ($FeTiO_3$)[16,17]. Chen[18] found that the intermediate phases ($Fe_2Ti_3O_9$ and Fe_2O_3) formed when the temperature was higher than 1000 ℃, and the stable phases (Fe_2TiO_5 and TiO_2) gradually formed when the temperature was higher than 1000 ℃. Gupta et al.[19] found that the TiO_2, hematite (Fe_2O_3) and CS phase were the stable phases when the oxidation temperature was lower than 850 ℃. Xiao et al.[20] found that the $FeTiO_3$ transformed to hematite and rutile when the oxidation temperatures ranged from 700 to 800 ℃, and pseudobrookite formed when the oxidation temperature reached 900 ℃. Although the isothermal oxidation of ilmenite by air has been studied intensively, the information on non-isothermal oxidation kinetics of ilmenite concentrate by air is still not sufficient, such as kinetic model, apparent activation energy and pre-exponential factor. On the other hand, the pre-oxidation process was an effective method to improve the reducibility of ilmenite concentrate. Therefore, it is necessary to clarify the non-isothermal kinetics and oxidation mechanism of ilmenite concentrate for the further application.
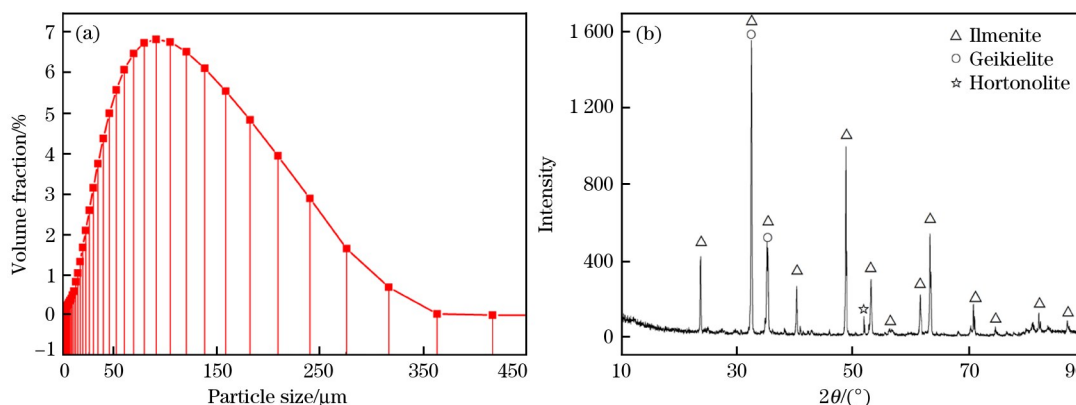
In the present study, the non-isothermal oxidation experiments of ilmenite concentrate at various heating rates under air atmosphere were carried out by thermogravimetry. According to the thermogravimetric (TG) and differential thermogravimetric (DTG) analysis data, the oxidation kinetic model function, kinetic parameters of apparent activation energy, and pre-exponential factor were evaluated by Málek and Starink methods. Moreover, the microstructure and phase composition of oxidation products were determined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS).

2. Experimental

2.1. Raw materials

The ilmenite concentrate was provided by Panzhihua Iron & Steel Company (Sichuan province, China). The particle size distribution of the ilmenite concentrate, as obtained using a Malvern Mastersizer 2000 particle size analyzer, is shown in Fig. 1(a). The analysis results show that 52.38% of the ilmenite concentrate particles have a diameter less than 74 μm, and the average particle diameter and specific surface area are 87.595 μm and 0.146 m$^2 \cdot$ g^{-1}, respectively.

Fig. 1.   Particle size distribution (a) and XRD pattern (b) of ilmenite concentrate.

The chemical composition of the ilmenite concentrate was characterized by X-ray fluorescence (Rigaku, model ZSX Primus II) and is shown in Table 1. The X-ray diffraction was obtained by a D/max 2200 X-ray diffractometer (Tokyo, Japan), a conventional copper target X-ray tube set at 30 kV and 30 mA. The X-ray source was CuKα radiation. Data were collected from 2θ of 10° to 90° with a step width of 0.20°, step time of 0.4 s, scanning speed of 6 (°)/min, divergence slit width of 0.20 mm, scatter slit width of 0.60 mm, and receiving slit width of 0.20 mm at room temperature. All samples were dried at 40 ℃ to a constant moisture in a vacuum oven; then, about 50.00 mg samples were added into the slide for packing prior to X-ray scanning. The XRD pattern indicates that ilmenite is the major mineral in the il-

Table 1
Chemical composition of ilmenite concentrate (wt.%)

TFe	FeO	Fe$_2$O$_3$	TiO$_2$	Al$_2$O$_3$	SiO$_2$	MgO	CaO	MnO	V$_2$O$_5$	S	P
31.43	34.87	6.16	47.29	1.01	3.26	5.72	0.85	0.64	0.06	0.135	0.005