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THERMAL TRANSFORMATIONS OF TITANIUM SLAG OF HIGH TITANIA CONTENT

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Abstract

Titanium raw materials play important role as a source of titanium and titanium dioxide. The investigation of the rate of oxidation and phase transformation of titanium slag in static air atmosphere by use of thermogravimetry (TG) and X-ray diffractometry (XRD) were presented. The investigation were carried out for three different particle size fractions to determine influence of this parameter on rate of reaction. To estimate kinetic parameters was used the kinetic model of contracting volume. The value of kinetic parameters show that influence of heating rate and particle size on rate of reaction is not so large. The thermogravimetric investigations of the oxidation of titanium slag in air atmosphere shown that reaction proceeds in two stages. The XRD investigation shown that titanium slag has the pseudobrookite structure and its diffraction pattern is very close to the diffractogram of magnesium titanate $MgTi_2O_5$ and iron magnesium titanium oxide (Fe–Mg–Ti–O). At elevated temperature the structure of slag transforms to the ferric pseudobrookite structure and excess titanium dioxide forms the rutile phase.

Keywords: oxidation, thermal transformations, titanium slag

Introduction

The titanium slag containing more than 75% TiO_2 is prepared by electrothermic reduction of ilmenite with carbon at elevated temperature. It is used as a raw material in the chloride technology of titanium dioxide production. To increase TiO_2 content, titanium slag is treated by thermal oxidation and acid leaching.

Titanium slag of high titania content is raw material which can be used to production of titanium dioxide. Received from titanium raw materials TiO_2 is the object of intensive investigations [1, 2].

The aim of presented work was the investigation of the rate of oxidation and phase transformation of titanium slag in static air atmosphere by use of thermogravimetry (TG) and high temperature X-ray diffractometry (XRD).

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Experimental

Samples and preparation

The composition of QIT titanium slag (QIT Fer et Titane Inc., Quebec, Canada) determined by X-ray fluorescence spectrometry (XRF spectrometer Philips 1480) was resulted in Ti – 47.4%, Fe – 8.1%, Mg – 3%, Si – 2.1%, Al – 1.9%. The titanium slag forms so-called ferrous pseodobrookite phase. The details of the titanium slag investigations with neutron diffraction and Mössbauer spectroscopy have been reported [3, 4].

Sample of titanium slag before measurement was grunded in a spherical mill. After grinding, sample was subject of screen analysis to receive suitable fractions of particles. Next samples were dried to constant mass in temperature 105°C.

Methods

The TG measurements of the oxidation rate of titanium slag samples under non-isothermal conditions were carried out using a Derivatograph C (MOM, Hungary) in static air atmosphere at temperature range 20 to 1000°C. A mass of sample in all runs was 100 mg. The reference material was alumina. Mass of sample and shape of crucible was chosen in order to eliminate the influence of diffusion on kinetics of process.

The experiments were performed for the three different grain size fractions, namely:

1 – 0.16–0.315 mm; 2 – 0.4–0.5 mm; 3 – 0.8–1.25 mm at heating rate 2.5, 5 and 10 K min^{-1}.

The X-ray powder diffractometry was used for identification of structural transformation of slag during temperature increasing.

The X-ray investigation of sample was carried out using Philips diffractometer type PW 1710 equipped with high temperature camera Anton Paar HTK 10. The operation of X-ray tube with Cu radiation was at voltage 45 kV and current 40 mA.

The X-ray diffraction measurements were also carried out for powdered samples of slag (fraction<0.02 mm) calcined for 1 h in furnace in static air atmosphere at temperature range 100–1000°C. Diffraction patterns were analysed using JCPDS PDF-2 powder diffraction data base.

Results

The rate of the solid state reaction is frequently limited by the reaction interface area. In the case of spherical, cylindrical or more complicated in shape particles the kinetic model of contracting volume can be used [5, 6].

$$\mathrm{d}\alpha/\mathrm{d}T=(A/\beta)\exp(-E/RT)(1-\alpha)^{2/3} \tag{1}$$

The experimental TG curves for different particle fractions of titanium slag recorded in static air atmosphere are presented in Figs 1 and 2. The oxidation of slag proceeds in two reaction stages and final mass increase depends upon the particle diameter

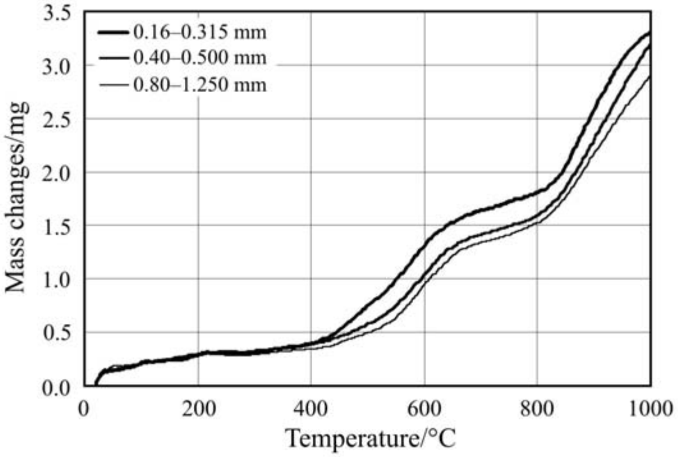

Fig. 1 TG curve of titanium slag at heating rate 5 K min^{-1}

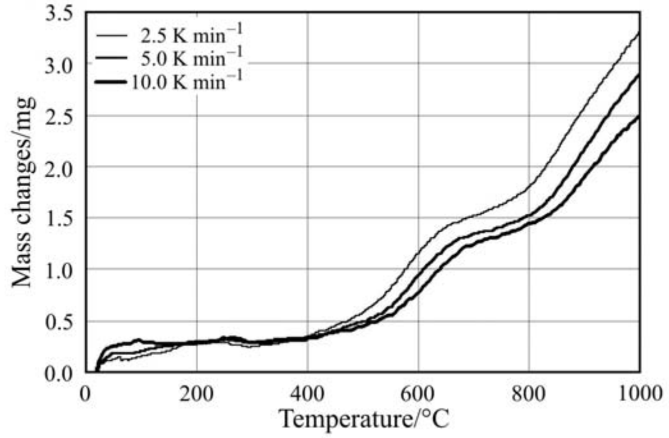

Fig. 2 TG curves of the 0.8–1.25 mm fraction of titanium slag at different heating rate

and heating rate. The mass increase for the fraction 1 to 3 is, respectively: 3.11, 3.17 and 3.69% at a heating rate 2.5 K min^{-1}.

On Fig. 3 was presented experimental results and curve calculated from the model (1). The calculation results show good approximation of TG curve with results obtained from this model. The activation energy for the first oxidation stage is in average 55.42 kJ mol^{-1} and systematic deviation correlated to heating rate or particle size is not observed. The activation energy for second oxidation stage is about three times higher and its mean value is 144.27 kJ mol^{-1}.

The explanation of observed on TG curves two stages of titanium slag oxidation is following. During heating of material in air atmosphere two consequent reaction occur, the oxidation of Ti^{3+} followed by Fe^{2+} oxidation according to equations

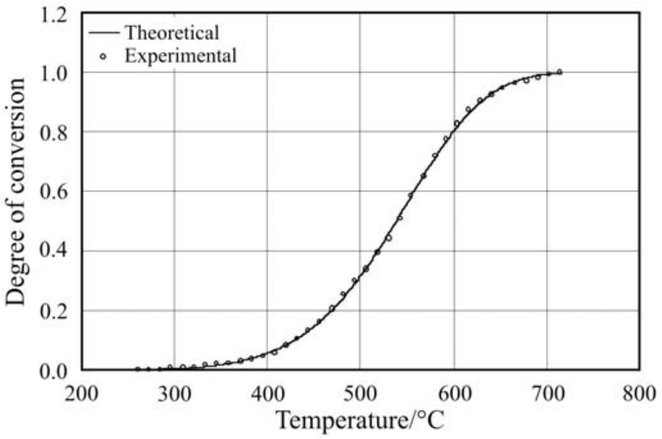

Fig. 3 TG curve for first stage of reaction and results obtained from the model, heating rate 2.5 K $\min^{-1}$ and grain size fraction 0.16–0.315 mm

$$2Ti^{3+}+1/2O_2=2Ti^{4+}+O^{2-} \tag{2}$$

$$2Fe^{2+}+1/2O_2=2Fe^{3+}+O^{2-} \tag{3}$$

what results from the fact that oxidation of ferrous cation in solid phase is inhibited by electron transfer reaction:

$$Fe^{3+}+Ti^{3+}=Fe^{2+}+Ti^{4+} \tag{4}$$

We can assume that the oxidation of Ti^{3+} and Fe^{2+} occurs almost in parallel reactions. The reactions proceed at reaction interface and ferrous cations oxidate when all neighbours Ti cations at reaction interface are in higher valence state. The reaction advances only in outer boundary layer of slag particles and the reaction rate decreases when the reacting substances in the particle shell are exhausted. The reaction becomes diffusionally controlled what corresponds to deflection of TG curve at temperature range 300–400°C. The oxidation is accelerated again when the structural changes in material begin to proceed and rutile phase forms and grows. As a result of this transformation and structure rearrangement in the boundary layer of particles are formed slits and cracks and outer layer of particle is destructed what enables further advance of reaction. The observed acceleration of reaction rate can be attributed to the ‘superheating’ of material.

The oxidation of slag and its structural changes are interconnected. The structural rearrangement consists in exchange of Ti and Fe between *A* and *B* sites in the pseudobrookite lattice. This process can be described by following equation:

$$(Fe, A)Ti_2O_5 \leftrightarrow (Fe_{1-x}, A)(Ti_{2-x}Fe_x)O_{5-2x}+xTiO_2 \tag{5}$$

and at oxygen atmosphere:

$$(Fe, A)Ti_2O_5+xO_2 \leftrightarrow (Fe_{1-x}, A)(Ti_{2-x}Fe_2)O_2+xTiO_2 \tag{6}$$

In the first reaction two kinds of vacancies are created: oxygen anion vacancy in basic structural lattice and iron vacancy in *A* sites. The former one can be compensated by oxygen from air atmosphere. Iron vacancy is compensated by diffusion to the reaction interface other cations as Ti^{3+} and Fe^{2+}. Iron ion Fe^{3+} having a smaller than Fe^{2+} radius can be substituted easier in the Ti^{4+} site forming acceptor admixture and oxygen vacancy. The oxygen atmosphere should shift the equilibrium to the right side of above equations accelerating the decomposition of pseudobrookite phase and rutile formation.

The diffractogram of commercial titanium slag over angular range $10<2\Theta<100$ is presented in Fig. 4. This investigation shows that titanium slag has the pseudobrookite structure and its diffraction pattern is the closest one to the diffractogram of the pure synthetic phase of magnesium titanate $MgTi_2O_5$ and iron–magnesium–titanium oxide (Fe–Mg–Ti–O) determined as sorelslag with unknown composition and crystal structure. The titanium slag contains a small amount of rutile phase.

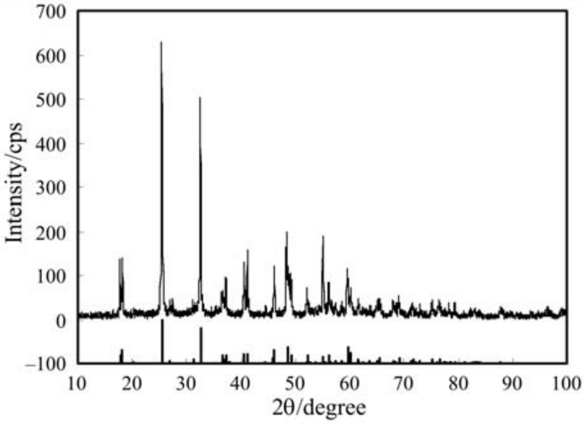

Fig. 4 Diffractogram of titanium slag with $MgTi_2O_5$ pattern

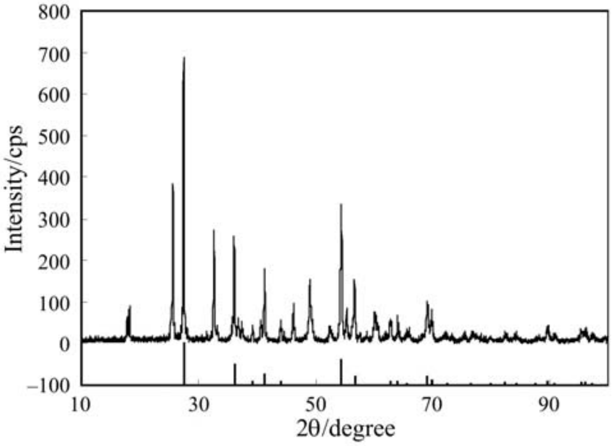

Fig. 5 Diffractogram of titanium slag calcined at 900°C with rutile pattern

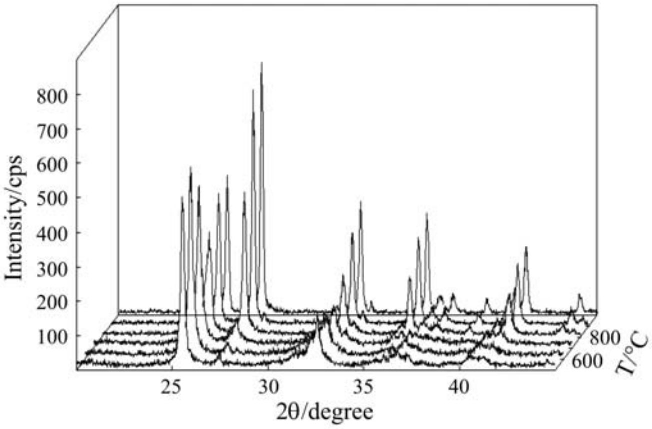

Fig. 6 Three dimensional plot of titanium slag X-ray diffractograms

In Fig. 5 is presented the diffraction pattern of slag calcined at 900°C. This pattern shows the increased amount of rutile and structure of pseudobrookite. The thermal transformations of slag are presented on the three-dimensional plot of diffraction patterns presented in Fig. 6. The plot over angular range $20<2\Theta<45$ shows the peaks of pseudobrookite and rutile. These plots illustrate the remarkable ferric pseudobrookite formation at temperature 800°C. In the sample calcined at 700°C appears rutile phase and can be observed rapid increase of the intensity of rutile peak in samples calcined at 800°C and above this temperature. The growth of rutile crystals begins at temperature range 700–800°C.

Conclusions

The TG investigations of the oxidation of titanium slag in air atmosphere shown that reaction proceeds in two stages. The final mass increase depends upon the particle diameter. A good approximation of TG curve was obtained for contracting volume model for both reaction stages. The activation energy for the first oxidation stage is in average 55.42 kJ mol^{-1} and for second stage is about three times higher and its mean value is 144.27 kJ mol^{-1}. The acceleration of oxidation reaction above temperature 700°C can be attributed to the structural transformation of slag occurring over temperature range 700–800°C resulting in rutile phase formation.

The XRD investigation shows that titanium slag has the pseudobrookite structure and its diffraction pattern is very close to the diffractogram of magnesium titanate $MgTi_2O_5$ and iron magnesium titanium oxide (Fe–Mg–Ti–O). At elevated temperature the structure of slag transforms to the ferric pseudobrookite structure and excess titanium dioxide forms the rutile phase. The rutile phase growth advances at temperature range 750 to 800°C.

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