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ESTIMATION OF KINETIC PARAMETERS OF THERMAL OXIDATION OF ILMENITE*

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Abstract

The aim of the presented work was the investigation of thermal oxidation of ilmenite in static air atmosphere. The investigations were carried out by use of a derivatograph (MOM, Hungary). The changes of crystallographic structure of investigated samples were identified by X-ray diffractometry on Philips PW-1710 diffractometer. In temperature above 500°C appears structure of hematite Fe_2O_3. On the basis of the thermogravimetric measurements, the contracting area and contracting volume models were found as the best fitting experimental data.

Keywords: ilmenite, kinetics, model, oxidation

Introduction

Ilmenites used as a titania raw material are obtained from the magma rocks. Ilmenite is very important mineral material for the production of titanium dioxide. The content of titania in ilmenite is about 40–50% TiO_2 but it is possible to take up TiO_2 content by thermal oxidation of material and following acid leaching. It is a method in order to obtain synthetic rutile used in titanium dioxide chloride technology.

The experimental work aimed at the investigation of thermal transformations of ilmenite in air atmosphere and testing kinetic models which can be used for the description the rate of this reaction.

Experimental

Commercial Norwegian ilmenite was used as experimental material. The first step was the determination of the elemental composition of this raw material. The sample of ilmemite was ground, dried and investigated on XRF spectrometer Philips 1480. The analyses resulted in TiO_2 – 44.4%, FeO – 34.8%, Fe_2O_3 – 11.6%, MgO – 4.1% and SiO_2 – 2.1%. The iron in ilmenite is on two levels of oxidation Fe^{2+} and Fe^{3+}.

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Thermal oxidation of ilmenite was investigated by means of a derivatograph (MOM, Hungary). Investigations were carried out in the temperature range from 20 to 1000°C. Sample of ilmenite before measurement was ground in a spherical mill (maximum diameter of particles was 0.04 mm) and dried to constant mass in temperature 105°C. The mass of sample used in the measurements was 100 mg. The crucible of plate type was used in thermoanalytical experiments. Mass of sample and shape of crucible was chosen in order to eliminate the influence of outer diffusion factors on kinetics of process. Several series of measurements at different rate of heating in static air atmosphere were carried out to check the influence of rate heating on kinetics of this process.

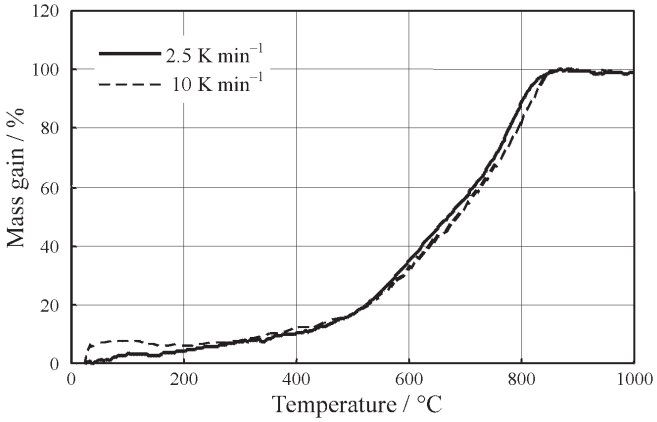

Fig. 1 Thermal behaviour of ilmenite

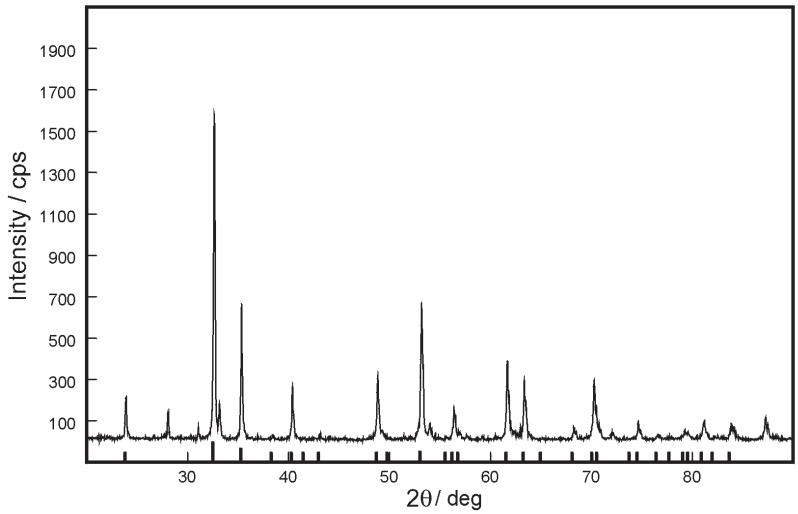

Fig. 2 Diffraction pattern of ilmenite at temperature 100°C with ilmenite standard

The results of measurements for rate of heating 2.5 and 10 K min^{-1} are presented in Fig. 1. The shape of curves is very close. In this condition kinetics of oxidation process is independent of the heating rate.

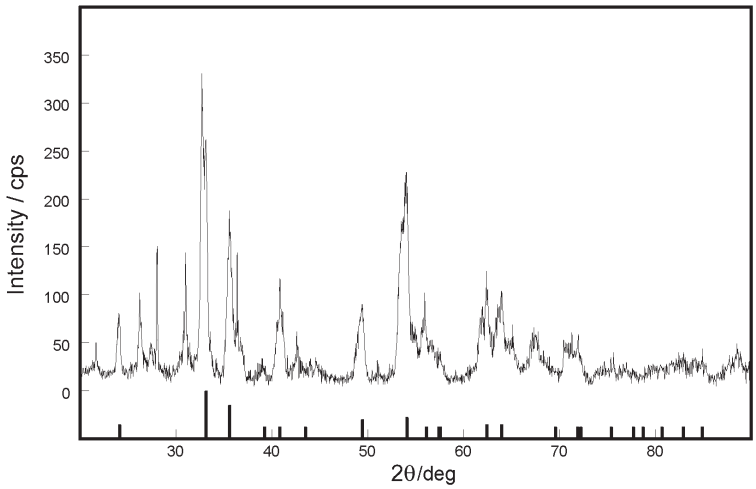

Fig. 3 Diffraction pattern of ilmenite at temperature 700°C with hematite standard

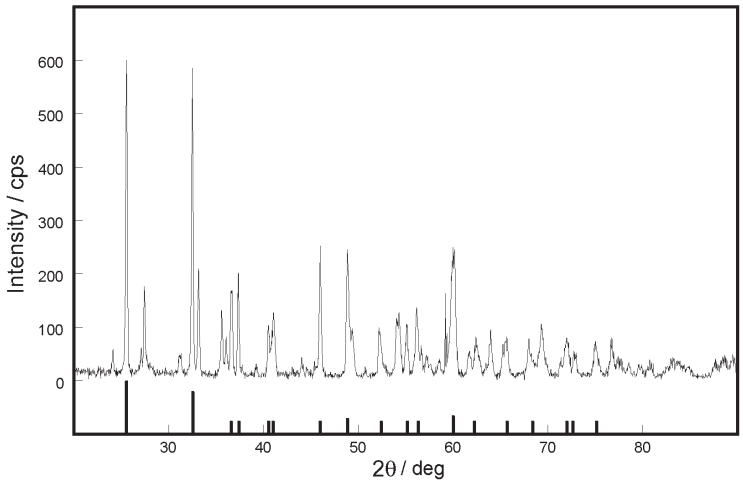

Fig. 4 Diffraction pattern of ilmenite at temperature 1000°C with pseudobrookite standard

Above 500°C acceleration of mass gain follows until 800°C where increase of mass was finished. Above 850 until 1000°C mass of sample is almost constant.

The samples for investigation of crystal structure on X-ray diffractometer were prepared in the following way. Samples of ilmenite were placed in furnace, and then heating began up to the required temperatures with an average heating rate of about

3 K min^{-1}. In selected temperatures sample was taken out from furnace and heating of remaining samples was continued.

Samples obtained in this way were investigated on X-ray diffractometer. X-ray diffraction data were collected on Philips 1710 powder diffractometer equipped with copper X-ray tube. Automatic divergence slit and 0.1 mm receiving slit were used during data collection. The operation of X-ray tube was at 40 kV and 35 mA. Intensity measurements were made at intervals of 0.02° in the range of 2θ from 10 to 90°.

Results are presented in Figs 2 to 4 where X-ray patterns are at temperatures 100, 700 and 1000°C. Figure 5 presents three dimensional plot of diffractograms in the temperature range from 100 to 1000°C at 100°C intervals and for 2θ angle range from 30 to 42°.

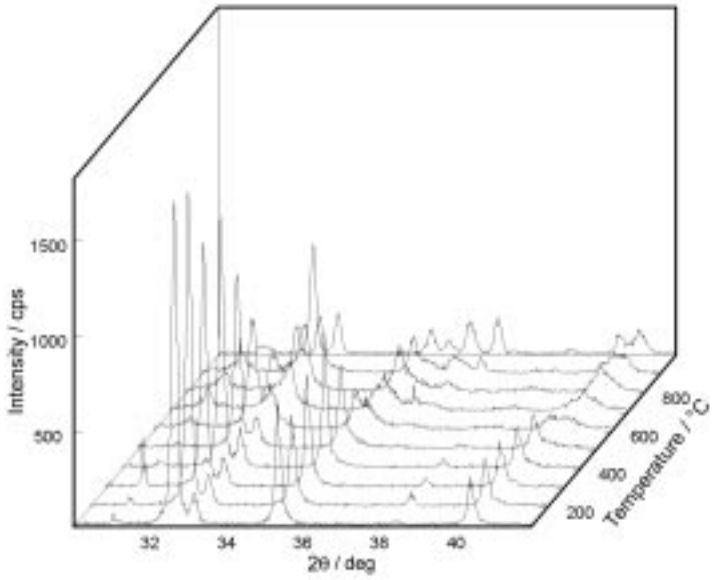

Fig. 5 Three dimensional plot of ilmenite X-ray pattern

Figure 5 shows that the structure of ilmenite $FeTiO_3$ well visible at 100°C (Fig. 2) slowly disappears to 800°C. At 500°C (Fig. 3) the structure of hematite Fe_2O_3 appears. In the temperature range from 800 to 900°C (Fig. 4) a new phase pseudobrookite Fe_2TiO_5 appears and simultaneously partial disappearance of structure of hematite follows.

From the presented investigations it can be concluded, that in the temperature range from 500 to 800°C the disappearance of ilmenite structure occurs and the structure of hematite appears and simultaneously we can observe main increase of sample mass in this range of temperatures. The increase of sample mass in this range of temperature is about 4%.

Assuming, that reaction of ilmenite oxidation is

$$4FeO+O_2 \rightarrow 2Fe_2O_3 \quad (1)$$

on the basis of increase of sample mass, can be estimated the content of Fe(II) in this raw material.

The analytical content of Fe(II) in ilmenite is 27.11%. Assuming the reaction of thermal oxidation (1), the calculated increase of mass after oxidation should be equal 3.88%. This calculated value is close to the value obtained from thermoanalytical experiments.

Main increase of mass observed during reaction of thermal oxidation is the result of oxidation of ilmenite. As a product of this process forms hematite. The pseudobrookite structure forms at higher temperature.

Results

The rate of reaction of thermal oxidation of ilmenite may be expressed as:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (2)$$

Considering a constant rate of temperature changes:

$$\frac{dT}{dt} = q \quad (3)$$

Equation (2) takes the form:

$$\frac{d\alpha}{dT} = \frac{A}{q}\exp\left(-\frac{E}{RT}\right)f(\alpha) \quad (4)$$

The function $f(\alpha)$ depends on the process rate controlling mechanism. In literature [1] there are well known rate equations used in kinetic analyses of solid state reactions. These kinetic models take into account geometrical factors, chemical process control, nucleation and diffusional limits.

To find the best fitting model of thermal oxidation of ilmenite we used method of the last squares minimisation of errors between the model and experimental data. We used the iterative procedure to find out the minimum of sum of square deviations.

$$F = \sum_{i=1}^{n}(T_{iexp} - T_i)^2 \quad (5)$$

The algorithm to minimise function (5) was the Marquart method for optimisation and Runge–Kutta method to solve the differential equation [2].

As a result of calculations and model selection we found the best fitting of experimental data is obtained for the models of contracting surface and contracting volume. In both cases the lowest values of sum of square deviations were received. The activation energy and pre-exponential factor for the kinetic model of contracting surface was E=30.88 kJ mol^{-1} and A=0.186 min^{-1} and for the kinetic model of contract-

ing volume was E=34.26 kJ mol^{-1} and A=0.333 min^{-1}. From this we can draw the conclusion, that the main influence on kinetics of oxidation process was the interfacial surface.

References

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